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Electroanalytical Determination of Two ACCase-inhibing Herbicides in Soybean Products. A Theoretical Insight

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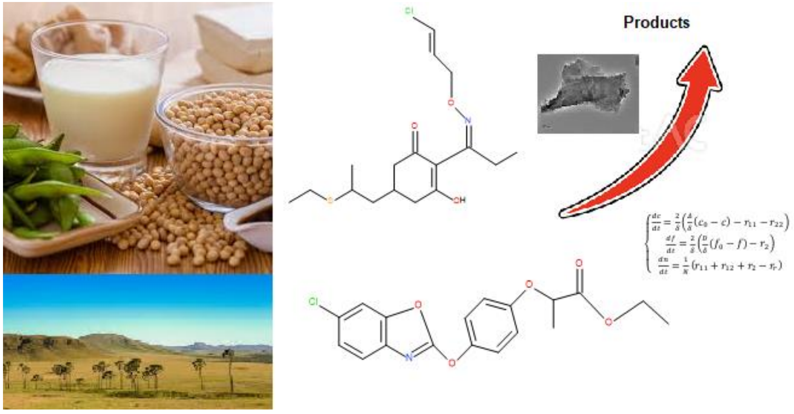
This study evaluates the possibility of electroanalytical detection of clethodim and fenoxaprop-p-ethyl in soybean crops and products. The electrochemical analysis may be performed at both the cathode and the anode, given the presence of donor and acceptor functional groups. Two mathematical models, each for the positive or negative polarity of the working electrode, were developed and analyzed using linear stability theory and bifurcation analysis. Either way, the electroanalytical behavior is effective and sufficient to quantify the nanomolar concentrations of both pesticides in mildly acidic and neutral medium for cathodic process and neutral to moderately alkaline in anodic. However, considering the moderately acidic environment of the soybean plant and its products, like also the electrochemical properties of both of the pesticide, the cathodic process is preferable.

Graphical abstract



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1. Introduction

Soybean products are among the most planted in Cerrado biome in Center-West administrative region of Brazil [1 – 4]. The soy plantation and the soybean production is one of the most important areas of the agricultural sector of Brazilian economy, reason why the soybean crops are very important for Brazilian federal government and the governments of Brazilian states, including the areas of Cerrado (Goiás, Mato Grosso, Mato Grosso do Sul, Federal District and parts of the states of Bahia, Tocantins, Maranhão, Piauí, Minas Gerais, São Paulo and Paraná). Minimal part of Cerrado lies within the borders of Paraguay (in the extremely eastern and north-

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eastern parts of Paraguayan departments of Amambay, Concepción and Canindeyú).

In order to enhance the fertility of soy crops by protecting them from gramine weeds, concurring with soy for growth resources, the herbicide preparations, including the cyclohexanediones and aryloxyphenoxypropionates, like clethodim and fenoxaprop-*p*-ethyl (Fig.1) [5 – 10], both authorized by the Brazilian regulator ANVISA. Their mechanism is based on Acetyl-CoA Carboxylase (ACCase) inhibition, leading to the failure in the cell membrane construction, which becomes letal for the weed.

Although they are effective for the soybean protection from weed, they may be toxic if enter the soybean products. For this and other reasons, the development of a rapid and efficient method for their quantification is actual, and the electroanalytical process (either cathodically or anodically) may be an excellent solution for this problem [11 – 14], as they provide an efficient, rapid and exact concentration determination, being relatively cheap.

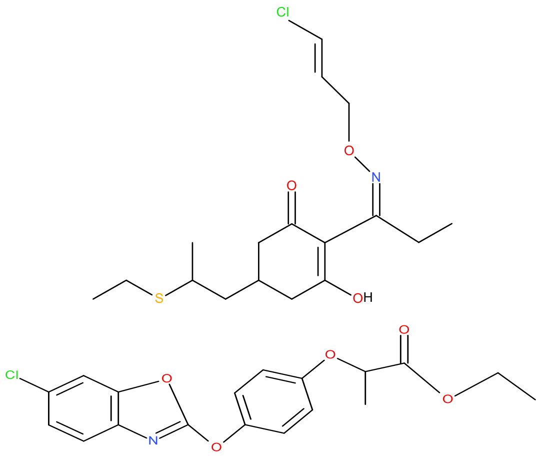

Fig.1. Clethodim and fenoxaprop-*p*-ethyl

As for now, no theoretical or experimental reports for the electrochemical methods for the quantification of both of the mentioned herbicides. Nevertheless, their chemical composition indicate that these compounds contain both donating and accepting groups [15 – 22], which leads to the conclusion that both cathodic and anodic processes are applicable to them. Moreover, although the cathodic electrochemical determination is preferable, the anodic determination is possible, if the strong oxidants are used as electrode modifiers.

Nevertheless, the electrochemical instabilities, typical for the similar electroanalytical and electrosynthetical processes [23 – 26] may impede the easy interpretation of the analytical signal or even lead to the electrochemical equipment to break down. On the other hand, the electrochemical instabilities may reveal the presence of a substance or a specific reaction involving the electroactive compound.

The analysis of the theoretical and experimental data shows that the electrochemical instabilities in non-autocatalytic electrochemical systems are caused by the influences of chemical and electrochemical processes on the double electric layer (DEL) ionic force, capacity and conductivity, like also the electrode surface material impedance.

Therefore, the theoretical *a priori* investigation of the system´s behavior, capable to detect the conditions of the most effective sensing interpretation, like also the conditions of the electrochemical instabilities, are important stage for the development of new electrochemical sensors, especially for new compounds and involving new electrode modifiers. Also, this investigation, involving the development and analysis of a mathematical model, permits to compare the similar electroanalytical systems. Therefore, the aim of this work is to investigate, from the mechanistical theoretical point of view, the possibility for two aryloxyphenoxypropionate ACCase inhibing herbicides electrochemical determination by cathodic and anodic scenario. It involves the mechanism suggestion and mathematical model analysis and interpretation, including also the comparison of the behavior of this system with that of the similar ones [27, 28].

2. Material and Methods

2. 1 Section I. Cathodic process

2.1.1 System and its modeling

If cathodic process, based on carbon nitride-modified cathode is used, it is more convenient for both clethodim and fenoxaprop-p-ethyl, due to two reasons:

- Mildly acidic medium, characteristic for soybean products, is suitable for this process
- Both of the herbicides possess electron accepting group, reason why their electrochemical behavior becomes more expressed on cathode.

The electroanalytical process on cathode is realized at environmental temperature and it is membraneless at working potentials. A membrane impeding the passage of the chloride-ion, product of the organic dechlorination, becomes required at more reductive cathodic potentials and lower pH, in which this dechlorination occurs.

In neutral, mildly and moderately acidic medium (3<pH≤7), maximally close to the soybean pH, and at relatively less cathodic potential (U > -1V), which is analyzed in the present work, clethodim and fenoxaprop-*p*-ethyl may be reduced by carbonyl and carboxyl group correspondently. Moreover, clethodim is also reduced by alkoxyme moiety, which gives it one more voltammogramic cathodic reduction peak.

For this reason, accepting certain assumptions [27 – 28], we describe the behavior of this system by the trivariant equation-set (1):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_{11} - r_{22}\right) \\ \frac{df}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(f_0 - f) - r_2\right) \\ \frac{dn}{dt} = \frac{1}{N}(r_{11} + r_{12} + r_2 - r_r) \end{cases} \qquad (1)$$

Herein δ is pre-surface layer thickness, c and f are clethodim and fenoxaprop-p-ethyl diffusion layer concentrations, D and Δ are their diffusion coefficients, n is carbon nitride oxidized form coverage degree, N is its maximal surface concentration and the parameters r stand for the correspondent reaction rates, calculated as (2 – 5):

$$r_{11} = k_{11}c(1-n) \qquad (2)$$

$$r_{12} = k_{12}c(1-n)^2 \exp(-ac) \qquad (3)$$

$$r_2 = k_2 f(1-n)^2 \exp(-bf) \qquad (4)$$

$$r_r = k_r f \exp\left(-\frac{2F\varphi_0}{RT}\right) \qquad (5)$$

Herein the parameters k correspond to the reaction rate constants, a and b are parameters describing the influences of ionic forms´ transformations during the chemical stages on DEL electrophysical properties, F is the Faraday constant, φ_0

stands for zero-charge related potential slope in DEL, R is the universal gas constant and T is the absolute temperature.

Taking into account that the pyridinic nitrogen atom in fenoxaprop-*p*-ethyl is protonated in acidic medium, influencing DEL in both oxidized and reduced forms, like also an ionic particle formation during the alkoxyme moiety reduction, interfering the DEL electrophysical properties, the oscillatory behavior in this system becomes more probable than in similar electroanalytical processes. Nevertheless, the carbon nitride modified electrode is still efficient electrode modifier for both ACCase inhibitor herbicide determination, as shown below.

3. Results and Discussion

In order to describe theoretically the electrochemical determination of clethodim and fenoxaprop-*p*-ethyl in acidic medium over carbon nitride-modified electrode, we analyze the differential equation set (1), like also the algebraic relations (2 – 5) by means of linear stability theory. The steady-state Jacobian matrix members for this system may be described as (6):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \qquad (6)$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_{11}(1-n) - k_{12}(1-n)^2\exp(-ac) + ak_{12}c(1-n)^2\exp(-ac)\right)\ 0 \qquad (7)$$

$$a_{12} = 0 \qquad (8)$$

$$a_{13} = \frac{2}{\delta}(k_{11}c + 2k_{12}c(1-n)\exp(-ac)) \qquad (9)$$

$$a_{21} = 0 \qquad (10)$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{D}{\delta} - k_2(1-n)^2\exp(-bf) + bk_2f(1-n)^2\exp(-bf)\right) \qquad (11)$$

$$a_{23} = \frac{2}{\delta}(2k_2f(1-n)\exp(-bf)) \qquad (12)$$

$$a_{31} = \frac{1}{N}(k_{11}(1-n) + k_{12}(1-n)^2\exp(-ac) - ak_{12}c(1-n)^2\exp(-ac)) \qquad (13)$$

$$a_{32} = \frac{1}{N}(k_2(1-n)^2\exp(-bf) - bk_2f(1-n)^2\exp(-bf)) \qquad (14)$$

$$a_{33} = \frac{1}{N}\left(-k_{11}c - 2k_{12}c(1-n)\exp(-ac) - 2k_2f(1-n)\exp(-bf) - k_r\exp\left(-\frac{2F\varphi_0}{RT}\right) + jk_rf\exp\left(-\frac{2F\varphi_0}{RT}\right)\right) \qquad (15)$$

In order to avoid the cumbersome expression during the determinant analysis, we introduce new variables and rewrite it as (16):

$$\frac{4}{\delta^2 C}\begin{vmatrix} -\kappa - \Xi & 0 & \Gamma \\ 0 & -\xi - J & P \\ \Xi & J & -\Gamma - P - \Omega \end{vmatrix} \qquad (16)$$

Opening the straight brackets, applying both Routh-Hurwitz stability criterion and monotonic instability condition and changing the signs to the opposite, we obtain the requirement set, expressed as (17):

$$\kappa(\xi\Gamma + \xi P + \xi\Omega + J\Gamma + J\Omega) + \Xi(\xi P + \xi\Omega + J\Omega)\begin{cases} > 0, steady - state\ stability \\ = 0,\ monotonic\ instability \end{cases} \qquad (17)$$

If −Det J>0, the Routh-Hurwitz stability criterion is valid, and the steady-state is thereby stable, providing an efficient steady-state determination of both of the analytes. Moreover, the wide stability region lets use this system in pharmaceutical formulations and biological liquids, like also in the environment.

This criterion is readily satisfied, if the kinetic parameters J and Ω are positive. In the vast majority of the cases, they both have positive signs and, considering that the other variables in the determinant are positive, it indicates the vast steady-state stability topological region. The electroanalytical process is mostly kinetically controlled, being capable of being driven to the diffusion-controlled mode in small concentrations of both of the pesticides.

In the absence of the side reactions or other factors, capable to compromise the analyte and (or) modifier stability, excluding the reactions, foreseen by the mechanism, the linearity between the electrochemical parameter and concentration is observed, providing an efficient analytical signal interpretation, which is really important for the herbicides concentration monitoring in soybean products.

The condition Det J=0 corresponds to the detection limit, manifested by the *monotonic instability*. It may be seen as an N-shaped part of the steady-state voltammogram and depicts the margin between the stable steady-states and unstable states and corresponds to the steady-state multiplicity. In other words, multiple steady-states, each one unstable, coexist in this point.

As for the oscillatory behavior, it is realized beyond the detection limit, in the case of the Hopf bifurcation realization. Its realization requires the presence of the positive-callback related positive addendums in main diagonal elements.

Observing the main diagonal elements (7), (11) and (15), we may observe that the oscillatory behavior becomes possible by DEL influences of the electrochemical stage, like also one of the chemical stages for each of the analytes. This factor is typical for the similar systems [27 – 28] and may be described by the positivity of the elements $jk_rf\exp\left(-\frac{2F\varphi_0}{RT}\right) > 0$, if j>0, $ak_{12}c(1-n)^2\exp(-ac) > 0$, if a>0 and $bk_2f(1-n)^2\exp(-bf) > 0$, if b>0, describing the similar cyclic phenomena on both DEL and surface during the chemical and electrochemical stages. These elements describe the positive callback, and this callback will depend on the system´s characteristics. For example, the oscillation frequency and amplitude will depend on the background electrolyte composition, which has been proven experimentally and theoretically [27, 28].

3.1 Anodic process

Taking into account that both clethodim and fenoxaprop-p-ethyl contain accepting group, these molecules aren´t electronically enriched. For this reason, the electrooxidation of both of the analytes requires higher energy and, consequently, the anode has to be modified by:

- strong oxidants as they are;
- substances, yielding strong oxidants *in situ* during the electrochemical stage.

Some examples of such substances are cobalt (III) oxyhydroxide and copper (II) sulfide, oxidized in neutral and alkaline medium, which yield in situ strong oxidants on the electrochemical stage (18 – 20):

$CuS + OH^- - e^- \rightarrow CuS(OH)$ (hydroxyl donor and proton recipient) (18)

$CoO(OH) + OH^- - e^- \rightarrow CoO_2 + H_2O$ (proton recipient) (19)

$CoO(OH) - e^- \rightarrow CoO_2 + H^+$ (proton recipient) (20)

This process will also occur at environmental temperature, at neutral to mildly alkaline pH (7≤pH<11,5), and it is membraneless. Both of the substances may be used to quantify either clethodim or fenoxaprop-p-ethyl, but it will require high anode potential and more complex sample preparation. Considering the chemical properties of both of the compounds in alkaline medium in the presence of strong oxidants (including N-oxidation and polymerization scenario for fenoxaprop-p-ethyl), we describe the behavior of this system by a trivariant equation-set (21)

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_1 - r_p\right) \\ \frac{df}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(f_0 - f) - r_{21} - r_{22} - r_p\right) \\ \frac{dn}{dt} = \frac{1}{N}\left(r_{11} + r_{21} + r_{22} + r_p - r_O\right) \end{cases} \quad (21)$$

Analysis of this model is quite similar to that described either in the previous section or in the articles [27 – 28]. It proves that, despite of the efficiency of the anodic electrochemical determination of the analytes, the cathodic scenario is preferable, as it is more compatible to both soybean composition (with mildly to moderately acidic pH) and herbicide functional group (both molecules contain strong accepting groups, reason why they are easily reduced by a cathodically promoted scenario). Nevertheless, if present, the polymerization scenario permits efficient removal of both of the pesticides from the environment and soybean formulation, which lets it contribute to the circular economy processes.

4. Conclusions

From the theoretical description of the electrochemical determination of two aryloxyphenoxypropionate ACCase inhibing herbicides by cathodic and anodic process it has been possible to conclude that most of them may be applied for clethodim and fenoxaprop-*p*-ethyl. The electroanalytical process is mostly kinetically controlled, passing to diffusion-controlled mode in small analytes concentrations. As for the oscillatory behavior in this system, it may be caused by DEL influence by direct and indirect electrochemical stages in both cathodic and anodic process. The system may be used as electroanalytical, providing the efficient analytical signal interpretation, nevertheless, considering the nature of both soybean products and quantified pesticides, the cathodic process is somehow more efficient from electroanalytical point of view. Nevertheless, the anodic process including the polymerization scenario permits the pesticides removal and immobilization in the polymer phase, which is important for the circular economy.

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Author Contributions

Volodymyr V. Tkach (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Tetiana V. Morozova (Data Curation, Conceptualization, Investigation; Supervision; Validation, Writing – Review and Editing); José Inácio Ferrão da Paiva Martins (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Isabel O'Neill de Mascarenhas Gaivão (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Yana G. Ivanushko (Investigatioon, Conceptualization, Data Curation, Methodology, Validation, Visualization); Mehmet Türkmenoğlu (Investigatioon, Conceptualization, Data Curation, Methodology, Validation, Visualization); Petro I. Yagodynets´ (Investigation, Conceptualization, Methodology, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing).

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