The Theoretical Description for Chlorantraniliprole Electrochemical Determination, Assisted by Squaraine Dye – Nano-CuS Composite

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The theoretical description for the chlorantraniliprole electrochemical determination, assisted by the hybrid composite of squaraine dye with CuS nanoparticles has been described. The correspondent reaction mechanism has been proposed, and the correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis. It has been shown that the chlorantraniprole electrochemical anodical determination on high potential may be efficiently provided by cupper sulfide nanoparticles, stabilized by the squaraine dye. On the other hand, the oscillatory and monotonic instability is also possible, being caused by DEL influences of the electrochemical stage.

Graphical abstract
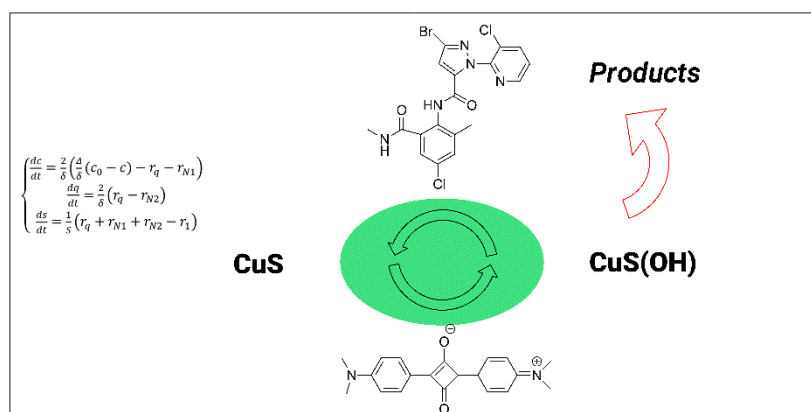
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1. Introduction

Chlorantraniliprole (Rynaxypyr, Fig. 1) is a selective insecticide of the ryanoid class [1-4]. It has been developed by DuPont, in order to control a wide range of pests including *Lepidoptera, Coleoptera, Diptera* and *Isoptera*.
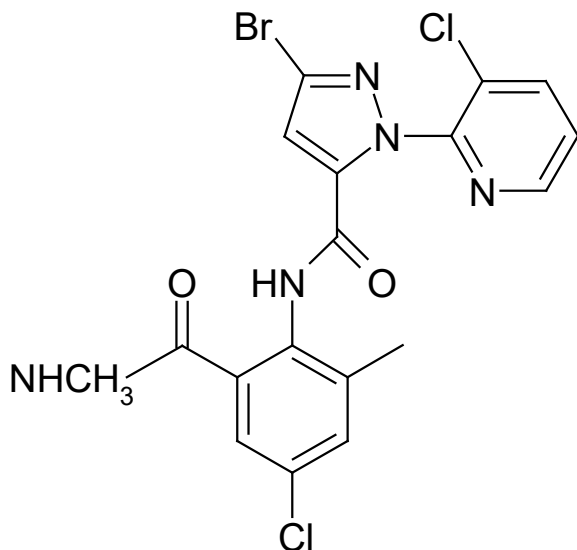
Fig. 1. Chemical structure of chlorantraniliprole.

In Uzbekistan, chlorantraniliprole is used as the active substance of zaragen pesticide [5-10]. It is characterized by a high level toxicity, including the cardiovascular symptoms like sinusoidal bradicardia, arrhythmia and ventricular extrasystolia. Moreover, this substance may be highly toxic to honey bees and aquatic organisms, which makes it an environmentally dangerous chemical. Thus, the development of an efficient and rapid method for its determination is really actual [11-14], and the electrochemical methods could give it a good service.

For now, no works about the chlorantraniliprole electrochemical determination have been published. Nevertheless, its analogous molecules like carbendazime, isoproturon, paraquat and diquat have been successfully determined by electrochemical way [15-21]. Also, chlorantraniliprole molecule contains the electroactive groups, reason why it is considered electrochemically active.

Both anodic and cathodic electrochemical determination may be compatible for the chlorantraniliprole molecule. Although cathodic determination is preferable, the anodic oxidation is also possible and may be efficient. Either way, the use of bear electrodes for electroanalysis becomes inefficient, due to the physical adsorption, overvoltage and electrode shape effects, enhancing the energy loss. Therefore, in order to enhance the efficacy of electroanalytical process, the electrode is modified [22-30]. The chemically modified electrodes diminish the energy losses and augment the catalytic activity and affinity between the sensor and the analyte.

In [22], an interesting electroanalytical process has been developed for inositol, using the copper sulfide nanoparticles. The process involved a highly energetic state of trivalent copper form, which may be useful for chlorantraniliprol electrochemical oxidation. In order to stabilize and mediate the electron transfer, the CuS nanoparticles are deposited over

a squaraine dye [23-28] or conducting polymer matrix [29-30]. It makes more efficient the electrochemical signal interpretation, as it becomes clearer.

Nevertheless, the use of novel electrode modifiers with novel analytes may be impeded by:

- the indecision concerning the exact mechanism of electrochemical reaction;
- necessity of determination of the parameter region, correspondent to the most efficient active substance and mediating action;
- the presence of electrochemical instabilities, yet described for the CoO(OH) synthesis [31-32].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the chlorantraniliprole electrochemical determination. Moreover, it is also capable compare the behavior of this system with that for the similar ones without any experimental essay.

So, the goal of this work is the mechanistic theoretic analysis of the chlorantraniliprole electrochemical determination, assisted by Squaraine dye – nano CuS composite. In order to achieve it, we realize the specific goals:

- suggestion of the mechanism of the reaction consequence, leading to the appearance of analytical signal;
- development of the balance equation mathematical model, correspondent to the electroanalytical system;
- analysis and interpretation of the model in terms of the electroanalytical use of the system;
- the seek for the possibility of electrochemical instabilities and for the factor, causing them;
- the comparison of the mentioned system´s behavior with the similar ones [33 – 35].

In the work [34], the electrochemical determination of chlorantraniliprole over a squaraine dye composite with silver (I, III) oxide has been given, and the conclusion about its efficiency in electroanalytical process has been made. As for copper sulfide, its oxidation yields trivalent copper sulfohydroxide, somehow more aggressive oxidant, capable to add one more oxidation scenario, compared to the work [34]. The presence of three oxidation scenarios instead of two makes the electrochemical instabilities more probable, as in similar processes [33-35] and this will be shown below.

2. Material and Methods

The composite may be yielded by copper sulfide chemical or electrochemical deposition on a squaraine dye. The nanoparticles' structure, arrangement and shape will depend on a dye chosen and on the synthesis conditions [22].

As chlorantraniliprole contains two pyridinic nitrogen atoms, strong oxidants act on them, yielding N-oxides. As the trivalent copper is highly energetic, it is capable to phenolize the benzolic ring with its subsequent transformation into a quinonic moiety (1-2):

$$CuS + OH^- - e^- \rightarrow CuS(OH) \qquad (1)$$

$$(2)$$
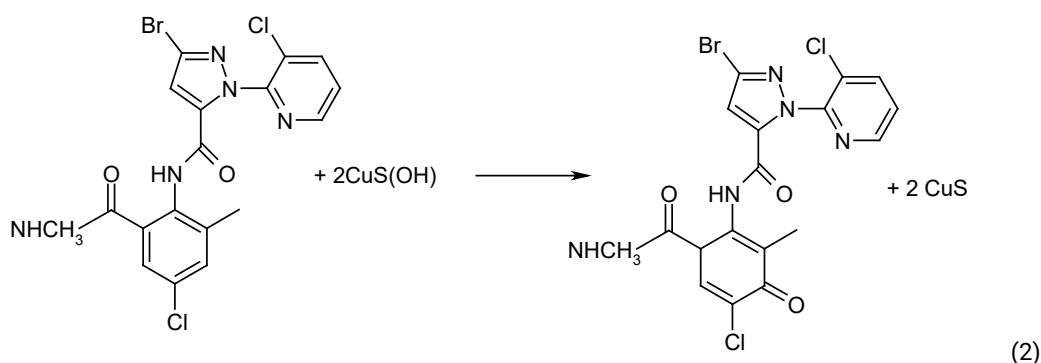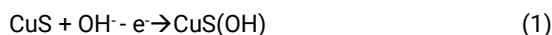
The *N*-oxidation of pyridinic ring is also possible, as a parallel scenario either for the pyridinic derivative, or for its quinonized form. Therefore, in order to describe the behavior of the electrochemical determination of chlorantraniliprole on the CuS-Squaraine dye modified electrode, we introduce three variables:

c – chlorantraniliprole concentration in the pre-surface layer;

q – quinonicform concentration in the pre-surface layer;

s – copper sulfide surface coverage degree.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we assume that the background electrolyte is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ, and the concentration profile in it is supposed to be linear. Also, we assume that, in the synthesis conditions, the quinonic low-molecular oxidation product, while formed, diffuses off the pre-surface layer. The mathematical model will be thereby analyzed by the method, mentioned in [36].

It is possible to show that the system´s behavior will be described by balance equation set as following (3):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_q - r_{N1}\right) \\ \frac{dq}{dt} = \frac{2}{\delta}\left(r_q - r_{N2}\right) \\ \frac{ds}{dt} = \frac{1}{S}\left(r_q + r_{N1} + r_{N2} - r_1\right) \end{cases} \qquad (3)$$

Here, Δ is the diffusion coefficient, S is the maximal CuS matrix surface coverage degree, and the parameters r are the correspondent reaction rates, which may be described as (4-7):

$$r_q = k_q c(1 - s)^2 \qquad (4)$$

$$r_{N1} = k_{N1} c(1 - s)^2 \qquad (5)$$

$$r_{N2} = k_{N2} q(1 - s)^2 \qquad (6)$$

$$r_1 = k_1 s \exp\left(\frac{F\varphi_0}{RT}\right) \qquad (7)$$

in which the parameters k are rate constants of the reactions, F is the Faraday number, φ_0 is the potential slope in DEL, relative to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature.

In acidic media, the pyridinic nitrogen atoms would be protonated, causing strong impact on double electric layer (DEL). But in neutral and basic media, this impact won't be realized. Therefore, the behavior of this system will be more stable and less dynamic, as shown in the next section.

3. Results and Discussion

In order to investigate theoretically the electroanalytical determination of chlorantraniliprole, assisted by squaraine dye – CuS composite, we analyze the equation-set (3) and algebraic relations (4-7) by means of linear stability theory. The steady-state Jacobian matrix members will be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \qquad (8)$$

in which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_q(1 - s)^2 - k_{N1}(1 - s)^2\right) \quad (9)$$

$$a_{12} = 0 \quad (10)$$

$$a_{13} = \frac{2}{\delta}\left(2k_q c(1 - s) + 2k_{N1}(1 - s)\right) \quad (11)$$

$$a_{21} = \frac{2}{\delta}\left(k_q(1-s)^2\right) \quad (12)$$

$$a_{22} = \frac{2}{\delta}\left(-k_{N2}(1-s)^2\right) \quad (13)$$

$$a_{23} = \frac{2}{\delta}\left(-2k_q c(1-s) + 2k_{N2}q(1-s)\right) \quad (14)$$

$$a_{31} = \frac{1}{S}\left(k_q(1-s)^2 + k_{N1}(1-s)^2\right) \quad (15)$$

$$a_{32} = \frac{1}{S}\left(k_{N2}(1-s)^2\right) \quad (16)$$

$$a_{33} = \frac{1}{S}\left(-2k_q c(1-s) - 2k_{N2}q(1-s) - 2k_{N1}(1-s) - k_1\exp\left(\frac{F\varphi_0}{RT}\right) - jk_1 s\exp\left(\frac{F\varphi_0}{RT}\right)\right) \quad (17)$$

As in the similar systems [33-35], the oscillatory behavior is possible in this system. Nevertheless, as on the chemical stages no ionic compounds formation, destruction and transformation occurs (in basic media), the unique factor responsible for the oscillatory behavior is the influence of the electrochemical stage on double electric layer capacitance and conductivity. It is described by the positivity of the element $jk_1 s\exp\left(\frac{F\varphi_0}{RT}\right) > 0$ if j<0. The oscillations are expected to be frequent and of small amplitude.

In order to investigate the steady-state stability, we apply the Routh-Hurwitz criterion to the equation-set (3). Avoiding cumbersome expressions, we introduce new variables and rewrite the determinant as (18):

$$\frac{4}{\delta^2 S}\begin{vmatrix} -\kappa - \varXi - \varLambda & 0 & \varSigma \\ \varXi & -T & P - \varSigma \\ \varXi + \varLambda & T & -\varSigma - P - \varOmega \end{vmatrix} \quad (18)$$

Opening the brackets and applying the Det J<0 requirement, salient from the criterion, we obtain the steady-state stability requirement, exposed as (19):

$$\varSigma(2\varXi + \varLambda) - (\kappa + \varXi + \varLambda)(2\varSigma + \varOmega) < 0 \quad (19)$$

As the second expression in the majority of parameter values, has more negative values than the first, the left part of the inequation (19) will be easily shifted to more negative values. Thus, this inequation describes an electroanalytically efficient diffusion and kinetically controlled electroanalytical system.

As in this case, there are no reactions, capable to compromise the analyte and modifier stability, the steady-state stability is correspondent to the linear dependence between the chlorantraniliprole concentration and the current (in this system, we describe the amperometric sensor), which is therefore observed in vast measure of the concentrations.

The detection limit is relatively low (in micro or nanomolar range, depending on the electrode shape and analysis conditions) and it is correspondent to the margin between the stable steady-states and unstable states. This margin is defined by the monotonic instability, described by the condition of Det J = 0, or:

$$\varSigma(2\varXi + \varLambda) - (\kappa + \varXi + \varLambda)(2\varSigma + \varOmega) = 0 \quad (20)$$

If the squaraine dye is substituted by a conducting polymer without pyridinic nitrogen atoms or other complex forming groups, the model will be the same. Yet if the conducting polymer contains them, the double electric layer and surface conductivity will be more effective on the chemical stage, thus the model will be transformed as analogous to [33-35]

4. Conclusions

From the analysis of the system with the chlorantraniliprole electrochemical determination as an anodic process, assisted by CuS – Squaraine Dye composite it is possible to conclude that:

- The system's behavior is less dynamic, while compared to the similar systems in acid media, due to the less intense influence of the process of double electric layer conductivity and capacitance.

- The electroanalytical process tends to be either kinetically or diffusion controlled with the easy realization of linear dependence between the concentration and the current.

- The oscillatory behavior tends to have less probability to be realized, compared with the acid media, due to the impossibility of DEL influence of the electrochemical stage.

Author Contributions

Volodymyr V. Tkach (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Marta V. Kushnir (Data Curation, Conceptualization, Investigation); Sílvio C. de Oliveira (Conceptualization, Investigation, Supervision, Formal Analysis), Hanifa Zh. Salomova (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Dilafruz B. Razhabova (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Dilfuza M. Musayeva (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Laziz N. Niyazov (Conceptualization, Investigation, Data Curation, Methodology, Validation, Visualization, Formal Analysis), Yana G. Ivanushko (Conceptualization, Investigation, Supervision, Formal Analysis), Oleksandra V. Ahafonova (Conceptualization, Investigation, Formal Analysis), Mariia P. Mytchenok (Conceptualization, Investigation, Formal Analysis), Bohdana Yu. Banul (Conceptualization, Investigation, Formal Analysis), Tetiana P. Honchar (Conceptualization, Investigation, Formal Analysis), Petro I. Yagodynets´ (Investigation, Conceptualization, Methodology, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing), Zholt O. Kormosh (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing), Lucinda Vaz dos Reis (Data Curation, Conceptualization, Investigation); Konon L. Bagrii (Data

Curation, Conceptualization, Investigation), Lyubov T. Strutynska (Data Curation, Conceptualization, Investigation), Inna P. Danyliuk (Data Curation, Conceptualization, Investigation), Nataliia M. Gordiyenko (Investigation, Conceptualization, Supervision, Validation, Writing − Original Draft, Writing − Review and Editing), Yulia V. Britsyna (Investigation, Conceptualization, Supervision, Validation, Writing − Original Draft, Writing − Review and Editing), Maryna M. Parkhomenko (Data Curation, Conceptualization, Investigation), Mariia M. Levon (Data Curation, Conceptualization, Investigation)

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