

Full Paper

The Theoretical Evaluation for the Possibility of Electrochemical Pyriproxyfen Detection in Water

Volodymyr V. Tkach,^{1,2,*} Sílvio C. de Oliveira,² Reza Ojani,³ Virgínia S. Neves,⁴ Michel O. Galeano Espínola⁵ and Petro I. Yagodynets¹

¹*Chernivtsi National University, 58012, Kotsyubyns'ky Str., 2, Chernivtsi, Ukraine*

²*Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil*

³*University of Mazandaran, 47416-95447, 3rd km. Air Force Road, Babolsar, Islamic Republic of Iran*

⁴*Instituto Federal de Educação, Ciência e Tecnologia da Bahia, 40301-015, Rua Emídio dos Santos, S/N, Barbalho, Salvador, BA, Brazil*

⁵*Universidad Nacional de Asunción, Facultad de Ciencias Químicas, 10,5 km. Ruta Mcal. Estigarribia, 1900, San Lorenzo, Distrito Capital, Paraguay*

*Corresponding Author, Tel.:+5521991809675

E-Mail: Nightwatcher2401@gmail.com

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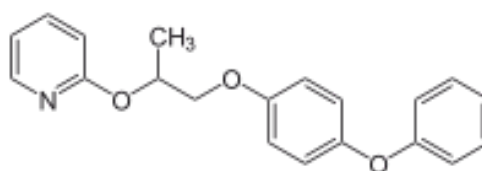
Abstract- The possibility of pyriproxyfen electrochemical detection in water (in neutral, or alkaline pH conditions) has been studied. During the analysis, pyriproxyfen is transformed in a yet studied quinone-hydroquinonic system before the electrochemical reaction. By means of mathematical model development and analysis, using the linear stability theory and bifurcation analysis, the analytical efficiency conditions have been detected, including the optimal pH and potential range. The oscillatory and monotonic instability conditions have also been detected. These instabilities may be caused by double electric layer influences of the electrochemical reaction. The analysis may be driven in the presence of different organic, hybrid and inorganic modifiers. Nevertheless, the specific conditions for electrode modifying material stability are required for the electrochemical analysis of pyriproxyfen.

Keywords- Pyriproxyfen, Electrochemical detection, Quinone-hydroquinonic electrochemical system, Mathematical modeling, Stable steady-state

1. INTRODUCTION

The neglected tropical diseases combat has always been of the priorities of the actual medicine [1]. Besides of new treatment methodologies it includes preventive actions [2], like vaccination, hygienization of tropical countries (in its majority, of low, or unequal development) and sterilization of host species. For example, the combat of *Aedes Aegypti* has been enhanced in Brazil, Colombia, Mexico and other Latin America countries, as a prevention action, realized, due to the epidemic outbreak of the Dengue, Chikungunya and, especially, Zika fevers [3], accompanied by the growth of microcephaly cases. The viruses of the mentioned diseases are capable to be transmitted by this mosquito and its sterilizing actual not only for the mentioned countries, but also for other tropical and subequatorial countries, including African, Asian and Oceanian countries.

One of the insecticides and larvicides, used to combat the transmitting type of mosquitoes is pyriproxyfen [4], approved in the US in 2001 and introduced in Brazil in 2014. It is a pyridinic derivative with the formula, represented below (Scheme 1):



Scheme 1. Pyriproxyfen chemical structure

Despite of the declarations, made by the Ministry of Health of Brazil and World Health Organization [5], relating the microcephaly cases exclusively to Zika fever, this hypothesis isn't completely evident [6], and the pyriproxyfen toxicity seems to be a valid alternative (or collaborating) factor. For this and other reasons, the development of an analytical technique, capable to detect its concentration is a really actual task [7] and the use of electrochemical methods, yet used for the detection and degradation some other pesticides [8–9], may be an interesting solution for it.

Despite of the absence (by far) of publication, describing concretely the electrochemical detection of pyriproxyfen, it's possible (due to the analyte chemical structure) to relate it to one of yet studied electrochemical processes – quinone-hydroquinonic electron transfer. Many electroanalytical techniques were used for it and many electrode modifiers were employed, like specific molybdenic acid ester [10], ionic liquid [11], cobalt oxy-hydroxide [12], conducting polymers [13–16] and even banana tissue [17]. On the other hand, the proper quinonic system has been used as a modifier for the detection of sulphite [18] and hydrazine [19]. In [20], both analyte and modifier were quinonic systems, being the modifier a conducting polymer (polyalizarine). Thus, the use of quinone-hydroquinonic oxidative-

reductive pair seems to be a way to viabilize the piriproxyfen detection by electrochemical way.

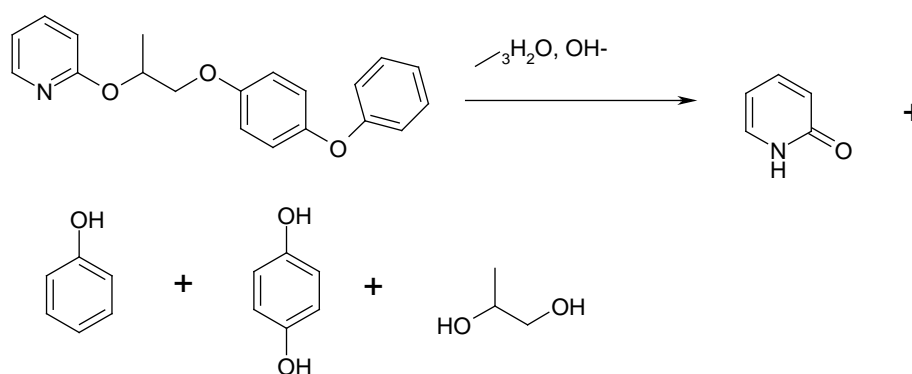
One of the ways to predict, by theoretical means, the behavior of a system, that hasn't been investigated by experimental way, is the mathematical modeling, or better, the analysis of the model, capable to describe adequately the system. It also permits to judge of its most probable reaction mechanism, detect the possibility of electrochemical instabilities and steady-state stability condition and compare its behavior with that of other systems without any experimental essay.

So, the general objective of this work is to investigate, by theoretical means, the possibility of electrochemical detection of pyriproxyfen in water. Its realization will require the reaching of specific objectives, like:

- developing the mathematical model;
- its analysis by means of linear stability theory;
- steady-state stability analysis, including the analysis of steady-state electroanalytical efficiency;
- oscillatory and monotonic instabilities' probability detection
- Comparison of the system's behavior with that of analogous systems [21–28].

2. SYSTEM AND ITS MODELING

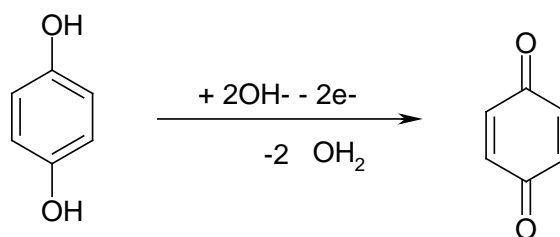
Being an aromatic ether, piriproxyfen may be hydrolyzed in alkaline solution, forming α -pyridone, hydroquinone, phenol and a glycol, according to the Scheme 2:



Scheme 2. Piriproxyfen hydrolysis in the alkaline solution

Due to the presence of two hydroxyl groups, conjugated with an aromatic system, hydroquinone, and especially its anion, will have the lowest oxidation potential, compared to other hydrolysis products. This is caused by higher level of mesomeric effect, than in the case of other mentioned compounds.

Hydroquinone, formed by hydrolysis, is, thus, transformed into its quinonic form (Scheme 3):



Scheme 3. Hydroquinone electrooxidation

When the electrode is chemically modified, the oxidation process is mediated and more complex, being described, conditionally, as reaction 1 and 2:



And it is pH-dependent.

In some conditions, due to anodic overpotential, phenolic compounds may be oxidized in the same potential range as hydroquinonic, so it is strongly recommended to use materials, capable to discern their oxidation peaks (e.g. the modifiers, used in [10-17] and [20]). Moreover, in this case the modifier may be stable to relatively high temperatures and slightly or moderately alkaline pH.

Taking in account the above reactions, and the electrode modifier, we describe mathematically the electrochemical oxidation process. So we introduce three variables:

c_1 – the pesticide pre-surface layer concentration;

c_2 – the hydroquinone pre-surface layer concentration;

θ – the modifier reduced form surface concentration.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte (a salt of an alkaline metal with some addition of alkali, or a weak-acid salt of an alkaline metal) is in excess, so we can neglect the migration flow. The pre-surface layer thickness is assumed to be constant, equal to δ , and the concentration profile of the analyte and the alkali, to be linear. The pesticide enters the layer, by means of its diffusion and is hydrolyzed, according to the Scheme 2. Thus, its balance equation will be rewritten as:

$$\frac{dc_1}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_1 \right) \quad (1)$$

In which Δ is its diffusion coefficient, c_0 , its bulk concentration and r_1 its hydrolysis rate. The hydroquinone appears during the pesticide hydrolysis, and, theoretically, the quantitative relation of their concentrations is 1:1. Then, it reacts with the electrode modifying substance. So, its balance equation will be rewritten as:

$$\frac{dc_2}{dt} = \frac{2}{\delta} (r_1 - r_3) \quad (2)$$

In which r_3 is the rate of the reaction (1).

The modifier is reduced, while oxidizing the hydroquinone. Its oxidized form is regenerated by electrochemical way. In this case, the balance equation for the surface concentration of the reduced form may be described as:

$$\frac{d\theta}{dt} = \frac{1}{\Gamma}(r_3 - r_4) \quad (3)$$

In which Γ is the modifier maximal surface concentration and r_4 is the rate of the reaction (2).

The correspondent reaction rates may be calculated as:

$$r_1 = k_1 c_1 \quad (4)$$

$$r_3 = k_3 c_2 (1 - \theta) \quad (5)$$

$$r_4 = k_4 \theta \exp\left(\frac{2F\phi_0}{RT}\right) \quad (6)$$

in which the parameters k are corresponding reaction rate constants, 2 is the number of electrons, transferred during a quinone-hydroquinonic transformation, $F=N_A \cdot e$ is a Faraday number, ϕ_0 is the potential slope, related to zero-charge potential, R is the universal gas constant and T is absolute temperature.

As it may be seen from the model, the behavior of the system has to be similar to the observed in [21–28]. The common and different features of the mentioned systems will be discussed below.

3. RESULTS AND DISCUSSION

To investigate the behavior of the system with the electrochemical detection of piriproxyfen *via* its alkaline-assisted hydrolysis, we investigate the equation set (1–3), taking in account the algebraic relations (4–6), by means of linear stability theory. The steady-state Jacobian functional matrix elements for this equation set may be calculated as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (7)$$

In which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - k_1 \right) \quad (8)$$

$$a_{12} = 0 \quad (9)$$

$$a_{13} = 0 \quad (10)$$

$$a_{21} = \frac{2}{\delta} k_1 \quad (11)$$

$$a_{22} = \frac{2}{\delta} (-k_2 (1 - \theta)) \quad (12)$$

$$a_{23} = \frac{2}{\delta} (k_2 c_2) \quad (13)$$

$$a_{31} = 0 \quad (14)$$

$$a_{32} = \frac{1}{F}(k_2(1 - \theta)) \quad (15)$$

$$a_{33} = \frac{1}{F}\left(-k_2c_2 - k_4 \exp\left(\frac{2F\varphi_0}{RT}\right) - jk_4\theta \exp\left(\frac{2F\varphi_0}{RT}\right)\right) \quad (16)$$

In which, the parameter j describes the influence of the electrochemical oxidation on the double electric layer (DEL).

In general features, this system resembles the yet described isomerization sensor [21]. But there are principal differences between two reactions, because isomerization is, generally, a slow process (even catalyzed), and the phenol ether alkaline hydrolysis may be slightly accelerated in special conditions (due to stable anion formation). So, their behaviors, besides of common characteristics, will present many different features.

Similarly to [21–28], *the oscillatory behavior* for this system is possible and it will be caused uniquely by influences of electrochemical oxidation on DEL capacitances, described by the positivity of main-diagonal element $-jk_4\theta \exp\left(\frac{2F\varphi_0}{RT}\right)$ (positive main-diagonal elements describe the positive callback).

These influences (and also, the oscillations' amplitude and frequency) will depend not only of the solution content and ionic force (made "stronger" by the presence of phenoxyde ions), but also on modifying material and its doping degree, like observed in analogous systems [29–35].

When the modifying material's behavior is oscillatory, due to its instability in strongly alkaline media (see [27] and [28] and [35] for $\text{CoO}(\text{OH})$), this factor may define the oscillatory behavior too.

The steady-state stability analysis, made by Routh-Hurwitz criterion is applied for this system. Applying this criterion and the $\text{Det } J < 0$ condition, surging of it, it's possible to obtain the steady-state stability requirement, expressed as:

$$\frac{4}{F\delta^2} K_1(k_2W(1 - \theta)) < 0 \quad (17)$$

In which $K_1 = -\frac{4}{\delta} - k_1$ is al and the parameter $W = k_4 \exp\left(\frac{2F\varphi_0}{RT}\right) + jk_4\theta \exp\left(\frac{2F\varphi_0}{RT}\right)$ may be positive, or negative, depending of the value of the parameter j . If it is positive, which occurs in the case of the absence, or fragility of oxidation effects in DEL capacitances, the left side of the inequation is always negative and the steady-state stability is warranted.

If $k_1 > \frac{4}{\delta}$, which is characteristic for relatively alkaline systems in high temperature, the reaction is diffusion-controlled. Yet, when pH is relatively closer to neutral, the hydrolysis may be relatively slow reaction and the process may be reaction-controlled.

In both cases K_1 will have high-module negative values and, case W is positive, the steady-state is stable and analytically efficient. So, to provide the analytical efficiency it is strongly recommended to use materials, resistant to high temperature and moderate and high alkaline

concentrations (examples: conducting polymers, carbon materials, CoO(OH) in moderately alkaline solutions, TiO₂ in moderately alkaline solutions, hybrid materials).

It is possible to join the most favorable analytical conditions in the table

Table 1. The most efficient electroanalytical conditions for piriproxyfen

Temperature	Alkalinity	Diffusion	Hydrolysis	Mediator
Low	High	Slow	Relatively slow, especially in high analyte concentrations	Stable
High	Moderate	Rapid	Relatively rapid	Stable, with some restrictions, concerning its use in very high pH conditions
High	High	Rapid	Very rapid	Material stability required

If the kinetic effect of electrochemical reaction is equal to its capacitance effect, the parameter W will be equal to zero, and the Jacobian determinant will be equal to nil. So, the *monotonic instability* will be realized.

Its condition, for this system, may be rewritten as: $j\theta = -1$.

Analysis in neutral media is possible, but, in this case, the hydrolysis is the part of solution pre-treatment. So, the detection will be indirect.

4. CONCLUSIONS

From the theoretical analysis of the problem of piriproxyfen electrochemical detection, it is possible to conclude that:

- The electrochemical analytic technique to detect piriproxyfen is capable to be realized, preferably in alkaline solutions and enhanced temperature, which requires the use of special electrochemical electrode modifiers.
- The modifier has to be stable, according to working pH solution.
- The oscillatory behavior in the system is possible and may be caused by influences of electrochemical oxidation in DEL. If the material is unstable in highly alkaline solution, its dissolution will also influence the oscillatory behavior.
- The steady-state stability is warranted by absences of the influences of electrochemical oxidation in DEL. The reaction will be diffusion-controlled, or reaction controlled, depending on pH, temperature and pesticide concentration.

- The monotonic instability for this system is possible and may be caused by the equality of the kinetic effect of electrochemical reaction to its capacitance effect.

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