



The Theoretical Evaluation for the Possibility of the CoO(OH)-Assisted Electrochemical Detection in Water

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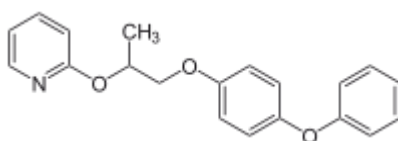
Abstract

The possibility of pyriproxyfen electrochemical detection in water (in neutral, or alkaline pH conditions), assisted by CoO(OH), has been studied. By means of mathematical model development and analysis, using the linear stability theory and bifurcation analysis, the analytical efficiency conditions have been detected. The oscillatory and monotonic instability conditions have also been detected.

Keywords: Intoxication prevention, Pyriproxyfen, Electrochemical detection, Cobalt (III) Oxyhydroxide, Mathematical modeling, Stable steady-state.

1. Introduction

The neglected tropical diseases combat is one of the priorities of the actual medical science [1], including new treatment methodologies and preventive actions [2], like vaccination, hygienization of tropical countries (mostly of low or unequal development) and the treatment of host species and transmitters. For example, the combat to *Aedes Aegypti* mosquito 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 the number of the cases of microcephaly and other diseases. The viruses of the mentioned diseases are capable to be transmitted by this mosquito, and *Aedes Aegypti* combat is 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:



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, due its chemical composition, analogous to that of other pesticides, causing microcephaly. Other statement valid for it is that not only the proper pesticide, but also its metabolites may be responsible for microcephaly. The authors of [6] have also alleged that Brazil, with the maximum of microcephaly cases, was the only country to use pyriproxyfen in drinking water.

Thus, 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 employing chemically modified electrodes, yet used for the detection and degradation some other pesticides [8 – 9], may be an interesting solution for it.

So far, the possibility of piriproxyfen electrochemical determination was only analyzed by theoretical means in [10], waiting for experimental approval. According to [10], the analysis is preferable to be realized in neutral or alkaline media, and the cobalt (III) oxyhydroxide, a p-type semiconductor, yet used in the detection of the similar compounds [11 – 12], may be also used in such analysis.

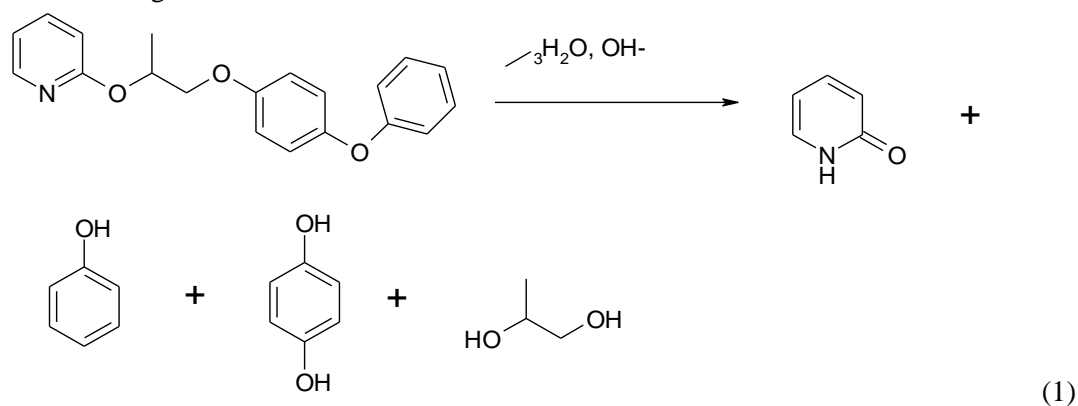
One of the ways to predict, by theoretical means, the behavior of a system, that hasn't been investigated by experimental way, is the mathematical modeling. It also permits to judge of its most probable reaction mechanism, detect the possibility of electrochemical instabilities and steady-state stability 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 CoO(OH)-assisted 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 [13 - 14].

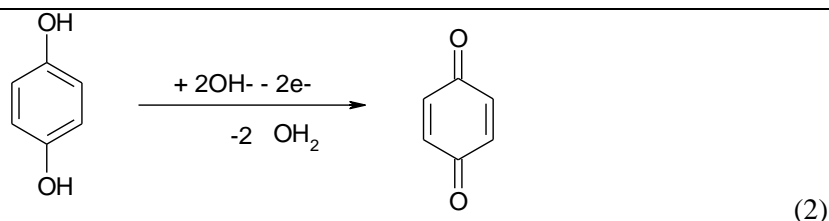
2. System and its modeling

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

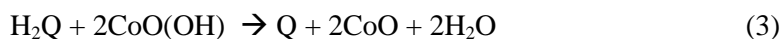


Due to the presence of two hydroxyl groups, conjugated with an aromatic system, hydroquinone, and especially its anion, will have the lowest oxidation potential, compared to other hydrolysis products. This is caused by higher level of mesomeric effect, than in the case of other mentioned compounds.

Hydroquinone, formed by hydrolysis, is, thus, transformed into its quinonic form:



CoO(OH) may be used for phenolic and hydroquinonic compounds [11, 14]. In this case, the reaction mechanism may be described as:



and it is pH-dependent.

Taking in account the equations the electrode modifier and the supposing the constant alkali concentration, we describe mathematically the electrochemical oxidation process, introducing three variables:

c_1 – the pesticide pre-surface layer concentration;

c_2 – the hydroquinone pre-surface layer concentration;

θ – the CoO 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 equation (1). Thus, its balance equation will be rewritten as:

$$\frac{dc_1}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_1 \right) \tag{5}$$

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:

$$\frac{dc_2}{dt} = \frac{2}{\delta} (r_1 - r_3) \tag{6}$$

In which r_3 is the rate of the reaction (3).

CoO is formed, while CoO(OH) is 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:

$$\frac{d\theta}{dt} = \frac{1}{\Gamma} (r_3 - r_4) \tag{7},$$

In which Γ is the modifier maximal surface concentration and r_4 is the rate of the reaction (4).

The correspondent reaction rates may be calculated as:"

$$r_1 = k_1 c_1 \tag{8}$$

$$r_3 = k_3 c_2 (1 - \theta) \tag{9}$$

$$r_4 = k_4 \theta \exp\left(\frac{2F\phi_0}{RT}\right) \tag{10}$$

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 [13 – 14]. 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 $\text{CoO}(\text{OH})$ -assisted electrochemical detection of piriproxyfen *via* its alkaline-assisted hydrolysis, we investigate the equation set (5 – 7), taking in account the algebraic relations (8 – 10), by means of linear stability theory. The steady-state Jacobian functional matrix elements for this equation set may be calculated as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{11}$$

In which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - k_1 \right) \tag{12}$$

$$a_{12} = 0 \tag{13}$$

$$a_{13} = 0 \tag{14}$$

$$a_{21} = \frac{2}{\delta} k_1 \tag{15}$$

$$a_{22} = \frac{2}{\delta} \left(-k_2(1 - \theta) \right) \tag{16}$$

$$a_{23} = \frac{2}{\delta} (k_2 c_2) \tag{17}$$

$$a_{31} = 0 \tag{18}$$

$$a_{32} = \frac{1}{\Gamma} (k_2(1 - \theta)) \tag{19}$$

$$a_{33} = \frac{1}{\Gamma} \left(-k_2 c_2 - k_4 \exp\left(\frac{2F \varphi_0}{RT}\right) - j k_4 \theta \exp\left(\frac{2F \varphi_0}{RT}\right) \right) \tag{20}$$

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

Similarly to [13 – 14], *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 $-j k_4 \theta \exp\left(\frac{2F \varphi_0}{RT}\right)$ (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 [13 -14].

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:

$$\frac{4}{\Gamma \delta^2} K_1 (k_2 W (1 - \theta)) < 0 \tag{21}$$

in which $K_1 = -\frac{\Delta}{\delta} - k_1$ is always negative and the parameter $W = k_4 \exp\left(\frac{2F \varphi_0}{RT}\right) + j k_4 \theta \exp\left(\frac{2F \varphi_0}{RT}\right)$ 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. This condition is satisfied for the vast parameter region. From the electroanalytical point of view, it is correspondent to the linear dependence between electrochemical parameter and concentration. So, CoO(OH) may be an excellent modifier for pyriproxyfen electrochemical detection.

If $K_1 > \frac{\Delta}{\delta}$, 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.

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. Conclusion

The theoretical analysis of the possibility of CoO(OH) assisted pyriproxyfen detection let us conclude that:

- The electrochemical analytic technique to detect pyriproxyfen by CoO(OH)-modified electrode is capable to be realized, in lightly alkaline solutions and enhanced temperature.
- The oscillatory behavior in the system is possible and may be caused by influences of electrochemical oxidation in DEL.
- 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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