

*Full Paper*

## **Isoproturon Electrochemical Oxidation as an Electroanalytic and Electrosynthetic System Theoretical Investigation**

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**Abstract-** The electrochemical oxidation of the pesticide isoproturon, followed by electrochemical polymerization of its product has been described from the theoretical point of view. The mathematical model, describing both processes, has been developed and analyzed. The system's behavior is similar to that observed in the processes of gabapentine and paracetamol detection and of so called "polythiophene paradox", and the stable steady-state is maintained easily and rapidly, being efficient either for electroanalytical, or for electrosynthetic process. The possibility of oscillatory and monotonic instabilities was also evaluated.

**Keywords-** Food safety, Intoxication prevention, Isoproturon, Electrochemical sensors, Electropolymerization, Stable steady-state

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### **1. INTRODUCTION**

Isoproturon is a herbicide, belonging to the family of substituted ureic derivatives [1–2]. It is absorbed by roots and leaves of plants and acts as an inhibitor of photosynthesis. In France, it

is one of the fifteen most used herbicides in mild winter cultures [3]. Nevertheless, it is very toxic not only to humans [4–5], but also to mammals, birds and fishes [6–7], and its toxicity mechanism includes the reaction of the products of its oxidation with porphyrinic complexes (chlorophyll, hemoglobin, hemocyanin, cytochromes, etc). The European Commission has authorized its use in the European Union, but has allowed its countries to establish their own norms of use [8]. In France its maximally permitted concentration in water is equal to 61  $\mu\text{g/L}$  [9], yet in the United Kingdom its use is forbidden [10]. In Canada, its reference concentration is limited to 9  $\mu\text{g/L}$  [11]. In Brazil, it is used in different cultures, like pineapple, banana and coffee [12]. So, the development of a method, capable to detect its concentration by rapid, precise, sensitive and exact manner is really actual task [13–14], and the use of electrochemical methods may give it a good service [15–17].

The use of electrochemical methods for pesticides' detection has been realized [18 – 20], and the chemically modified electrodes were employed. The use of these methods had some advantages, like rapidity, sensitivity, precision and affinity to the analyte. Nevertheless, their development and use may encounter some problems, like:

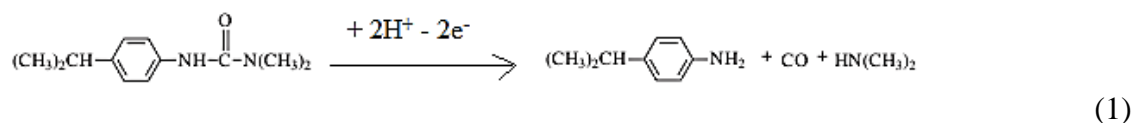
- indecision, concerning the mechanism of analyte and(or) modifier electrochemical behavior;
- appearance of instabilities, like oscillatory and monotonic behavior, characteristic for such systems;
- the possibility of the concurrence of two parallel mechanisms of the electrochemical process, or two successive electrochemical and(or) chemical transformations.

All these problems may be resolved only with the development and analysis of a mathematical model, describing the electroanalytical system. So, the aim of this work is the mechanistic theoretic analysis of the possibility of isoproturon conducting-polymer assisted electrochemical detection. In order to achieve it, we realize the specific goals like:

- suggestion of the mechanism of the electroanalytical 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 role of hybrid mechanism, appearing in the conducting polymer, saturated with radical sites;
- 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.

## 2. SYSTEM AND ITS MODELING

The mechanism of the isoproturon electrochemical oxidation includes the transfer of two electrons and two protonic attacks, leading to *p*-isopropylaniline formation.



The oxidation product is then electropolymerized, and the presence of polypyrrole favors it [17]. The electropolymerization is realized by classic Díaz mechanism, and the monomer units may be linked either in the positions 2 and 6, or via amino group. So, in this system in fact, an electropolymerization of electrochemically synthesized monomer is realized, and its behavior will resemble that characteristic for gabapentine electrochemical oxidation [21–22], classical electropolymerization systems [23–26] and the systems with polythiophene paradox [27–28].

To describe its behavior, we use three variables:

$c$  – the pesticide concentration in the pre-surface layer;

$\theta$  – the pesticide coverage degree;

$\mu$  – the monomer 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  $\delta$ .

It is possible to show that the system may be described by three typical balance equations as following:

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left( \frac{\Delta}{\delta} (c_0 - c) + r_{-1} - r_1 \right) \\ \frac{d\theta}{dt} = \frac{1}{G} (r_1 - r_{-1} - r_2) \\ \frac{d\mu}{dt} = \frac{1}{M} (r_2 - r_3) \end{cases} \quad (2)$$

In which  $\Delta$  is the diffusion coefficient,  $c_0$  is the pesticide bulk concentration.  $r_1$ ,  $r_{-1}$ ,  $r_2$  and  $r_3$  are adsorption, desorption, electrooxidation and electropolymerization rates,  $G$  and  $M$  are the pesticide and monomer maximal surface concentrations.

The process rates may be described as:

$$r_1 = k_1 (1 - \theta - \mu) c \exp(\alpha\theta) \quad (3)$$

$$r_{-1} = k_{-1} \theta \exp(-\alpha\theta) \quad (4)$$

$$r_2 = k_2 \theta \exp\left(\frac{F\phi_0}{RT}\right) \quad (5)$$

$$r_3 = k_3 \mu^x \exp\left(\frac{nF\phi_0}{RT}\right) \quad (6)$$

In which the parameters  $k$  stand for corresponding rate constants,  $\alpha$  is a parameter, describing the pesticide particles' interaction,  $F$  is Faraday number,  $\phi_0$  is the potential slope in double electric layer (DEL), related to zero-charge potential,  $R$  is the universal gas constant and  $T$  is absolute temperature and  $x$  is the monomer polymerization reaction order.

In general features, this model is correspondent to the classic case of two successive electrochemical reactions, and its application in the case of isoproturon will be discussed below.

### 3. RESULTS AND DISCUSSION

To investigate the behavior of the system with electrochemical oxidation of isoproturon, followed by electropolymerization of its product, we analyze the equation set (2) by means of the linear stability theory and bifurcation analysis. The Jacobi functional matrix, the members of which are calculated for the steady-state, may be described as:

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

in which:

$$a_{11} = \frac{2}{\delta} \left( -\frac{\Delta}{\delta} (c_0 - c) - k_1 (1 - \theta - \mu) \exp(\alpha\theta) \right) \quad (8)$$

$$a_{12} = \frac{2}{\delta} (k_1 c \exp(\alpha\theta) - \alpha k_1 c (1 - \theta - \mu) \exp(\alpha\theta) + k_{-1} \exp(-\alpha\theta) - \alpha k_{-1} \theta \exp(-\alpha\theta)) \quad (9)$$

$$a_{13} = \frac{2}{\delta} (k_1 c \exp(\alpha\theta)) \quad (10)$$

$$a_{21} = \frac{1}{G} (k_1 (1 - \theta - \mu) \exp(\alpha\theta)) \quad (11)$$

$$a_{22} = \frac{1}{G} \left( -k_1 c \exp(\alpha\theta) + \alpha k_1 c (1 - \theta - \mu) \exp(\alpha\theta) - k_{-1} \exp(-\alpha\theta) + \alpha k_{-1} \theta \exp(-\alpha\theta) - k_2 \exp\left(\frac{F\phi_0}{RT}\right) + j k_2 \theta \exp\left(\frac{F\phi_0}{RT}\right) \right) \quad (12)$$

$$a_{23} = \frac{1}{G} \left( -k_1 c \exp(\alpha\theta) - h k_2 \theta \exp\left(\frac{F\phi_0}{RT}\right) \right) \quad (13)$$

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

$$a_{32} = \frac{1}{M} \left( k_2 \exp\left(\frac{F\phi_0}{RT}\right) - jk_2\theta \exp\left(\frac{F\phi_0}{RT}\right) - jk_3\mu^x \exp\left(\frac{nF\phi_0}{RT}\right) \right) \quad (15)$$

$$a_{33} = \frac{1}{M} \left( hk_2\theta \exp\left(\frac{F\phi_0}{RT}\right) - xk_3\mu^{x-1} \exp\left(\frac{nF\phi_0}{RT}\right) + hk_3\mu^x \exp\left(\frac{nF\phi_0}{RT}\right) \right) \quad (16)$$

Observing the expressions (8), (12) and (16), it is possible to conclude, that the *oscillatory behavior* for this system is possible, due to the presence of the positive addendums in the main diagonal elements. These addendums are referent to the positive callback.

These elements are similar to those observed in analogous systems [21–28] and define the electrochemical oscillations, caused by surface and DEL instabilities, observed experimentally in [23] and explained theoretically in [24]. The oscillatory behavior is more probable, than in classical electroanalytical systems involving conducting polymers, due to electropolymerization factor [25] and surface influences.

To investigate the *steady-state stability*, we investigate the equation set (2), applying Routh-Hurwitz criterion. We introduce new variables, in order to avoid the cumbersome expressions, so the Jacobian determinant will be rewritten as:

$$\frac{2}{\delta GM} \begin{vmatrix} -\kappa - X & \Lambda & P \\ X & -\Lambda - \Omega & -P - \Delta \\ 0 & \Omega - \xi & \Delta - \xi - \lambda \end{vmatrix} \quad (17)$$

Opening the brackets, we obtain the steady-state stability condition, expressed in the form of:

$$(-\kappa - X)(-\Lambda\Delta + \Lambda\xi + \Lambda\lambda + \Omega\xi + \Omega\lambda - \Omega\Delta - \xi P - \xi\Delta) + X(P\Omega - P\xi - \Omega\Delta + \Lambda\xi + \Lambda\lambda) < 0 \quad (18)$$

**Table 1.** The stable steady-state kinetics of the system

Polymer active surface	Analyte concentration	Controlling Process	Electroanalytical Efficiency	Electrosynthetical Efficiency
Narrow	Low	Diffusion	Yes	Conditioned to the resulting polymer morphology
	High	Adsorption	Yes	Yes.
Wide	Low	Diffusion	Yes	Conditioned to the resulting polymer morphology
	High	Diffusion or adsorption	Yes	Yes

In this case, the steady-state stability is less probable, than in a common case of CP-assisted electrochemical analysis. Nevertheless, as in similar systems [21–28] in the case of the negativity of the parameters  $\Delta$ ,  $\Omega$ ,  $\xi$  and  $\lambda$ , defining the fragile DEL influences of

electrochemical reactions, and the positivity of  $\Lambda$ , defining the surface behavior with repulsion of adsorbed particles, the condition (18) is satisfied.

The stable steady-state is efficient either for electroanalytic (linear dependence between concentration and electrochemical parameter), or for electrosynthetic (the electropolymerization is, kinetically, steady) purposes. Depending on the analyte concentration and the polymer morphology the reaction may be diffusion- or adsorption controlled (See Table 1).

When the impact of surface and electrochemical destabilizing factors is equal to that of the factors stabilizing the system, the *monotonic instability is formed*. It's correspondent to the detection limit, and its condition for this system is:

$$(-\kappa - X)(-\Lambda\Delta + \Lambda\xi + \Lambda\lambda + \Omega\xi + \Omega\lambda - \Omega\Delta - \xi P - \xi\Delta) + X(P\Omega - P\xi - \Omega\Delta + \Lambda\xi + \Lambda\lambda) < 0 \quad (18)$$

When the impact of surface and electrochemical destabilizing factors is equal to that of the factors stabilizing the system, the *monotonic instability is formed*. It's correspondent to the detection limit, and its condition for this system is:

$$(-\kappa - X)(-\Lambda\Delta + \Lambda\xi + \Lambda\lambda + \Omega\xi + \Omega\lambda - \Omega\Delta - \xi P - \xi\Delta) + X(P\Omega - P\xi - \Omega\Delta + \Lambda\xi + \Lambda\lambda) = 0 \quad (19)$$

In this case, the system enters in one of the multiple steady-states, each one is unstable and is destroyed, when the system conditions are changed.

The autocatalytic behavior isn't possible in the electrooxidation process, but is probable in electropolymerization. In this case, the model is modified. The autocatalysis, in this case, is one more cause for the oscillatory behavior.

#### 4. CONCLUSION

The theoretical mechanistic analysis of isoproturon electrochemical oxidation, followed by electropolymerization of its product, let us conclude that:

- The stable steady-state is easy to maintain, and it is efficient either for electroanalytic, or for electrosynthetic purpose. The synthetic efficiency is conditioned to the resulting polymer morphology;
- Depending on the conducting polymer active surface and the analyte concentration, the process may be diffusion- or adsorption controlled. The steady-state stability, despite of being correspondent to less vast parameter region, than for similar systems, is easy to maintain;
- The oscillatory and monotonic instabilities are possible and may be caused by surface and electrochemical instabilities. They are more probable, then for a classic case of electrochemical sensing, due to the presence of surface instabilities and two consequent electrochemical stages influencing to DEL.

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