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Research Paper / Araştırma Makalesi

Mathematical Description for Fipronil Electrochemical Detection Assisted by Cobalt (III) Oxyhydroxide

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ABSTRACT

The possibility of fipronil pesticide electrochemical determination assisted by cobalt (III) oxyhydroxide was determined in this study. The redox pair $CoO(OH)/CoO_2$ was used in this process. The correspondent mathematical model was developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown that the oxyhydroxide may be applied as an efficient electrode modifier in the detection of fipronil in neutral and lightly alkaline media. Electrochemical response was clear and easy to interpret. The possibility of oscillatory and monotonic instabilities was also verified.

Keywords: Intoxication prevention, Fipronil, Cobalt (III) oxyhydroxide, Electrochemical sensors, Stable steady-state

Kobalt (III) Oksihidroksit Yardımıyla Fipronilin Elektrokimyasal Tespiti İçin Matematiksel Açıklama

ÖZ

Bu çalışmada, kobalt (III) oksihidroksit kullanılarak fipronil pestisidinin elektrokimyasal tespit olasılığı belirlenmiştir. Bu işlemde redoks çifti $CoO(OH)/CoO_2$ kullanılmıştır. Karşılık gelen matematiksel model, doğrusal kararlılık teorisi ve bifurkasyon analizi vasıtasıyla geliştirilmiş ve analiz edilmiştir. Oksihidroksidin, nötr ve hafif alkali ortamda fipronilin saptanmasında etkili bir elektrot değiştirici olarak uygulanabileceği gösterilmiştir. Elektrokimyasal cevabın açık ve kolay anlaşılır olduğu belirlenmiştir. Titreşimli ve monotonik istikrarsızlık olasılığı da çalışmada doğrulanmıştır.

Anahtar Kelimeler: Zehirlenme önleme, Fipronil, Kobalt (III) oksihidroksit, Elektrokimyasal sensörler, Kararlı hal

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INTRODUCTION

Fipronil (Figure 1) (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl) pyrazole-3-carbonitrile) is used as a broad-spectrum insecticide, employed to control the population of dangerous insects [1 – 5]. It is also used as drug for treatment and prevention of parasitic infections, generally for veterinary use [2]. Its mechanism of action includes disruption of chloride passage through GABA–mediated channels in nerve cell membranes, resulting in terminal neurologic malfunction. Being an active substance of different commercial formulations like Regent®, Frontline®, Termidor®, 4fleas®, Activo®, Alfamed® among others, it is used against beetles, ticks, seas, termites and other pests and currently registered in more than 70 countries worldwide for the control of insect pests in more than hundred crops like corn, soybean, sugar cane and wheat.

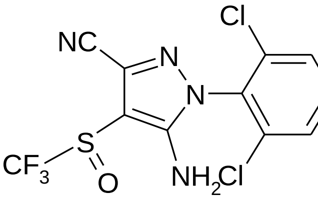


Figure 1. Fipronil's chemical structure

Fipronil is classed by the World Health Organization as Class II moderately hazardous pesticide [6]. Its major metabolite (Figure 2) [7] in vertebrates and invertebrates appears to be fipronil sulfone [8]. On plants and in soils, fipronil undergoes a photoextrusion reaction, yielding a desulfinyl derivative [8]. There have been limited studies of the degradation of fipronil on the surface (skin) of domestic species, particularly dogs and cats. It has been reported that basic conditions (pH > 7) and increased temperatures will induce hydrolysis of fipronil [9], conditions, that may occur on the skin surface of mammals.

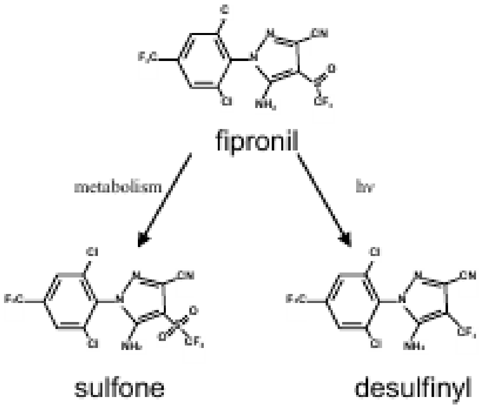


Figure 2. Fipronil metabolism (Reproduced from [7])

The selective toxicity of fipronil therefore depends on the relative rate of conversion to the more persistent and less selective sulfone metabolite and desulfinyl photoproduct [10]). Desulfinyl photoproduct, in particular, has a 10 fold greater selectivity for mammalian GABA chloride channels than the parent compound [8]. No directly applicable data are available on the influence of degradation products on the toxicity of Fipronil applied to target animals.

The intoxication symptoms include sweating, nausea, vomiting, headache, abdominal pain, dizziness, agitation, weakness, and tonic-clonic seizures [11–12]. The U.S. EPA has classified fipronil as a group C (possible human) carcinogen based on an increase in thyroid follicular cell tumors in both sexes of the rat [12].

Its ecotoxicity for crustaceans, insects and zooplankton is very high [13]. Its half-life lasts four months to one year depending on the media. It is relatively stable in water, but it´s not so stable in soil, due to its photolysis. Thus, the development of a precise, exact, rapid and efficient method of its quantification is really actual task [14–16].

For now, two works concerning fipronil electrochemical determination are known, both, authored by Brazilian groups [17–18]. The conditions of the electrooxidation were neutral or lightly alkaline, so cobalt (III) oxyhydroxide, yet used for the detection of the similar compounds [19–20] would be used as an active substance. As fipronil is hard to be oxidized, due to the presence of the acceptor groups (like pyridinic nitrogen heteroatom – CF_3, - $SOCF_3$, - CN) it's more convenient to employ CoO(OH) as a reducent, so the redox pair CoO(OH) – CoO_2 has to be used.

On the other hand, the development of new electroanalytical systems may confront the problems like:

- the indecision in the modifier mechanism of action;
- the compatibility of the modifier with the pharmaceutical tissue or biological object (some modifiers, used *in vitro* may be non-compatible with *in vivo* sensing);
- the presence of electrochemical instabilities, accompanying both electrochemical synthesis of cobalt (III) oxyhydroxide [21], and electrochemical oxidation and electrooxidative polymerization of organic molecules [22-23].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the electroanalytical system. By modeling 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 possibility of fipronil electrochemical quantification, assisted by the cobalt (III) oxyhydroxide. In order to achieve it, specific goals include:

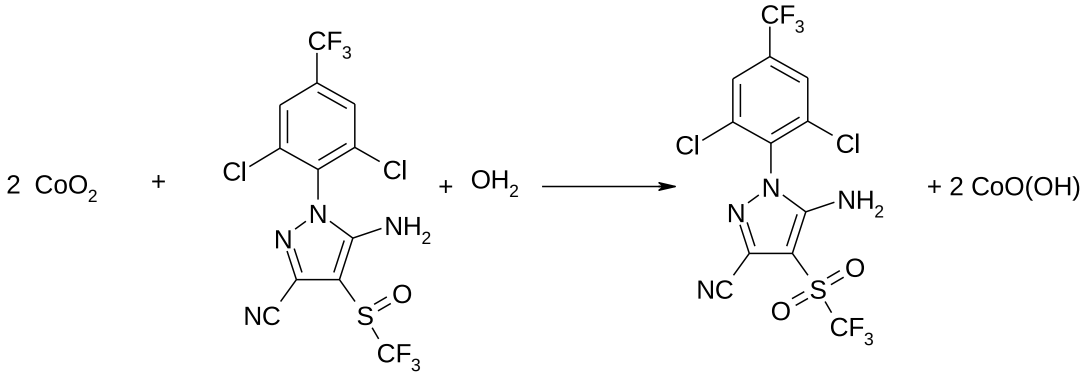
- suggestion of the mechanism of the electroanalytical reaction consequence, leading to the appearance of analytical signal;
- development of the balance equation mathematical model, correspondent to the electroanalytical system;
- analysis and interpretation of the model in terms of the electroanalytical use of the system;
- the 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 [24–28].

SYSTEM and ITS MODELING

As it was mentioned, in this system, CoO(OH) electro-oxidation in alkaline media is used. This process may be described as:

$$CoO(OH) + OH^- - e^- \rightarrow CoO_2 + H_2O \qquad (1)$$

Fipronil is being oxidized by cobalt (IV)oxide in aqueous media, restoring CoO(OH) (2).



(2)

So, in order to describe this system, supposing the excess of alkali, we introduce two variables:

f – fipronil concentration in the pre-surface layer;
θ – CoO(OH) 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.

Fiprponil enters the pre-surface layer by means of its diffusion and reacts with cobalt (IV) oxide. Thus, its balance equation can be rewritten as:

$$\frac{df}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(f_0 - f) - r_1\right) \qquad (3)$$

in which Δ is the diffusion coefficient, f_0 is the fipronil bulk concentration and r_1 is its reaction rate with cobalt (IV) oxide.

Cobalt(III) oxyhydroxide, covering the entire electrode surface at the beginning of the electroanalytical process, is electro-oxidized and restored by reaction of its oxidation product with fipronil. So, its balance equation may be rewritten as:

$$\frac{d\theta}{dt} = \frac{1}{G}(r_1 - r_2) \qquad (4)$$

in which G is CoO(OH) maximal surface concentration, and r_2 its oxidation rate.

The correspondent reaction rates may be described as:

$$r_1 = k_1 f(1-\theta)^2 \qquad (5)$$
$$r_2 = k_2\theta \exp\left(\frac{F\varphi_0}{RT}\right) \qquad (6)$$

In which the parameters k are correspondent reaction rate constants, n is the number of electrons transferred, F is the Faraday number, φ_0 is the DEL potential slope in the double, related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature.

In general, the behavior of this system obeys the classical bivariant model, and its electroanalytical aspects will be discussed below.

RESULTS and DISCUSSION

In order to investigate the behavior of the system with the electrochemical detection of fipronil over cobalt(III)oxyhydroxide, we analyze the equation set (3-4) by means of linear stability theory. The steady-state members of Jacobian functional matrix may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \qquad (7)$$

In which

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_1(1-\theta)^2\right) \qquad (8)$$
$$a_{12} = \frac{2}{\delta}\left(2k_1 f(1-\theta) \quad \right) \qquad (9)$$
$$a_{21} = \frac{1}{G}(k_1(1-\theta)^2) \qquad (10)$$
$$a_{22} = \frac{1}{G}\left(-k_1(1-\theta)^2 - k_2\exp\left(\frac{F\varphi_0}{RT}\right) - jk_2\theta\exp\left(\frac{F\varphi_0}{RT}\right)\right) \qquad (11)$$

In order to avoid the cumbersome expressions, we introduce new variables, so the Jacobian determinant will be rewritten as:

$$\frac{2}{\delta G}\begin{vmatrix} -\kappa - \Xi & \Omega \\ \Xi & -\Omega - \Phi \end{vmatrix} \qquad (12)$$

For the bivariant systems, the conditions of the steady-state stabilities and the principal instabilities may be joined in the table:

Steady-state stability	Tr J<0, Det J>0
Oscillatory instability	Tr J=0, Det J>0
Monotonic instability	Tr J=0, Det J=0

It is possible to show that, *the oscillatory behavior* in this system is possible, as in the similar ones [24–28]. It may be only caused by the DEL influences of the electrooxidation of cobalt oxyhydroxide, described by the positivity of the main diagonal element $-\Phi = -k_2 \exp\left(\frac{F\varphi_0}{RT}\right) - jk_2\theta \exp\left(\frac{F\varphi_0}{RT}\right)$. The general condition for the oscillatory instability for this system is:

$$\begin{cases} \frac{2}{\delta}(-\kappa - \Xi) = \frac{1}{G}(\Omega + \Phi) \\ \kappa\Omega + \Phi + \Xi\Phi > 0 \end{cases} \quad (18)$$

And it may only be realized in the case of the negativity of Φ (as the rest of the parameters may only be positive). The oscillations are expected to be frequent and of small amplitude. Mostly, they are realized beyond the detection limit.

The *steady-state stability* for this system may be described as:

$$\begin{cases} \frac{2}{\delta}(-\kappa - \Xi) - \frac{1}{G}(\Omega + \Phi) < 0 \\ \kappa\Omega + \Phi + \Xi\Phi > 0 \end{cases} \quad (19)$$

and it is warranted to be satisfied, as the only element, capable to be negative is Φ, and its negativity, as it was described above, is linked to the strong influences of the electrochemical stage in DEL. So, if these influences are not so strong, Φ is positive, so the upper inequation left side tends to possess more negative values, and the lower inequation left side tends to possess more positive values, which is correspondent to the steady-state stability.

As there are no side reactions involving the medium, the electroanalytical efficiency of the stable steady-state isn’t compromised, so the steady-state stability is correspondent to the linear dependence between the electrochemical parameter and concentration. The electroanalytical process tends to be diffusion-controlled, and its conditions are similar to those described in [19 – 20].

The *monotonic instability* in this system is possible, being caused by the equality between the stabilizing influences and the destabilizing ones of the electrochemical process influences on DEL. It is correspondent to the detection limit and its condition may be described as:

$$\begin{cases} \frac{2}{\delta}(-\kappa - \Xi) - \frac{1}{G}(\Omega + \Phi) < 0 \\ \kappa\Omega + \Phi + \Xi\Phi = 0 \end{cases} \quad (20)$$

The detection limit may be obtained from this model, if the set (20) is resolved from the point of view of fipronil concentration. It may be found for different media, but the knowledge of reaction constant and DEL parameters´ values is required.

The composite of CoO(OH) with a conducting polymer may be used in this analysis. Nevertheless, the formed CoO_2 may overoxidize chemically some polymers, which may influence strongly the electroanalytic function of the composite. So, it is recommended to use a relatively stable polymer (like polythiophene, formed by the polymerization of bithiophene) or overoxidized polymer. This aspect of this system will be described in our next works.

CONCLUSIONS

From the theoretical investigation of the possibility of the fipronil electrochemical detection, assisted by cobalt(III) oxyhydroxide it is possible to conclude that:

- CoO(OH) may serve as an excellent modifier for fipronil electrochemical determination. The system is electroanalytically efficient, although CoO(OH) is used as a reducent;
- The electroanalytical process tends to be diffusion-controlled;
- The oscillatory behavior in this system is possible, being caused only by DEL influences of the electrochemical process. The amplitude is expected to be small and dependent on the solution composition.

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