Full Paper

The Mathematical Evaluation for the Use of the Conducting Polymers, Saturated with Radical Sites, in Carbendazim Electrochemical Detection

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Abstract- The possibility of use of conducting polymer (CP), saturated by radical growth centers, as an electrode modifier for carbendazim electrochemical detection has been evaluated by mechanistic way. A mechanism of its electrochemical transformation has been suggested and two mathematical models for oxidation and reduction stages were developed and analyzed by means of linear stability theory and bifurcation analysis. It was proved that, despite of the mechanism´s hybrid character, the conducting polymer, saturated with radical sites, may be an excellent electrode modifier for carbendazim electrochemical detection. The possibility of the oscillatory behavior in this system has also been verified, and it may be possible on both radical formation and recombination stages, being caused by surface and electrochemical factors.

1. INTRODUCTION

The growing demand of food has promoted the use of pesticides – substances, capable to prevent or annihilate organisms, undesired in agriculture. [1]. they are bioactive to biological especies, capable to interfere the production, processing, keeping and transport of food [2-3].

Carbendazim (Fig. 1), being a carbamate of benzimidazole, is a fungicide of wide specter of use in different countries, mostly developing. It may be used in Brazil with apples, cereals, cotton, beans, soya and citric fruits with the use limit of 300 g/ha [4]. Nevertheless, it is very toxic to human and mammals [5-7], and its mechanism of toxicity includes the direct testicular action. The European Union has established its residual limit concentration to 100 ppb, yet in the United States its use isn´t approved [8-9].
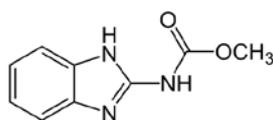
Fig. 1. Carbendazim

The carbendazime is absorbed by plants in roots, seeds and leaves, being transferred, afterwards, to the entire plant. As it is intensively used, it´s become a pollutant, very persistent in soil, in water, wastes and food [10]. So, the developing of a precise, exact, rapid and sensitive method of its detection in different ecological matrixes is an actual task [11-13], and the electrochemical methods, involving chemically modified electrodes, yet used for other substances [14-18], including pesticides like paraquat [17] and diquat [18], seems an interesting solution for it.

Some electrochemical methods for carbendazim electrochemical detection have been developed [19-22]. Usually, they employed carbon materials [19-21] and silicon [22]. On the other hand, the conducting polymers, combining the properties of plastics with metal conductivity and being easy to modify, also have the electroanalytical use [23-25], being also applied to carbendazim [25].

Carbendazim may be acquired either in the general market of chemical products, for example, from Sigma Aldrich, or with producers, like Syngenta, or in the shops, specified in the sell of fertilizers and pesticides. The analysis may also be used to detect carbendazim concentration in different commercial forms

Nevertheless, the main problems that the development of new electroanalytical processes may encounter are:

- Indecision in the most probable mechanism of the analyte oxidation. For example, three probable mechanisms were suggested in [19-21] and in [25] for carbendazime, and all of them may be posed in doubt;

- indecision in the electroanalytical action of the electrode modifier with the analyte and the possibility of hybrid character of its mechanism;
- The possibility for the electrochemical instabilities, capable to accompany the similar systems involving the electrochemical oxidation and reduction of different organic compounds (including electropolymerization) [26-29].

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 carbendazim conducting-polymer assisted electrochemical detection. In order to achieve it, we realize the specific objectives:

- 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 ([30-34]).

2. SECTION I. RADICAL FORMATION. SYSTEM AND ITS MODELING

For carbendazim electrooxidation, there are different mechanisms, but the most related and most probable is the exposed below:

(1)
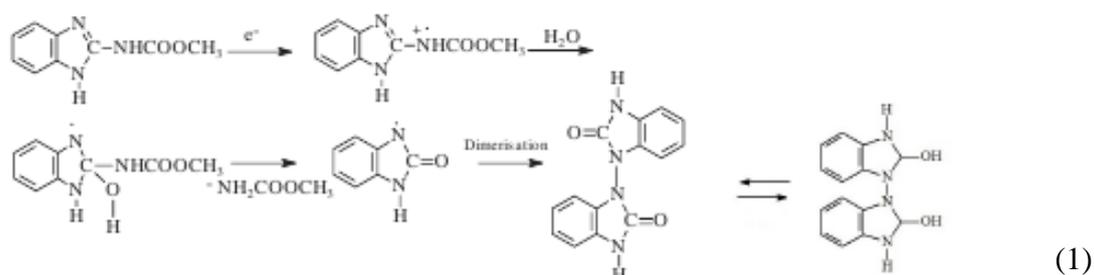
For this case, a classical two-dimensional model [30] may be applicable. The variables introduced are:

c – carbendazim pre-surface concentration;

θ – its 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.

It is possible to show, that the balance equations for pesticide pre-surface and surface concentrations may be written as:

$$\begin{cases} \dfrac{dc}{dt} = \dfrac{2}{\delta}\left(\left(\dfrac{D}{\delta}(c_0 - c)\right) + r_{-1} - r_1\right) \\ \dfrac{d\theta}{dt} = \dfrac{1}{G}(r_1 - r_{-1} - r_2) \end{cases} \tag{2}$$

In which D is the pesticide diffusion coefficient, c_0 its bulk concentration G its maximal surface concentration, r_1, r_{-1} and r_2 are adsorption, desorption and radical formation rates. The correspondent process rates may be calculated as:

$$r_1 = k_1 c (1 - \theta) \exp(a\theta) \tag{3}$$

$$r_{-1} = k_{-1} \theta \exp(-a\theta) \tag{4}$$

$$r_2 = k_2 \theta \exp(\frac{F\gamma\theta}{RT}) \tag{5},$$

In which the parameters k stand for rate constants of correspondent reactions, a is a variable describing the interaction of adsorbed pesticide particles, F is the Faraday number, γ is the variable, describing the influence of pesticide coverage on double electric layer (DEL) capacitance, R is the universal gas constant and T is the absolute temperature.

3. RESULTS AND DISCUSSION

3.1. Section I

As the two-dimensional equation set, describing the first stage of the mechanism, is classic, it will be described in a brief way.

The equation set (2) is analyzed by means of linear stability theory. The Jacobi functional matrix, the elements of which are calculated for a stable steady-state, may be represented as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{6},$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{D}{\delta} - k_1(1-\theta)\exp(a\theta)\right) \tag{7}$$

$$a_{12} = \frac{2}{\delta}\left(k_1 c\exp(a\theta) - ak_1 c(1-\theta)\exp(a\theta) + k_{-1}\exp(-a\theta) - ak_{-1}\theta\exp(-a\theta)\right) \tag{8}$$

$$a_{21} = \frac{1}{G}\left(k_1(1-\theta)\exp(a\theta)\right) \tag{9}$$

$$a_{22} = \frac{1}{G}\left(-k_1 c\exp(a\theta) + ak_1 c(1-\theta)\exp(a\theta) - k_{-1}\exp(-a\theta) + ak_{-1}\theta\exp(-a\theta) - k_2\exp(\frac{F\gamma\theta}{RT}) - \gamma k_2\theta\exp(\frac{F\gamma\theta}{RT})\right) \tag{10}$$

As in [30], the *oscillatory behavior* in this system is possible, being caused by surface and electrochemical instabilities. The main-diagonal element (10) contains positive addendums, defining the positive callback. They are positive in the cause of the positivity of a, defining the adsorbed particles' attraction and in the case of the negativity of γ, defining strong DEL influences of the electrochemical stage and radical formation.

To simplify the Jacobi determinant analysis, avoiding the appearance of cumbersome expressions, we introduce new variables, for the determinant to be rewritten as:

$$\frac{2}{\delta G}\begin{vmatrix} -\kappa - \Omega & \Lambda \\ \Omega & -\Lambda - \Xi \end{vmatrix} \tag{11}$$

As the condition Tr J<0 is easy to be satisfied, the main condition for *steady-state stability* is that of Det J>0. Opening the brackets, we obtain the steady-state stability requirement, rewritten as:

$$\kappa\Lambda + \kappa\Xi + \Omega\Xi > 0 \tag{12},$$

And it is certainly satisfied in the case of the positivity of surface behavior parameter Ω and electrooxidation parameter Ξ. These values define the repulsion between pesticide particles and the absence, or insufficient impact of DEL influences of electrochemical process.

As this condition is difficult to be unsatisfied, it is possible to affirm that the stable steady-state in the radical formation process is established easily and rapidly, which shows that the electroanalytical process must be efficient (with the satisfaction of conditions, mentioned in the next section). The linear dependence between electrochemical parameter and concentration is maintained in wide parameter range. Depending on the pesticide concentration, and polymer adsorption capacity, the reaction may be diffusion-controlled or adsorption-controlled. In small pesticide concentrations it must be diffusion-controlled, and in relatively big concentrations, adsorption-controlled.

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:

$$\kappa\Lambda + \kappa\Xi + \Omega\Xi = 0 \tag{13}$$

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 radical behavior is an important and interesting stability factor for this system, and its analysis will be represented in the section below.

3.2. Section II. The radical recombinations and their adducts

If the conducting polymer is saturated with radical sites, they may be used as traps for radical particles. It may be used not only in electroanalysis, but also in material modification [33-34].

In the case of the product of carbendazim electrooxidation, the radical may recombine either with the same one, or with the radical site on the polymer backbone.

$$\tag{14}$$
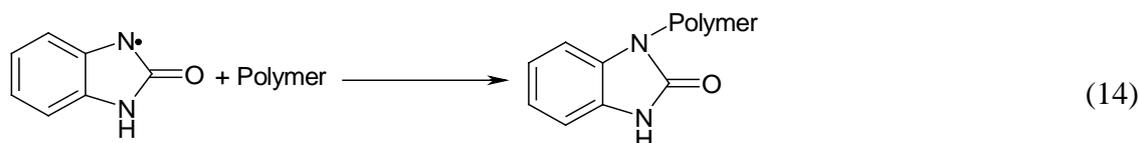
After the radical recombination, its products are reduced to form alcoholic compounds (1). The electrode's potential is then changed. The low-molecular dimeric alcohol is desorbed from the electrode surface, while formed. Yet the product of the reduction of the adduct of the radical-polymer recombination remains on the surface.

Supposing, that at the initial moment, the pesticide radicals cover the entire surface, and that the proton concentration is maintained steady, to describe this stage, we introduce two variables:

Δ – the radical dimer surface coverage degree;

σ – the modified polymer surface coverage degree, supposing the supposed above.

In this stage, the two-dimensional mathematical balance equation set will be described as:

$$\begin{cases} \dfrac{d\Delta}{dt} = \dfrac{1}{P}\left(r_3 - r_5\right) \\ \dfrac{d\sigma}{dt} = \dfrac{1}{X}\left(r_4 - r_6\right) \end{cases} \tag{15}$$

In which the parameters P and X are maximal surface concentrations of correspondent substances, r_3 and r_4 are recombination rates, r_5 and r_6 are reduction rates.

The correspondent reaction rates may be calculated as:

$$r_3 = k_3 (1 - \Delta - \sigma)^2 \exp(-b(1 - \Delta - \sigma)) \tag{16}$$

$$r_4 = k_4 (1 - \Delta - \sigma) \exp(-f((1 - \Delta - \sigma))) \tag{17}$$

$$r_5 = k_5 \Delta \exp\left(-\frac{2F\rho\Delta}{RT}\right) \exp(-g\Delta) \tag{18}$$

$$r_6 = k_6 \sigma \exp\left(-\frac{2nF\chi\sigma}{RT}\right) \tag{19}$$

In which the parameters k are rate constants of correspondent reactions, the parameters b and f describe the radicals' interaction one with another and with the surface, g stands for the parameter, describing the particles' interaction during the formation of the soluble alcohol, ρ and χ describe the influences of the electrochemical processes on double electric layer.

As in the first section, this system is described by a two-dimensional equation set. Nevertheless, as the process is occurring only on the surface, it may suffer influences of surface and electrochemical instabilities, which will be described below.

3.2.1 Results and discussion (section II)

As in the previous section, we analyze the equation set (15) by means of linear stability theory and bifurcation analysis. The Jacobi functional matrix for it will be described as

$$\begin{pmatrix} j_{11} & j_{12} \\ j_{21} & j_{22} \end{pmatrix} \tag{20}$$

In which:

$$j_{11} = \frac{1}{P} \left(\begin{array}{c} -2k_3(1-\Delta-\sigma)\exp(-b(1-\Delta-\sigma)) + bk_3(1-\Delta-\sigma)^2 \exp(-b(1-\Delta-\sigma) - k_5 \exp\left(-\frac{2F\rho\Delta}{RT}\right)\exp(-g\Delta) + \\ + gk_5\Delta\exp\left(-\frac{2F\rho\Delta}{RT}\right)\exp(-g\Delta) + \frac{2F\rho}{RT}k_5\Delta\exp\left(-\frac{2F\rho\Delta}{RT}\right)\exp(-g\Delta) \end{array} \right) \tag{21}$$

$$j_{12} = \frac{1}{P}\left(-2k_3(1-\Delta-\sigma)\exp(-b(1-\Delta-\sigma)) + bk_3(1-\Delta-\sigma)^2 \exp(-b(1-\Delta-\sigma))\right) \tag{22}$$

$$j_{21} = \frac{1}{X}\left(-k_4 \exp(-f((1-\Delta-\sigma))) + fk_4(1-\Delta-\sigma)\exp(-f((1-\Delta-\sigma)))\right) \tag{23}$$

$$j_{22} = \frac{1}{X}\left(-k_4 \exp(-f((1-\Delta-\sigma))) + fk_4(1-\Delta-\sigma)\exp(-f((1-\Delta-\sigma))) - k_6 \exp\left(-\frac{2nF\chi\sigma}{RT}\right) + \frac{2nF\chi}{RT}k_6\sigma\exp\left(-\frac{2nF\chi\sigma}{RT}\right)\right) \tag{24}$$

As in the similar models [30-34] and in the section 1 the *oscillatory behavior* in this system is possible, being caused by surface and electrochemical factors. But now, due to the interaction between radicals and polymer, the attraction may be promoted not only by two neighbor radicals, but also between the radicals and the radical sites on the polymer surface, which gives more chances for the oscillatory behavior, than in the case of [30]. Moreover, as the low-molecular alcohol is dissolved after the reaction, its dissolution may also be accompanied by an attraction between its molecules.

By the *steady-state stability* analysis, analogous to that described in the section I, it is possible to prove, that the stable steady-state is formed rapidly and is maintained by the absence or fragility of surface and DEL-influences of the radicals' and adducts' reactions. The reaction on this stage is controlled by the radical formation.

The general steady-state stability, conditioned to the radical concentration steady-state, described as:

$$r_2 = r_3 + r_4 \tag{25},$$

is maintained in the zones of steady-state stabilities of the systems, described in the sections I and II. The general reaction is controlled by the factors, described in the first section.

4. CONCLUSION

The steady-state stability analysis for the carbendazim electrochemical detection on conducting polymers may show that:

- The steady-state is easy to maintain stable. The electroanalytical response has to be efficient. The linear dependence between the concentration and electrochemical parameter is maintained in vast parameter range;
- The steady-state stability may only be compromised by surface and electrochemical instabilities. The general reaction my be diffusion-controlled or adsorption-controlled, depending on the pesticide concentration and the active surface of the polymer;
- On the stage of radical recombination, the oscillatory behavior is more probable, that on the initial stage, but in both of them it is caused by the same factors.

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