

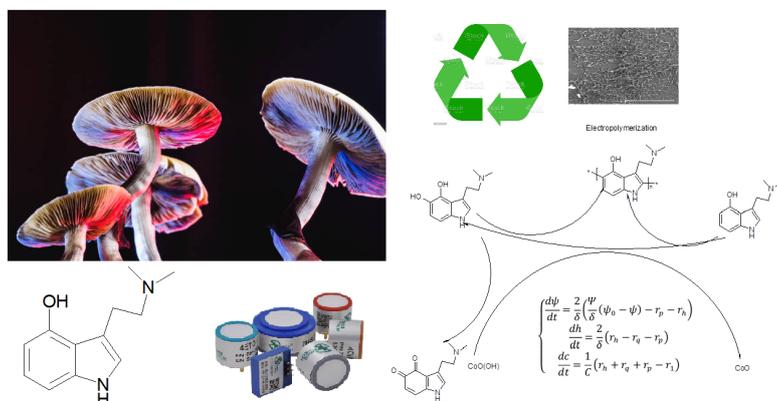
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The Theoretical Description for Psilocin Electrochemical Determination over Cobalt Oxyhydroxide

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The possibility of psilocin electrochemical determination and electropolymerization over cobalt (III) oxyhydroxide-modified anode is evaluated from the mathematical point of view. This process may be aimed for rapid and sensitive psilocin electrochemical determination method and for psilocin conversion to a green conducting polymer composite. Psilocin is thereby oxidized yielding either micro- or macromolecular product, being both of them important for the economical and green conducting polymer composite for electrocatalysis, electroanalysis and energy conversion. The analysis of the correspondent mathematical model confirms, that, despite of the high probability of the oscillatory behavior, the electrochemical process is efficient from both analytical and synthetical point of view.

Graphical abstract



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1. Introduction

Psilocin [1–4] (Fig. 1) is a common toxin of the psychedelic mushrooms like *Ps. Mexicana* and *Ps. Cubensis*. Besides of the presence of the substance in the proper mushroom pulp, it is also formed in organism from other *Psilocybe* toxins, mainly from psilocybin. It is an indolic compound, similar to bufotenin and serotine.

Its toxic effects include hallucinogenic action [5–7], which is dose-related, reason why the development of an efficient electroanalytical process is really actual.

Moreover, being an indolic compound, substituted by donor groups, it is interesting as a monomer for a conducting

polymer, analogous to those yet synthesized from other indoles [8–12]. The indoles are generally electropolymerized via the positions 3 and 5. If the position 3 is occupied, the electropolymerization is given towards the position 2.

Both phenolic hydroxyl and tertiary amine group lower the psilocin oxidation and polymerization potentials, leading to the enhanced electrochemical activity. It is even more expressed on chemically modified electrodes, which augment the electroanalytical activity and sensitivity and favors the composite material formation [11–12].

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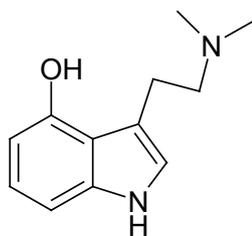


Fig. 1. Psilocin.

As for cobalt (III) oxyhydroxide, it is a suitable modifier candidate, due to its interesting properties. It is a p-type semiconductor, alternative to titanium dioxide, but with more expressed electrochemical activity [13–15], due to the presence of trivalent cobalt, capable of being either reductor or oxidant. Moreover, the CoO(OH)-modification interchange may also be useful for electroanalytical purposes. Other advantage of CoO(OH) is its possibility to be intercalated into the carbon or conducting polymer matrix [13–14]. Therefore, cobalt (III) oxyhydroxide might be efficiently used in psilocin electrochemical determination and assisted electropolymerization.

Nevertheless, the presence of electrochemical instabilities in both CoO(OH) electrosynthesis [15] and electropolymerization process [16–17] may destabilize the system, due to the high impact of the chemical and electrochemical stages on double electric layer (DEL) ionic force and related parameters (conductivity, capacitance, resistance). Those instabilities may lead to the problems in the electrochemical equipment integrity and in analytical signal formation. On the other hand, their presence may serve for the psilocin identification, due to the specific behavior pattern.

Therefore, the goal of this work is to investigate from the theoretical mechanistic point of view the CoO(OH)-assisted electrochemical sensing of psilocin, including both micromolecular electrooxidation and electropolymerization scenario. Also, the behavior of this system will be compared with that of the similar ones [18–21].

2. Material and Methods

2.1 System and its modeling

Taking into account the donor groups, which make part of psilocin molecules, its oxidation potential lowers, if compared to the unsubstituted indole. Moreover, the oxidation will be given by either pyrrolic or benzenic rings.

The electropolymerization is foreseen to occur towards the positions 2 and 5. Moreover, the phenolization of the benzenic ring hydrogen atoms will be given to the positions 5 or 7, being the products capable of participating in the electropolymerization as second monomers.

Considering the behavior similarity of α - and γ -hydroquinone derivatives, like also the *ortho*-effect in phenolization, in order to simplify the modeling, we consider α -hydroquinone formation as predominant. The behavior of the electroanalytical-electrosynthetic system will be thereby expressed on the Fig. 2.

Cobalt (III) oxyhydroxide is, for its turn, regenerated on electrochemical stage (1):

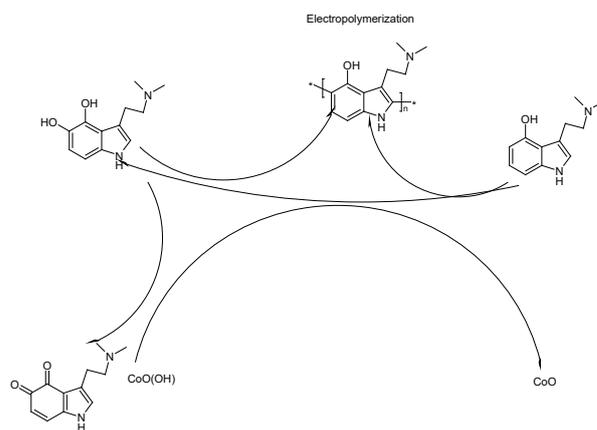


Fig. 2. The scheme of psilocin electrooxidation over CoO(OH)-modified electrode.

Therefore, taking into account the above cited statements and taking some assumptions [18–21], we describe the behavior of psilocin electrochemical determination and electropolymerization over cobalt (III) oxyhydroxide by a trivariate balance equation set, including the participation of the micromolecular oxidation product participation in the electropolymerization process (2):

$$\begin{cases} \frac{d\psi}{dt} = \frac{2}{\delta} \left(\frac{\Psi}{\delta} (\psi_0 - \psi) - r_p - r_h \right) \\ \frac{dh}{dt} = \frac{2}{\delta} (r_h - r_q - r_p) \\ \frac{dc}{dt} = \frac{1}{C} (r_h + r_q + r_p - r_1) \end{cases} \quad (2)$$

Herein, ψ is the psilocin concentration in the pre-surface layer; Ψ its diffusion coefficient, ψ_0 its bulk concentration, δ the pre-surface layer thickness, h is hydroquinonic derivative concentration, c is cobalt (II) oxide surface coverage degree, C is cobalt (II) oxide maximal surface concentration and the parameters r stand for the correspondent reaction rates, calculated as:

$$r_h = k_h \psi (1 - c)^2 \exp(-a\psi) \quad (3)$$

$$r_q = k_q h (1 - c)^2 \exp(-ah) \quad (4)$$

$$r_p = k_p \psi^x h^y (1 - c)^z \exp(-ah) \exp(-a\psi) \quad (5)$$

$$r_1 = k_1 c \exp\left(\frac{F\varphi_0}{RT}\right) \quad (6)$$

Herein, the parameters k stand for the correspondent reaction rate constants, the parameter a described the double electric layer (DEL) influences of the chemical stages, x , y and z are the assisted electropolymerization reaction orders, $F = N_A \cdot e$ is the Faraday number, φ_0 is the zero-charge related potential slope, R is the universal gas constant, T is the absolute temperature.

High DEL impact of the chemical and electrochemical stages of this process makes highly probable the oscillatory behavior, which is manifested even more clearly than in the similar systems. Nonetheless, the electrochemical system is efficient from both electroanalytical and electrosynthetic point of view, as shown below.

3. Results and Discussion

The behavior investigation of psilocin CoO(OH)-assisted electrochemical determination is given by equation-set (2)

analysis by means of the linear stability theory. The steady-state Jacobian matrix members will be described as (7):

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

In which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Psi}{\delta} - k_h(1-c)^2 \exp(-a\psi) + ak_h\psi(1-c)^2 \exp(-a\psi) - xk_p\psi^{x-1}h^y(1-c)^z \exp(-ah) \exp(-a\psi) + ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) \right) \quad (8)$$

$$a_{12} = \frac{2}{\delta} (ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) - yk_p\psi^x h^{y-1}(1-c)^z \exp(-ah) \exp(-a\psi)) \quad (9)$$

$$a_{13} = \frac{2}{\delta} (2k_h\psi(1-c) \exp(-a\psi) + zk_p\psi^x h^y(1-c)^{z-1} \exp(-ah) \exp(-a\psi)) \quad (10)$$

$$a_{21} = \frac{2}{\delta} (k_h(1-c)^2 \exp(-a\psi) - ak_h\psi(1-c)^2 \exp(-a\psi) - xk_p\psi^{x-1}h^y(1-c)^z \exp(-ah) \exp(-a\psi) + ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi)) \quad (11)$$

$$a_{22} = \frac{2}{\delta} (ak_q h(1-c)^2 \exp(-ah) - k_q(1-c)^2 \exp(-ah) + ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) - yk_p\psi^x h^{y-1}(1-c)^z \exp(-ah) \exp(-a\psi)) \quad (12)$$

$$a_{23} = \frac{2}{\delta} (-2k_h\psi(1-c) \exp(-a\psi) + 2k_q h(1-c) \exp(-ah) + zk_p\psi^x h^y(1-c)^{z-1} \exp(-ah) \exp(-a\psi)) \quad (13)$$

$$a_{31} = \frac{1}{C} (k_h(1-c)^2 \exp(-a\psi) - ak_h\psi(1-c)^2 \exp(-a\psi) + xk_p\psi^{x-1}h^y(1-c)^z \exp(-ah) \exp(-a\psi) - ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) - r_1) \quad (14)$$

$$a_{32} = \frac{1}{C} (-ak_q h(1-c)^2 \exp(-ah) + k_q(1-c)^2 \exp(-ah) - ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) + yk_p\psi^x h^{y-1}(1-c)^z \exp(-ah) \exp(-a\psi)) \quad (15)$$

$$a_{33} = \frac{1}{C} \left(-2k_h\psi(1-c) \exp(-a\psi) - 2k_q h(1-c) \exp(-ah) - zk_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) - k_1 \exp\left(\frac{F\phi_0}{RT}\right) + jk_1 c \exp\left(\frac{F\phi_0}{RT}\right) \right) \quad (16)$$

Observing the elements (8), (12) and (16), we conclude, that Hopf bifurcation, realized in the presence of the positive addendums, is possible. Moreover, it is more probable than in the similar systems [18–21]. Being related to the positive callback, this bifurcation describes the oscillatory behavior.

As in the similar systems, the oscillations frequency and amplitude will be highly dependent on the electrolyte composition, including pH. First of all, the psilocin monomer is ionized by different manner in acidic, neutral and alkaline media. Also, the DEL conductivity, capacitance and impedance will depend on its ionic composition. Therefore, the type of the oscillatory behavior, described by the positivity of the DEL-related addendums $ak_h\psi(1-c)^2 \exp(-a\psi) > 0$, $ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) > 0$, $ak_p\psi^x h^y(1-c)^z \exp(-ah) \exp(-a\psi) > 0$ if $a > 0$ (for chemical stages) and $jk_1 c \exp\left(\frac{F\phi_0}{RT}\right) > 0$ (for electrochemical stage), and the oscillation patterns will be defined by the background electrolyte composition.

Avoiding the cumbersome expressions during the determinant analysis, we rewrite the Jacobian determinant as (17), introducing new simplified variables:

$$\frac{4}{\delta^2 C} \begin{vmatrix} -\kappa - \Xi - \Lambda & -\Pi & T + P \\ \Xi - \Lambda & -\Sigma - \Pi & T + K - P \\ \Xi + \Lambda & \Sigma + \Pi & -T - K - P - \Omega \end{vmatrix} \quad (17)$$

Which, taking into account the determinant properties, may be rewritten as (18):

$$\frac{4}{\delta^2 C} \begin{vmatrix} -\kappa - \Xi - \Lambda & -\Pi & T + P \\ 2\Xi & 0 & -2P - \Omega \\ -\kappa & \Sigma & -K - \Omega \end{vmatrix} \quad (18)$$

Applying the Routh-Hurwitz criterion and Det J < 0 condition, salient from it, we obtain the steady-state stability requisite as (19):

$$\begin{aligned} & -\kappa(2P\Sigma + \Omega\Sigma + 2\Pi P + 2\Pi\Omega) \\ & -\Xi(2P\Sigma + \Omega\Sigma + 2\Sigma T + \Sigma P) \\ & -\Pi K - \Pi\Omega - 2P\Lambda\Sigma - \Lambda\Omega\Sigma \\ & < 0 \end{aligned} \quad (19)$$

Or, changing the signs to the opposite, as (20):

$$\begin{aligned} & \kappa(2P\Sigma + \Omega\Sigma + 2\Pi P + 2\Pi\Omega) \\ & + \Xi(2P\Sigma + \Omega\Sigma + 2\Sigma T + \Sigma P) \\ & - \Pi K - \Pi\Omega + 2P\Lambda\Sigma + \Lambda\Omega\Sigma \\ & > 0 \end{aligned} \quad (20)$$

The requisite (20) defines an efficient diffusion and kinetically controlled system, in which the linear dependence between the psilocin concentration and electrochemical parameter (in this case, current).

The requisite (20) is realized in the case of the positivity of the kinetic parameters Ξ , Λ , Σ and Ω . Really, in the case of the positivity of those parameters, the left side of the expression (20) will be shifted towards more positive values, providing an efficient analytical signal interpretation, is observed in a vast concentration range. From electrosynthetic point of view,

this system is related to an efficient well-developed polymer surface formation.

As for the *detection limit*, it is defined by monotonic instability, delimiting the margin between the stable steady-states and unstable states. Its condition for this system is (21):

$$\begin{aligned} &\kappa(2P\Sigma + \Omega\Sigma + 2PP + 2\Pi\Omega) \\ &+ \varepsilon(2P\Sigma + \Omega\Sigma + 2\Sigma T + \Sigma P \\ &- \Pi K - \Pi\Omega) + 2P\Lambda\Sigma + \Lambda\Omega\Sigma \\ &= 0 \end{aligned} \quad (21)$$

The simultaneous electrochemical determination of mushroom indoles and human indolic hormones on cobalt(III) oxyhydroxide is possible. The behavior of this case will be strongly dependent on the possibility of two indolic analytes ionization and copolymerization and will be evaluated in our next works.

4. Conclusions

From the theoretical analysis of psilocin CoO(OH)-assisted electrochemical determination and electropolymerization it was possible to conclude that this process is an efficient both diffusion and kinetically controlled electroanalytical and electrosynthetic system. The oscillatory behavior in this system is possible, being highly probable. The oscillation frequency and amplitude depend strongly on the background electrolyte nature, due to DEL impact of electrochemical and chemical stages. Nonetheless, the electroanalytical process is efficient and the analytical signal interpretation is clear.

Author Contributions

Volodymyr V. Tkach (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Mykhailo M Kucher (Conceptualization, Investigation, Supervision, Formal Analysis); Marta V. Kushnir (Data Curation, Conceptualization, Investigation); Yana G. Ivanushko (Conceptualization, Investigation, Supervision, Formal Analysis), Yüksel Akinay (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Necdet Karakoyun (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Petro I. Yagodynets (Investigation, Conceptualization, Methodology, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing), Zholt O. Kormosh (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing).

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