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The Theoretical Description For The Electrochemical Pyrogallol And Hydroxyquinol Electrochemical Determination Over CoO(OH)-Modified Electrode

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Abstract

The theoretical description for hydroxyquinol and pyrogallol electrochemical determination in food and wastewater has been made in this work. The efficiency of the cobalt (III) oxyhydroxide for this determination is verified from either electroanalytical and electrosynthetical point of view, as it also provides the assisted electro(co)polymerization. The stable steady-state is easy to obtain and maintain, which confirms the efficiency of the electrode modifier and the easy interpretation of analytical signal.

Keywords: *hydroxyquinol, pyrogallol, cobalt (III) oxyhydroxide, electrochemical sensors, electrochemical oscillations, stable steady-state*

Introduction

Phenol [1 – 4] is one of the most widespread pollutants in the pharmaceutical and food industry wastewaters. One of the most popular methods for its removal consists in its mineralization, by which it is fistly oxidized to polyphenolic compounds, and then to carbon dioxide and water (Fig. 1).

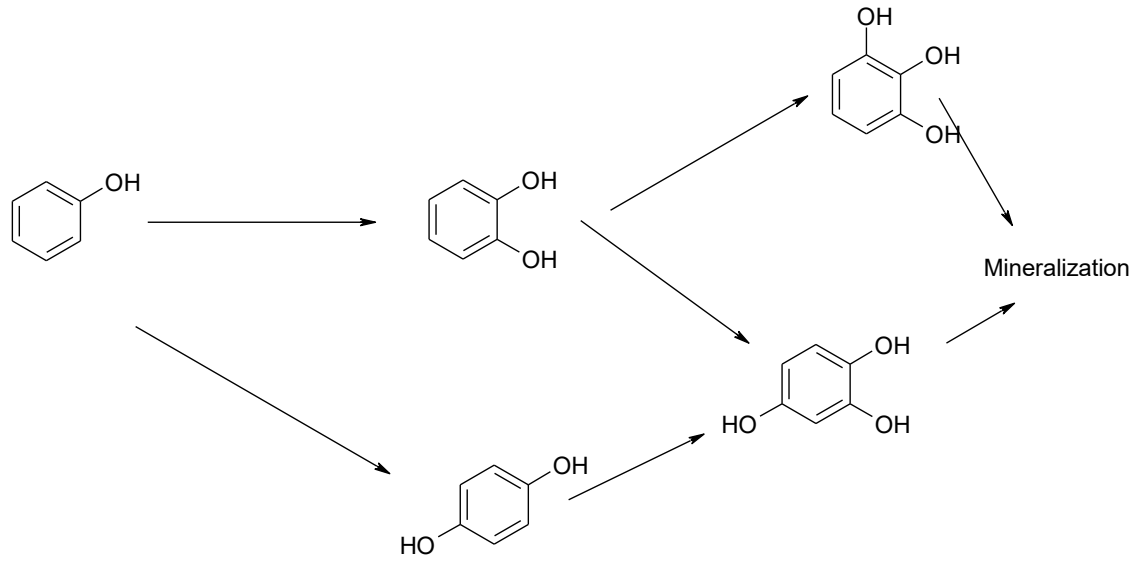

Fig. 1. Phenol gradual oxidation and mineralization.

Either the proper phenol or the products of its gradual oxidation are natural compounds. For example, the proper phenol and 1,4-hydroquinone are among the toxins of yellow stainer mushroom *Agaricus xanthodermus* [5 – 10]. 1,2-Hydroquinone is decarboxylate of protocatechic acid, pyrogallol (1,2,3-trihydroxybenzene) is decarboxylate of gallic acid. The derivatives of both of the acids may be found in fruit juices, wines, biodiesel etc. As for hydroxyquinol (1,2,4-trihydroxybenzene), it is a natural antioxidant, a fructose fermentative dehydratation product. Its derivatives (ethers and esters) are natural aromatizers and sweeteners. For example, sesamol is a hydroxyquinol ether, responsible for the taste of Turkish delights including lokum, tahini halva and baklava. It also may be found in ayran, tan and doug milk drinks and traditional Inebolu simit from Kastamonu. For this and other reasons, the development of a rapid and efficient method for both hydroxyquinol and pyrogallol determination is really actual [11 – 14].

Cobalt (III) oxyhydroxide [15 – 21] (alone and in composite with conducting polymers) has become a popular electrode modifier for electroanalytical systems. It is a semiconducting material, similar to titanium dioxide, but more electroactive. It may be an interesting electrode modifier for phenolic and polyphenolic compounds electrochemical determination and electropolymerization. Therefore, the goal of this work is to investigate theoretically the hydroxyquinol and pyrogallol electrochemical determination over cobalt (III) oxyhydroxide. This aims to find the condition of the parameter range for the best analytical signal interpretation, the oscillatory and monotonic instabilities condition and the comparison of the behavior of this system with that of the similar ones [22 – 28].

System And Its Modeling

Both pyrogallol and hydroxyquinol may be oxidized by both micro and macromolecular oxidation scenarios. Nevertheless, hydroxyquinol may be oxidized by more scenarios in relation to pyrogallol. Both of them form conducting polymers and may form either homopolymer or copolymer. Assuming that the copolymerization is more probable, that the homopolymerization of each of the compounds, we

consider only the copolymerization scenario in the model. The behavior of electroanalytical system is described on the Fig. 2.

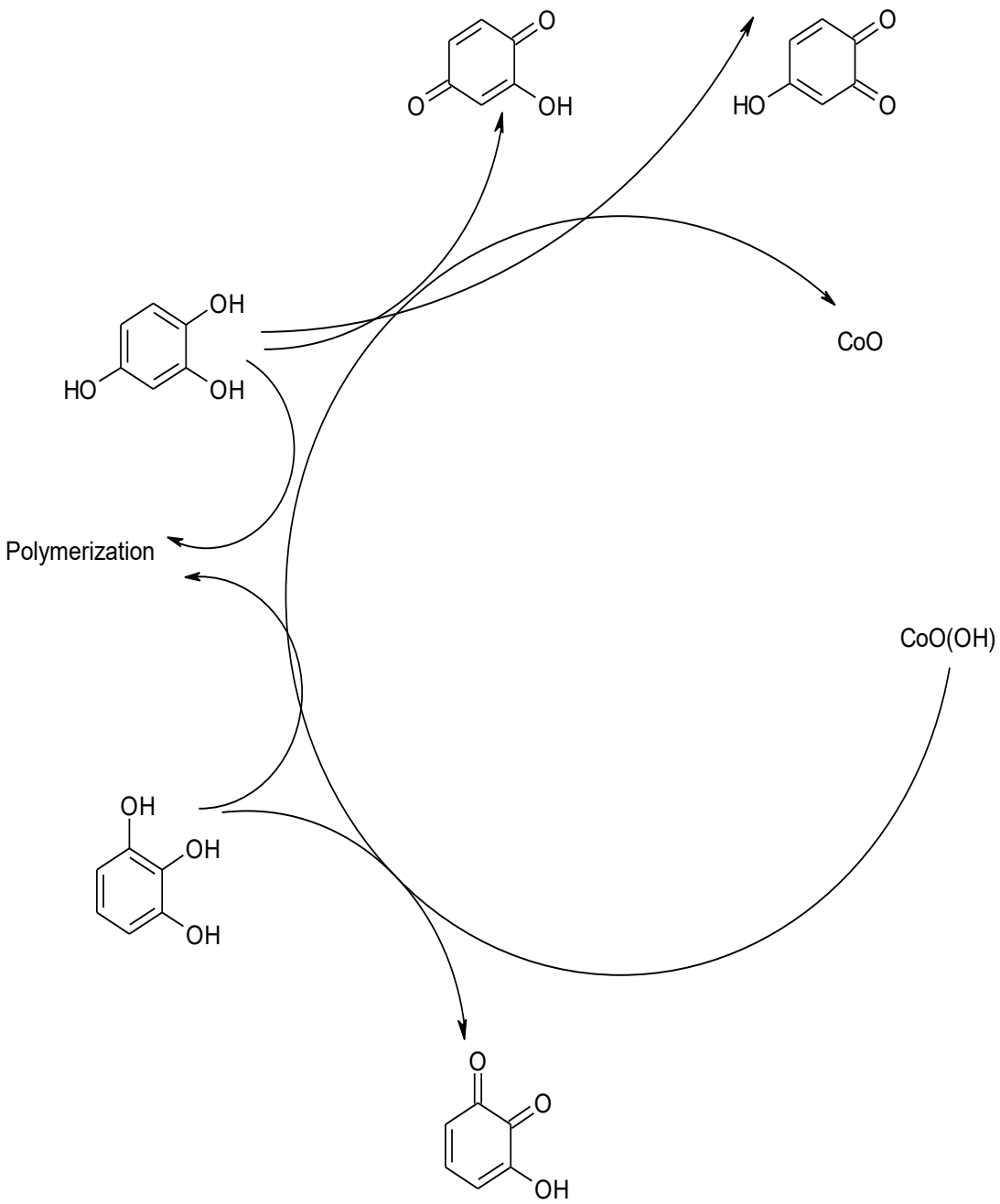

Fig. 2. The schematic representation of electroanalytical process.

Therefore, taking into account the above-mentioned statements and taking some assumptions [22 – 28], we describe the system´s behavior by a trivariant equation-set (1):

$$\begin{cases} \frac{dh}{dt} = \frac{2}{\delta}\left(\frac{H}{\delta}(h_0 - h) - r_{11} - r_{12} - r_p\right) \\ \frac{dp}{dt} = \frac{2}{\delta}\left(\frac{P}{\delta}(p_0 - p) - r_{21} - r_p\right) \\ \frac{dc}{dt} = \frac{1}{C}\left(r_{11} + r_{12} + r_{21} + r_p - r_c\right) \end{cases} \quad (1)$$

Herein, h and p are hydroxyquinol and pyrogallol concentrations in the pre-surface layer; H and P are their diffusion coefficients, h_0 and p_0 are their bulk concentrations, c is the cobalt (II) oxide surface coverage degree, C is this maximal concentration and the parameters r are their correspondent reaction rates, which, in neutral media, may be calculated as:

$$r_{11} = k_{11}h(1-c)^2 \quad (2)$$

$$r_{12} = k_{12}h(1-c)^2 \quad (3)$$

$$r_{21} = k_{21}p(1-c)^2 \quad (4)$$

$$r_p = k_p h^x p^y (1-c)^z \quad (5)$$

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

In which the parameters k are the correspondent reaction rate constants, x, y and z are polymerization reaction orders, F is the Faraday number, φ_0 is the zero-charge related potential slope, R is the universal gas constant and T is the absolute temperature.

In neutral media, the ionization is phenolic compounds is reduced, being, therefore, neglected. So, in this case the oscillatory behavior will be less probable than in alkaline media, and the electroanalytical process will be more stable, as shown below.

Results And Discussion

In order to investigate the stability of the system with the hydroxyquinol and pyrogallol electrochemical determination over CoO(OH)-modified electrode in neutral media, we investigate the equation-set (1) by means of linear stability theory. The steady-state Jacobian matrix components may be described as:

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

Herein:

$$a_{11} = \frac{2}{\delta}\left(-\frac{H}{\delta} - k_{11}(1-c)^2 - k_{12}h(1-c)^2 - xk_p h^{x-1}p^y(1-c)^2\right) \quad (8)$$

$$a_{12} = \frac{2}{\delta}\left(-yh^x p^{y-1}(1-c)^2\right) \quad (9)$$

$$a_{13} = \frac{2}{\delta}\left(2k_{11}h(1-c) + 2k_{12}h(1-c) + zk_p h^x p^y (1-c)^{z-1}\right) \quad (10)$$

$$a_{21} = \frac{2}{\delta}\left(xk_p h^{x-1}p^y(1-c)^2\right) \quad (11)$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{P}{\delta} - k_{21}(1-c)^2 - yh^x p^{y-1}(1-c)^2\right) \quad (12)$$

$$a_{23} = \frac{2}{\delta}\left(2k_{21}p(1-c) + zk_p h^x p^y (1-c)^{z-1}\right) \quad (13)$$

$$a_{31} = \frac{1}{C}\left(k_{11}(1-c)^2 + k_{12}h(1-c)^2 + xk_p h^{x-1}p^y(1-c)^2\right) \quad (14)$$

$$a_{32} = \frac{1}{C}\left(k_{21}(1-c)^2 + yh^x p^{y-1}(1-c)^2\right) \quad (15)$$

$$a_{33} = \frac{1}{C}\left(-k_{11}h(1-c) - 2k_{12}h(1-c) - 2k_{21}p(1-c) - zk_p h^x p^y (1-c)^{z-1} - k_c \exp\left(\frac{F\varphi_0}{RT}\right) + jk_c c \exp\left(\frac{F\varphi_0}{RT}\right)\right) \quad (16)$$

In neutral media, the chemical stage do not affect the double electric layer, reason why *the oscillatory behavior* will be caused by the only factor of DEL impact of the electrochemical stage, described by the positivity of $jk_c c \exp\left(\frac{F\varphi_0}{RT}\right) > 0$, if j>0. This factor is common for all the similar systems [22 – 28] and defines also the dependence of the oscillation frequency and amplitude from the background electrolyte composition.

Avoiding the cumbersome expression during the determinant analysis, we introduce new variables and rewrite the determinant as (17):

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

Applying the Det J<0 requisite, salient from Routh-Hurwitz critetion, we obtain the *steady-state stability condition*, expressed as (18):

$$-\kappa(\xi\Lambda + T\Lambda + P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega + P\Omega) - \Sigma(\xi\Lambda + T\Lambda + P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega - PN - \xi\Lambda - \xi\Phi) - \Xi(P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega + P\Omega) < 0 \quad (18)$$

Which may be rewritten as (19):

$$\kappa(\xi\Lambda + T\Lambda + P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega + P\Omega) + \Sigma(\xi\Lambda + T\Lambda + P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega - PN - \xi\Lambda - \xi\Phi) + \Xi(P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega + P\Omega) > 0 \quad (19)$$

Defining a highly stable electroanalytical system, in which the linear current-concentration dependence range will be wider than for alkaline media [21 – 28]. For this reason, neutral or neutralized pH may be recommended for the electroanalytical process, which will be both diffusion or kinetically controlled, with higher impact of the kinetical factor.

As for the detection limit, it defines the margin between stable steady-states and unstable states. Being described by the *monotonic instability,* its condition is exposed as (20):

$$\kappa(\xi\Lambda + T\Lambda + P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega + P\Omega) + \Sigma(\xi\Lambda + T\Lambda + P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega - PN - \xi\Lambda - \xi\Phi) + \Xi(P\Lambda + \xi\Phi + \xi N + \xi\Omega + T\Omega + P\Omega) = 0 \quad (20)$$

If phloroglucinol (1,3,5-trihydroxybenzene) or an etherified phenolic derivative is used as a second analyte, the electropolymerization scenario may become the only oxidation scenario for this compound. In this case, the balance equation-set will be rewritten as (21):

$$\begin{cases} \frac{dh}{dt} = \frac{2}{\delta}\left(\frac{H}{\delta}(h_0 - h) - r_{11} - r_{12} - r_p\right) \\ \frac{dp}{dt} = \frac{2}{\delta}\left(\frac{P}{\delta}(p_0 - p) - r_p\right) \\ \frac{dc}{dt} = \frac{1}{C}\left(r_{11} + r_{12} + r_p - r_c\right) \end{cases} \quad (21)$$

This case (for neutral and alkaline media) will be analyzed in our next works.

Conclusions

From the analysis of the system with hydroxyquinol and pyrogallol electrochemical determination over CoO(OH), it was possible to conclude that that it is an efficient process from both electroanalytical and electrosynthetical points of view, providing an economical and green conducting polymer synthesis and phenolic compounds analysis in food and wastewater. The linear dependence between the analyte concentration and electrochemical parameter is easy to form in an efficient kinetically-controlled system. For its turn, the oscillatory behavior is expected to be probable due to the double electric layer structure changes during the process on electrochemical stage. Either way, its probability is lower in neutral than in alkaline medium. The probability of the oscillatory behavior and the oscillation amplitude will be highly dependent on the solution background electrolyte composition.

Conflict of interest

The authors declare that there is no conflict of interests regarding this publication

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