Letters in Applied NanoBioScience
Open-Access Journal (ISSN: 2284-6808)

Article
Volume 13, Issue 3, 2024, 136
https://doi.org/10.33263/LIANBS133.136

The Theoretical Description for Electrochemical Hydroxyquinol and Phloroglucinol Electrochemical Detection Over CoO(OH)-Modified Electrode

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Received: 17.04.2023; Accepted: 22.06.2023; Published: 27.07.2024

Abstract: The theoretical description for hydroxyquinol and phloroglucinol 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 an electroanalytical or electrosynthetical point of view, as it also provides assisted electro(co)polymerization. The stable steady-state is easy to obtain and maintain, confirming the electrode modifier's efficiency and the easy interpretation of curves for direct and indirect determination. This process may also efficiently remove phenolic compounds from the pharmaceutical wastewater.

Keywords: hydroxyquinol; phloroglucinol; cobalt (III) oxyhydroxide; electrochemical sensors; electrochemical oscillations; stable steady-state

1. Introduction

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

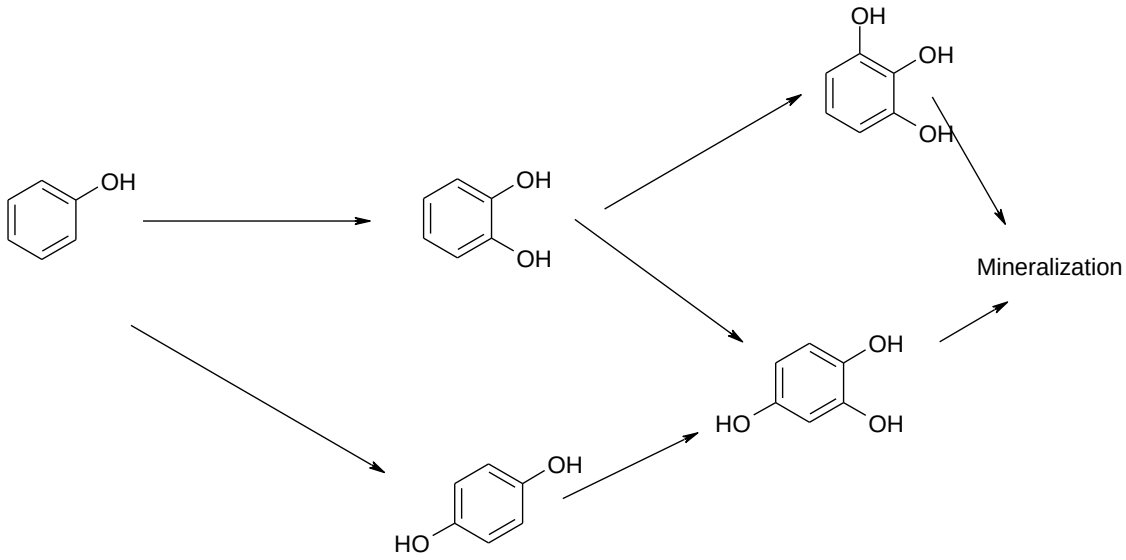

Figure 1. Phenol gradual oxidation and mineralization.

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 the yellow stainer mushroom *Agaricus xanthodermus* [5–10]. 1,2-Hydroquinone is decarboxylate of protocatechic acid, and pyrogallol (1,2,3-trihydroxybenzene) is decarboxylate of gallic acid. The acids' derivatives may be found in fruit juices, wines, biodiesel, etc. Triphenols, which are pyrogallol (1,2,4-trihydroxyquinone), hydroxyquinol (1,2,4-trihydroxybenzene), and phloroglucinol (1,3,5-trihydroxyquinone) are also important intermediates of phenol mineralization and important natural compounds.

Hydroxyquinol (1,2,4-trihydroxybenzene) 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.

Phloroglucinol (1,3,5-trihydroxybenzene) may be either an industrial effluent or a metabolism product of certain plants and microorganisms. It is also a base for phlorotannins. Its name is explained by its flowerish scent ("phloro-") and sweet taste ("glucinol"). As a triphenol, it exists in the form of two tautomers (Fig. 2)

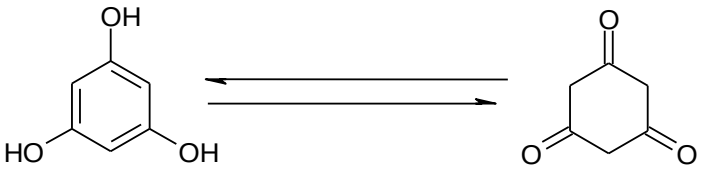

Figure 2. Phloroglucinol tautomerism.

It is widely used in dye synthesis and as a veterinary drug for gallstone treatment in cattle. It is also used as a monomer for conducting polymers. For this and other reasons,

developing a rapid and efficient method for hydroxyquinol and phloroglucinol 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, this work aims to theoretically investigate hydroxyquinol and phloroglucinol 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 similar ones [22–28].

2. Materials and Methods

Hydroxyquinol may be electrooxidized by either α- or γ-hydroquinonic scenarios. It may also be electropolymerized. As for phloroglucinol, in the analysis conditions, it may only participate in the macromolecular electrooxidation scenario, yielding a (co)polymer (Figure 3).

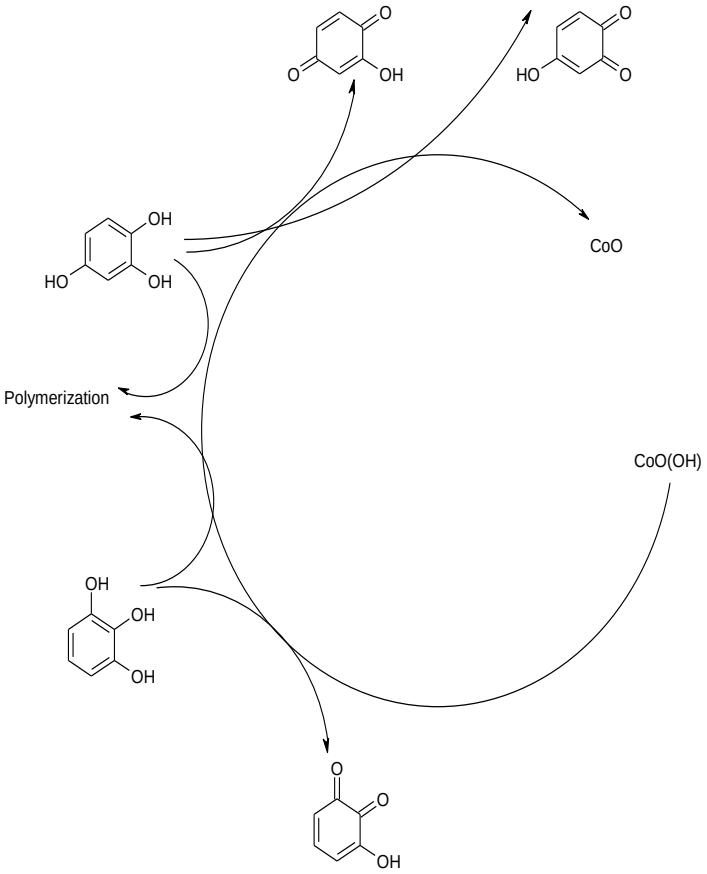

Figure 3. The schematic representation of the electroanalytical process.

In this scheme, the electrochemical determination and quantification of hydroxyquinol will be direct, and for phloroglucinol, it will be indirect. 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):

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

Herein, h and p are hydroxyquinol and phloroglucinol 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:

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

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

$$r_p = k_p h^x p^y (1-c)^z \quad (4)$$

$$r_c = k_c c \exp\left(\frac{F\varphi_0}{RT}\right) \quad (5)$$

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 of phenolic compounds is reduced and, 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.

3. Results and Discussion

To investigate the system's stability with the hydroxyquinol and phloroglucinol electrochemical determination over CoO(OH)-modified electrode in neutral media, we investigate the equation-set (6) using linear stability theory. The steady-state Jacobian matrix components may be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (6)$$

Herein:

$$a_{11} = \frac{2}{\delta}\left(-\frac{H}{\delta} - k_{11}(1-c)^2 - k_{12}h(1-c)^2 - xk_p h^{x-1}p^y(1-c)^2\right) \quad (7)$$

$$a_{12} = \frac{2}{\delta}(-yh^x p^{y-1}(1-c)^2) \quad (8)$$

$$a_{13} = \frac{2}{\delta}\left(2k_{11}h(1-c) + 2k_{12}h(1-c) + zk_p h^x p^y (1-c)^{z-1}\right) \quad (9)$$

$$a_{21} = \frac{2}{\delta}\left(xk_p h^{x-1}p^y(1-c)^2\right) \quad (10)$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{P}{\delta} - yh^x p^{y-1}(1-c)^2\right) \quad (11)$$

$$a_{23} = \frac{2}{\delta}\left(zk_p h^x p^y (1-c)^{z-1}\right) \quad (12)$$

$$a_{31} = \frac{1}{C}\left(k_{11}(1-c)^2 + k_{12}h(1-c)^2 + xk_p h^{x-1}p^y(1-c)^2\right) \quad (13)$$

$$a_{32} = \frac{1}{C}\left(yh^x p^{y-1}(1-c)^2\right) \quad (14)$$

$$a_{33} = \frac{1}{C}\left(-k_{11}h(1-c) - 2k_{12}h(1-c) - zk_p h^x p^y (1-c)^{z-1} - k_c \exp\left(\frac{F\varphi_0}{RT}\right) + jk_c c \exp\left(\frac{F\varphi_0}{RT}\right)\right) \quad (15)$$

In neutral media, the chemical stage does 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 similar systems [22–28] and also defines 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 (16):

$$\frac{4}{\delta^2 C}\begin{vmatrix} -\kappa - \Xi - \Sigma & -P & \Lambda + \Phi \\ -\Sigma & -\xi - P & \Phi \\ \Xi + \Sigma & P & -\Lambda - \Phi - \Omega \end{vmatrix} \quad (16)$$

which, considering the determinant properties, will be rewritten as (17):

$$\frac{4}{\delta^2 C}\begin{vmatrix} -\kappa - \Xi - \Sigma & -P & \Lambda + \Phi \\ -\Sigma & -\xi - P & \Phi \\ -\kappa & 0 & -\Omega \end{vmatrix} \quad (17)$$

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

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

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 a 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 (19):

$$-P(\kappa\Omega + \Xi\Omega + \kappa\Lambda) - \xi(\kappa\Omega + \Xi\Omega + \Sigma\Omega + \kappa\Lambda + \kappa\Phi) = 0 \quad (19)$$

The phenolization scenario [27], yielding the 1,2,3,5-tetrahydroxybenzene, may also be possible. This oxidation scenario mimics the action of pyrogallol hydroxytransferase and may be realized by CoO(OH) in a lightly alkaline medium. In this case, the direct detection of both hydroxyquinol and phloroglucinol becomes more efficient.

4. Conclusions

From the analysis of the system with hydroxyquinol and phloroglucinol electrochemical determination over CoO(OH), it was possible to prove that it is an excellent electroanalytical electrode modifier and electropolymerization initiator for phenolic compounds analysis in food and wastewater and electropolymerization. The linear concentration dependence range is easily achieved in a kinetically controlled system. In turn,

the oscillatory behavior is expected to be probable due to the double electric layer ionic force cyclic changes in the electrochemical stage, affecting the steady-state stability. Either way, its probability is lower in neutral than in an alkaline medium. The probability of the oscillatory behavior and the oscillation amplitude will depend highly on the electrolyte composition of the solution background.

Funding

This research received no external funding.

Acknowledgments

Volodymyr V. Tkach acknowledges the Engineering Faculty of the University of Porto and the University of Trás-os-Montes and Alto Douro for their support during these difficult times for Ukraine and its research.

Conflicts of Interest

The authors declare no conflict of interest.

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