

The Theoretical Description for Economical and Green Electrochemical Detection and Removal of Heavy Metals by a Conducting Polymer Material, Based on Poisonous Mushrooms *C. Orellanus*, *P. Involutus*, and *A. Xanthodermus*

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Abstract: This work is a theoretical evaluation of heavy metal cations' electrochemical determination and removal from wastewater by means of their oxidation in the presence of a conducting polymer based on poisonous mushrooms. As their main toxins are phenolic, their possible electro(co)polymerization and the complex formation of the phenolic toxins in the polymer phase with the heavy metal cations are possible. The mathematical modeling of the system's behavior confirms its efficiency for the electrochemical determination and removal of heavy metals from natural waters and wastewater. The procedure is foreseen to be realized in an economical and green manner.

Keywords: heavy metals; poisonous mushrooms; *Cortinarius orellanus*; *Paxillus involutus*; *Agaricus xanthodermus*; conducting polymers; electrochemical removal; electrochemical sensors; electrochemical oscillations; stable steady-state

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1. Introduction

The term “heavy metals” was introduced by German chemist Leopold Gmelin in 1817. This term became so popular that it has given its name to the musical style known as “heavy metal rock” [1 – 4].

As for now, more than forty definitions for the term “heavy metals” are commonly accepted, but generally, all the metals beginning with vanadium are considered as “heavy”. Most are transition metals capable of forming stable complex compounds [5 – 8].

Heavy metal cations are among the most aggressive pollutants in the environment. They may occur even in food and drinks (including those of traditional recipes [9]). These cations are highly toxic, provoking different intoxication symptoms. For this and other reasons, the determination and removal of heavy metals concentrations are really effective, and electrochemical methods may be a good solution for this problem [10 – 14].

Besides cathodic deposition, which is used in different systems of wastewater treatment [13 – 15], anodic extraction may also be used [16 – 17]. Generally, it is based on the electrooxidation of a metallic cation or of a surface material in the presence of this cation, thereby yielding a more oxidized form and(or) a stable complex.

In order to implement this function, the anode will be modified by a conjugated dye [17], its polymer, or another conducting polymer possessing complex-forming functional groups. Those monomers and polymers are generally synthetic [18 – 25], but they may be substituted by natural analogous compounds.

In this aspect, toxic mushrooms may be an interesting source of monomers. Besides being highly renewable, they do not participate in the trophic chain of human and most animal organisms. It’s important to mention the mushrooms *Cortinarius Orellanus*, *Paxillus involutus*, and the yellow stainer *Agaricus Xanthodermus*, which contain phenolic compounds capable of being used as monomers for economic and green conducting polymers (Fig. 1):

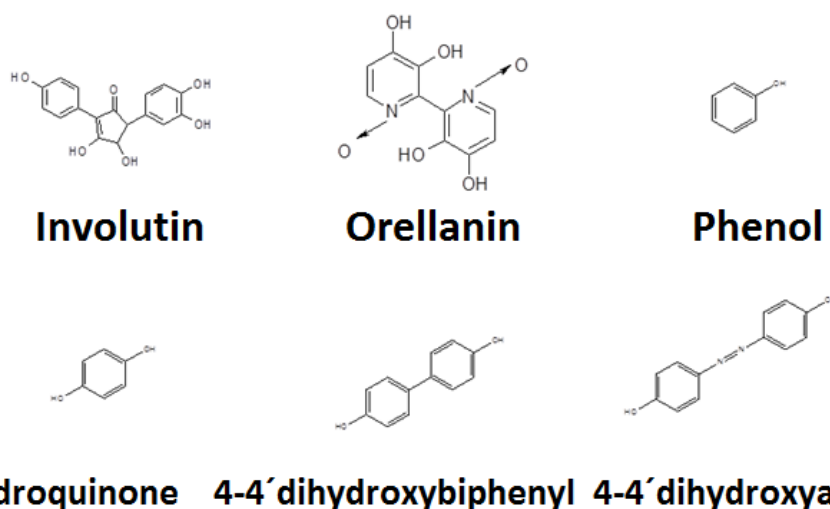


Figure 1. The phenolic mushroom toxins, potentially used as monomers.

This list includes interesting compounds, including 4-4'-dihydroxyazobenzene, the only endogenous azo-dye found in nature.

Considering the possibility of two tautomeric forms for orellanin (Fig. 2):

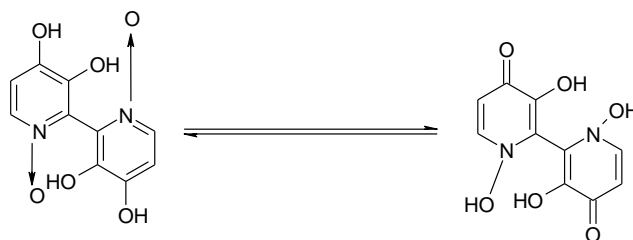


Figure 2. Two tautomeric forms for orellanin.

It is possible to conclude that the orellanin unit may be used to coordinate heavy-metal cation in stable complexes and, in some cases, even coordination polymers.

Therefore, in this work, we theoretically investigate the possibility of using conducting (co)polymers of mushroom phenols for heavy metal cation concentration measurement and removal. For this purpose, the system's behavior will be described by a balance differential equation set, which will be analyzed by linear stability theory and bifurcation analysis to detect the steady-state stability requirements, like the oscillatory and monotonic instability conditions. Also, the behavior of the system will be compared with that of similar ones [25 – 28].

2. Materials and Methods

In this work, we describe the simplest case, in which the metallic element has two or more valent states, and the cation, present in water, corresponds to one of the lower oxidation states (like Mn^{2+} , Fe^{2+} , Co^{2+} , Cu^+). Therefore, the complex formation with the phenols will be given in the first stage, being the cation, thereby electrooxidized yet in the polymer phase. This, in turn, will be accompanied by the attraction between the macromolecules, which will bring the surface aspect to the system's behavior (Fig. 3).

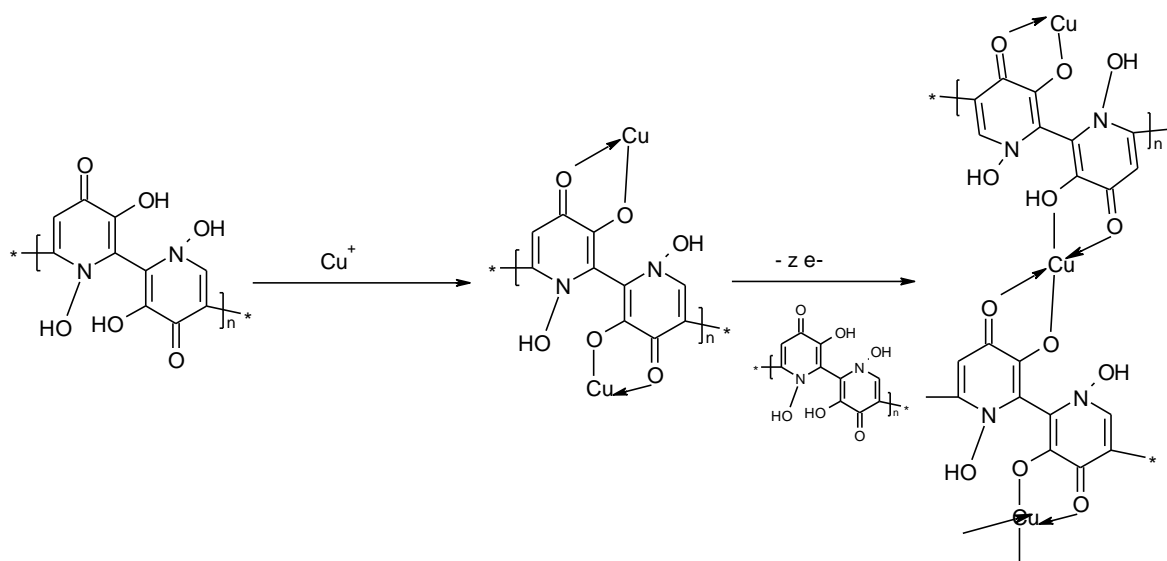


Figure 3. The scheme for retention and detection of heavy metal cation by two macromolecules. Example of copper (I) and orellanin unit.

Therefore, one more type of polymerization will be added (coordination polymerization), the metallic cation will be oxidized, and ionic and coordination bonds will bond two macromolecules via the metallic cation. Therefore, the surface factor, absent in similar systems [27 – 28], but observed in some experimental processes [25 – 26], enters the process, enhancing the probability of the oscillatory behavior in this case.

Taking some assumptions [27 – 28], we describe the potentiostatic behavior of this system by a bivariate balance differential equation set (1):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_{c1} - r_{c2} \right) \\ \frac{dp}{dt} = \frac{1}{P} (r_{c1} + r_{c2} - r_0) \end{cases} \quad (1)$$

In which c is the pre-surface concentration of the metallic ion, c_0 is its bulk concentration, Δ is the diffusion coefficient, δ is the pre-surface layer thickness, p is the modified polymer surface coverage degree, P is its maximal surface concentration, and the parameters r are correspondent reaction rates, calculated as:

$$r_{c1} = k_{c1}c(1 - p) \exp(-ac) \quad (2)$$

$$r_{c2} = k_{c2}c(1 - p) \exp(-ac) \quad (3)$$

$$r_0 = k_0p \exp(-bp) \exp\left(\frac{zF\varphi_0}{RT}\right) \quad (4)$$

in which the parameters k are the correspondent reaction rate constants, a and b are variables, describing, correspondently, the DEL impact of the ionic forms transformation during the chemical stage and the attraction between macromolecules during the electrochemical stage, z is the number of transferred electrons, F is the Faraday number, φ_0 is the potential slope related to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature.

The balance equations correspond to the process's sequence, leading to the electrochemical determination(removal) of the heavy metal cations in(from) the wastewater, including diffusion, chemical, and electrochemical reactions. The model may differ depending on the metal detected(removed), as shown, inclusively, at the end of the next section.

Generally, the behavior of this system becomes similar to that of the system observed by our group for the overoxidized conducting polymer [27]. Nevertheless, the surface interaction factor of macromolecules during the electrochemical stage will make the behavior more dynamic, augmenting the probability of oscillatory and monotonic instabilities. Nevertheless, those instabilities do not strongly affect the system's efficiency, which remains high, as shown below.

3. Results and Discussion

In order to investigate the behavior of the system with the heavy metal cation determination and elimination on poisonous mushroom polyphenoles' polymers modified electrode, we analyze the balance differential equation set (1), considering the algebraic relations (2 – 4) by means of linear stability theory. The steady-state Jacobian matrix members may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (5)$$

In which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{A}{\delta} - k_{c1}(1-p) \exp(-ac) + ak_{c1}c(1-p) \exp(-ac) - k_{c2}(1-p) \exp(-ac) + ak_{c2}c(1-p) \exp(-ac) \right) \quad (6)$$

$$a_{12} = \frac{2}{\delta} (k_{c1}c \exp(-ac) + k_{c2}c \exp(-ac)) \quad (7)$$

$$a_{21} = \frac{1}{p} (k_{c1}(1-p) \exp(-ac) + ak_{c1}c(1-p) \exp(-ac) - k_{c2}(1-p) \exp(-ac) + ak_{c2}c(1-p) \exp(-ac)) \quad (8)$$

$$a_{22} = \frac{1}{p} \left(-k_{c1}c \exp(-ac) - k_{c2}c \exp(-ac) - k_o \exp(-bp) \exp\left(\frac{zF\phi_0}{RT}\right) + (b + j)k_o p \exp(-bp) \exp\left(\frac{zF\phi_0}{RT}\right) \right) \quad (9)$$

The main conditions of the steady-state stability and the most important instabilities are exposed in Table 1:

Table 1. The main stability conditions for the bivariate equation sets.

Steady-state stability	Tr J < 0, Det J > 0
Oscillatory instability (Hopf bifurcation)	Tr J = 0, Det J > 0
Monotonic instability (Saddle-node bifurcation)	Tr J < 0, Det J > 0

In order to simplify the determinant analysis, we introduce new variables, rewriting the determinant as:

$$\frac{2}{\delta P} \begin{vmatrix} -\kappa - \mathcal{E} & \Sigma \\ \mathcal{E} & -\Sigma - \Omega \end{vmatrix} \quad (10)$$

In which:

$$-\frac{2}{\delta} (\kappa - \mathcal{E}) - \frac{1}{P} (-\Sigma - \Omega) = Tr J \quad (11) - \text{Jacobian matrix trace}$$

$$\frac{2}{\delta P} (\kappa \Sigma + \kappa \Omega + \mathcal{E} \Omega) = Det J \quad (12) - \text{Jacobian matrix determinant}$$

Such as in the work [28], the oscillatory behavior via Hopf bifurcation is possible in this case. Moreover, it is even more probable than in [28], due to the presence of the surface behavior factor experimentally observed in [25 – 26].

The realization of the oscillatory behavior by Hopf bifurcation is given by the presence of the positive elements in the matrix main diagonal (which is necessary to satisfy the main condition Tr J=0). These elements are: $ak_{c1}c(1-p) \exp(-ac) > 0$ and $ak_{c2}c(1-p) \exp(-ac) > 0$, if $a > 0$, $(b + j)k_o p \exp(-bp) \exp\left(\frac{zF\phi_0}{RT}\right) > 0$, if $b > 0$ and/or $j > 0$. This positivity defines the oscillatory behavior caused by the capacitance effect of DEL (in the case of the positivity of a and j) and the surface instability (in the case of the positivity of b). The oscillation frequency and amplitude depend on the wastewater's ionic composition and the background electrolyte used. Mathematically, the condition of the oscillatory behavior will be described as (13):

$$\begin{cases} -\frac{2}{\delta} (\kappa - \mathcal{E}) - \frac{1}{P} (-\Sigma - \Omega) = 0 \\ \frac{2}{\delta P} (\kappa \Sigma + \kappa \Omega + \mathcal{E} \Omega) > 0 \end{cases} \quad (13)$$

In the case of the negativity of these elements, steady-state stability is warranted. Its condition will be described as (14):

$$\begin{cases} -\frac{2}{\delta} (\kappa - \mathcal{E}) - \frac{1}{P} (-\Sigma - \Omega) < 0 \\ \frac{2}{\delta P} (\kappa \Sigma + \kappa \Omega + \mathcal{E} \Omega) > 0 \end{cases} \quad (14)$$

Really, if the variables a, b, and j have null or negative values, the left side of the first inequation of (14) will be more negative, stabilizing the system and ensuring the efficiency of

the process from both electroanalytical and removal points of view. From the electroanalytical point of view, this condition will define the linear dependence between the electrochemical parameter and concentration, providing an easy interpretation of the analytical signal. As for the process, it will be kinetically controlled.

As for the detection limit, it is correspondent to the monotonic instability, defined by the condition of $\text{Det } J=0$, or (15):

$$\begin{cases} -\frac{2}{\delta}(\kappa - \varepsilon) - \frac{1}{p}(-\Sigma - \Omega) < 0 \\ \frac{2}{\delta p}(\kappa\Sigma + \kappa\Omega + \varepsilon\Omega) = 0 \end{cases} \quad (15)$$

At this point, the margin between the stable, steady states, and unstable states is formed. A multiplicity of unstable steady-states corresponds to this margin. The system chooses one of them, and it is destroyed if the system conditions are changed.

If two cations of the same metal but in two oxidation states (like Fe^{2+} and Fe^{3+}) are present, the balance equation set becomes trivariate (16):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_{c1} - r_{c2} \right) \\ \frac{dc^*}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c^*_0 - c^*) - r_{c^*1} - r_{c^*2} \right) \\ \frac{dp}{dt} = \frac{1}{p} (r_{c1} + r_{c2} + r_{c^*1} + r_{c^*2} - r_0) \end{cases} \quad (16)$$

And this process, which by this, will be more accomplished by the presence of two cations, will be analyzed in our next works.

4. Conclusions

From the behavior investigation of the system with the heavy metal cations electrochemical detection and elimination, assisted by a conducting polymer, based on mushroom polyphenols, based on *C. orellanus*, *P. involutus*, and *A. Xanthodermus* it was possible to conclude that the polyphenolic conducting polymer, based on natural source, maybe na efficient anode modifier for heavy metal cation removal and determination in natural waters and wastewaters. The behavior of the process becomes more accomplished due to the presence of surface instability, augmenting the probability of the oscillatory behavior. Nevertheless, it is an efficient process controlled by the kinetics of the chemical and electrochemical reactions that make up part of it.

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Conflicts of Interest

The authors declare no conflict of interest.

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