

Evaluation of voltammetric method for the determination of electrodeposited copper in citrate medium validated by ICP-OES

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ABSTRACT

Copper (Cu) is a toxic pollutant and its presence in wastewater, even at low concentrations, can have a significant environmental impact. In this work, a method for the determination of Cu was developed using a voltammetric technique involving a platinum electrode in citrate medium. Cu at a ppb level was determined by both chronoamperometry (CA) and anodic linear scanning voltammetry (ALSV), and the results were compared to those from inductively coupled plasma optical emission spectroscopy (ICP-OES). The results obtained were similar, having a deviation of 2.56%. The least squares method was used to evaluate the correlation between the ALSV and ICP-OES results. Statistical analyses showed a 95% confidence interval.

Keywords: Anodic linear scanning voltammetry, chronoamperometry, copper.

1. INTRODUCTION

Copper (Cu) and copper-based alloys are used in a variety of applications that are necessary for a reasonable standard of living [1]. Cu is one of the most investigated metallic catalysts, mainly due to its industrial importance [1, 2]. Industries, such as metallurgy, mining, and electronics, generate Cu as an effluent. Currently, wastewater treatment, instead of eliminating the problem completely, leads to the exchange of the metal from the liquid phase to the solid phase, which is still highly toxic and must be stored in landfills [3-6].

Cu electrodeposition has been widely used as an aluminum replacement in the connector industry [1, 7]. It also plays a key role in the electronics industry, especially in the manufacturing of printed and interconnected circuits, fabrication of microelectronic devices, and nanotechnology applications [8, 9]. Organic additives are commonly used in the acidic baths of copper sulfate electrodeposition to improve the quality of the deposits, including physical and mechanical properties such as gloss, hardness, smoothness, and ductility [10-12].

Among the various organic additives studied in the literature, citrate has been the most popular, especially in the electrodeposition of copper alloys [13, 14]. In terms of electrochemical techniques, electrodeposition is promising due to its high sensitivity and recovery of Cu in its solid state, which allows its reutilization. Additionally, electrodeposition has the advantages of low operation cost and high efficiency in the removal of metallic ions [7]. It is therefore necessary to use analytical techniques capable of identifying copper traces, such as graphite furnace atomic absorption spectroscopy (GFAAS), flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). These techniques, together with electrochemical techniques, are the most widely used for the determination of traces of heavy metals [15-17].

Electroanalytical technique validations using ICP-OES and ICP-MS are limited in the literature. A

few researchers [18-20], have used redissolved solution voltammetry to preconcentrate various metals, in order to provide low limits of detection and quantification. Oliveira *et al.* [18] developed a biochar-modified carbon paste electrode for use with differential pulse adsorptive stripping voltammetry (DPAdSV) for the determination of copper (II) ions in distillate samples (cachaça, vodka, gin, and tequila). Validation of the sensor was performed by ICP-OES, with the results concordant with a confidence interval of 95%.

Saidin *et al.* [19] studied the use of the multi-walled carbon nanotubes (MWCNTs) paste electrode modified with the tetracarbonylmolybdenum(0) nanocomposite to determine Cu(II) by using square wave anodic stripping voltammetry (SWASV). The response of the MWCNT paste electrode modified is linearly related to the concentration of Cu(II) in the 0.1 nM to 1.0 μ M range, and the limit of detection is 80 pM. The method was applied to the analysis of Cu(II) in water samples, and the results agreed well with those obtained by inductively coupled plasma optical emission spectrometry (ICP-OES).

Zamhari *et al.* [20] reported the simultaneous electrochemical detection of Co(II) and Cu(II) by 1-diazo-2-naphthol-4-sulfonic acid/MWCNTs modified glassy carbon electrode (GCE) by differential pulse anodic stripping voltammetry (DPASV) in a batch system. The method was successfully applied in real water samples and the results were in good agreement with those obtained by ICP-OES.

The objective of this work was to develop a method for the determination of potentiostatically deposited Cu in citrate medium by chronoamperometry (CA) and anodic linear scanning voltammetry (ALSV), with validation by argon ICP-OES.

2. MATERIALS AND METHODS

Analytical grade reagents were used, with solutions of these reagents prepared with deionized water (Milli-Q system). Electroanalytical studies were performed using a potentiostat/galvanostat (model PGSTAT 30, Autolab). Physical characterization measurements were obtained using a scanning electron microscope (SEM model XL-30, Philips) coupled to an energy-dispersive X-ray (EDX) microanalyzer. Quantification measurements were performed using an ICP-OES (model Optima 4300 DV, Perkin Elmer Instruments).

The two electrochemical cells of the Pyrex[®] glass, capacity 50 mL, and Teflon[®] tamp caps were used for the electrodeposition and electrodisolution of the Cu deposits. The platinum working electrode (99.95%, Degussa), with surface area = $8.0 \times 10^{-3} \text{ cm}^2$, was pre-polished with 1200 grit silicon carbide sandpaper. A platinum plate (99.95%, Degussa), 0.5 cm^2 in size, and saturated calomel, were used as the auxiliary and reference electrodes, respectively. For copper deposition, the solution used was composed of: $0.05 \text{ mol}\cdot\text{L}^{-1} \text{ CuSO}_4\cdot 5\text{H}_2\text{O}$, $0.03 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$, $0.02 \text{ mol}\cdot\text{L}^{-1} \text{ H}_3\text{C}_6\text{H}_5\text{O}_7$, and $0.2 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7$. The electrodisolution solution contained: $0.02 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$, $0.03 \text{ mol}\cdot\text{L}^{-1} \text{ H}_3\text{C}_6\text{H}_5\text{O}_7$, and $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7$.

For the ICP-OES experiments, two calibration curves were composed of 0.5, 1.0, 2.5, and $5.0 \text{ mg}\cdot\text{L}^{-1}$ Cu solutions prepared with 10% (v/v) HNO_3 in electrodisolution solution.

Initially, Cu deposition/dissolution was investigated using chronoamperometry (CA) and anodic linear scanning voltammetry (ALSV). All of the experiments were performed in triplicate at a scanning rate of $5.0 \text{ mV}\cdot\text{s}^{-1}$ and pH 5.9. The operating conditions used for ICP-OES were: radiofrequency power = 1330 W; argon gas plasma flow rate = $15 \text{ L}\cdot\text{min}^{-1}$; nitrogen gas flow rate = $0.5 \text{ L}\cdot\text{min}^{-1}$; nebulizer flow rate = $0.8 \text{ L}\cdot\text{min}^{-1}$; sample flow rate = $1.4 \text{ mL}\cdot\text{min}^{-1}$; number of replicates of each sample = 3; and processed signal = peak area (3 pixels).

The samples for ICP-OES analysis were prepared using chronoamperometric Cu deposition for 600 s, followed by electrodisolution by ALSV using the same electrolyte medium, without the presence of metal. Cu electrodisolution was performed in a fixed volume, using deposits from various potentials (-0.30, -0.50, -0.70, and -0.90 V). Aliquots of each were taken and diluted with water in a ratio of 1:1 to minimize interference effects.

The dissolved electrochemical mass was calculated, indirectly, by using the experimentally determined anodic charge, Equation (1) [21].

$$m = \frac{E_q Q_a}{F} \quad (1)$$

where E_q is the chemical equivalent ($\text{g}\cdot\text{mol}^{-1}$), Q_a is the anodic charge (C), and F = Faraday's constant ($96485 \text{ C}\cdot\text{mol}^{-1}$).

3. RESULTS

3.1 Electrochemical behavior study

Initial experiments of Cu electrodeposition were carried out using Cu salts in the presence of Na_2SO_4 , which acts as a support electrolyte. This method serves the functions of increasing the conductivity of the solution and minimizing the mass transport migration of electroactive species associated with citric acid/sodium citrate metal complexation [22]. From an electrochemical point of view, the use of complexing agents is of interest since they decrease the concentrations of free metal ions in solution, preventing the rapid deposition of cations onto the electrode surface that leads to the formation of rough, brittle deposits having displacement tendencies [22].

In electroplating, complexants are commonly added to the bath, with the purpose of reducing the amount of free cations in solution. This is because a portion of the metal of interest is complexed, while a portion of the cations are free in solution to be electrodeposited. With less free cations in solution, the electrodeposition reaction is slower, and forms better quality electrodeposits. Conversely, if the complexing agent is not added to the bath, the metal (cation) rapidly deposits onto the electrode surface, forming rough and brittle electrodeposits.

Chronoamperometry was used to investigate Cu electroactivity, using a platinum substrate in sulfate/citric acid/sodium citrate medium, with electrochemical behavior characteristic of an irreversible process being observed. The process of deposit formation/growth was observed, verifying the influence of potential inversion from -0.30 to -0.90 V. Cu deposition began around -0.20 V [23], with no current maxima being observed. The appearance of a single oxidation process was observed at -0.03 V, Figure 1.

As the sweep traveled to regions of more negative inversion potential, there was an increase in the amount of Cu deposited. This was due to the energy supplied to the system being increased, allowing a larger quantity of species in solution to be reduced, while also increasing the peak dissolution potentials, indicating that more copper was dissolved. This was supported by a calculation of the current efficiency process [14].

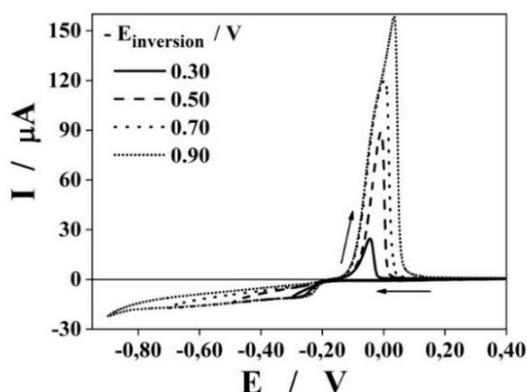


Figure 1: Cyclic voltammograms of the electrodeposition/electrodissolution of Cu using various inversion potentials registered in a $0.1 \text{ mol}\cdot\text{L}^{-1}$ citrate bath on a platinum surface.

The current efficiency (η) of the process, which is the ratio of the anodic species dissolution region and cathodic species deposition region loads, was calculated using experimentally determined cathodic and anodic charge values from the electrodeposition of electroactive species from the potential inversion differences of the Cu electrodeposition [24, 25]. As shown in Table 1, this calculation involves the ratio of the anodic/cathodic load being multiplied by 100. As mentioned earlier, as the inversion potential is increased to more negative values, the efficiency of the process is also increased.

Table 1: Current efficiency (η) of the Cu electrodeposition process in a 0.1 mol L⁻¹ citrate bath, at various inversion potentials recorded by chronoamperometry.

$E_{inv.}$ (V)	Q_c (catodic charge at mC)	Q_a (anodic charge at mC)	η (%)
-0.30	1.60	1.01	61
-0.50	7.86	6.71	85
-0.70	1.85	1.62	88
-0.90	2.49	2.21	89

The voltammograms shown in Figure 2 were recorded during ALSV experiments, in which two electrochemical cells were used. The first cell contained deposition solution Cu salts and additives, while the second cell contained electrodisolution solution. The composition of the electrodisolution solution was similar to that used for the CA experiments, with the exception of the concentration of Na₂SO₄ being 0.01 instead of 0.03 mol·L⁻¹ to balance the withdrawal of copper salts and maintain the same ionic strength.

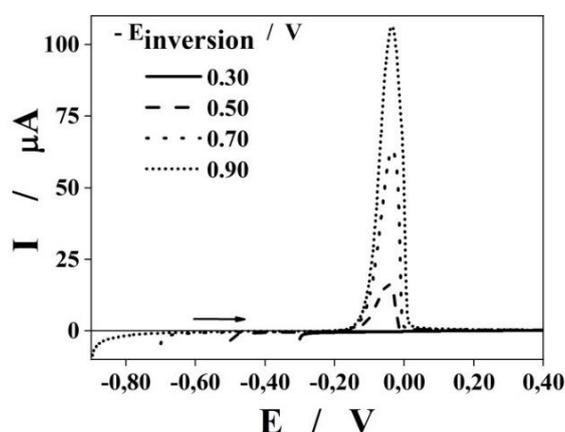


Figure 2: Linear voltammograms of Cu anodic electrodisolution using various inversion potentials registered in a 0.1 mol·L⁻¹ citrate bath on a platinum surface.

Deposition of electroactive species was performed by starting at a fixed initial potential of 0.40 V (a more negative region), and reaching a final variable potential of -0.30 V to -0.90 V. During the deposition process, for all of the final potential values, no current maxima were observed during Cu ($\text{Cu}^{2+} \rightleftharpoons \text{Cu}^0$) reduction. The dissolution process is presented in Figure 2, where a scan can be seen from variable initial potentials, equal to the final deposition potentials, to a fixed final potential.

During the sweep, copper dissolution ($\text{Cu}^0 \rightleftharpoons \text{Cu}^{2+}$) was observed as a single process, showing that the more negative the initial potential, the greater the area of the peaks obtained. This is because more of the metal was dissolved from the previous stage of Cu deposition ($\text{Cu}^{2+} \rightleftharpoons \text{Cu}^0$) and metallic copper formation. Therefore, the metallic Cu layer that formed on the surface of the substrate increased as the potential was increased.

The differences observed in the current efficiency values of Cu electrodeposition using the two techniques indicated a higher amount of deposit formation occurred during the process of CA versus ALSV. For the more positive inversion potentials (up to -0.50 V), the yield decreased considerably with ALSV, while the other potentials presented satisfactory yields, similar to those from CA. In both techniques, the potential of -0.90 V presented the highest current efficiency, and was chosen for studies of electrodeposition morphology, using a potentiostatic deposition time of 2,400 s.

The morphological analysis of Cu is shown in Figure 3A. Using a magnification of 5,000x, type morphology was observed, and remained constant regardless of the time or deposition potential applied. A homogeneous and uniform distribution of grains of different sizes was observed throughout the substrate surface. This morphology was also seen by Li, Du and Mei [26] in studies of electrodeposition of Cu, TiN and ZrO₂ simultaneously in Ni deposits from a citrate bath in the presence of additives, and the results shows that

the nanocomposite coating exhibits nodular-like structure with aggregated granules dispersed on the coating surface.

The EDX spectrum using a 100x magnification for this deposit shows the three characteristic peaks for copper identification, with no platinum identification peaks, due to the formation of a compact layer film covering completely the substrate, Figure 3B.

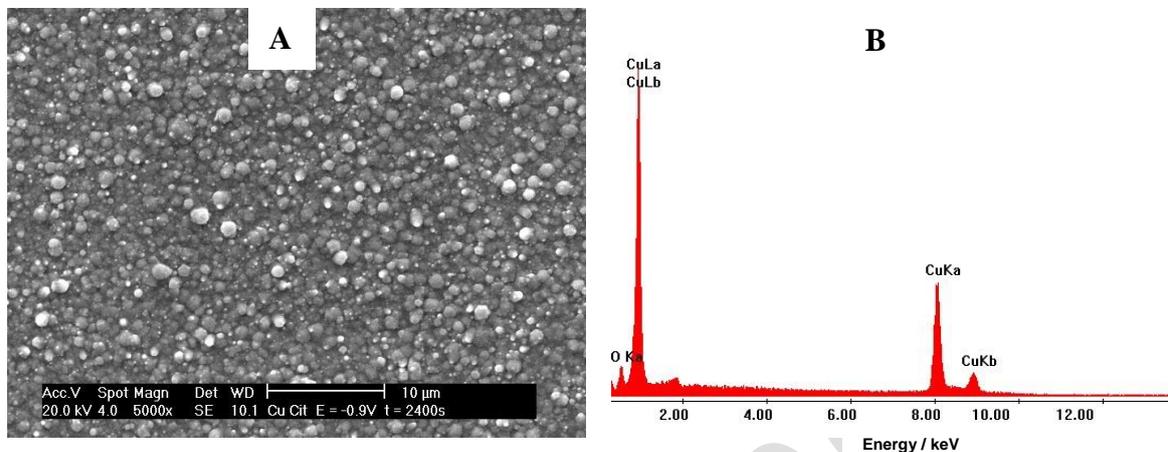


Figure 3: SEM micrograph (A) and EDX spectrum (B) of electrodeposits of Cu in a $0.1 \text{ mol}\cdot\text{L}^{-1}$ citrate bath on platinum, $E_{\text{dep}} = -0.90 \text{ V}$ for 2400 s.

3.2 Optimization of ICP-OES parameters for the determination of copper

First, a Cu emission wavelength was experimentally determined. Figure 4 shows a graph of intensity versus concentration for $\lambda = 324.752$ and 327.393 nm . Based on the calibration curves, both wavelengths had similar linearities, with correlation coefficients on the order of 0.9999.

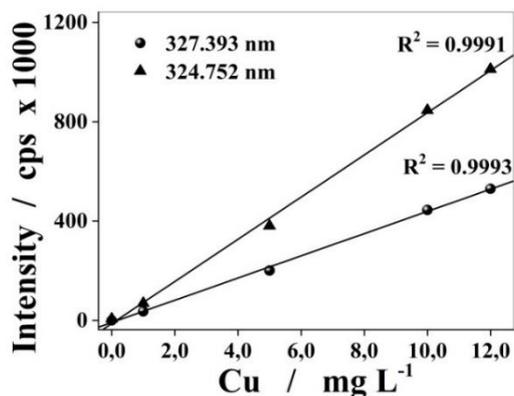


Figure 4: Cu concentration vs. wavelength intensity for ICP-OES.

Although they had similar linearities, it was observed that for $\lambda = 324.52 \text{ nm}$, the slope of the curve was greater, indicating greater sensitivity (angular coefficient = $84,896 \text{ cps}/(\text{mg}\cdot\text{L}^{-1})$, where cps = cycles per second). In contrast, for $\lambda = 327.393 \text{ nm}$, the angular coefficient was $44,707 \text{ cps}/(\text{mg}\cdot\text{L}^{-1})$. Therefore, the $\lambda = 324.752 \text{ nm}$ was selected for use, since it presented a 47% increase in sensitivity.

The effect of the support electrolyte in the electrodisolution medium on the Cu signal was evaluated. However, it was observed that the saline content of this medium caused a disruption in the plasma, leading to extinguishment. Therefore, the salt composition of the electrolyte medium was changed to a 50% composition of the original solution. Subsequently, a study was carried out using nitric acid medium and electrodisolution bath, to compare their effects on the Cu emission signal, Figure 5.

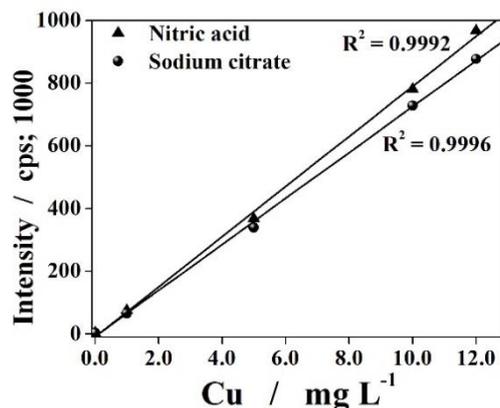


Figure 5: Cu concentration versus wavelength intensity in nitric acid medium and citric acid/sodium citrate medium for ICP-OES.

According to the results, there was a small decrease in sensitivity for the sodium citrate medium, specifically at higher Cu concentrations. This loss is demonstrated by comparing the values of the angular coefficients of the two curves. In the nitric acid medium, an angular coefficient of 79,863 cps/(mg·L⁻¹) was calculated, while an angular coefficient of 73,280 cps/(mg·L⁻¹) was calculated for the dissolution solution.

A possible explanation for this decrease in sensitivity may be due to spectral interferences from high levels of sodium emission, or an alteration in plasma temperature, since part of the plasma energy is absorbed by sodium ionization, because the presence of interfering elements, such as Na, K, and Ca that emit specific spectrum could change the background intensity, decreasing the signal to background ratio, consequently increasing detection limits [27].

3.3 Validation of the electrochemical method for the determination of Cu using ICP-OES

To certify the results obtained using the CA and ALSV techniques, it was necessary to validate the results obtained by ICP-OES. However, the Cu deposition time had to be adjusted due to the sensitivity of this emission technique. In this case, deposition times between 20 and 600 s were investigated, with 600 s for potentiostatic deposition being chosen.

The electrodeposits were subsequently dissolved in electrodeposition solution by ALSV. The content of Cu dissolved was calculated, indirectly, by the calculation of the electrochemical mass of Cu dissolved using the anodic charge, obtained from Faraday's law (Equation 1). Subsequently, the results were compared to those quantified by ICP-OES, Table 2.

Table 2: Cu contents determined by ALSV and ICP-OES in the dissolution potential range studied.

E _{inv.} (V)	ALSV	ICP-OES	RELATIVE ERROR (%)
	Cu (mg L ⁻¹) ± sd	Cu (mg L ⁻¹) ± sd	
-0,30	0,057 ± 0,001	0,052 ± 0,010	+ 8,77
-0,50	0,132 ± 0,001	0,145 ± 0,004	- 9,84
-0,70	0,181 ± 0,032	0,167 ± 0,021	+ 7,73
-0,90	0,195 ± 0,009	0,188 ± 0,006	+ 3,59
		Average	+2.56%

sd (standard deviation).

The Cu content values determined by both methods were very close. It was calculated that the copper content determined by the electroanalytical method versus the atomic emission method showed an average relative error of 2.56%. However, it was also noted that the error present is suggestive of a random distribution and is not specific to either one of the techniques. The relative error was calculated using the results of the electrochemical technique as a reference. In comparison to the errors calculated in this work, Saidin *et al.* [19] reported an average relative error of 0.83%, and Zamhari *et al.* [20] found errors ranging from -7.98 to +4.17% in real water samples analyzed, which average to a total error of -0.55%, and the results were in good agreement with those obtained by ICP-OES (p>0.05).

Figure 6 shows the Cu contents obtained from the comparison of the ALSV and ICP-OES methods, in which the least squares method was used to evaluate the correlation between the two techniques, defined by a linear regression line ($R = 0.9831$). In this figure, the symbols correspond to the means of the Cu concentrations obtained by ALSV and ICP-OES at different potentials of electrodisolution (Table 1), representing a 95% confidence interval. The confidence interval for the statistical tests performed in this work was in agreement with the results presented by Oliveira *et al.* [18]. The results showed that the electroanalytical techniques of CA and ALSV have high precision for Cu determination. The graph was constructed using the least squares method, with a 95% confidence interval.

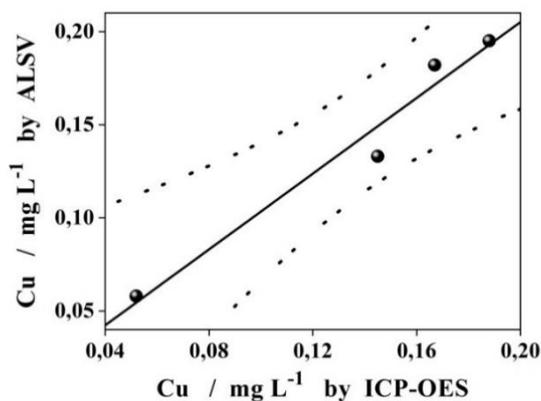


Figure 6: Least squares graph for the results obtained in the determination of Cu using ALSV and ICP-OES at different dissolution potentials.

4. CONCLUSIONS

The electrochemical electroconductivity assays performed for copper, using a platinum substrate in sulfate/citric acid/sodium citrate medium, showed electrochemical behavior characteristic of an irreversible process, with a well-defined oxidation peak at -0.03 V. The results obtained by chronoamperometry (CA) and anodic linear scanning voltammetry (ALSV) versus those quantified by inductively coupled argon plasma optical emission spectrometry (ICP-OES), were found to be very close, having a randomly distributed average error of 2.56%. The least squares method was used to evaluate the correlation between the two techniques (ALSV and ICP-OES), and the results of the statistical tests performed presented a 95% confidence interval.

It is therefore, possible to affirm that the electroanalytical techniques used (CA and ALSV) in this work, prove to be efficient for the determination of copper (at a ppb level), as attested by validation with ICP-OES.

5. ACKNOWLEDGEMENTS

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6. BIBLIOGRAPHY

- [1] ICSG – International Copper Study Group, *The World Copper Factbook 2020*, Lisbon, Portugal, 2020. 67p. Available in: <https://www.icsg.org/index.php/component/jdownloads/finish/170/3046>.
- [2] SILVA, L.A., VICTOR, M.M., LOPES, W.A., *et al.*, “Cobre: produção industrial e aplicações”, *Química Nova*, v. 42, n. 10, pp. 1154-1161, Nov. 2019.

- [3] GU, J-N., LIANG, J., CHEN, C., *et al.*, “Treatment of real deplating wastewater through an environmental friendly precipitation-electrodeposition-oxidation process: Recovery of silver and copper and reuse of wastewater”, *Separation and Purification Technology*, v. 248, n. 1, p. 117082, Oct. 2020.
- [4] CARVAJAL-FLÓREZ, R., CARDONA-GALLO, S.A., “Technologies applicable to the removal of heavy metals from landfill leachate”, *Environmental Science and Pollution Research*, v. 26, pp. 15725-15753, Apr. 2019.
- [5] COLLIVIGNARELLI, M.C., ABBÀ, A., BESTETTI, M., *et al.*, “Electrolytic Recovery of Nickel and Copper from Acid Pickling Solutions Used to Treat Metal Surfaces”, *Water, Air, & Soil Pollution*, v. 230, pp. 101-113, Apr. 2019.
- [6] HOSSAIN, R., NEKOU EI, K.R., MANSURI, I. *et al.*, “Sustainable Recovery of Cu and Sn from Problematic Global Waste: Exploring Value from Waste Printed Circuit Boards”, *ACS Sustainable Chemistry & Engineering*, v.7, n. 1, pp. 1006-1017, 2019.
- [7] DA SILVA, T.R., MAJUSTE, D., BAUER, J. *et al.*, “Effect of zinc ions on copper electrodeposition in the context of metal recovery from waste printed circuit boards”, *Hydrometallurgy*, v. 198, pp. 105513-105524, 2020.
- [8] SUNDARAM, R.M., SEKIGUCHI, A., SEKIYA, M. *et al.*, “Copper/carbon nanotube composites: research trends and outlook”, *Royal Society Open Science*, v. 5, pp. 180814-180834, Oct. 2018.
- [9] GRANADO, L., KEMPA, S., GREGORIADES, L.J. *et al.*, “Improvements of the Epoxy-Copper Adhesion for Microelectronic Applications”, *ACS Applied Electronic Materials*, v.1, n. 8, pp. 1498-1505, Jul. 2019.
- [10] PAGNANELLI, F. “Shape evolution and effect of organic additives in the electrosynthesis of Cu nanostructures”, *Journal of Solid State Electrochemistry*, v. 23, pp. 2723-2735, Aug. 2019.
- [11] GIURLANI, W., ZANGARI, G., GAMBINOSSI, F. *et al.*, “Electroplating for Decorative Applications: Recent Trends in Research and Development”, *Coatings*, v. 8, pp. 260-284, Jul. 2018.
- [12] LI, M., WEI, G., WANG, J. *et al.*, “Copper plating from non-cyanide alkaline baths”, *Surface Review and Letters*, v. 21, n. 1, pp. 1450009-1450015, 2014.
- [13] SANTOS, H.S., CORREA, A.A., GROMBONI, M.F. *et al.*, “Electrodeposition study of the Cu-Zn-Mo system in citrate/sulfate medium”, *Eclética Química Journal*, v. 44, n. special, pp. 26-35, Nov. 2019.
- [14] MELO, L.C., LIMA NETO, P., CORREIA, A.N. “The influence of citrate and tartrate on the electrodeposition and surface morphology of Cu-Ni layers”, *Journal of Applied Electrochemistry*, v. 41, n. 4. pp. 415-422, 2011.
- [15] MAJEED, H.J., EFTEKHARI, M., GHEIBI, M. *et al.*, “Synthesis and application of cerium oxide nanoparticles for preconcentration of trace levels of copper in water and foods followed by flame atomic absorption spectrometry”, *Journal of Food Measurement and Characterization*, v. 13, pp. 339-346, 2019.
- [16] KILIÇ, H.D., SEDA, D., DONMEZ, K.B. *et al.*, Application of stripping voltammetry method for the analysis of available copper, zinc and manganese contents in soil samples”, *International Journal of Environmental Analytical Chemistry*, v. 98, n. 4, pp. 308-322, 2018.
- [17] BIYANI, M., BIYANI, R., TSUCHIHASHI, T. *et al.*, “DEP-On-Go for Simultaneous Sensing of Multiple Heavy Metals Pollutants in Environmental Samples”, *Sensors*, v. 17, s17010045, 2017.
- [18] OLIVEIRA, P.R., LAMY-MENDES, A.C., RESENDE, E.I.P., *et al.*, “Electrochemical determination of copper ions in spirit drinks using carbon paste electrode modified with biochar”, *Food Chemistry*, v. 171, pp. 426-431, Mar. 2015.
- [19] SAIDIN, M.I., ISA, I.M., AHMAD, M. *et al.*, “Square wave anodic stripping voltammetry of copper(II) at a MWCNT paste electrode modified with a tetracarbonylmolybdenum(0) nanocomposite”, *Microchimica Acta*, v. 90, n. 4, pp. 1441-1448, Apr. 2016.
- [20] ZAMHARI, M., NUMNUAM, A., LIMBUT, W., *et al.*, “Simultaneous Electrochemical Detection of Co(II) and Cu(II) by 1-Diazo-2-Naphthol-4-Sulfonic Acid/MWCNTs Modified Electrode”, *Electroanalysis*, v. 29, n. 10, pp. 2348-2357, Oct. 2017.

- [21] BOWER, V.E., DAVIS, R.D., “The electrochemical equivalent of pure silver - A value of the Faraday”, *Journal of Research of the National Bureau of Standards*, v.85, n.3, pp.175-191, May./Jun. 1980.
- [22] AGOSTINHO, S.M.L., VILLAMIL, R.F.V., AGOSTINHO NETO, A., *et al.*, “O eletrólito suporte e suas múltiplas funções em processos de eletrodo”, *Química Nova*, v. 27, n. 5, pp. 813-817, Jun, 2004.
- [23] SNOOK, G.A., BOND, A.M., FLETCHER, S., “The use of massograms and voltammograms for distinguishing five basic combinations of charge transfer and mass transfer at electrode surfaces”, *Journal of Electroanalytical Chemistry*, v. 526, n. 1-2, pp. 1-9, May. 2002.
- [24] DEO, Y. GUHA, S., SARKAR, K. *et al.*, “Electrodeposited Ni-Cu alloy coatings on mild steel for enhanced corrosion properties”, *Applied Surface Science*, v. 515, p. 146078, 2020.
- [25] KONGSTEIN, O.E., HAARBERG, G.M., THONSTAD, J. “Current efficiency and kinetics of cobalt electrodeposition in acid chloride solutions. Part I: The influence of current density, pH and temperature”, *Journal of Applied Electrochemistry*, v. 37, n. 6, pp. 669-674, 2007.
- [26] LI, B., DU, S., MEI, T. “Pulse electrodeposited Ni-Cu/TiN-ZrO₂ nanocomposite coating: microstructural and electrochemical properties”, *Materials Research Express*, v. 6, n. 9, p. 096433, 2019.
- [27] KIM, J., ANAWATI, J. AZIMI, G. “Matrix complexity effect on platinum group metals analysis using inductively coupled plasma optical emission spectrometry”, *Journal of Analytical Atomic Spectrometry*, v. 33, n. 8, pp. 1310-1321, Aug. 2018.

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