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ELECTROANALYSIS OF COPPER IONS BY SENSOR BASED ON CARBON PASTE AND EDTA

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Abstract: In this article we have set ourselves the objective of developing new functional materials applied in electroanalysis. The aim is to develop new modified electrodes having analytical performance by immobilizing an organic film based on Disodium ethylenediaminetetraacetate dihydrate (EDTA) on the surface of carbon paste electrode (CPE). We performed electrochemical analysis traces of copper ions by the technique of square wave voltammetry (SWV) and cyclic voltammetry (CV). The objective of studying the electrochemical reactivity of the electrodes produced is to consider their use as voltammetric sensors dedicated to the detection of copper ions. The EDTA cation chelator power to improve the analytical characteristics of our electrodes, gives a high sensibility and stability, for determination of Cu(II) in a solution.

Keywords: EDTA; cyclic voltammetry; sensor; square wave voltammetry

INTRODUCTION

Sensitive and selective detection of heavy metal ions is particularly critical and challenging research area. Including several metal ions Cu(II) exposes essentiality as micronutrient element, it similarly has considerable value in biochemistry and metabolic processes of various living organisms [1,2]. Absence of Cu(II) may be to blame for the anemia, ischemic heart diseases, bone demineralization, cardiovascular effects, skin diseases etc. [3]. But recently, due to contamination instead of being an essential element, excessive doses of Cu(II) ion become threatening life issue for the living organisms [4]. Therefore, a number of methods and technologies have been produced for the sensitive and selective detection of metal ions. Highly identified techniques are liquid chromatography, atomic emission spectroscopy, spectrophotometry, and inductively coupled plasma mass spectrometry [5–10] etc.

several researchers based on the utilization of electrochemical sensors due to many advantages such as high sensitivity, rapidity of response, simplicity, low cost, miniaturized and automated devices [11,12]. In recent years, the development of innovative materials and new manufacturing processes has seen an increase due to improvement in research activities in the formulation of electrochemical sensors for the detection of heavy metals have considerably [13,14].

Carbon paste electrodes (CPE) have become a subject of development and research. CPE's are considerably more convenient, the electrode material cheaper and easy to handle and prepare with the desired composition and predetermined properties [15,16]. The electrochemical response of CPE varies mostly on the properties of the modifier species. The modification of the CPE can be done in several methods [17–20] and the immobilization method [21].

EXPERIMENTAL

— Apparatus

Voltammograms were recorded using a voltalab potentiostat model PGSTAT 100, controlled by voltalab master 4. The three-electrode electrolytic cell was utilized. As a working

electrode modified paste electrode, with a geometric area 0.1256 cm². A reference electrode was a saturated calomel electrode (SCE) while the counter electrode was a Pt wire.

— Reagents

Graphite powder (Carbone, Lorraine, ref 9900, French), CuSO₄ and all other reagents utilized were of analytical grade. All chemicals were employed without further purification. The supporting electrolyte was trisHCl buffer (pH = 5.06). Distilled water was utilized for all preparation of the solution. All chemicals employed for handling were of analytical grade.

— Preparation of the CPE

The carbon paste electrode (CPE) was made by hand mixing graphite powder and paraffin oil. The resulting paste was grounded into a PTFE cylindrical tube electrode. The electrode obtained was dried at room temperature. Electrical contact was made with a carbon bar. Modified CPE electrodes (EDTA-CPE) were prepared by immobilizing EDTA by soaking the prepared CPE electrode in a solution containing the EDTA solution.

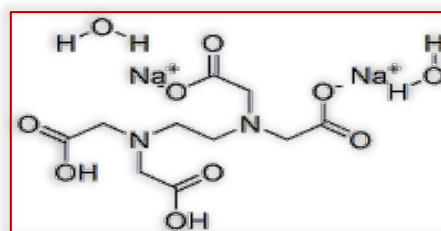


Figure 1. Molecule of disodium ethylenediaminetetraacetate dihydrate

RESULTS AND DISCUSSION

The influence of pH on EDTA immobilized on the CPE surface was studied in the pH range between 4 and 8 (Figure 2). By comparing the results obtained for the four pHs studied, we find that the highest activity and current densities are recorded at slightly acidic pH at pH 5. The pH 5 is therefore retained for the rest of the manipulations.

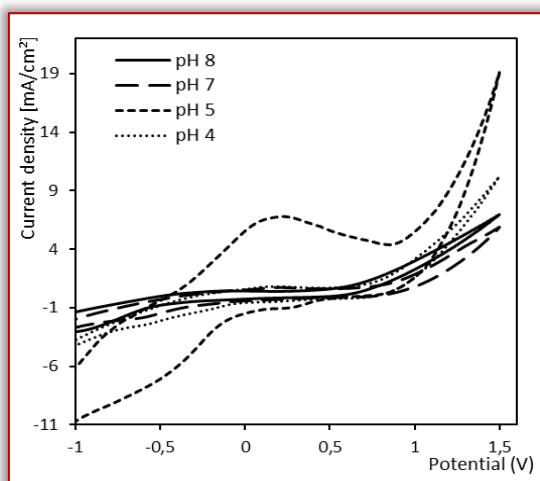


Figure 2. Cyclic voltammograms recorded in a Tris HCl solution at different pH, scan rate 100 mV/s.

Figure 3 illustrates the cyclic voltammograms recorded for the carbon paste electrode and the carbon paste electrode modified by the organic molecule, in a trisHCl electrolytic medium. The appearance of the voltammogram has completely changed in the existence of the EDTA molecule on the carbon surface, which proves the modification of the base electrode corresponding to the reaction proposed below:

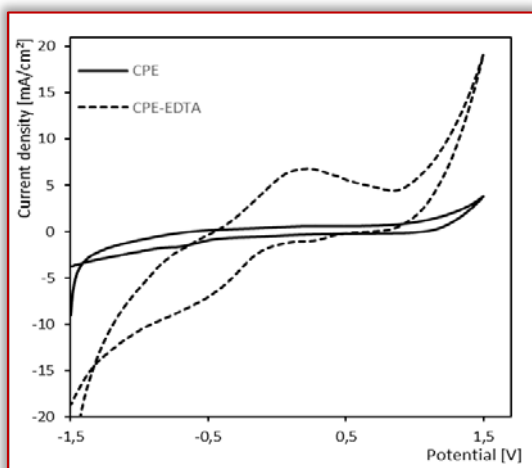
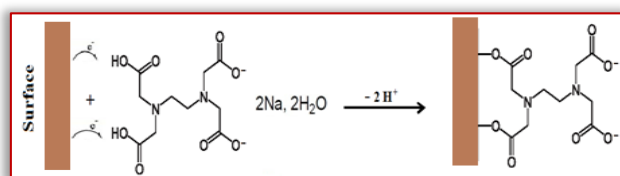


Figure 3. Cyclic voltammograms recorded in buffer solution (pH 5.06), CPE (a) and EDTA-CPE (b), Scan rate 100 mV/s.



Scheme 1. The proposed mechanism for the immobilization of the EDTA molecule on the surface of CPE.

In order to study the ability of EDTA on detection, the comparative study of the capacity for determining Cu (II) ion concentration by the CPE / EDTA electrode before and after preconcentration in a solution contains Cu²⁺ ions have been studied. The modified EDTA was preconcentrated in the analysed solution containing 70 mg/l copper ions in TrisHCl buffer solution. The CPE/EDTA electrode has two overlaid redox peaks of SWV significant for Cu (II) ions,

however, the CPE / EDTA electrode after preconcentration in Cu (II) ions has a superior current density than the modified electrode after preconcentration (Figure 4), result to the selective chelation capacity of EDTA molecules towards Pb (II) ions. VC method confirmed this result figure 5.

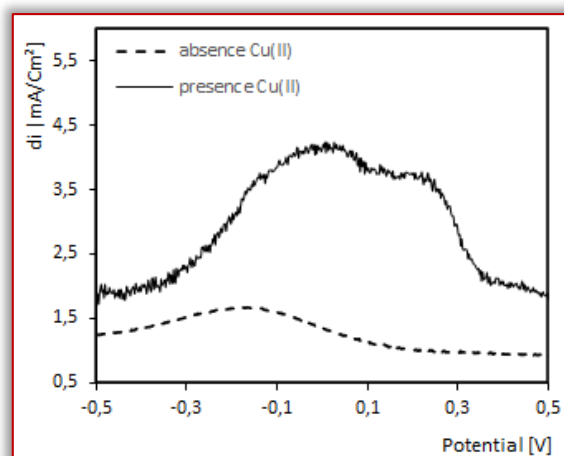


Figure 4. SQW voltammograms recorded for EDTA-CPE in buffer solution (pH 5.06), before and after preconcentration in copper solution, scan rate 100 mV/s.

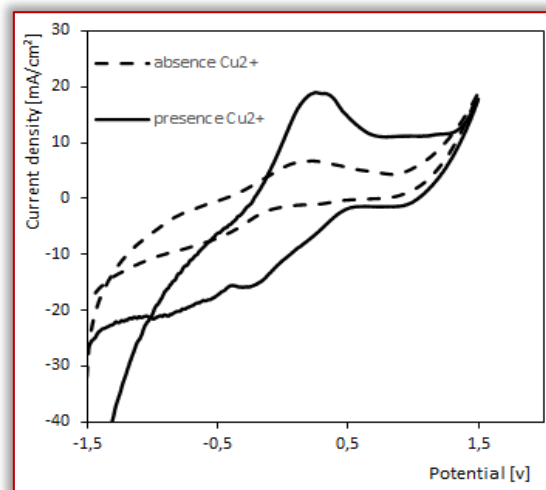


Figure 5. Cyclic voltammograms recorded for EDTA-CPE in buffer solution (pH 5.06), before and after preconcentration in copper solution, scan rate 100 mV/s.

The Figure shows typical curves, respectively, of CV and SWV recorded for the EDTA-CPE electrode, on solutions containing Cu(II) concentrations between $3,01 \times 10^{-4}$ mol/l à $4,816 \times 10^{-3}$ mol/l. The densities of the oxidation and reduction peaks increase linearly with the concentration of copper ions (Figure 6).

The linear calibration equation is as follows:

$$i_{P_{\text{anodique}}} \text{ (mA)} = 187,6 [\text{Cu}^{2+}] \text{ (mol l}^{-1}\text{)} + 2,7803, \\ R^2 = 0,9033$$

$$i_{P_{\text{cathodique}}} \text{ (mA)} = -201,6 [\text{Cu}^{2+}] \text{ (mol l}^{-1}\text{)} - 3,2372, \\ R^2 = 0,9143$$

According to Miller and Miller, the basic deviation of the mean current (SD) determined at the oxidation potential of copper for seven voltammograms of the solution contains Cu (II) concentrations in the pure electrolyte be able to be formed by l'equation:

$$SD = \frac{1}{(n-2)} \sum_{j=0}^n (i_j - I_j)^2 \quad (10)$$

where i_j is the experimental value of the current calculated at manipulation j and I_j is the corresponding value recalculated at the same concentration using the calibration equation. The calculated S.D. value was utilized for the determination of limit detection (DL, $3 \times \text{S.D.} / \text{slope}$) and limit quantization (QL, $10 \times \text{S.D.} / \text{slope}$). From this equation we deduce the following values:

≡ Detection limit (DL): 2.4×10^{-4} mol/l

≡ Limit quantification (QL) : $8,3 \times 10^{-4}$ mol/l

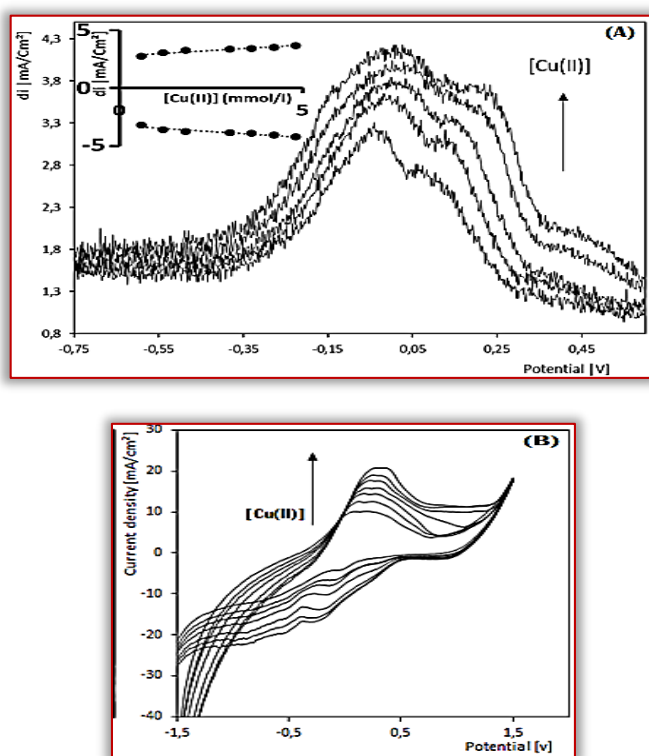
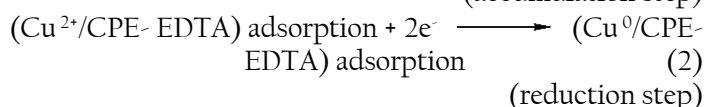
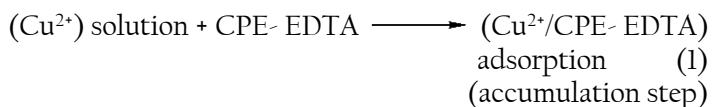
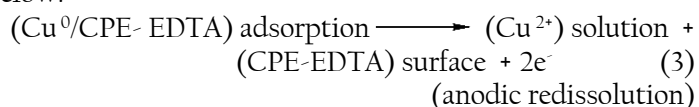


Figure 6. SQW (A) and CV (B) voltammograms obtained in EDTA-CPE, in buffer solution containing different concentrations of copper. Inset: Calibration curve obtained by analyzing copper ions in the range comprised between 3,01 and 4,16 mol/l.

After determining the calibration curves for the electroanalysis of Cu(II) ions, we propose the following mechanism:



The peak P2 corresponds to the phenomenon of oxidation of Cu and of salting out of Cu^{2+} , by following the mechanism below:



CONCLUSION

In this work we have studied the possibility of determining the Cu(II) ions by the carbon paste electrode modified by EDTA. The EDTA-CPE electrode prepares by self-assembly

method. The latter showed a great activity vis-à-vis the chelation of Cu^{2+} ions. Copper (II) analysis is possible by monitoring the oxidation peak of Pb^{2+} ions in the electrolytic solution. We work on the validation of the recommended method and the study of the interference of different metals for example Cd^{2+} , Hg^{2+} , etc.

References

- [1] Feier B., B'ajan I., Fizes I., an, Floner D., Cristea C., Geneste F., S'andulescu R. (2015) Highly selective electrochemical detection of Copper(II) using N, N'bis(acetylaceton) ethylenediimine as a receptor, *Int. J. Electrochem. Sci.* 10:121–139.
- [2] Niu L.M., Luo H.Q., Li N.B., Song L. (2007). Electrochemical detection of copper(II) at gold electrode modified with a self-assembled monolayer of penicillamine, *J. Anal. Chem.* 62:470–474.
- [3] Romana D.L., Olivares M., Uauy R., Araya M. (2011). Risks and benefits of copper in light of new insights of copper homeostasis, *J. Trace Elem. Med. Biol.* 253–13.
- [4] L.M. Gaetke, C.K. Chow. (2003). Copper toxicity, oxidative stress, and antioxidant nutrients, *Toxicology* 189:147–163.
- [5] Gillicuddy N. Mc, Nesterenko E.P., Nesterenko P.N., Jones P., Paull B. (2013). Chelation chromatography of alkaline earth and transition metals using monolithic silica column with bonded N-hydroxyethyliminodiacetic acid functional groups, *J. Chromatogr. A* 1276:102–111.
- [6] Lopes F.S., Junior O.A., Gutz I.G.R. (2010). Fully electrochemical hyphenated flow system for preconcentration cleanup, stripping, capillary electrophoresis with stacking and contactless conductivity detection of trace heavy metals, *Electrochem. Commun.* 12:1387–1390.
- [7] Xiaodong W., Qiuling Y., Zhidong Y. (2011). Qingwen, Determination of cadmium and copper in water and food samples by dispersive liquid-liquid microextraction combined with UV-vis spectrophotometry, *Microchem. J.* 97:249–254.
- [8] Kamal G., Yadollah N., Omid O., Ammar M. (2011). Sulfur-nanoparticle-based method for separation and preconcentration of some heavy metals in marine samples prior to flame atomic absorption spectrometry determination, *Talanta* 85:763–769.
- [9] Li W., Simmons P., Shrader D., Herrman T.J., Dai S.Y. (2013). Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper iron, manganese and zinc in animal feed and fertilizer, *Talanta* 11:243–48.
- [10] Dai B., Cao M., Fang G., Liu B., Dong Xv., Pan M., Wang S. (2012). Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS, *J. Hazard. Mater.* 219–220:103–110.
- [11] Beilsteins Handbuch der organischen Chemie (1971) Bd IX, U5, Springer Verlag, Berlin 4234.
- [12] Nikolski B.P., Krylow L.I., Zakhvataev B.B. (1973) *Radiokhimija* 15: 810-813.
- [13] Gao H, Qi X, Chen Y, Sun W (2011) Electrochemical deoxyribonucleic acid biosensor based on the self-assembly film with nanogold decorated on ionic liquid

- modified carbon paste electrode. *Anal Chim Acta* 704: 133-138.
- [14] Wang J. (2003) Nanoparticle-based electrochemical DNA detection. *Anal Chim Acta* 500: 247-257.
- [15] Svancara I., Vytras K., Barek J., Zima J. (2001) Carbon paste electrodes in modern electroanalysis. *Critical Reviews in Analytical Chemistry* 31: 311-345.
- [16] Rice M.E., Galus Z., Adams R.N. (1983) Graphite paste electrodes: Effects of paste composition and surface states on electron-transfer rates. *J Electroanal Chem Interfacial Electrochem* 143: 89-102.
- [17] Reddy S., Swamy B.K., Chandra U., Sherigara B.S., Jayadevappa H. (2010) Synthesis of CdO nanoparticles and their modified carbon paste electrode for determination of dopamine and ascorbic acid by using cyclic voltammetry technique. *Int J Electrochem Sci* 5: 10-17.
- [18] Tanuja S.B., Swamy B.E.K., Vasantakumar K.P. (2016) Electrochemical Response of Dopamine in Presence of Uric Acid at Pregabalin Modified Carbon Paste Electrode: A Cyclic Voltammetric Study. *J Anal Bioanal Tech* 7: 1.
- [19] Gilbert O., Chandra U., Swamy B.K., Char M.P., Nagaraj C., et al. (2008). Poly (alanine) modified carbon paste electrode for simultaneous detection of dopamine and ascorbic acid. *Int J Electrochem Sci* 3: 1186-1195.
- [20] Gilbert O., Swamy B.K., Chandra U., Sherigara B.S. (2009) Electrocatalytic oxidation of dopamine and ascorbic acid at poly (Eriochrome Black-T) modified carbon paste electrode. *Int J Electrochem Sci* 4: 582-591.
- [21] Shankar S.S., Swamy B.K., Ch U., Manjunatha J.G., Sherigara B.S. (2009) Simultaneous determination of dopamine, uric acid and ascorbic acid with CTAB modified carbon paste electrode. *Int J Electrochem Sci* 4: 592-601.



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