

A Novel Hybrid Composite Formed by Reaction of 4,5-Diphenyl-2-Imidazolethiol with Hexacyanoferrate (III) and Subsequent Reaction with Copper (II): Preparation, Characterization and a Voltammetric Application for Determination of L-Glutathione

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A novel Hybrid composite formed by interaction of 4,5-Diphenyl-2-Imidazolethiol and copper hexacyanoferrate (III) (CuHDIT) was characterized by Fourier transform infrared spectra (FTIR), x-ray diffraction (XRD), scanning electron and energy dispersive (SEM). CuHDIT was incorporated into a graphite paste electrode and the electrochemical studies were conducted with cyclic voltammetry. The cyclic voltammogram of the modified graphite paste electrode with CuHDIT, showed two redox couple with formal potential $E^{0'} = 0.24$ and 0.74 V (vs Ag/AgCl_(sat.), KCl, 1.0 mol L^{-1} ; $\nu = 20 \text{ mV s}^{-1}$), attributed to the $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Fe}^{2+}(\text{CN})_6/\text{Fe}^{3+}(\text{CN})_6$ redox processes respectively. The redox second redox couple (0.74V) presents an electrocatalytic response for determination of L-Glutathione. The modified electrode showed a linear response from 5.0×10^{-5} to $9.0 \times 10^{-4} \text{ mol L}^{-1}$. The method showed a detection limit of $5.33 \times 10^{-5} \text{ mol L}^{-1}$ with a relative standard deviation of $\pm 2\%$ ($n = 3$) and amperometric sensitivity of $12.52 \text{ mA mol L}^{-1}$.

Keywords: 4,5-Diphenyl-2-Imidazolethiol, Hexacyanoferrate (III), L-glutathione, cyclic voltammetry, graphite paste electrode.

1. INTRODUCTION

In electroanalytical chemistry, the modification of electrodes with new materials have been studied extensively in recent years, because chemically modified electrodes (CMEs) posses distinct

advantages over conventional electrodes in numerous applications areas including electrocatalysis and electrochemical sensors [1]. One of the advantages of CMEs is their ability to catalyze the oxidation and reduction of sites involved in electronic transfer reactions, there by increasing their sensitivity and selectivity of some electroactives species [2-4]. In addition, chemically modified carbon paste electrodes possess advantages of ease of preparation, ease of regeneration, stable response, very low Ohmic resistance [5] and CMEs posses distinct advantages over mercury electrodes because of their possible toxicity or because of rapid deterioration of electrode response [6]. Platinum and gold electrodes form surface oxide, causing complications with analytical applications also [7]. In this view point the graphite paste electrode offers advantages over methods of modification above mentioned.

In this paper, carbon paste electrode was modified with a new type of composite based on complexing of the 4,5-diphenyl-2-imidazoethiol following two stages; first with potassium hexacyanoferrate (III) and then cupric ions (CuHDIT). The modified graphite paste electrode with CuHDIT was characterized by cyclic voltammetry. We demonstrated that the modified paste electrode presents a responses towards L-Glutathione.

L-glutathione can exist in oxidized (GSSG) and reduced (GSH) forms [8] and it is involved in many cellular functions, especially in antioxidant defense [9]. The glutathione redox ratio is the major non-protein thiol in living cells [10].

GSH is capable of scavenging reactive oxygen and nitrogen species, which ar thought to contribute to the development of many common diseases including cancer, heart attack, stroke, arthritis [11].

Several methods have been described in the literature for determination of L-Glutathione, such as spectrophotometry [12, 13], potentiometry [14], high-performance liquid chromatography [15-18], spectrofluorimetry [19] and voltammetry [20-22].

Most of them are less susceptible to interference problems with sample preparation, as they often require extraction and pre-concentration steps [10]. However, electrochemical methods, present the advantages of simplicity and high sensitivity.

2. EXPERIMENTAL

2.1. Reagents and solutions

All reagents solutions and supporting electrolytes were prepared using Milli-Q water. L-Glutathione were used without further purification and all reagents and solvents were of analytical grade (Merck or Aldrich) and were used as purchased. All solutions and supporting electrolytes were prepared using Milli-Q water. The L-Glutathione solutions were prepared immediately before use and were deaerated with purified nitrogen. This procedure was adopted because this species can be oxidized to L-Glutathione by atmospheric oxygen.

2.2. Techniques

The spectra in the in-fared region were obtained by a Nicolet 5DXB FT-IR spectrometer (Nicolet Instruments, Madison, WI). The pastils for analysis were prepared using 150 mg of previously dried KBr PA of the Synth brand and 1.5 mg (1.0% (w/w)) of each sample. A minimum of 64 “scans” with a resolution of $\pm 4 \text{ cm}^{-1}$ in a band of 4000 to 400 cm^{-1} was used. The X ray diffraction patterns (XRD) spectroscopy were obtained using a Siemens D 5000 diffractometer with $\text{CuK } \alpha$ ($\lambda 1.5406 \text{ \AA}$ radiation), submitted to 40 kV, 30 mA, $0.05^\circ \text{ s}^{-1}$ and exposed to radiation from 5 up to 50° (2θ). The scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) of the any materials were obtained using a JEOL JSM T-300 microscope. The samples were adhered over aluminum holders and covered with a thin layer (20–30 nm) of gold in Sputter Coater Bal-Tec SCD-050. The cyclic voltammetry readings were obtained by potentiostat of Microquímica (MQPG-01) on a scale ranging from - 0.2 to 1.0 V (versus Cl). The electrochemical system was composed of three electrodes: a working electrode (internal diameter 0.5mm) of graphite paste modified with 20% CuHDIT, 25 μL Nujol, as reference electrode ($\text{Ag}/\text{AgCl}_{(\text{sat.})}$), and an auxiliary electrode made of platinum. In the electrochemical cell, the L-Glutatione solutions used in voltammetric experiments were prepared immediately before use and were deaerated with purified nitrogen.

2.3. Synthesis

2.3.1. Reaction of Hexacyanoferrate (III) and Copper with DIT to form CuHDIT

The CuHDIT composite were prepared as follows: 1.0 g of 4,5-diphenyl-2-imidazoethiol (DIT) was added to 25 mL of a solution of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ potassium hexacyanoferrate (III). The mixture was stirred for 1h at room temperature. The solid phase was then filtered and washed thoroughly with deionized water. The material resulting from this first phase were oven dried at 70°C and designated as HDIT. In the second stage, the HDIT was added to a solution of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of copper (II) chloride and the mixture was stirred for 1h at room temperature and then the solid was thoroughly filtered, washed with deionized water and dried at 70°C . The materials resulting from this stage were described by CuHDIT.

2.4. Preparation of the graphite paste electrode modified with CuHDIT

The graphite paste electrode modified with CuHDIT (GPE- CuHDIT) was prepared by mixing 20 mg of CuHDIT with 90 mg of graphite (Aldrich) and 50 μL of mineral oil. The electrode body was produced from a glass tube of 3 mm i.d. and 14 cm height, containing graphite paste. A copper wire was inserted through the opposite end of the glass tube to establish electrical contact. After homogenizing the mixture, the modified paste was carefully positioned on the tube tip to avoid possible air gaps, which often enhances electrode resistance. The external surface of the electrode was smoothed on soft paper. A new surface can be produced by scraping out the old surface and replacing the graphite paste.

2.5. Procedure

Initially, cyclic voltammograms (CV) were recorded for study the sensibility of L-Glutathione, by graphite paste electrode modified with CuHDIT. The supra analite solutions were prepared immediately before use and were deaerated with nitrogen. In most of the experiments, 1.0 mol L⁻¹ KCl (pH~7.2) was used as the supporting electrolyte. The catalytic and or sensibility current was estimated by the difference between the electrode current in the presence of analite compounds and that which is established in the blank solution.

3. RESULTS AND DISCUSSION

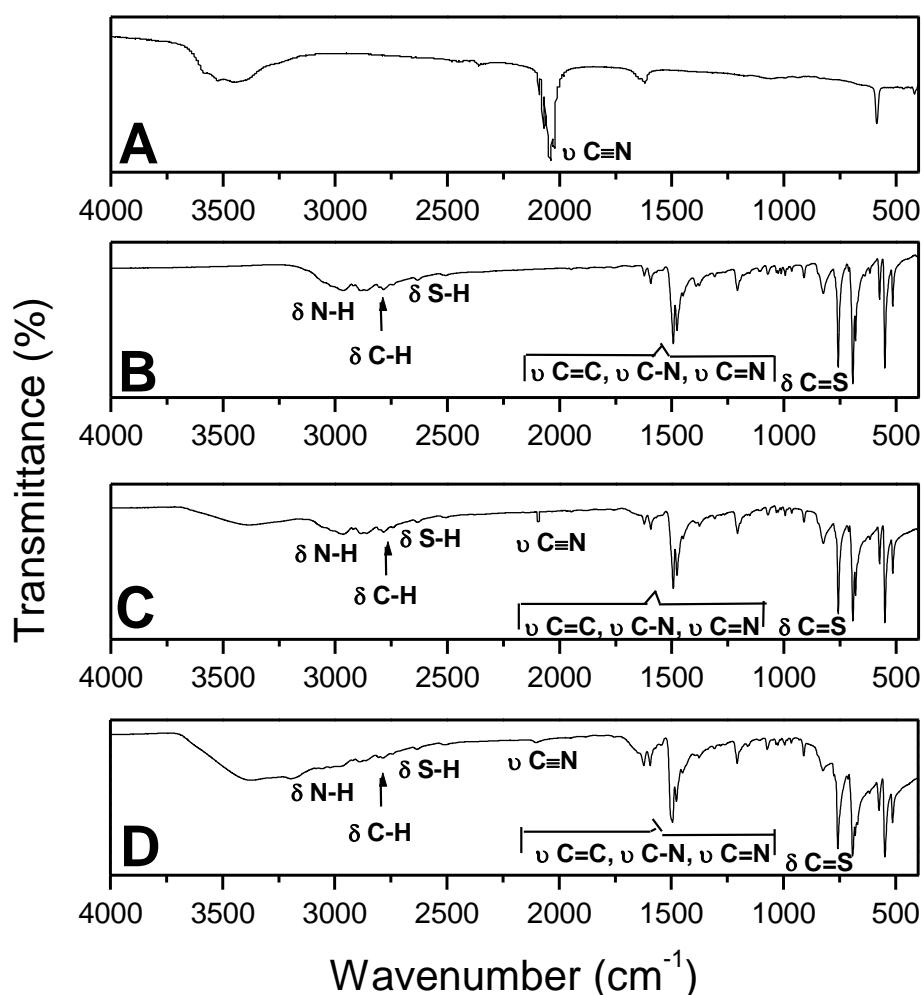


Figure 1. Vibrational spectrum of: (A) Potassium Hexacyanoferrate (III), (B) DIT, (C) HDIT and (D) CuHDIT.

The vibrational spectrum of potassium hexacyanoferrate (III), as illustrated in Figure 1 (A), showed an absorption band at about ~ 2112 and 2030 cm^{-1} which is a typical band of the material,

stretching which corresponds to the cage-shaped structure of $C\equiv N_{(\nu C\equiv N)}$ [23].

Figure 1 (B), (C) and (D) illustrate the vibrational spectra of DIT, HDIT and CuHDIT, respectively.

Figure 1 (B) refers to the vibrational spectrum of the DIT ligand, and exhibits characteristic bands of this compound such as the bands ranging from 1300 to 1530 cm^{-1} , related to the axial deformation vibrations of the imidazole ring bonds [23]. The broad and intense band at 2970 cm^{-1} was assigned to the axial deformation $N-H_{(\delta N-H)}$ [24, 25].

In the region between 3200 and 3500 cm^{-1} the bands observed were attributed to the axial deformation of $N-H_{(\nu N-H)}$, these bands probably overlap the bands attributed to the axial deformation of $C-H_{(\nu C-H)}$ ring bonds [23, 26].

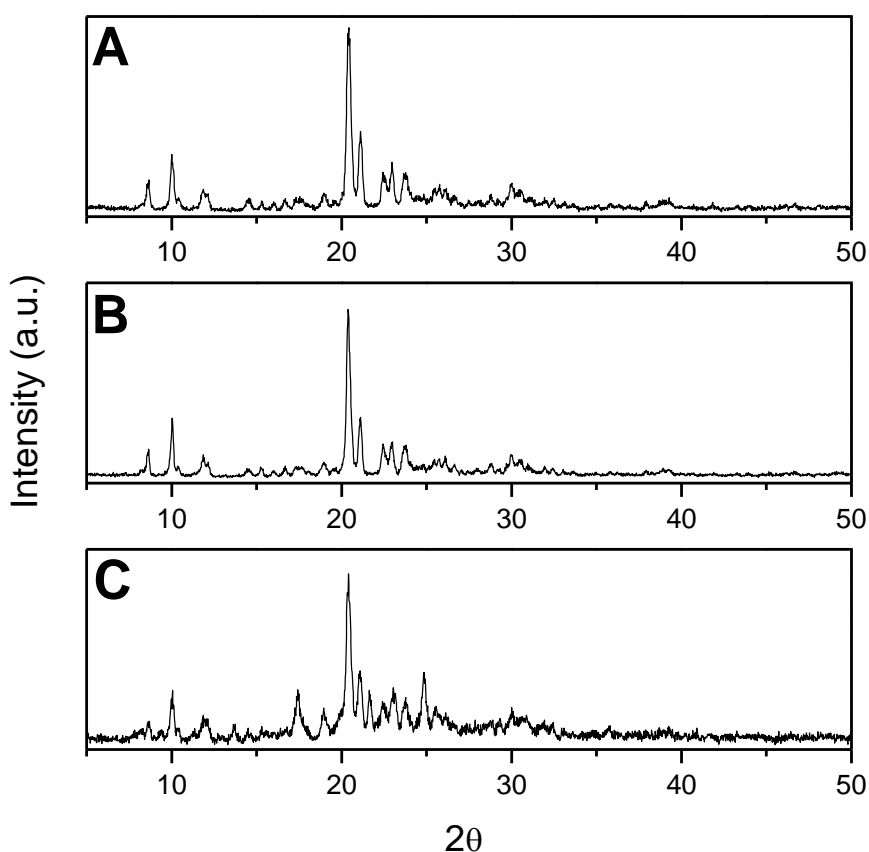


Figure 2. XRD of: (A) DIT, (B) HDIT e (C) CuHDIT.

Additionally, the Figure 1 (B), (C) and (D), the band is related to the stretching of the $C=S$ group ($\nu C=S$) around 768 cm^{-1} [27]. The spectra of the compounds in which the $C=S$ group is attached to a nitrogen atom showed an absorption band in the region of axial deformation usual $C=S_{(\delta C=S)}$, and many others in the region between 1563 and 700 cm^{-1} are assigned to the axial deformation of the $C=S_{(\delta C=S)}$, and $C-N_{(\delta C-N)}$ respectively [28].

A significant vibration, which can be observed in the spectra (C) and (D) are related to the vibrations of type $C\equiv N_{(\nu C\equiv N)}$ around 2042 cm^{-1} , characteristic of the stretching of the potassium hexacyanoferrate (III) [20], and the composite (HDIT) the $\nu C\equiv N$ is displaced about 49 cm^{-1} relative to the hexacyanoferrate (III) potassium.

As an application of this novel composite, DIT was firstly reacted with hexacyanoferrate (III), and then with Cu^{+2} to form (CuHDIT). The success of synthesis was verified by vibrational spectroscopy (FTIR) as illustrated by Fig. 1 (C) and (D).

Figures 2 (A), (B) and (C) corresponds to the XRD patterns of DIT, HDIT and CuHDIT respectively. According to the XRD patterns obtained, a crystallinity quite common. The DIT, HDIT and CuHDIT showed the following characteristics $2\theta = 8.53; 10.23; 12.01; 14.53; 15.25; 15.97; 16.81; 17.53; 19.09; 20.63; 22.83; 23.91; 25.83; 27.54; 28.03; 28.87; 30.43; 39.22$. So by the Scherrer equation [29], the size of the particles was estimate to be 288 nm for HDIT and 212 nm for CuHDIT.

The scanning electron microscopy (SEM) of the DIT, HDIT and CuHDIT with an increase of 10.000X, respectively. The scanning electron microscopy of DTI, HDIT and CuHDIT showed the presence of dispersed microparticles with sizes of around 9.0 and 10.0 micrometers, did not exhibit significant change in the size and topology of the materials.

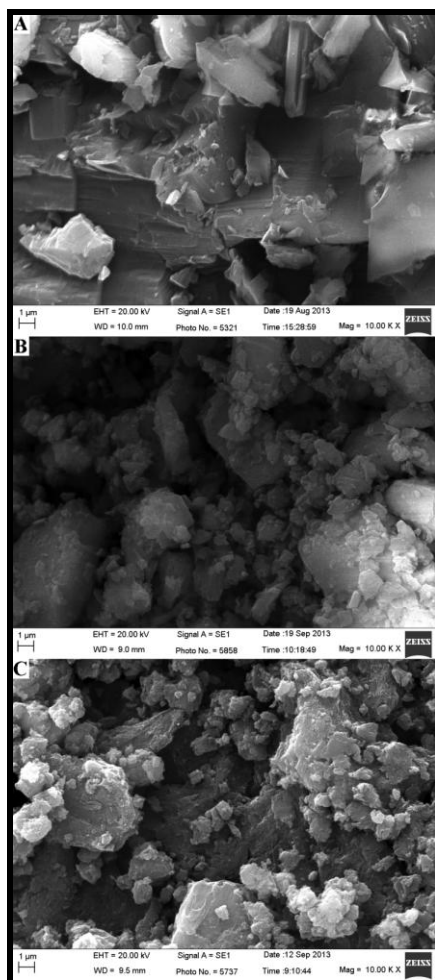


Figure 3. SEM of: (A) DIT; (B) HDIT and (C) CuHDIT.

Figures 4 (A), (B) and (C) show energy dispersive spectroscopy analyses (EDS) for DIT, HDIT and CuHDIT samples respectively. It was observed in the EDS spectrum of DIT (A) revealed the presence of C, N and S. In the EDS spectrum for HDIT (B) the presence of C, N, S and Fe. For the composite materials CuHSDIT (C) revealed C, N, S, Fe and Cu, which clearly shows the success in the preparation of CuHDIT.

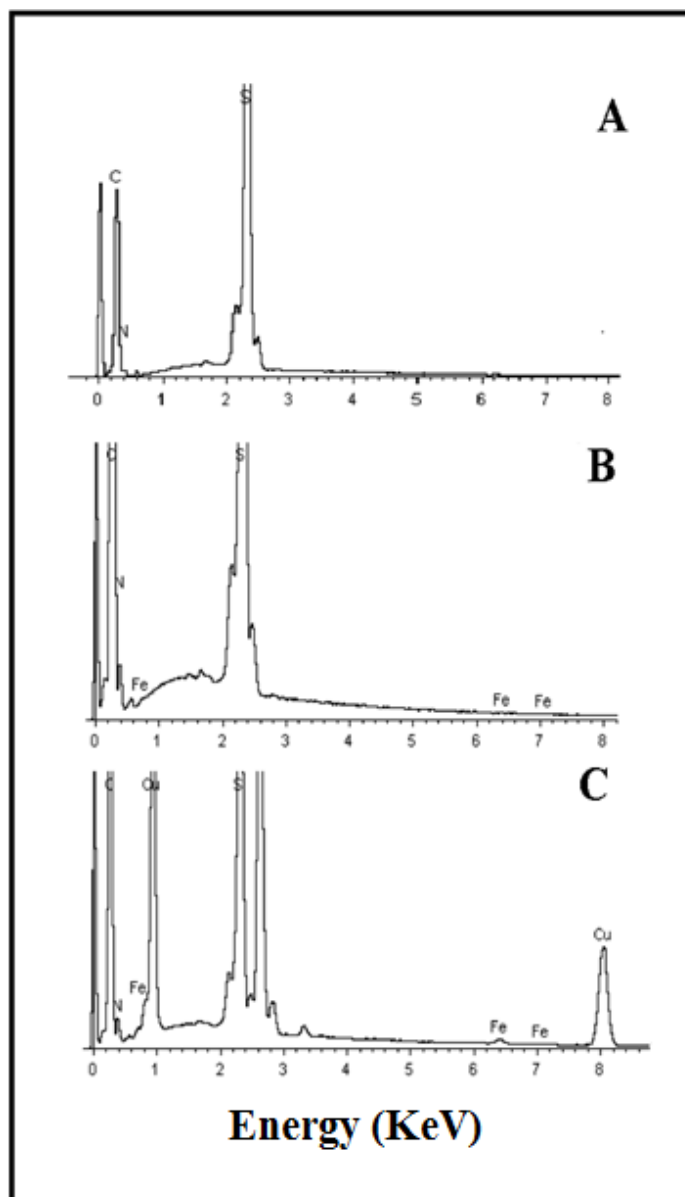


Figure 4. EDS of: (A) DIT, (B) HDIT e (C) CuHDIT.

CuHDIT was characterized by cyclic voltammetry as shown in Fig. 5. With the voltammogram of CuHDIT (20% w/w), a redox pair (peak I) was observed with a midi potential $E^{0'} = 0.24$ V and a redox pair (peak II) was observed with a $E^{0'} = 0.74$ V ($v = 20$ mV s⁻¹; KCl 1.0 M), attributed to the redox process $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and $\text{Fe}^{\text{II}}(\text{CN})_6/\text{Fe}^{\text{III}}(\text{CN})_6$.

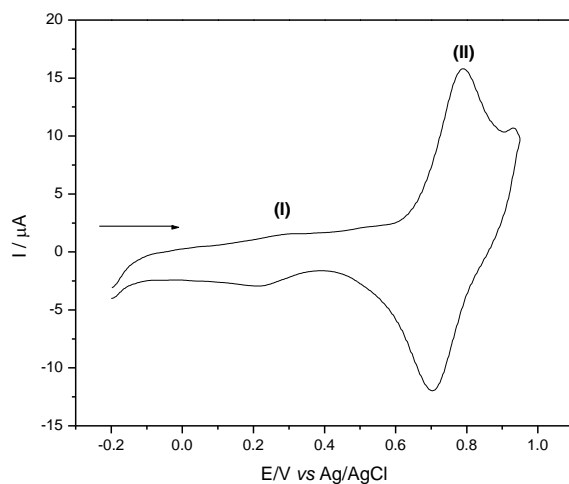


Figure 5. Cyclic voltammograms of graphite electrode modified with CuHDIT ($\text{KCl } 1.0 \text{ mol L}^{-1}$; $\nu = 20 \text{ mV s}^{-1}$; 20% (w/w)).

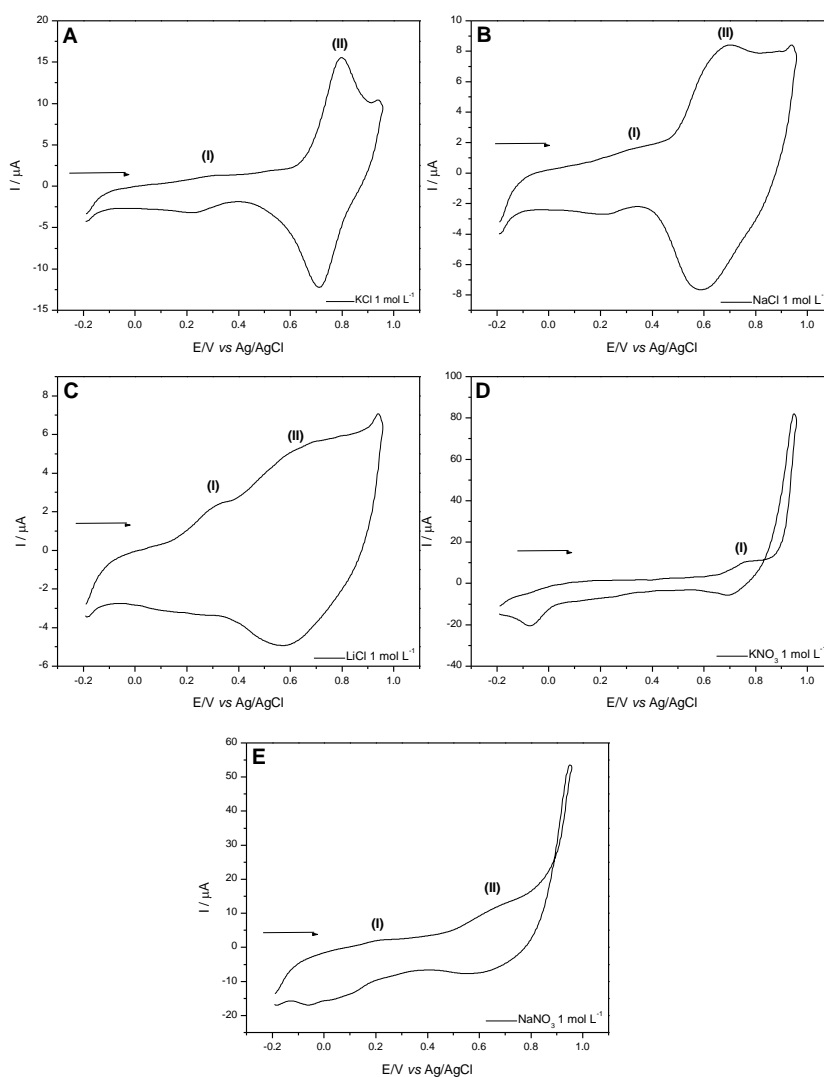


Figure 6. Cyclic voltammograms of graphite electrode modified with CuHDIT: (A) KCl, (B) NaCl, (C) LiCl, (D) KNO_3 and (E) NaNO_3 (1.0 mol L^{-1} ; $\nu = 20 \text{ mV s}^{-1}$; 20% (w/w)).

Studies on various supporting electrolytes (KCl, NaCl, LiCl, KNO₃ and NaNO₃) for studies of cations and anions are illustrated in Fig. 6. It was observed that the nature of the cations affected the average potential (E^{θ}) and the current intensities, but was not verified any interference of anions with exception of chloride (Cl⁻).

As shown in Table 1, which are also lists the main electrochemical parameters of the compounds and their respective hydration radii.

Table 1. Relation of the diameter of hydrated cations with the electrochemical parameters of CuHDIT ($v = 20\text{mV s}^{-1}$, $1,0\text{ mol L}^{-1}$, 20% w/w).

Electrolytes	$ I_{pa}/I_{pc} _{(I)}$	$\Delta E_{p(I)}$ (V)*	$E^{\theta}_{(I)}$ (V)**	$ I_{pa}/I_{pc} _{(II)}$	$\Delta E_{p(II)}$ (V)*	$E^{\theta}_{(II)}$ (V)**	Diameter of the hydrated cation (nm)***
KCl	0.40	0.06	0.24	0.70	0.08	0.74	0.240
NaCl	-	-	-	1.21	0.09	0.62	0.360
LiCl	-	-	-	0.65	0.04	0.60	0.470
KNO ₃	-	-	-	0.91	0.06	0.72	0.240
NaNO ₃	-	-	-	0.45	0.05	0.62	0.360

* $\Delta E_p = [E_{pa} - E_{pc}]$

** $E^{\theta} = [E_{pa} + E_{pc}] / 2$

*** Ref [30]

Analogous to studies on CuHDIT [31] and for being a compound analogous to Prussian blue, these materials exhibit a zeolite structure type, presenting cavities that allow the inflow and outflow of some metal ions with smaller hydration radii [32-34].

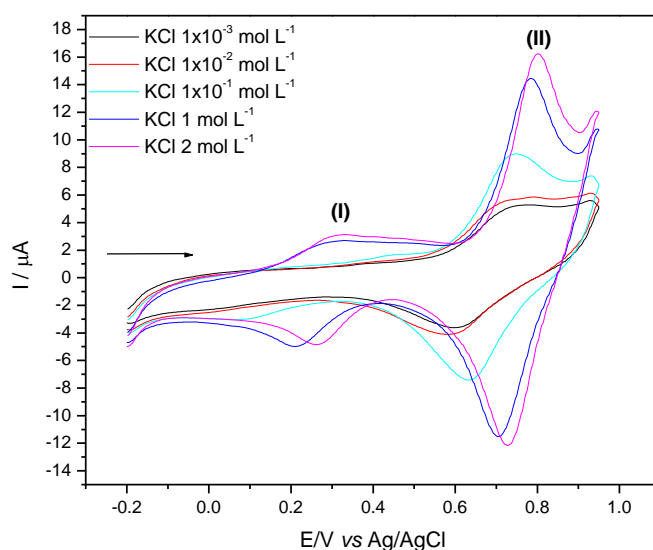


Figure 7. Cyclic voltammograms of the graphite paste electrode modified with CuHDIT at different concentrations (KCl; $v = 20\text{ mV s}^{-1}$; 20% (w/w)).

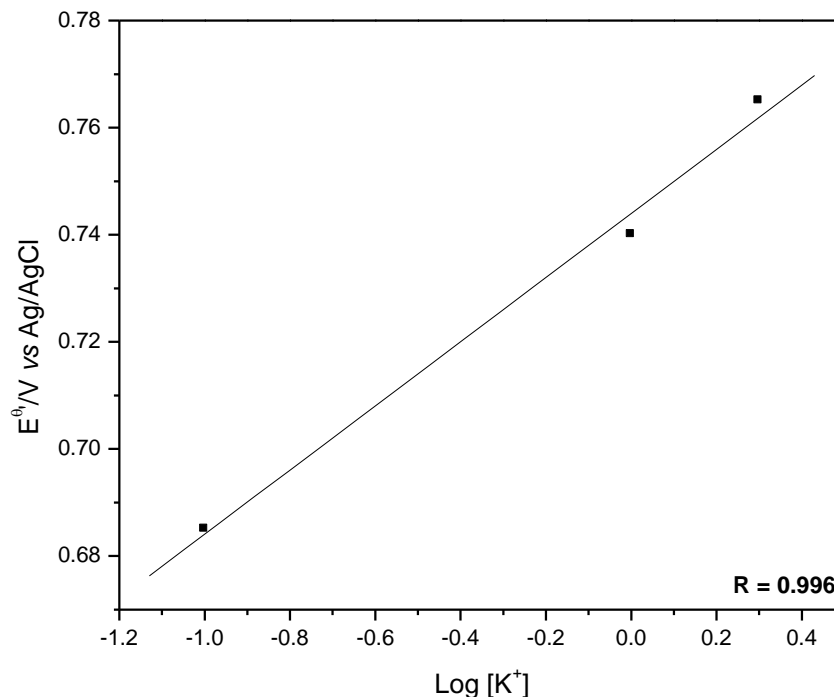


Figure 8. Average potential (E^{θ}) of graphite paste modified with CuHDIT as a function of KCl concentration.

For this reason, the cations K^+ (smaller hydration radii - Table 1) diffuse more easily between these cavities, resulting in a better electrochemical response of the modified electrode. With the data presented in Table 1, it was concluded that the electrolyte of KCl (K^+) showed a better voltammetric performance compared to the others electrolytes.

Fig. 7 illustrates the cyclic voltammograms obtained with different concentrations of KCl (1.0×10^{-3} to 2.0 mol L^{-1}). There is a small shift in formal potential to more positive values with increasing electrolyte concentration.

Fig. 8 shows that the average formal potential values (E^{θ}) shifted linearly ($R=0.996$) to more positive potentials by varying the concentration of KCl from 1.0×10^{-3} to 2.0 mol L^{-1} . This study enabled to see that for the graphite paste electrode modified with CuHDIT, the slope line is of 56 mV per decade of concentration of potassium ions, indicating that the behavior exhibited by the electrode moves close to quasi nernstian process with the transfer of one electron [35, 36].

The equations below describe the ratio of the concentrations of electrolytes in material CuHDIT.

Fig. 9 shows the cyclic voltammogram at different pH values (2-8). It was observed that at pHs 2 to 8 there is no significant change in the peak current and there is not shift of the average peak potential, which can affirm that the hydrogen ion concentration does not affect the electrochemical process.

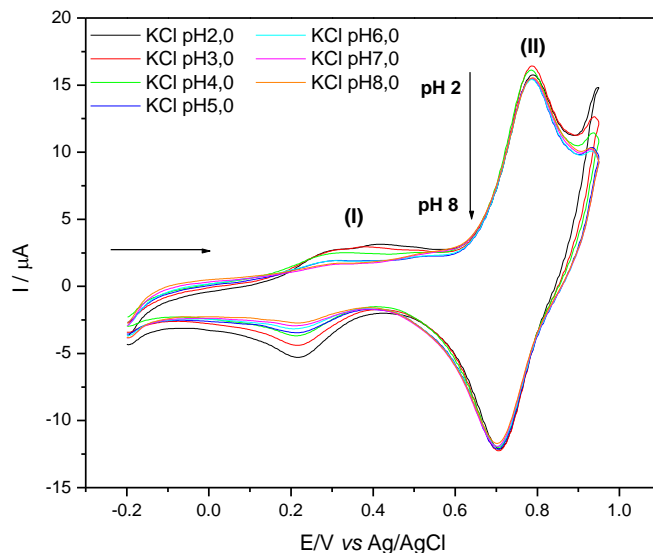


Figure 9. Cyclic voltammograms of graphite paste electrode modified with CuHDIT at different pH values ($\nu = 20 \text{ mV s}^{-1}$; KCl 1.0 mol L^{-1} ; 20% (w/w)).

Fig. 10 illustrates the cyclic voltammogram of CuHDIT at different scan rates (10 to 80 mV s^{-1}), it was observed that by increasing the scan rate there is an increased anodic peak current and also a small shift of the average potential to more positive values [35].

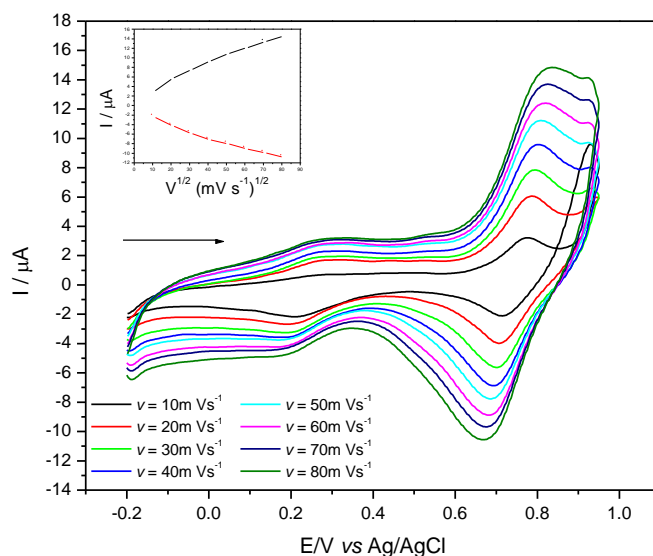


Figure 10. Cyclic voltammograms of CuHDIT at different scan rates (KCl 1.0 mol L^{-1} ; 20% (w/w)).
 Inserted Graphic: dependence of peak current intensity (anodic and cathodic) as a function of scan rate.

Furthermore, as illustrated by Fig. 10 (Inserted Graphic), the current intensities of the anodic and cathodic peak have a linear relationship with the square root of the scan rate, thus characterizing a diffusional process [36].

3.1. Electroanalytical application of composite CuHDIT electrocatalytic oxidation of L-Glutatione

Fig. 11 illustrates the voltammetric behavior of the graphite paste electrode modified with CuHDIT for the electro-oxidation of L-Glutatione in 1.0 mol L^{-1} KCl. The graphite paste unmodified electrode in a solution of KCl 1.0 mol L^{-1} in the absence (curve A) and presence of L-Glutatione (curve B) did not show a redox pair in the potential range studied between -0.2 and 1.0 V . After the addition of L-Glutatione there was an increase in the anodic peak current intensity (curve D) when compared with the graphite paste electrode modified with CuHDIT in absence of L-Glutatione (curve C). There was an increase in the anodic current intensity of the peak at 0.77 V and a small shift to more negative potentials. Thus, it was determined that with de adding aliquots of the L-Glutatione, the analite was oxidized by an electrocatalyst oxidation process on the electrode surface.

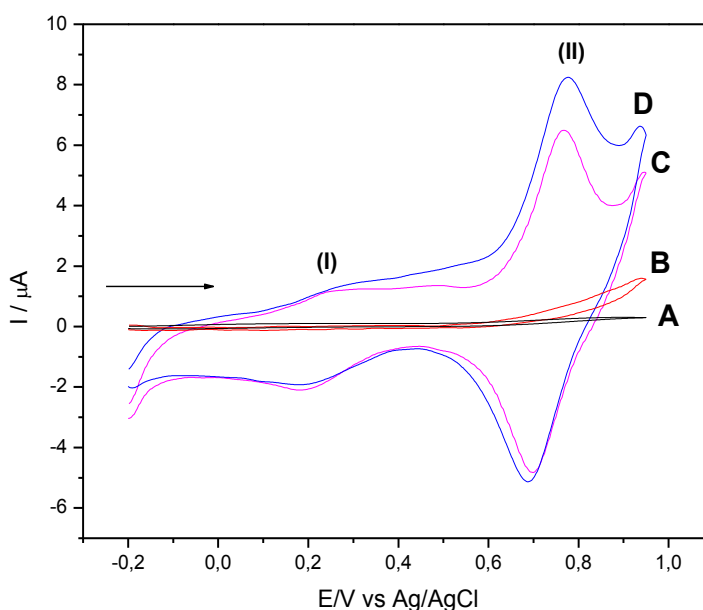
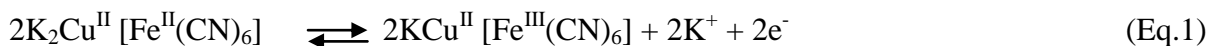


Figure 11. Cyclic voltammograms: (A) of the graphite paste electrode; (B) graphite paste electrode and $9.0 \times 10^{-4} \text{ mol L}^{-1}$ of L-Glutatione; (C) graphite paste electrode modified with CuHDIT and (D) graphite paste electrode modified with CuHDIT and $9.0 \times 10^{-4} \text{ mol L}^{-1}$ of L-Glutatione (KCl 1.0 mol L^{-1} ; 20 mV s^{-1} ; $20\%(\text{w/w})$).

The electrocatalytic oxidation of L-Glutatione occurs as follows: Fe^{3+} produced during anodic scan, chemically oxidize the molecule L-Glutatione when it is reduced to Fe^{2+} , which will again be electrochemically oxidized to Fe^{3+} .

To this system, the electrocatalytic process can also be represented according to the equations 1 and 2:



Thus L-Glutatione is oxidized at the electrode surface, and this process occurs in the potential of 0.77 V. The oxidation process does not occur in this potential when is used glassy carbon electrode or unmodified carbon paste (Fig. 11 B).

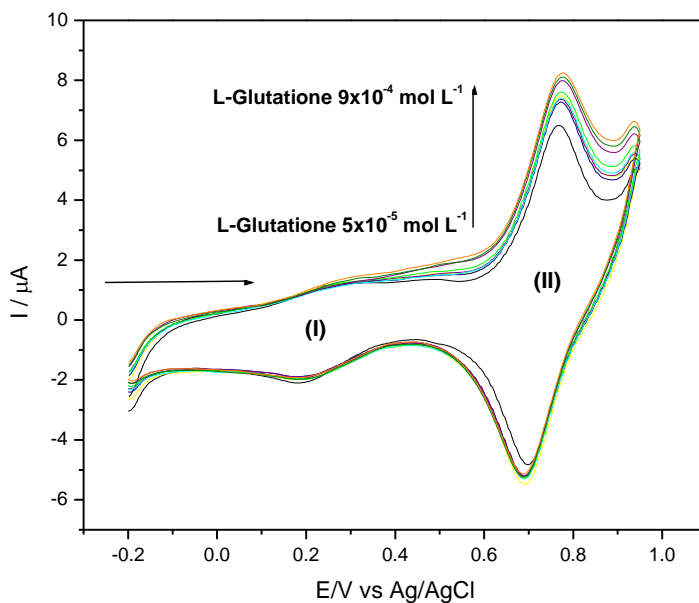


Figure 12. Cyclic voltammograms of applications of various concentrations of L-Glutatione graphite paste electrode modified with CuHDIT ($\text{KCl } 1.0 \text{ mol L}^{-1}$; 20 mVs^{-1} ; 20% (w/w)).

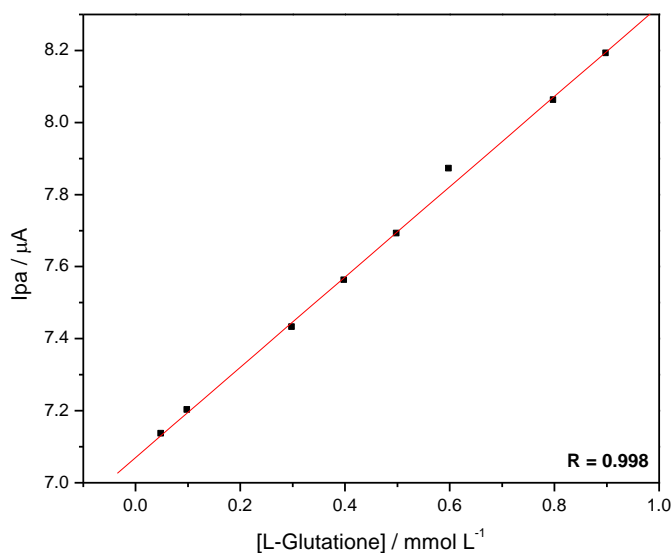


Figure 13. Analytical curve for the determination of L-Glutatione using the graphite paste electrode modified with CuHDIT ($\text{KCl } 1.0 \text{ mol L}^{-1}$; 20 mV s^{-1} ; 20%(w/w)).

The peak potential is not affected by the concentration of sulfite and the catalytic current is also linear with the square root of scan rate. The behavior of electrochemical oxidation of L-Glutatione in the CuHDIT. Fig. 13 illustrates the analytical curve used to determinate L-Glutatione. The modified electrode showed a linear response from 5.0×10^{-5} to 9.0×10^{-4} mol L⁻¹ with the corresponding equation $Y(\mu\text{A}) = 7.07017 + 12.53 \times 10^2 [\text{L-Glutatione}]$, and a correlation coefficient of $r=0.998$. The method showed a detection limit of 5.33×10^{-5} mol L⁻¹ with a relative standard deviation of $\pm 2\%$ ($n = 3$) and amperometric sensitivity of 12.52 mA mol L⁻¹.

4. CONCLUSION

A preliminary characterization by FTIR and cyclic voltammetry of a composite formed by interaction of a 4,5-diphenyl-2-imidazolethiol (DIT) potassium hexacyanoferrate (III) adsorption and subsequent reaction of copper (CuHDIT) was conducted using graphite paste electrode.

The cyclic voltammogram of the modified graphite paste electrode with CuHDIT, showed two redox couple, a redox pair (peak I) was observed with a midi potential $E^{\theta'} = 0.24$ V and a redox pair (peak II) was observed with a $E^{\theta'} = 0.74$ V ($v = 20$ mV s⁻¹; KCl 1.0 M), attributed to the redox process $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and $\text{Fe}^{\text{II}}(\text{CN})_6/\text{Fe}^{\text{III}}(\text{CN})_6$.

The redox couple presents electrocatalytic property for L-Glutatione. Quantitation in millimolar range of sulfite in pharmaceutical can be achieved using graphite paste electrode modified with CuHDIT. The modified electrode showed a linear response from 5.0×10^{-5} to 9.0×10^{-4} mol L⁻¹ with the corresponding equation $Y(\mu\text{A}) = 7.07017 + 12.5278 \times 10^2 [\text{L-Glutatione}]$, and a correlation coefficient of $r=0.998$. The method showed a detection limit of 5.33×10^{-5} mol L⁻¹ with a relative standard deviation of $\pm 2\%$ ($n = 3$) and amperometric sensitivity of 12.52 mA mol L⁻¹. Additionally the modified electrode showed a excellent stability and good reproducibility during experiments.

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