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Voltammetric Studies of Cobalt Hexacyanoferrate Formed on the Titanium (IV) Phosphate Surface and its Application to the Determination of Sulfite

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Titanium (IV) Phosphate (TiPh) composite was prepared using a easily methodology of the synthesis. As a second step, TiPh was reacted with Cobalte (TiPhCo) and subsequent hexacyanoferrate was added (TiPhCoHCF). A preliminary characterization of the precursor and resulting materials was carried out using spectroscopic and voltammetric techniques. The electrochemical behaviour of the composite (TiPhCoHCF) was verified by means of a graphite paste electrode using cyclic voltammetry in a potential range of -0.2 to 1.0 V (*vs* Ag/AgCl*)*. The cyclic voltammogram of the modified electrode containing TiPhCoHCF exhibited two redox couples. The first process (peak I) presented a formal potential (E^{θ}') = 0.37 V *vs* Ag/AgCl attributed to the redox process $Co^{(II)}$ / $Co^{(III)}$ and other more defined redox couple, (peak II), showed a E^{θ}' = 0.67 V *vs* Ag/AgCl which was attributed to the redox process $[Fe^{(II)}(CN)_6]$ /$[Fe^{(III)}(CN)_6]$. The second redox couple exhibited an electrocatalytic activity towards the oxidation of sulfite. The titanium phosphate modified graphite paste electrode showed a linear response from 2.0×10^{-3} to 1.0×10^{-2} mol L^{-1} with the corresponding equation Y(μA) = $24.78 + 8.56 \times 10^{3}$ [Sulfite], and a correlation coefficient of $r = 0.997$. The method showed a detection limit of 6.51×10^{-4} mol L^{-1} with a relative standard deviation of ± 5% ($n = 3$) and amperometric sensitivity of 9.19×10^{-3} A mol L^{-1}

Keywords: Titanium phosfate; cobalte hexacyanoferrate; voltammetry; graphite paste electrode

1. INTRODUCTION

In the last years a great effort has been devoted to develop chemically modified electrodes for several applications [1-5]. Modified electrodes use the specific interactions of the electrodes modifying materials with solution species in order to achieve higher selectivity and catalytic effects [6]. Other approach has been modifying electrodes with ion-exchange materials to adsorb electroactive species.

The ion-exchange materials used have been polymers, transition metal oxides and clays [1]. In this context composite based on titanium (IV) hydrogen phosphates are potentially promising inorganic materials for modify electrodes due its property of metal cations sorption.

The titanium (IV) hydrogen phosphates composite is specially interesting because of their high chemical stability, photochemical reactivity and amphoteric character [7-9]. The effect of phosphates on the surface acid-base and associated catalytic properties, strongly depends on the preparation method used [10,11].

Recently we report the preparations and voltammetric studies of Titanium (IV) Phosphate copper hexacyanoferrate (TiPhCuHCF) prepared from Titanium (IV) phosphate [12] for electrocatalytical determination of N-acetylcysteine. This method is characterized by its simplicity and rapidly in composite preparation.

As a complementary investigation, in order to obtain interesting solid electroactive materials as a potential sensor candidate, this work report the chemically modification of Titanium (IV) Phosphate (TiPh) by the so using two different steps of the synthesis : Initially, the material obtained from Titanium (IV) Phosphate (TiPh) was treated with Co^{2+} (TiPhCo) and than a second step was conducted with a subsequent reaction with hexacyanoferrate to give rise to a new hybrid composite (TiPhCoHCF, where CoHCF means cobalte hexacyanoferrate), which is a Prussian Blue analog, widely used for several electrocatalytical applications [13]. The idea is to combine the ion exchange properties with good ionic conductor of TiPh and this combination will facilitate charge transfer between CoHCF and TiPh due to the cation diffusion within the CoHCF mediated by TiPh component In this paper the novel material, after initial optimization conditions, was tested in the electrocatalysis of Sulfite.

2. EXPERIMENTAL

2.1. Reagents

All reagents were analytical grade (p.a Merck) and deionized water, with Milli-Q Gradient system from Millipore was used. The solutions of Sulfite were prepared immediately before use.

2.2. Techniques

2.2.1. Fourier transform infrared spectra

Fourier transform infrared spectra were recorded on a Nicolet 5DXB FTIR 300 spectrometer. Approximately 600 mg of KBr was grounded in a mortar with a pestle, and sufficient solid sample was grounded with KBr to make a 1wt % mixture to produce KBr pellets. After the sample was loaded, the sample chamber was purged with nitrogen for at least 10 min. prior the data collection. A minimum of 32 scans was collected for each sample at a resolution of 4 cm^{-1}.

2.2.2. X ray diffraction

The X ray diffraction patterns (XRD) were obtained using a Siemens D 5000 diffractometer with CuKα (λ 1.5406 Å radiation), submitted to 40 kV, 30 mA, 0.05^o s^{-1} and exposed to radiation from 5 up to 80^o (2θ).

2.2.3. Electrochemical measurements

For cyclic voltammetric measurements was employed a potentiostat from Microchemistry, MQP1 model. The electrochemical system used was composed of three electrodes: platinum electrode used as auxiliar, $Ag/AgCl_{(s)}$ as a reference and modified graphite paste as a working electrode. The working electrode consists of a glass tube with 15 cm long, with a inner diameter of 0.30 cm and external diameter of 0.5 cm with the internal cavity connected by a copper wire to establish the electrical contact.

The cyclic voltammetry technique was employed to study the electrochemical behavior of titanium (IV) phosphate modified with Silver hexacyanoferrate.

The catalytic current was established by the difference between the current measured in the presence of sulfite and in its absence. The solutions were bubbled with nitrogen for 10 minutes before the measurements.

2.2.4. Diffuse reflectance

The diffuse reflectance spectra of the bulk solid binuclear complex were recorded between 350 and 800 nm on a Guided Wave model 260 spectrophotometer, using a tungsten-halogen lamp as the radiation source, and detectors of Si and Ge.

2.3. Preparation of graphite paste electrode modified with TiPhCoHCF

The graphite paste modified with TiPhCoHCF was prepared from a mixture containing 40% (w / w) of 40 mg TiPhCoHCF with 60 mg graphite powder (Aldrich) and 30 μL of mineral oil.

2.4. Preparation of titanium (IV) modified with phosphoric acid (TiPh)

The synthesis of titanium phosphate [12] was performed as described below: in a round-bottom flask was added 35ml of phosphoric acid P.A. (85%), 20 mL of titanium isopropoxide (IV) ($Ti[OCH(CH_3)_2]_4$) and 10 mL deionized water under strong agitation. The turbid solution formed was allowed to stand in the dark for one day. After the solid phase formed, it was separated by a sintered plate funnel and dried at room temperature. The material was stored in desiccators and described as TiPh.

2.5. Binuclear complex formation with the TiPh

The preparation of the binuclear complex has been prepared in two steps; initially it was added 1.0 g of TiPh into 50 mL of 1.0×10^{-2} mol L^{-1} Co^{2+} solution (50% ethanol / water). This mixture was stirred for 60 minutes at room temperature and solid phase was then filtered and washed thoroughly with ethanol / water mixture several times, the prepared material was dried at temperature above 343,15 K. The material was described as TiPhCo. In a second step, the TiPhCo was added to an aqueous solution containing 1.0×10^{-3} mol L^{-1} potassium ferricyanide ($K_3[Fe(CN)_6]$). The solution was stirred for 2 hours then the precipitate was filtered, washed exhaustively with deionized water and dried at room temperature. The material formed was described as TiPhCoHCF.

3. RESULTS AND DISCUSSION

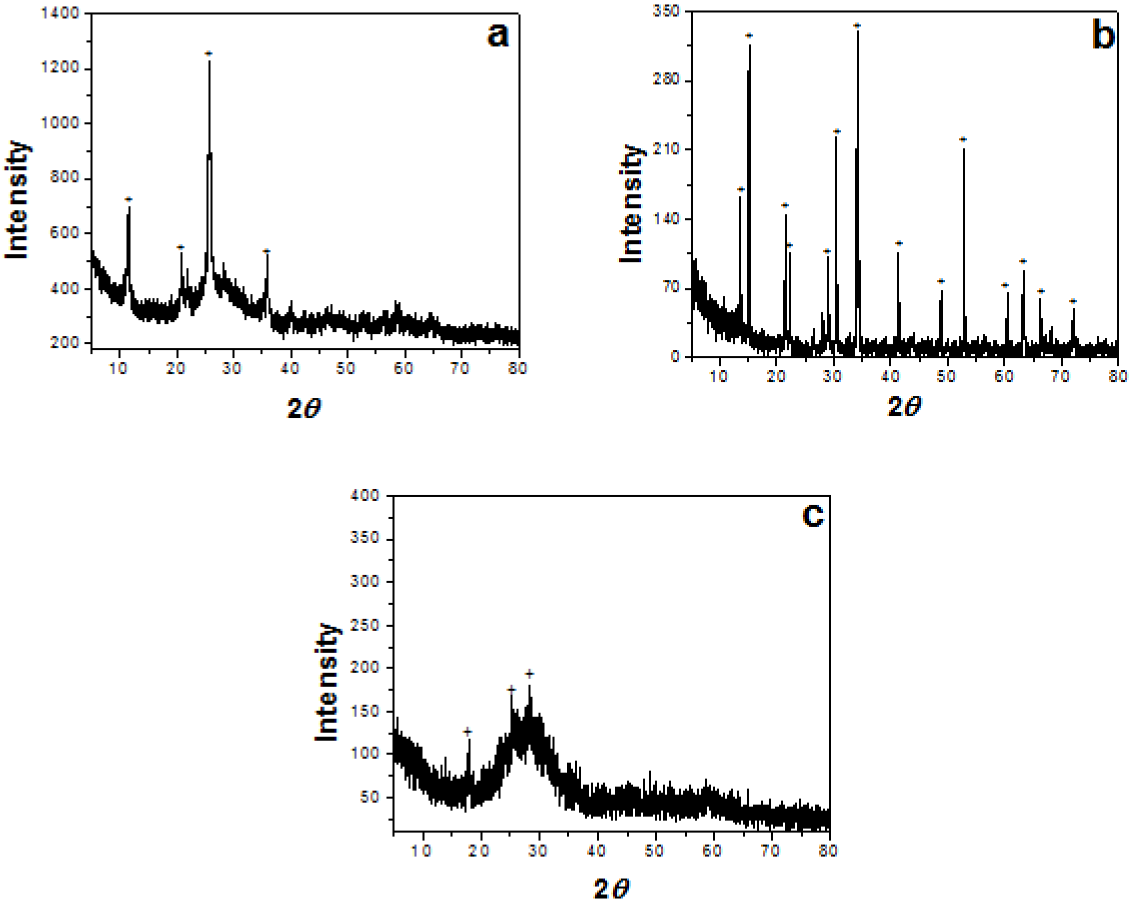

Figure 1. X-ray diffractogram of: **(a)** TiPh, **(b)** Potassium hexacyanoferrate and **(c)** TiPhCoHCF

The X-ray diffractogram of the TiPh is represented in Figure 1(a). The four intense peaks found in the diffractogram of the TiPh are in the regions of 11.55, 20.73, 25.60 and 35.72 degrees. Through the Search-Match software in order to elucidate the crystalline characteristic of the compound formed in the new synthetic route proposed, was determined that these peaks are characteristic of the compound $Ti_3(PO_4)_4$, whose file is the database JCPDS # 52-327. The X-ray diffractogram of the potassium hexacyanoferrate (HCF) is represented in Figure 1(b). The HCF has high crystallinity and was observed a intense peaks in the diffractogram are found in the regions of 13.65, 15.11, 21.49, 22.36, 29.05, 30.49, 34.12, 41.38, 49.05, 52.84, 60.24, 63.02, 66.19 and 72.15 degrees..

The X-ray diffractogram of TiPhCoHCF is represented in Figure 1(c), its amorphous part is noticeably sharper. TiPhCoHCF shows three intense peaks in the regions of 17.90, 25.38 and 28.56 degrees, both peaks are very pronounced in the diffractogram. In both materials (TiPh and TiPhCoHCF) two peaks near at 2θ 25.0 and 2θ 27.0° which correspond to anatase and rutile phases were observed [33].

The Figure 2(c) illustrates the spectrum in the infrared region of the TiPh, it was detected a broad band in the region of 3400 cm^{-1} which was attributed to symmetrical and asymmetrical –OH stretch, there is also a narrow and medium band in 1620 cm^{-1} that was assigned to H–O–H bond of water and a strong absorption at 1035 cm^{-1} which was attributed to v (P=O) stretching. The band observed at 1400 cm^{-1} was attributed to δ (POH) stretching [15,16]. The bands presented with values of 518 and 607 cm^{-1} correspond to links O–Ti–O [17]. The Figure 2(b) illustrates the spectrum in the infrared region of the TiPhCoHCF. The spectra (c) and (b) showed the same peaks observed in spectrum (c) except for a peak at 2136 cm^{-1} found only on the curve (b). This peak, assigned to v (C≡N) stretching shows the formation of cobalt hexacyanoferrate composite [18-20] formed at the surface of the starting material TiPh.

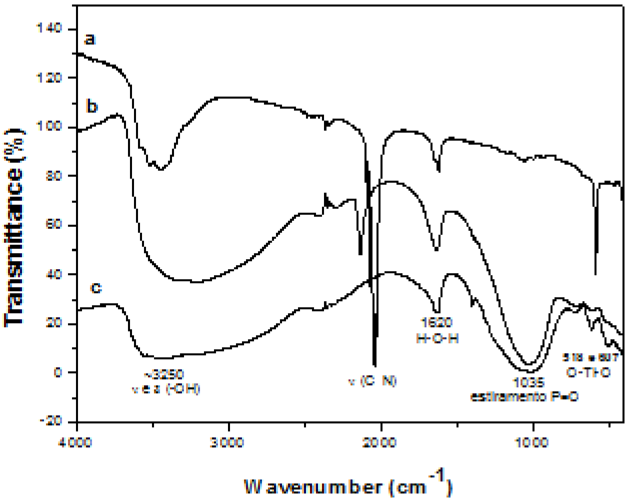

Figure 2. Infrared spectrum of: **(a)** HCF, **(b)** TiPh and **(c)** TiPhCoHCF

This peak is 108 cm^{-1} shifted with to higher energy with relation to potassium hexacyanoferrate (Fig. 2(a)).This behavior is in according to one described in the literature [18,19] and is attributed to both the kinematic coupling that occurs when a second mass is attached to the CN unit as well as to the fact that the N lone pair is antiboding with respect to the C≡N bond.CoHCF has been known to have strong absorption in the ultraviolet–visible range [21,22], whose absorption peaks appear at 390 and and 530 nm, respectively.

The diffuse reflectance of he supported binuclear species TiPhCoHCF after deconvolution, exhibit clearly two absorptions with λ_{max} 437 nm and 504 nm (see Figure 3a). These bands were attributed to LMCT (ligand to metal charge transfer) and MMCT (metal to metal charge transfer) process in the TiPh and in the [Co^{II}CNFe^{III}] moieties, respectively. These assigments were made by analogy with those described in the literature for the binuclear complex. The electronic transitions observed in the range 362–445 nm (Figure 3b) are due to strong charge-transfer absorption from ligand-orbital to vacant titanium orbital (ligand to metal charge-transfer, LMCT bands) which are strongly affected by the chemical nature of the ligands giving colours to the complexes [23].

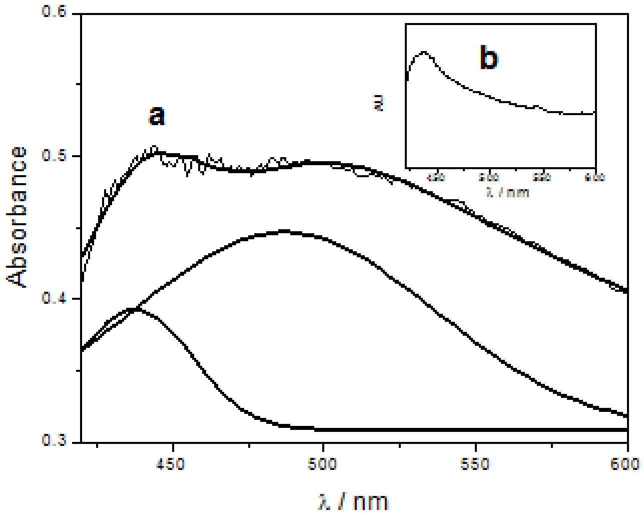

Figure 3. Diffuse Reflectance of: **(a)** TiPhCoHCF, after deconvolution and **(b)** TiPh.

3.1. Electrochemical characterization of TiPhCoHCF

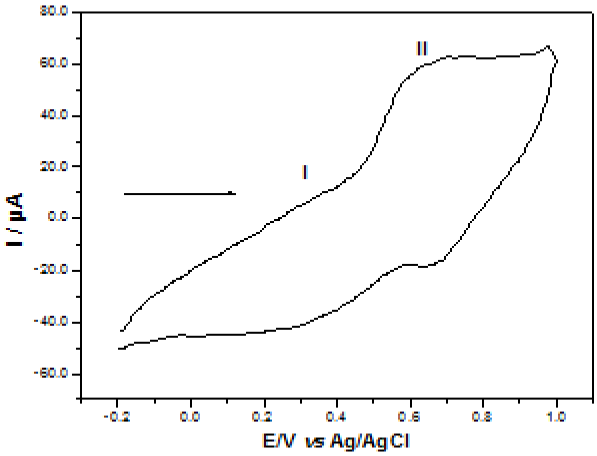

Figure 4. Cyclic voltammogram of graphite paste modified with TiPhCoHCF (v = 20 mV s^{-1}, KCl 1.0 molL^{-1})

Figure 4 illustrates the cyclic voltammogram of TiPhCoHCF. The material was characterized by cyclic voltammetry. It was possible to clearly observe a well defined redox couple (peak II) with an formal potential $E^{\theta\prime}$ = 0.67V *vs* Ag/AgCl which was attributed to the redox process $[Fe^{(II)}(CN)_6]$ / $[Fe^{(III)}(CN)_6]$ and other less defined redox couple (peak I) with formal potential $E^{\theta\prime}$ = 0.37V *vs* Ag/AgCl attributed to the redox process $Co^{(II)}$ / $Co^{(III)}$ [24,25]. This formal potential is in concordance with the value previously reported for cobalt hexacyanoferrate modified electrodes [26].

3.1.1. Voltammetric studies

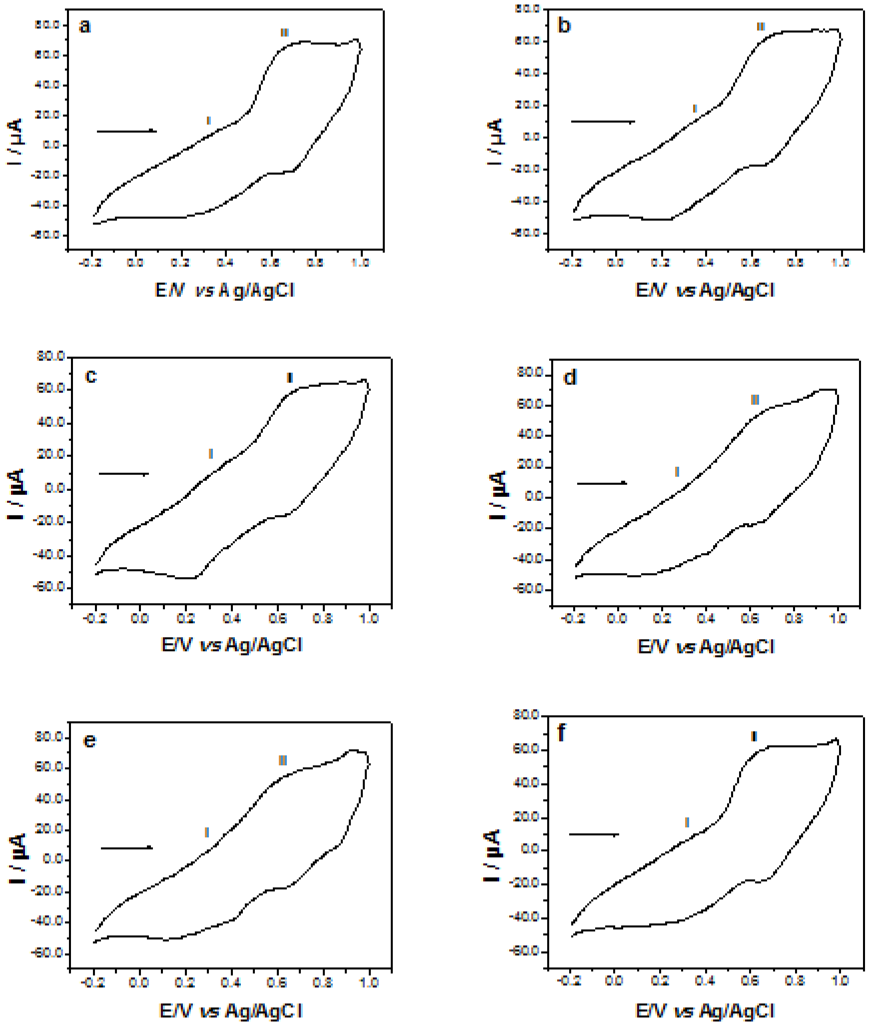

Figure 5. Influence of the nature of cations in the graphite electrode modified with TiPhCoHCF: a)KCl, b)NaCl, c)LiCl, d)$NaClO_4$ e)$NaNO_3$ f)KNO_3 (v = 20 mv s^{-1}; 1.0 mol L^{-1}).

The process of oxidation and reduction of the modified compounds on the surface of TiPhCoHCF occurs initially, the balance of cation present in the electrolyte to the electrode surface containing the material [17,27]. Different supporting electrolytes were used in the study of cations (LiCl, NaCl and KCl) and anions (KNO_3, $NaNO_3$ and Na_2SO_4). Through this study we observed that the nature of the cations affected the formal potential (E^{θ}') and the current intensities. The cyclic voltammograms obtained from studies of the influence of cations and anions are illustrated in Figure 5. Studies performed with different cations of the nitrate showed that not only the current intensity as well as the formal potential of redox couple processes (E^{θ}') are influenced by the cation nature, and these potentials are shifted to more anodic regions in the following sequence: $K^+ > Na^+ > Li^+$.

It is known that compounds such as Prussian blue and analogues exhibit structures with zeolite cavity, in order words, channels that allow the insertion of small molecules and ions that behave as zeolites [27-29]. By having smaller radius of hydration, the K^+ cation lodge more easily in the pores of the zeolite structure [27,28]. Table 1 lists the main electrochemical parameters of the compounds mentioned above and their radii of hydration.

Table 1. Main voltammetric parameters of TiPhCoHCF in the presence of different supporting electrolytes.

Electrolyte	*(E^{θ}')$_1$ (V)	*(ΔEp)$_1$(V)	Diameter of the hydrated cation (nm)
KCl	0.682	0.066	0.240
NaCl	0.681	0.075	0.360
LiCl	0.675	0.080	0.470
$NaClO_4$	0.679	0.074	0.360
$NaNO_3$	0.667	0.044	0.360
KNO_3	0.670	0.028	0.240

* $E°$' (V) = (E_{pa} + E_{pc})/2 e ΔEp (V) = |E_{pa} - E_{pc}|

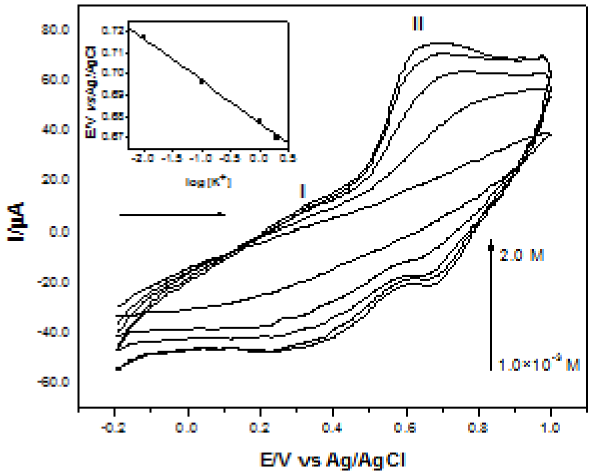

Figure 6. Cyclic voltammogram of graphite paste electrode modified with TiPhCoHCF in several concentrations (1.0×10^{-3} – 2.0 mol L^{-1}). (Inserted graphic: Formal potential (E^{θ}') of graphite paste modified with TiPhCoHCF a function of log concentration of KNO_3)

Figure 6 illustrates the cyclic voltammograms at different concentrations of KNO_3 (1.0×10^{-3} to 2.0 mol L^{-1}). Peak II showed a shift of potential ($E^{\theta\prime}$) to more negative values with increasing concentration of electrolytes. Increasing the concentration of KNO_3 observed the important participation of the K^+ ion in the redox process, where the potential shift was due to the change in the activity of these ions [27]. For the graphite paste electrode modified with TiPhCoHCF the slope of this line was 20 mV per decade concentration of potassium ions concentration indicating an almost Nernstian process [27,30] and two electrons are involved.

Figure 7 shows the cyclic voltammogram at different pH values (2-8). It was observed that varying the hydrogen ion concentration there is no change in current intensity of the anodic and cathodic peak as well as in other electrochemical

The inserted graphic in Figure 7 shows the effect of pH on the anodic current intensity (I_{pa}) of the modified graphite paste electrode. Its clear that the hydrogen ion concentration does not participate in the redox process, in order words, the formal potential ($E^{\theta\prime}$) of the redox process and other electrochemical parameters remained unchanged at different values of pH, but we chose pH 7.0, because the possibility of investigation of biological systems.

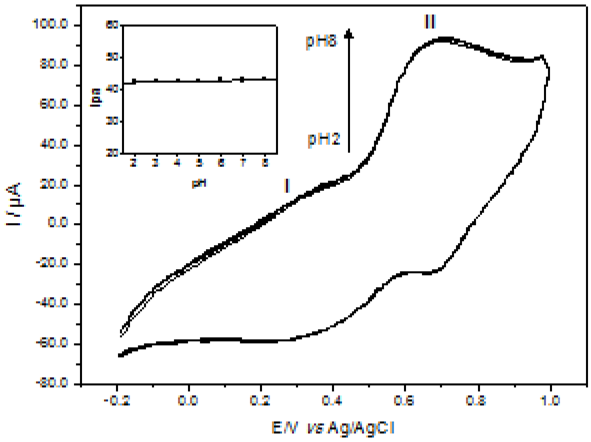

Figure 7. Cyclic voltammogram of graphite paste modified with TiPhCoHCF to different pH values (2 - 8); (KNO_3 1.0 mol L^{-1}, v = 20 mV s^{-1}). Inserted graphic: Dependence of current intensity of peak *II* in function of pH (2-8).

Figure 8 illutrates the cyclic voltammogram of TiPhCoHCF, respectively, at different scan rate (10 - 100 mV s^{-1}). With increasing scan rate, there is an increased current intensity of peak I and II and a shift of the peak II potential more positive. Through this study we chose the rate 30 mVs^{-1} for assembly of the analytical system, due to better performance voltammetric. Table 2 list the electrochemical parameters of TiPhCoHCF at different scan rate.

Figure 8 (inserted graphic) shows the linear dependence between the current intensity of the peak anodic/ cathodic and the square root of scan rate, characterizing thus a diffusion process [30]

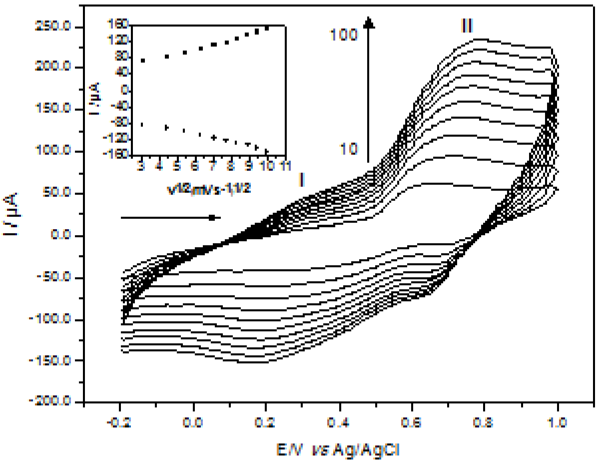

Figure 8. Cyclic voltammogram of TiPhCoHCF different scan rates: *10 - 100* mV s^{-1}; (KNO$_3$ 1.0 mol L^{-1}; pH 7.0). (Inserted graphic: Dependence of intensity current peak *I* (anode and cathode) with the square root of scan rate

Based on the results above, was chosen KNO$_3$ (1.0 mol L^{-1}, pH 7.0; v = 30 mV s^{-1}) to be used in subsequent voltammetric investigation.

As an application of the modified graphite paste electrode with TiPhCoHCF, after optimization of the voltammetric system, it was tested in the determination of sulfite.

Figure 9 illustrates the electrochemical behavior of graphite paste modified in the absence (curve a) and presence (curve b) sulfite 1.0×10^{-2} mol L^{-1}, both showed no redox couple in the range of potential studied (-0.2 to 1.0V). The curves c and d represent the cyclic voltammogram of graphite paste electrode modified with TiPhCoHCF in the absence and presence of sulfite 1.0×10^{-2} mol L^{-1}, respectively, showing that the TiPhCoHCF can be used for the electrocatalytic determination of sulfite.

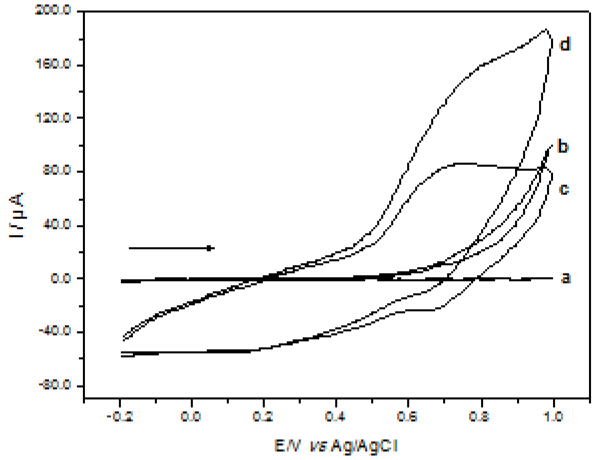

Figure 9. Cyclic voltammogram of: a) graphite paste electrode; b) graphite paste electrode in presence of 1.0×10^{-2} mol L^{-1} of Sulfite; c) graphite paste electrode modified with TiPhCoHCF; d) graphite paste electrode modified with TiPhCoHCF in presence of 1.0×10^{-2} mol L^{-1} Sulfite (KNO$_3$ 1.0 mol L^{-1} ; v = 30 mV s^{-1})

The electrocatalytic oxidation of SO_3^{2-} occurs as showed by equatios. 1 and 2: Fe^{3+} produced during anodic scan, chemically oxidize the molecule SO_4^{2-} when it is reduced to Fe^{2+}, which will again be electrochemically oxidized to Fe^{3+}. The Electrochemical and chemical processes can be represented according to equations 1 and 2 respectively:

$$Ti(H_2PO_4^-)_4K_2Co^{(II)}[Fe^{(II)}(CN)_6] \rightleftarrows Ti(H_2PO_4^-)_4Co^{(III)}[Fe^{(III)}(CN)_6] + 2K^+ + 2e^- \ (0.67\ V)$$

Eq. 1

$$Ti(H_2PO_4^-)_4Co^{(III)}[Fe^{(III)}(CN)_6] + SO_3^{2-} + 2K^+ + H_2O \rightleftarrows Ti(H_2PO_4^-)_4K_2Co^{(II)}[Fe^{(II)}(CN)_6] + SO_4^{2-} + 2H^+$$

Eq. 2

Thus SO_3^{2-} is oxidized at the electrode surface, and this process occurs in the potential of 0.67 V. The oxidation process does not occur in this potential when is used glassy carbon electrode or unmodified graphite paste. The peak potential is not affected by the concentration of SO_3^{2-} and the catalytic current is also linear with the square root of scan rate.

Figure 10 illustrates the electrochemical behavior of TiPhCoHCF in the presence of different concentrations of sulfite (2.0×10^{-3} a 1.0×10^{-2} mol L^{-1}). There was a linear increase in anodic current intensity with the addition of the analyte, which allowed us to confection a analytical curve.

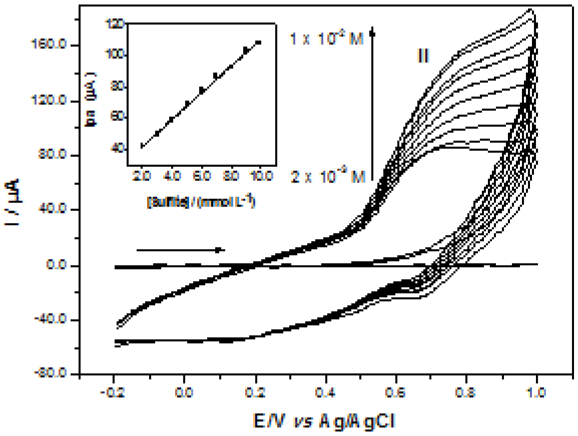

Figure 10. Cyclic voltammograms of the applications of various concentrations of sulfite using a graphite paste electrode modified with TiPhCoHCF. (Inserted graphic: Analytical curve (KNO_3 1.0 mol L^{-1}, pH 7.0; v = 30 mV s^{-1})

Figure 11 (inserted graphic) illustrates the analytical curve used to determinate sulfite. The modified electrode showed a linear response from 2.0×10^{-3} to 1.0×10^{-2} mol L^{-1} with the corresponding equation $Y(\mu A) = 24.78 + 8.565 \times 10^3$ [Sulfite], and a correlation coefficient of $r = 0.997$. The method showed a detection limit of 6.51×10^{-4} mol L^{-1} with a relative standard deviation of ± 5% ($n = 3$) and amperometric sensitivity of 9.19×10^{-3} A mol L^{-1}.

The detection limit was calculated using the following formula (Eq. 3):

$$DL = \frac{SD \times 3}{S} \qquad \text{Eq. 3}$$

Where SD is the standard deviation of 10 measurements of blank, at least three standard curves containing concentrations near and the supposed limit of quantification and S (sensitivity) is the slope of analytical curve [31].

4. CONCLUSION

In this study it was concluded that titanium oxide modified with phosphoric acid (TiPh), followed by an adsorption of a metal ion (Co^{2+}), interacted strongly with potassium hexacyanoferrate (TiPhCoHCF) forming a binuclear complex highly electroactive. The composite formed was characterized by techniques such as FT-IR, XDR and cyclic voltammetry.

The cyclic voltammogram of the modified electrode containing TiPhCoHCF exhibited two redox couples. The peak I with an formal potential (E^{θ}') = 0.37V *vs* Ag/AgCl attributed to the redox process $Co^{(II)}$ / $Co^{(III)}$ and other more defined redox couple, peak II, with E^{θ}' = 0.67V *vs* Ag/AgCl which was attributed to the redox process $[Fe^{(II)}(CN)_6]$ /$[Fe^{(III)}(CN)_6]$. The second redox couple exhibited an electrocatalytic activity towards the oxidation of sulfite. The modified electrode showed a linear response from 2.0×10^{-3} to 1.0×10^{-2} mol L^{-1} with the corresponding equation Y(μA) = 24.78 + 8.56×10^{3} [Sulfite], and a correlation coefficient of r = 0.997. The method showed a detection limit of 3.75×10^{-4} mol L^{-1} with a relative standard deviation of ± 5% (n=3) and amperometric sensitivity of 6.51×10^{-4} A mol L^{-1}.

Additionally, the modified titanium phosphate modified electrode is the easy to prepare and the voltammetric analysis require no pre-treatment step of the sample and are easy , allowing their surfaces are quickly renewed thereby decreasing the time spent in performing the analytical measurements.

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