

Electrocatalytic Detection of Hydrazine Using Chemically Modified Electrodes with Cobalt Pentacyanonitrosylferrate Adsorbed on the 3–Aminopropylsilica Surface

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Abstract

Cobalt pentacyanonitrosylferrate on the aminopropylsilica silica gel surface (SiCoNP) was previously prepared following two steps. The electrochemical behavior of SiCoNP modified electrode showed two redox couples, the first and second redox couples were observed at anodic potential (Epa)₁ = 0.36 and 0.60 V vs. Ag/AgCl attributed to the oxidation of Co^(II) to Co^(III) and Fe^(II)(CN)₅NO/Fe^(III)(CN)₅NO, respectively. The modified carbon paste electrode with SiCoNP was tested in the hydrazine electrooxidation. In the hydrazine electrooxidation, the H⁺ release was observed and the two metal centers are involved in this process. The proposed mechanism has been described and based on studies of the effect of hydrogen ion concentration in the redox process of bivalent compound formed. Thus a large increase in hydrogen ion concentration promotes the formation of an intermediate electroactive species with an anodic peak at 0.56 V. The nature of this species is not well established but may be related to protonation of cyanide or NO groups present. The modified graphite paste electrode presented a limit of detection of 2.38×10⁻⁴ mol L⁻¹ and amperometric sensitivity of 1.37×10⁻⁶ A.mol⁻¹.L.

Keywords: 3–aminopropylsilica, cobalt pentacyanonitrosylferrate, cyclic voltammetry, carbon paste electrode, hydrazine

1. Introduction

The chemically modified electrodes (CMEs) can mediate electron reactions kinetically unfavorable on unmodified substrates, showing enhancement of selectivity, inhibiting surface fouling while contributing towards the improvement of the analytical response of an analyte compared to unmodified or bulk electrodes. The CMEs can act as an electrocatalyst or as electrochemical sensors, increasing their sensitivity and selectivity (Baldwin & Thomsen, 1991; de Sá, Paim, & Stradiotto, 2014; El-Desoky & Ghoneim, 2011; Mattos, do Carmo, Oliveira, & Stradiotto, 2008; Pournaghi-Azar & Sabzi, 2003; Salimi, Abdi, & Khayatiyan, 2004; Sartori, Zezza, Paim, & Stradiotto, 2014; Sedenho et al., 2015).

Several organic and inorganic electroactives species are used in the preparation of modified electrodes, among them worth mentioning the cyanoferrates as hexacyanoferrates (HCF) and pentacyanonitrosylferrates (PCNF) (Dastangoo & Poureshghi, 2015). These compounds are represented by the structure [Fe^(III)(CN)₅L]⁻², were L is CN or NO wich exhibits reversible electron transfer and has been cleverly immobilized on the surface of electrodes (Dastangoo & Poureshghi, 2015; de Sá, Paim, Bicalho, & do Carmo, 2011; Sakthivel, Sivakumar, Chen, & Lun-Cheng, 2016).

Complexes of cyanoferrates has been extremely used for catalytic electrooxidation of compounds such as: L-cysteine (Sakthivel et al., 2016); N-acetylcysteine (de Sá et al., 2011; do Carmo, Da Silva, & Stradiotto, 2003); thiosulfate (Sabzi,

2005); hydrazine (Costa et al., 2010; Jayasri & Narayanan, 2007; Luo et al., 2015); ascorbic acid (Razmi & Harasi, 2008) and dopamine (Razmi, Agazadeh, & Habibi-A. B., 2003

Luo et al. (2015) developed an analytical method to determine hydrazine and nitrite using CoHCF nanoparticles-graphene modified with glassy carbon electrode. Electrochemical behavior of hydrazine and nitrite was studied by cyclic voltammetry and revealing the synergetic electrocatalytic function of reduced graphene oxide and cobalt hexacyanoferrate nanoparticles. The quantitative measurements of hydrazine and nitrite were carried out by amperometry and differential pulse voltammetry, respectively. The limit of detection for hydrazine was found to 6.9×10^{-8} mol L⁻¹ at 0.66 V operating potential (vs. Ag/AgCl) in 0.1 mol L⁻¹ phosphate buffer (pH 6.5).

Costa et al. (2010) used a ruthenium (III) hexacyanoferrate (Ru(HCF)) film coated on a glassy carbon electrode (to make hydrazine oxidation electrocatalyze). Cyclic voltammograms of Ru(HCF) film showed two redox processes attributed to Ru^(III)/Ru^(IV) and Fe^(II)/Fe^(III). Electrocatalytic oxidation of hydrazine was studied and some electrochemistry parameters was found, such as transfer coefficient (α) of ~0.31–0.36.

Jayasri & Narayanan (2007) incorporated manganese hexacyanoferrate (MnHCF) into a carbon paste electrode (CPE) and electrocatalytic oxidation of hydrazine was also studied under hydrodynamic and chronoamperometric conditions. The anodic current increases linearly with the increase in the hydrazine concentration in the range of 3.33×10^{-5} to 8.18×10^{-3} mol L⁻¹. The limit of detection was found to 6.65×10^{-6} mol L⁻¹.

Ahmar et al. (2013) developed an electrochemical sensor based on palladium nanoparticles immobilized on ethylenediamine cellulose. The prepared catalyst was immobilized on the surface of glassy carbon electrode using drop casting method to produce an electrochemical sensor toward hydrazine. A linear relationship was observed between the differential pulse voltammetry currents and the limit of detection of 1.5×10^{-6} mol L⁻¹.

The high specific surface area, porosity and thermal stability presented in silica and silica based materials are responsible for the great interest in applying them as support for electron mediators molecules in CPEs (Degefa, Chandravanshi, & Alemu, 1999; Shams, Alibeygi, & Torabi, 2006). Actually, in modified electrodes is divided into analysis with preconcentration using the technique of anodic stripping (Jaafariasl, Shams, & Amini, 2011; Torabi, Shams, Zolfigol, & Afshar, 2006), or as a substrate for incorporation of redox mediators (do Carmo, Gabriel, Bicalho, Picon, & Paim, 2011; do Carmo et al., 2011; Shams, Babaei, Taheri, & Kooshki, 2009).

de Sá et al. (2011) published the preparation and characterization of chemically modified electrodes with 3-aminopropylsilica and copper pentacyanonitrosylferrate applied in the voltammetric determination of N-acetylcysteina, the linear range was found between 9.9×10^{-5} and 8.9×10^{-4} mol L⁻¹ showed a detection limit of 4.18×10^{-5} mol L⁻¹ and an amperometric sensitivity of 3.02×10^{-2} A.mol⁻¹ L.

In order to use the cyanoferrate complexes properties in combination with modified silica, the goal of this paper was report the formation of the 3-aminopropylsilica with cobalt pentacyanonitrosylferrate (SiCoNP) and the direct and facile application in detection of hydrazine by cyclic voltammetry using modified carbon paste electrode with 3-aminopropylsilica and cobalt pentacyanonitrosylferrate.

2. Method

2.1 Reagents

All reagents were obtained from Merck or Sigma-Aldrich. The solutions were prepared with deionized water from the Milli-Q system from Millipore at a resistivity no less than 18.2 M Ω cm⁻¹ at 25 °C. The hydrazine solutions were prepared immediately before their use in the voltammetric analysis.

2.2 Synthesis of Bivalent Complex on the Silica

The 3-aminopropylsilica and cobalt pentacyanonitrosylferrate complex was synthesized by adding of 2.0 g of 3-aminopropylsilica in 25 mL of 1.0×10^{-3} mol L⁻¹ (pH 2) of sodium nitroprusside Na[Fe(CN)₅NO]. This mixture was stirred for 1.0 h. The solid phase was filtered and washed with deionized water. The solid was immediately added to a solution of 1.0 mol L⁻¹ of Co²⁺ ions at pH 2, stirred for 1.0 hours at room temperature and the solid phase was filtered and washed with deionized water. The material was dried and described as SiCoNP.

2.3 Preparation of the Carbon Paste Electrode Modified with SiCoNP

The chemically modified carbon paste electrodes were prepared by mixing containing 20% (w/w) (SiCoNP / carbon powder) and 30 μ L of mineral oil (de Sá et al., 2011). The electrode body was produced from a glass tube of 3 mm i.d. and 14 cm height, containing carbon paste. A copper wire was inserted through the opposite end to establish electrical contact. The electrode external surface was smoothed with soft paper. A new surface can be produced by scraping out the old surface and replacing the carbon paste (do Carmo et al., 2003; do Carmo et al., 2015).

2.4 Fourier Transform Infrared Measurements

The vibrational spectra of the materials were performed on a Nicolet 5DXB FTIR 300 spectrometer (Nicolet Instruments, Madison, WI). Approximately 150 mg of KBr was ground in a mortar/pestle, and sufficient solid sample was ground with KBr to produce a 1% (w/w) of each sample. A minimum of 64 scans were collected for each sample at a resolution of $\pm 4 \text{ cm}^{-1}$ in a band of $4000\text{-}400 \text{ cm}^{-1}$.

2.5 Electrochemical Measurements

Electrochemical experiments were carried out using a potentiostat model MQPG1. A conventional cell with three electrodes was used: carbon paste electrode modified with SiCoNP as working electrode, $\text{Ag}/\text{AgCl}_{(s)}$ (KCl , 3.0 mol L^{-1}) as reference electrode, and platinum wire ($3.0 \text{ cm} \times 0.1 \text{ cm}$) as auxiliary electrode. Before conducting all electrochemical experiments, the electrochemical cell was saturated with nitrogen for 15 min. All experiments were performed at room temperature. At most experiments, a 1.0 mol L^{-1} of Na_2SO_4 (pH 7.0) support electrolyte was employed at a scanning rate of 20 mV s^{-1} .

3. Results

Figure 1 show the vibrational spectrum in the infrared region of 3-aminopropyl silica gel (Si) and of cobalt pentacyanonitrosylferrate adsorbed on the 3-aminopropyl silica gel surface (SiCoNP). A broad strong absorption at 3448 cm^{-1} corresponding to the axial deformation of the vsOH group was observed (de Sá et al., 2011; Yang, El-Nahhal, Chuang, & Maciel, 1997).

There was an absorption at 1630 cm^{-1} , attributed to the angular deformation of the O–H deformation from H_2O ($\delta\text{O-H}$). At 1100 cm^{-1} is shown an asymmetric stretching vibrations relative to Si-O-Si ($\delta\text{Si-O-Si}$) that corresponds the skeleton of 3-aminopropyl silica gel is shown at 1100 cm^{-1} , such as the absorption at 480 cm^{-1} which is related to the bond O-Si-O ($\delta\text{O-Si-O}$) (de Sá et al., 2011; Yang et al., 1997).

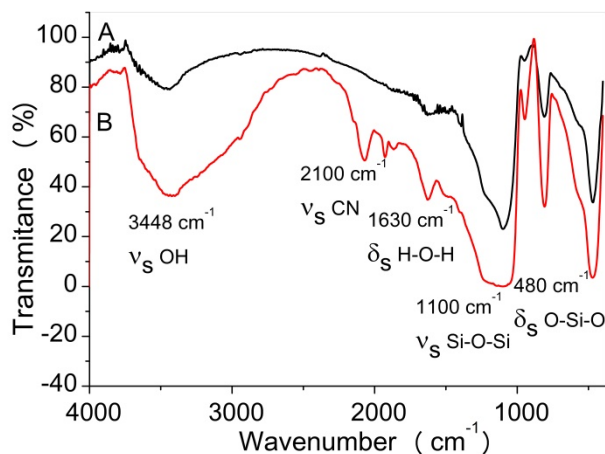


Figure 1. (A) Spectrum in the infrared region of Si and (B) SiCoNP

Figure 1-B show the absorption spectrum in the infrared region of SiCoNP. The spectra presents a vibration at $\sim 2100 \text{ cm}^{-1}$ related to the symmetric stretching $\text{C}\equiv\text{N}$ (vsCN) and small band at 1949 cm^{-1} attributed to symmetric stretching NO (vsNO) that are characteristic of the cobalt pentacyanonitrosylferrate (de Sá et al., 2011; Fulcher, Crowell, Bayliss, Holland, & Jezorek, 1981).

The electrochemical behavior of SiCoNP modified electrode in 1.0 mol L^{-1} of Na_2SO_4 is shown in Figure 2. The electrode exhibit two redox couples: the first redox couple (I) has an anodic potential $(E_{pa})_1$ at 0.36 V (vs. Ag/AgCl) attributed to the oxidation of $\text{Co}^{(II)}$ to $\text{Co}^{(III)}$, the respective reduction was seen at potential of 0.25 V (vs. Ag/AgCl). The second redox couple (II) exhibits an anodic potential $(E_{pa})_2$ at 0.60 V (vs Ag/AgCl) attributed to $\text{Fe}^{(II)}(\text{CN})_5\text{NO}/\text{Fe}^{(III)}(\text{CN})_5\text{NO}$ of the binuclear complex formed, the respective reduction was seen at potential of 0.55 V (vs. Ag/AgCl). These redox processes are described by the equation 1.

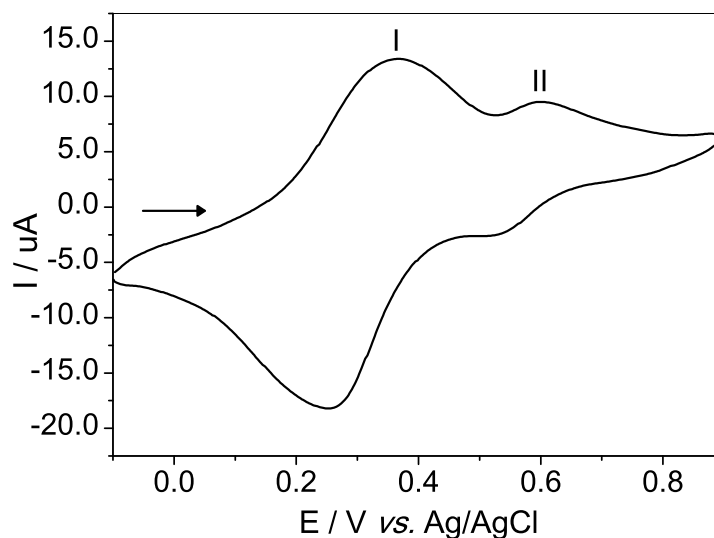


Figure 2. Cyclic voltammogram of SiCoNP in 1.0 mol L⁻¹ of Na₂SO₄; pH 7.0; (v = 20 mV s⁻¹)

According to Figure 3 and the studies conducted with different cations of alkali metals, it can be observed that both the anodic current as the first midpoint potential (E_m)₁ were not changed, but the I_{pa}/I_{pc} had different values. The electrochemical parameters of SiCoNP studied are listed in Tables 1 and 2. The midpoint potential (E_m) of carbon paste electrode modified with SiCoNP in presence of sodium salts (Cl⁻, NO₃⁻, SO₄²⁻, ClO₄⁻) was maintained constant for first and second redox couples. In the redox process of second peak (II), the NH₄⁺ ion interference is probably due to its major hydrated radius that difficult to entry in the crystalline reticulum.

Table 1. Voltammetric data of carbon paste electrode (SiCoNP) in the different supporting electrolytes to the first redox process (I).

<i>Cation</i>	<i>[I_{pa}/I_{pc}]</i>	<i>ΔE_p (V)</i>	<i>(E_m)₁ (V)</i>
Li ⁺	0.88	0.16	0.29
Na ⁺	0.69	0.11	0.29
K ⁺	0.77	0.15	0.29
NH ₄ ⁺	0.85	0.17	0.29

*ΔE_p = E_{pa} - E_{pc}

Table 2. Voltammetric data of carbon paste electrode (SiCoNP) in the different supporting electrolytes to the second redox process (II).

<i>Cation</i>	<i>[I_{pa}/I_{pc}]</i>	<i>ΔE_p (V)</i>	<i>(E_m)₂ (V)</i>
Li ⁺	0.92	0.23	0.56
Na ⁺	1.11	0.08	0.56
K ⁺	1.20	0.07	0.56
NH ₄ ⁺	Nd	nd	nd

*ΔE_p = E_{pa} - E_{pc}

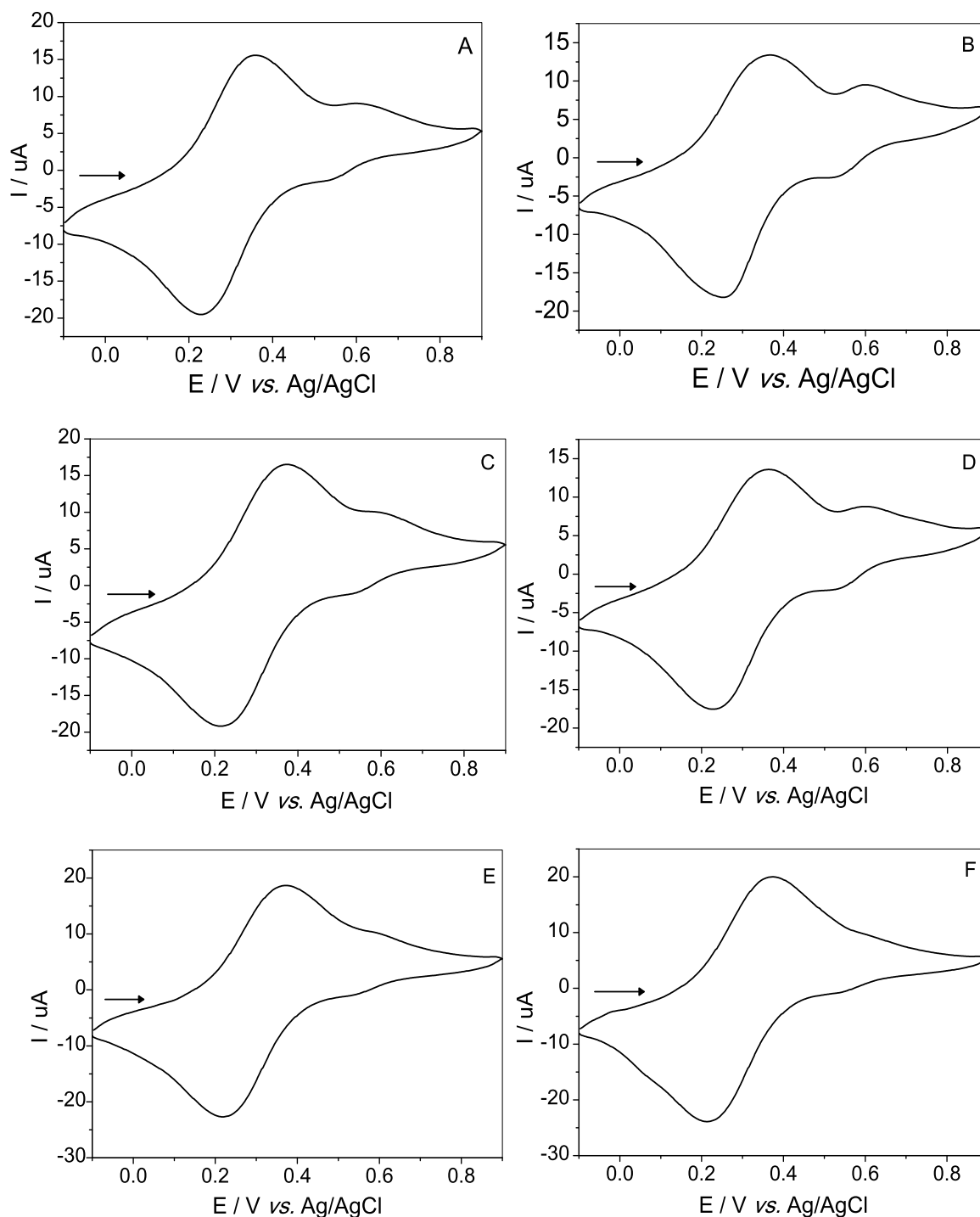


Figure 3. Cyclic voltammograms of carbon electrode modified with SiCoNP in different supporting electrolytes: A)

KCl; B) Na_2SO_4 ; C) LiCl; D) NaCl; E) KNO_3 ; F) NH_4Cl (1.0 mol l^{-1} ; 20 mV s^{-1})

Figure 4 shows the cyclic voltammograms for different concentrations of Na_2SO_4 support electrolyte of 1.0×10^{-2} to 2.0 mol L^{-1} . The effect of Na^+ ion in the redox process was easily observed with the formal potential change. While increasing in the concentration of Na_2SO_4 , the potential shifts and this behavior was assigned to the change in the activity of these ions (de Sá et al., 2011).

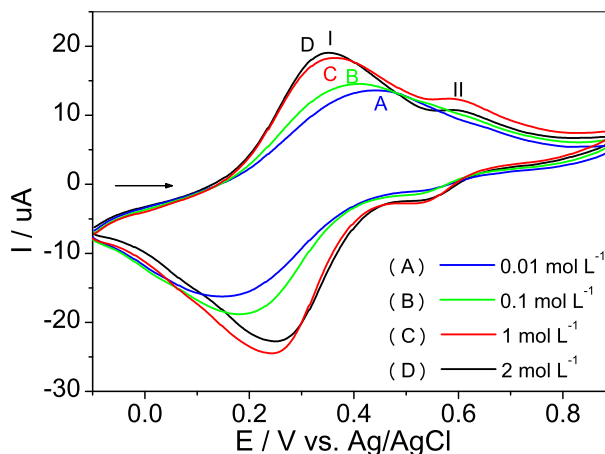


Figure 4. Cyclic voltammograms of carbon electrode modified with SiCoNP in different supporting electrolyte concentrations of Na_2SO_4 (1.0×10^{-2} to 2.0 mol L^{-1})

The concentration of the supporting electrolyte chosen to continue the ensuing studies was 1.0 mol L^{-1} of Na_2SO_4 due to better voltammetric parameters.

Figure 5 shows the cyclic voltammogram at different pH values (2.0 to 8.0). It was found that with the variation in hydrogen ion concentration (pH 8.0 to 4.0), the two redox processes, $(\text{Em})_1$ and $(\text{Em})_2$, remained practically unchanged. However, at $\text{pH} < 3$ an irreversible process occurs at 0.56 V (Figure 5, peak III). The existence of this new process has been assigned the formation of intermediary electroactive species likely to occur in high hydrogen ion concentrations.

Similar behavior was observed in the carbon paste electrode modified with iron nitroprusside FeNP at high hydrogen ion concentrations ($\text{pH} < 3$) (do Carmo, Silva, & Stradiotto, 2002).

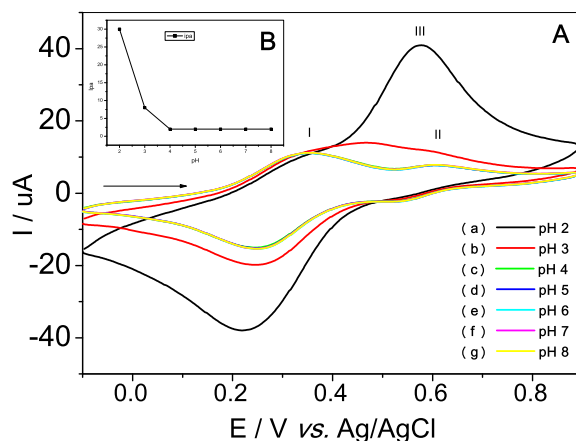


Figure 5. (A) Cyclic voltammograms of the carbon paste electrode modified with SiCoNP at different pH values: a) 2.0; b) 3.0; c) 4.0; d) 5.0; e) 6.0; f) 7.0; g) 8.0 ($v = 20 \text{ mV s}^{-1}$; Na_2SO_4 1.0 mol L^{-1}). (B) Figure I_{pa} vs. pH

Figure 6 (A) illustrates the cyclic voltammograms of SiCoNP at different scan rates (10 – 100 mV s^{-1}). As expected, an increasing the scan rate provided an increase in the current intensity for peak I and II. The linear relationship between anodic/cathodic peak and the square root of scan rate shown in Figure 6 (B) indicates a reversible reaction where the electroactive species follow the diffusion process (Bard & Faulkner, 2001; Zaib & Athar, 2015).

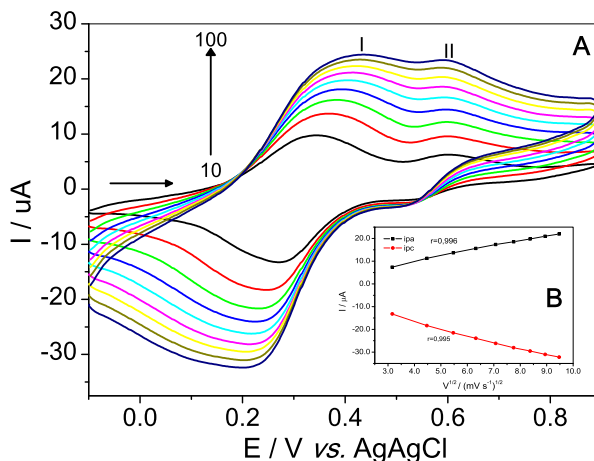


Figure 6. (A) Cyclic voltammograms of the carbon paste electrode modified with SiCoNP at different scan rates (10-100 mV s⁻¹). (B) Dependence on current intensity of the anodic and cathodic peaks (I) with the square root of the scan rate

Figure 7 shows an application of SiCoNP in the electrocatalytic detection of hydrazine using a modified carbon paste electrode. The curves (a) and (c) represent the carbon paste electrode unmodified in the absence and after addition of 9.0×10⁻³ mol L⁻¹ of hydrazine, respectively, and it was observed that in the potential range of -0.1 to 0.9 V the carbon paste electrode without modification showed no electroactivity. The Figure 7 (b) shows the behavior of carbon paste electrode modified with SiCoNP in the absence of hydrazine. It was observed that, in the presence of 9.0×10⁻³ mol L⁻¹ of hydrazine, there was an increase in the intensity of anodic current with the emergence of a new anodic peak at 0.58 V vs Ag/AgCl shown in curve (d). The anodic peak intensity increases proportionately with increasing concentration of hydrazine as showed by Figure 7. The verified increase of current intensity is due to the electrocatalysis of hydrazine by the electron mediator SiCoNP (de Sá et al., 2015).

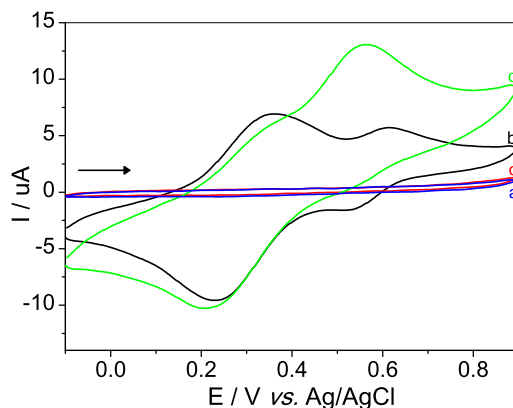
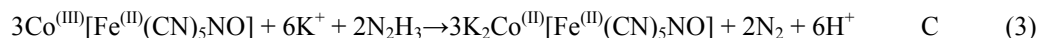
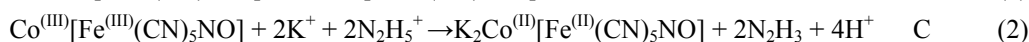
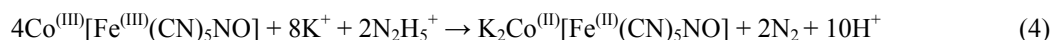


Figure 7. Cyclic voltammogram: a) carbon paste electrode; b) modified carbon paste electrode with SiCoNP in absence of hydrazine; c) carbon paste electrode in presence of 9.0×10⁻³ mol L⁻¹ of hydrazine; d) carbon paste electrode modified with SiCoNP after addition of 9.0×10⁻³ mol L⁻¹ of hydrazine (1.0 mol L⁻¹ of Na₂SO₄; v = 20 mV s⁻¹)

The hydrazine aliquots addition were conducted in the electrolyte solution pH 7.2, so under these conditions there is a predominance of N₂H₅⁺ species as the pKa of the hydrazine is 7.9 [31]. The ion hydrazinio releases protons to oxidize the metal center, reducing Fe (III) to Fe (II) (Razmi-Nerbin & Pournaghi-Azar, 2002), as represented by following equations (1-4)



Global chemical reaction



Thus the hydrazine oxidation occurs on the surface of carbon paste electrode modified with SiCoNP with the release of

H^+ , and the two metal centers involved in this process. The proposed mechanism has been described and based on studies of the effect of hydrogen ion concentration in the redox process of the compound binuclear formed. Therefore, a large increase in hydrogen ion concentration promotes the formation of an intermediate electroactive species with an anodic peak at 0.56 V. The nature of this species is not well established but may be related to protonation of cyanide or NO groups present.

According to the results contained in the analytical curve in Figure 8, the established range obtained was 5.0×10^{-4} to 3.8×10^{-3} mol L⁻¹. The linear response showed a correlation coefficient of $r = 0.998$, with a detection limit of 2.38×10^{-4} mol L⁻¹, amperometric sensitivity of 1.37×10^{-6} A.mol⁻¹.L. The linear range was established with an equation $Y(\mu A) = 1.79 + 1,372 [\text{Hydrazine}]$, with a relative standard deviation of $\pm 0,04$.

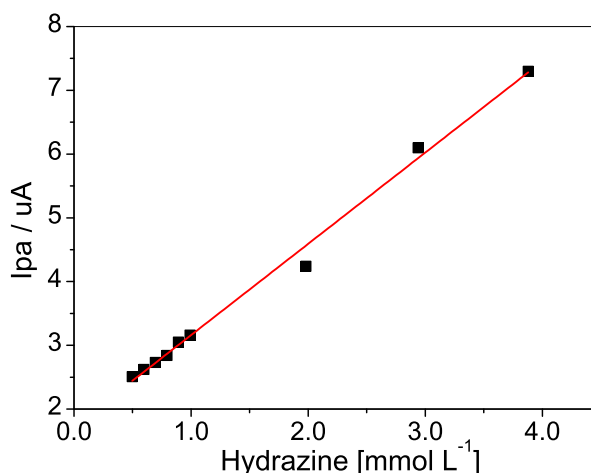


Figure 8. Analytic curve of the anodic peak current as a function of hydrazine concentration using the carbon paste electrode modified with SiCoNP (1.0 mol L⁻¹ of Na₂SO₄; $v = 20$ mV s⁻¹).

4. Conclusions

The 3-aminopropyl silica gel adsorbed with cobalt pentacyanonitrosylferrate (SiCoNP) was prepared and characterized by FT-IR that shown a vibration at ~ 2100 cm⁻¹ related to the symmetric stretching C \equiv N (vsCN) and a band at 1949 cm⁻¹ attributed to symmetric stretching NO (vsNO, that are characteristic of the cobalt pentacyanonitrosylferrate. The electrochemical behavior of carbon paste electrode with SiCoNP was performed using voltammetry. The material was successfully tested in electrocatalytic detection of hydrazine using a carbon paste electrode modified with SiCoNP. The linear range was found between 5.0×10^{-4} and 3.8×10^{-3} mol L⁻¹ for detection of hydrazine, showing a limit of detection of 2.38×10^{-4} mol L⁻¹ and an amperometric sensitivity of 1.37×10^{-6} A. mol⁻¹ L. The electrochemical sensor SiCoNP has potential characteristics to be applied in the detection of hydrazine, industrial quality control, boiler water monitoring and environmental analysis.

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