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Full Paper

Clay Effect in the Electrochemical Stabilization of Colloidal CoO(OH) Applied as a Modified Electrode

Lucéli Roloff[a], Elisangela Muncinelli Caldas Barbosa[b]; Filipe Quadros Mariani[a]; Andressa Galli[a], and Fauze Jaco Anaissi[a*]

[a]*Universidade Estadual do Centro-Oeste, Setor de Ciências Exatas e da Terra, Departamento de Química, Laboratório de Materiais e Compostos Inorgânicos, Rua Simeão Varela de Sá, 03, CEP: 85040-080, Guarapuava, PR, Brazil.*
[b]*Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul, CEP 95180-000, Farroupilha, RS, Brail.*

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Abstract: In this work, a mixed material was prepared using a montmorillonite clay (denominated imported sodic, IS) modified with colloidal cobalt (Co). The obtained mixed material (ISCo) was characterized by X-ray diffractometry and simultaneous thermal analysis and used to modify the surface of a platinum electrode for electrochemical determination of oxalic acid. The electrochemical behavior of the ISCo material was evaluated by cyclic voltammetry and the performance as a sensor for oxalic acid was assessed by square wave voltammetry. The platinum electrode showed no response to peak current when the oxalic acid concentration was increased in the range of 4.99×10^{-4} to 4.95×10^{-3} mol L^{-1}. On the other hand, the platinum electrode modified with the mixed material presented a linear response in the studied range with a detection limit of 2.55×10^{-4} mol L^{-1}.

Keywords: clays; cobalt oxide-hydroxide; electrochemical techniques; mixed materials

1. INTRODUCTION

In recent decades, efforts have been made to develop new chemically modified electrodes, which can be used directly and rapidly in analytical tests for the determination of important substances, such as pesticides [1], trace metals [2], dopamine [3], ascorbic acid [3] and oxalic acid [4], etc. Materials such as polymers, oxides, zeolites, inorganic or organic films are used to immobilize different electroactive species at the electrodes surface used as amperometric sensors. Electrodes modified with clay, mainly montmorillonite type, have attracted the attention of many electrochemical [5-10] due to ion exchange properties of the clay, the lamellar structure and its adsorption capacity and intercalation of various compounds [11-13].

Electrodes modified with clays are prepared by depositing thin films of material containing clay of conductive materials such as Pt, Au, SnO_2, glassy carbon or pyrolytic graphite [14]. The film of the material containing clay is formed by depositing and drying of a colloidal clay suspension. The type, the particle size and the way of drying clays are critical factors for obtaining a film with stability, uniformity and thickness [14,15]. It is interesting to use clay to modify the electrode surface due to its chemical and physical properties to control the sensitivity or the selectivity of the electrode for the species in solution. The negative aspect of using clays is that these materials are not electronically conductive. The charge transport within the clay film can be increased with the use of electroactive species. Several strategies have been developed, among which stands out the use of cations redox active sites inside the crystal lattice (iron, cobalt or copper for cationic clays and nickel, cobalt or manganese in anionic clays) to transfer electrons from the intercalated íons to the conductive substrate [15-18]. Another possibility to increase the transport of charges is the use of a conductive polymer (polypyrrole, p. ex.) in the lamella of the clay [19]; or the intercalation of a conductive composite material [20].

In this work was prepared a mixed material

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[*] Corresponding author. E-mail: anaissi@unicentro.br / fjanaissi@gmail.com

using as host matrix a clay of the type montmorillonite, called sodic imported, modified with colloidal cobalt. The mixed material was characterized by X-ray diffraction technique, and the electrochemical behavior was studied by cyclic voltammetry (CV) and tested as a sensor for oxalic acid by square wave voltammetry (SWV).

2. MATERIAL AND METHODS

All material used (volumetric flasks, spatulas, beakers, etc.), underwent an adopted cleaning procedure to ensure the absence of any organic waste that could interfere with the measurements. For this, it was used a sulfonitric solution [H_2SO_4 and HNO_3, 1:1 (v/v)], with subsequent exhaustive washing with distilled water and boil for 1 hour in distilled water. All reagents used are analytical grade and were used as received without additional purification. Glycerin ($C_3H_8O_3$, Synth), cobalt acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$, Vetec) and ethanol ($C_2H_6O$, Biotec) were used for the preparation of colloidal cobalt. Oxalic acid ($C_2H_2O_4$, Sigma-Aldrich) and sodium hydroxide (NaOH, Vetec) were used respectively in the preparation of stock solutions of oxalic acid [0.25 mol L^{-1}] and the supporting electrolyte [0.50 mol L^{-1}], wherein the solutions were prepared with ultrapure water previously heated. All solutions were prepared using ultrapure water originated from a purification unit Milli-Q, Millipore Corporation origin. The stock solution of oxalic acid with a concentration 0.25 mol L^{-1} was added to the supporting electrolyte in the electrochemical cell, in aliquots of 4.99×10^{-4} mol L^{-1}.

Preparation of Colloidal Cobalt and Mixed Material

Under stirring, in 100 mL of glycerine were dissolved 4.0 g of cobalt acetate tetrahydrate. It was added, then 42 mL of alcoholic NaOH (ethanol) and 42 mL of ethanol. After three days, it was obtained the cobalt colloidal gel, which was washed with ultrapure water to remove sodium and acetate ions as well as impurities like colloidal metal and glycerin. In the colloidal suspension of clay was added 50 mL of cobalt gel under stirring for 24 h. The gelatinous material formed was dispersed in water, and separated by decantation.

Modification of Working Electrode Surface

The modified electrodes were prepared by casting technique (solvent evaporation). A 1.0 µL aliquot of the suspension of the material was deposited on the surface of the base sensor. The electrode surface was dried at room temperature until complete evaporation of the solvent, the modified electrode was named CME-ISCo.

Characterization

The X-ray diffraction (XRD) was obtained using the beam line Synchrotron XRD1 of the Brazilian National Synchrotron Light Laboratory (LNLS). The energy used was 7,00021 keV, wavelength in the iron edge 1.77115 Å with Si crystal monochromators with special cuts for Si faces (111) with a peak at 16.4163 and FWHM 0.0038 degrees and Si (333) with a peak at 57.9353 and FWHM 0.0260 degrees. The step width used was 0.5 degrees. Simultaneous thermal analyses were obtained with the simultaneous thermogravimetric analyzer TGA/DTA Seiko SII, model 6300, operating with a heat ramp of 10 °C min^{-1}, in the temperature range of 30 - 1200 °C, in a nitrogen atmosphere.

Study of Electrochemical Behavior

Electrochemical experiments were performed in a potentiostat/galvanostat BASi, EPSILON model, coupled to a computer equipped with the software Epsilon-EC, BASi, Version 1.6.70. It was used a glass cell, in the conventional configuration of three electrodes, namely; the reference electrode: Ag/AgCl in NaCl 3 mol L^{-1}, working electrode: platinum with an area of 2 mm^2 and auxiliary electrode platinum wire. To eliminate the dissolved O_2 in the solution, nitrogen gas was purged for 5 minutes before each series of measurements.

The cyclic voltammetry measurements (CV) were carried out in the presence of the analyte oxalic acid aliquots (4.9×10^{-3} mol L^{-1}), employing a potential range of -500 to 500mV *vs* Ag/AgCl (amid 0.5 mol L^{-1} of NaOH) at different scanning speeds (10 to 300 mV s^{-1}). The CVs were obtained immediately after drying the working electrode at room temperature. The square wave voltammetry (SWV) was used for the quantitative determination of oxalic acid. For this, the technical parameters were evaluated characterized by the study of variation of the frequency of application of the potential pulses (*f*), of the scan increment (ΔE_s) and potential amplitude pulse (*a*). The SWV measures for the quantitative determination of oxalic acid were made in the optimized experimental conditions, and obtaining the optimized values of amplitude 80 mV, frequency 200 s^{-1} and increased 2 mV. The SWV were measured immediately after drying the working electrode at room temperature and recorded in the potential range from -450 mV to 400 mV *vs* Ag/AgCl.

3. RESULTS AND DISCUSSION

X-Ray Diffractometry (XRD)

Figure 1 shows the X-ray diffractograms of the clay IS (d_{001} clay = 12.46 Å) [21], and mixed material ISCo (d_{001} MM = 15.26 Å). It can be observed a shift in the peak 001 in the MM-ISCo, which is associated with increased basal interlayer distance indicating intercalation of the colloidal cobalt between the clay lamellae (Δd_{001} = 2.80 Å). Besides the peak 001, it may be noted the patterns of pure clay in the diffractogram of the mixed material where also appear overlapping peaks relating to the colloidal cobalt (Co) organic compounds used in the preparation of the colloidal suspension, suggesting the presence of CoO(OH) in the crystalline phase.

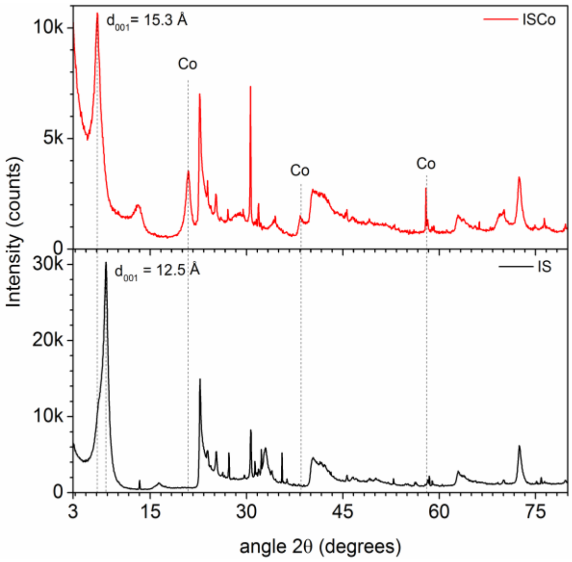

Figure 1. X-ray diffraction pattern for clay IS and mixed material ISCo.

Simultaneous thermal analysis (TGA-dTGA/DTA)

The simultaneous thermal analysis curves (STA) allow evaluation of thermal properties of the clay IS and mixed materials (MM-ISCo) since the thermal decomposition curves provide the percentages of the fragments of mass lost as a function of temperature. The TGA/DTA curves of colloidal cobalt, where the thermal behavior can be divided into three stages of loss of mass [23]. The thermal process reveals that the first weight loss occurs in the onset temperature (T_{onset} = 70 °C) peak and is probably associated with the release of weakly H_2O absorbed molecules (2.07 equivalents). The primary process, assigned to loss of glycerin, was observed in T_{onset} = 210 °C peak and involved the loss 1.35 equivalents.

The Figure 2A show the TGA/DTA curves of the clay IS. The differential thermal analysis (DTA) curves have endothermic peaks characteristic of water molecules, and hydroxyl group adsorbed in the clay structure [21]. Figure 2B show the STA curve for the MM-ISCo. This shows characteristically three processes of loss of mass. The first involves that of weakly-bonded water molecules until 100 °C. The second is related to the loss of glycerin (205 °C), and the third to the process of decomposition of CoO(OH) at 380 °C. Comparatively, the DTA curves (Fig. 2) for the MM-ISCo have an endothermic peak characteristic of leaving of water molecules, and the behavior is similar to the TGA curve in which they are grouped into sodic clay (above 200 °C). The DTA curves also have two exothermic peaks characteristic of the decomposition of colloidal cobalt (380 °C), and hydroxyl groups adsorbed on the clay structure (1100 °C). By analyzing the thermal behavior, it is possible to conclude that the MM-ISCo prepared from the sodic montmorillonites interact strongly with the colloidal cobalt.

Electrochemical Study

One of the initial studies for the investigation of the proposed mixed materials behavior consisted in the operation of the scanning speed. Thus, the cyclic voltammograms (Figure 3) are presented at different scan rates for the $Pt_{(naked)}$ electrode and the CME-ISCo. The peaks (II and III) in the voltammogram related to CME-ISCo (Figure 3B) are assigned to the Co(II)/Co(III) process [21] and indicating that the process is adsorptive [22]. The peak (I) is seen in the two graphs (Figure 3A and 3B) is possibly attributed to proton (H^+) adsorption. Also, according to Figure 3B, it can be observed that the increase in scan rate promoted an increase in the intensity of the peak current in the electro-oxidation of the mixed material, evidencing what happened in the redox process.

The series of CVs in function of scan rate of the CME-ISCo in the presence of oxalic acid (pH 12) is shown in Figure 4A. With the increase of the scan rate, there is an increase of the anodic peak current. In this manner, the peak (I) is attributed to the oxidation of oxalic acid (irreversible process) and peak (II) the presence of an interfering, possibly proton (H^+) adsorption (Figure 4A). The peak current varies linearly with the scan rate in the range from 10 to 300 mV s^{-1}, graph Figure 4B, indicating that the process is adsorptive [22].

The graph of the logarithm of current density against the logarithm of the scan rate (Figure 4C) and shows linear behavior with slope 0.7. This value is close to that found in the literature for systems controlled by adsorption of species, which provides a slope of 1.0 [22]. Through this response, it might be said that the oxalic acid oxidation process is controlled by adsorption of species to the electrodic surface.

In Figure 5 is presented a square wave voltammogram (SWV) obtained for the CME-ISCo, against successive additions of oxalic acid. It is observed that the peak current increases proportionally with increasing concentration to the CME-ISCo.

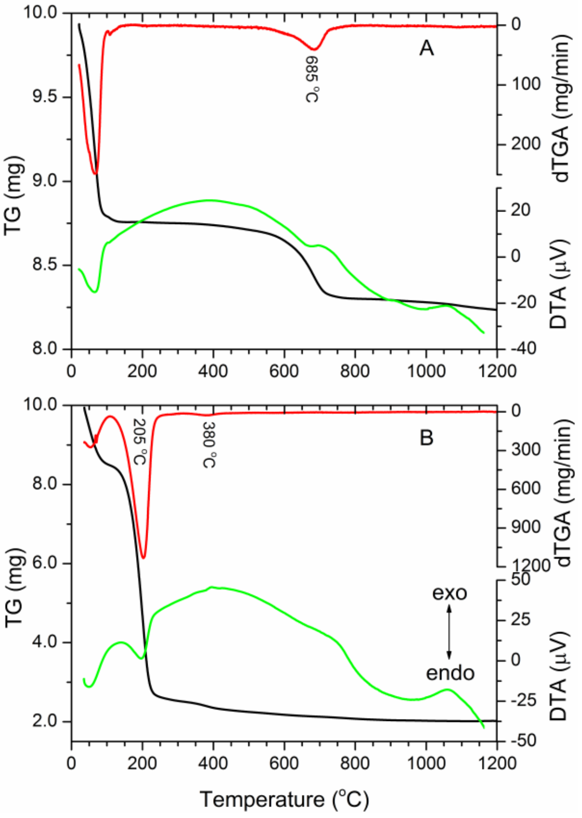

Figure 2. Thermal analysis curves (TGA-dTGA/DTA) for clay IS (A) and mixed material ISCo (B).

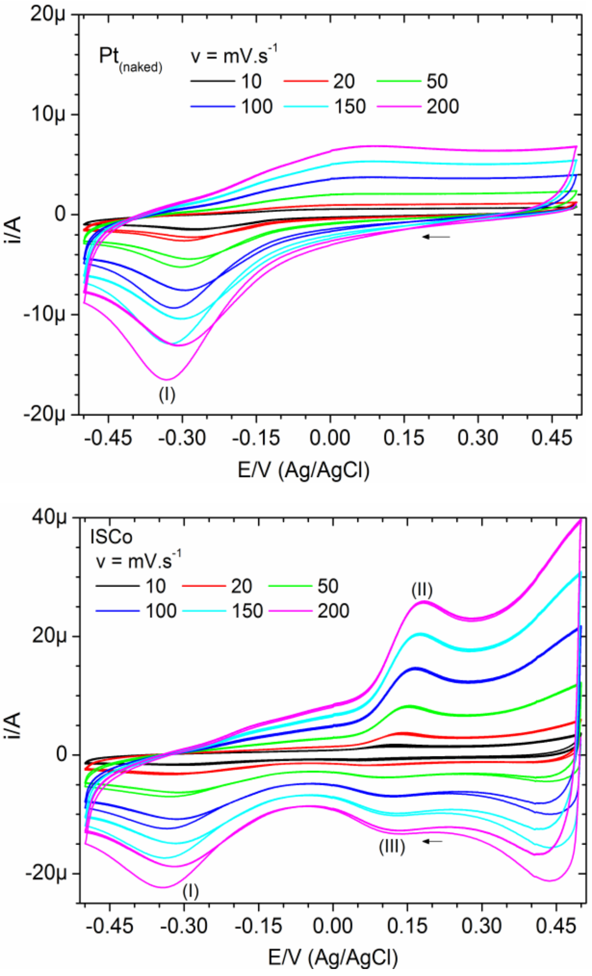

Figure 3. CVs of the electrode (A) $Pt_{(naked)}$ and (B) CME-ISCo at different scan rate in aqueous NaOH solution (0.5 mol L^{-1}).

From the data obtained from the SWVs for CME-ISCo (Figure 5), it was built an analytical curve by the standard addition method (Figure 6). The detection limit (DL) was calculated based on the Equation 1. Ten whites were registered to estimate the standard deviation of the arithmetic mean, which is imperative to evaluate the response of the methodology.

$$DL = 3 \times S_b/b \qquad \text{Equation 1}$$

Where S_b is the standard deviation of the blank signal mean in the pure electrolyte and b is the sensitivity of the analytical curve, that is, the slope at a significance level of 95% confidence. The DL calculated for the CME-ISCo was 2.55×10^{-4} mol L^{-1}. The quantification limit (QL) was calculated using Equation 2.

$$QL = 10 \times S_b/b \qquad \text{Equation 2}$$

The value of QL calculated for CME-ISCo was

2.55×10^{-3} mol L^{-1}.

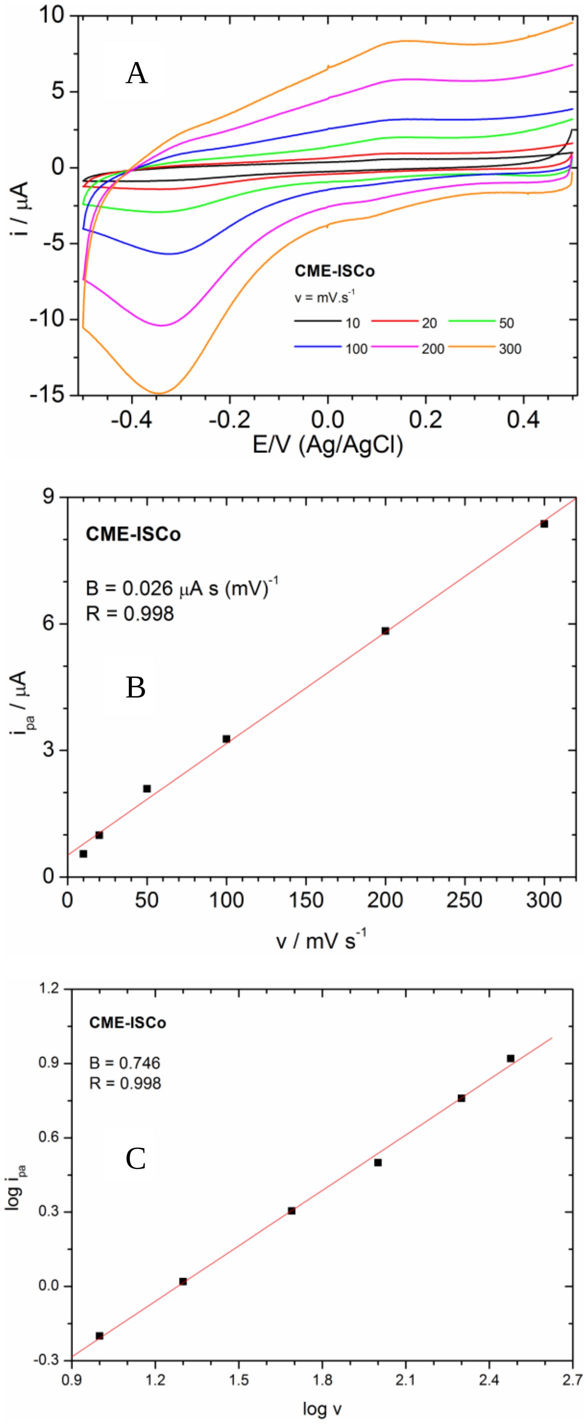

Figure 4. A) CVs of CME-ISCo at different scan rate in the presence of oxalic acid (4.9×10^{-3} mol L^{-1}). B) Graph of the dependence of the anodic peak current in function of scan rate for oxalic acid to CME-ISCo. C) Dependence of the logarithm of the peak current intensity as a function of the logarithm of the scan rate to oxalic acid on CME-ISCo. Electrode in the aqueous NaOH solution (0.5 mol L^{-1}).

Precision was evaluated based on the degree of repeatability and reproducibility of the proposed sensor regarding the Relative Standard Deviation (RSD), according to Equation 3, and which corresponds to the inverse signal-noise (S/N).

$$\% RSD = S/x \,.\, 100\% \qquad \text{Equation 3}$$

The repeatability is estimated considering 10 successive measurements in the same solution containing 4.9×10^{-3} mol L^{-1} of oxalic acid, under the same conditions of the analytical curve. Table 1 shows the values of the peak current to the oxalic acid repeatability of the CME-ISCo.

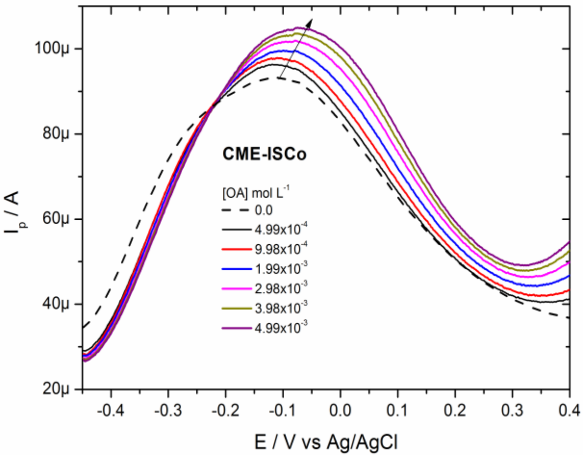

Figure 5. SWVs CME-ISCo, at different concentrations of oxalic acid solution $f = 200$ s^{-1}, $a = 80$ mV e $\Delta E_s = 2$ mV in aqueous NaOH solution (0.5 mol L^{-1}).

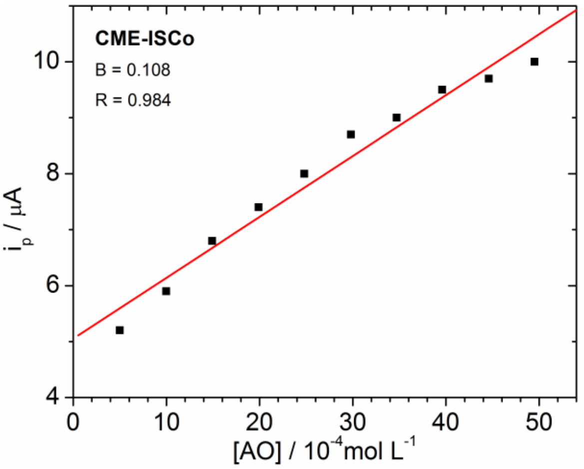

Figure 6. The graph of the linear relationship between current peak intensities and oxalic acid concentration to (in the range of 4.99×10^{-4} to 4.95×10^{-3} mol L^{-1}), in aqueous NaOH solution (0.5 mol L^{-1}).

Reproducibility was studied considering 5 different measures, in different solutions and at 5 different sensors solution containing 4.9×10^{-3} mol L^{-1}

oxalic acid, under the conditions deemed optimized. Table 2 shows the values of the peak current to the oxalic acid reproducibility of CME-ISCo. The relative standard deviation was then calculated according to equation 3.

Table 1. The CME-ISCo repeatability study.

Replicate	1	2	3	4	5	6	7	8	9	10
i_p (µA)	107	107	106	106	106	106	106	106	106	106
Mean	106.2 µA					**Standard Deviation**		0.707 µA		
RSD (%)	0.666									

Table 2. The CME-ISCo repeatability study.

Replicate (CME-ISCo)	1	2	3	4	5
i_p (µA)	106	107	106	108	110
Mean	**Standard Deviation**		**RSD (%)**		
107.4 µA	0.707 µA		0.658		

According to the results shown in Tables 1 and 2 respectively, it was observed that the proposed sensor has good repeatability and reproducibility for the analytical determination of oxalic acid, as the relative standard deviations found for the same were low. Previous studies [23] using only cobalt gel to modify the electrode surface indicate that there is a need to make cycling for electrode activation and to occur the onset of pairs of redox characteristic of the cobalt peaks, as well as stabilization peak current. In the case of uISng the mixed materials ISCo there is no need of the electrode surface activation, the clay provides a chemical and electrochemical stability which allows a redox process involving cobalt from the first cycle, thereby emphasizing a synergistic effect is favorable for electrochemical material applications mixed clay/colloidal cobalt.

4. CONCLUSION

The results evidenced the viability of using the electrode modified with the mixed materials ISCo, using square wave voltammetry for determination of oxalic acid. This effect was due to the clays provide attractive properties for the modification of electrodes due to its stability and low cost, coupled with the easy preparation of the electrode. The cyclic voltammograms of mixed materials showed well-defined peaks attributed to the redox process Co(II)/Co(III), the highest resolution at high scanning rates. The results showed that the oxidation reaction of oxalic acid is an irreversible process and that the process speed is controlled by adsorption of species in the electrodic surface. From the optimization of experimental parameters, the analytical curve for oxalic acid was obtained with a detection limit of 2.55 × 10^{-4} mol L^{-1} for modified electrode with mixed materials ISCo, which proves a good performance material.

5. ACKNOWLEDGMENTS

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