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Electrochemical Oxidation of Sulfite in Aqueous Solution by Glassy Carbon Electrode Modified with Polymeric Co(II) Meso-Tetrakis (2-Thienyl)Porphyrin

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Sulfite electro-oxidation mediated by a glassy carbon electrode modified with electropolymerized Co(II) meso-tetrakis (2-thienyl)porphyrin (Co(II)TTP) was studied. The GC/pCo(II)TTP electrode has demonstrated its catalytic capacity toward sulfite oxidation. Besides, the modified electrode is very stable and its activity stays unchanged over more than 21 days of air and light exposure.

Keywords: Cobalt meso-tetrakis (2-thienyl)porphyrin, sulfite oxidation, electrocatalytic oxidation, modified electrode, amperometric sensor

1. INTRODUCTION

Sulfite, sulfur anhydride, or sulfur dioxide is, undoubtedly, the additive most widely used as food preservative due to its antioxidant and antimicrobial properties. However, high levels of this compound produce toxic effects[1]: for example, it has been found that high levels of this compound can produce adverse reactions on asthma patients[2], and can also produce a change in the organoleptic properties of food and drinks when this compound is used at high concentrations[3, 4]. Taking into account what has been mentioned before, and due to the fact that its use limitations are established by law in most countries, sulfite ion concentration determination in the environment, food and other materials becomes an important issue.

Several methods for sulfite ion determination have been developed, which include amperometry[5,6], spectrophotometry[7,8], electrochemistryf9,10], enzymatic techniques[11,12], and flow injection chemiluminescence (FIA-CL) methods[13,14]. Electrochemical reduction of sulfite aqueous solutions has been the subject of several investigations dating from the 30's, and a large variety of electrode materials has been studied, including mercury, gold, platinum bismuth, copper, and graphite modified with iron phthalcocyanine[15-17].

In turn, electrochemical techniques provide plausible results under laboratory conditions. On electroanalysis, modified electrodes have the capable potential to satisfy the requirements of a sensor to be fast and exact[18, 19]. The preparation methods for these electrodes include molecular layers bound by adsorption and electropolymerization, amongst others[20- 22]. For an efficient electrode surface modification it is needed an electroactive species such as porphyrins, which are capable of forming stable complexes with a large variety of metals. The presence of transition metals in coordination with the porphyrin ring (metalloporphyrins) benefits its catalytic and electro-catalytic characteristics, where the peripheral groups can be also used to control the interaction.

It is widely known that sulfite anion (SO_3^{2-}) in aqueous dissolution establishes balance among the different molecular forms of this species, bisulfite (HSO_3^-), and sulfur dioxide (SO_2), Ec 1. A part reacts with compounds that have carbonyl groups and it is called bound sulfite; the other part is called free $SO_{2,}$ in which its respective concentrations will depend, principally, on the pH [23].

$$SO_3^{2-} + 2H^+ \rightleftarrows HSO_3^- + H^+ \rightleftarrows SO_2 + H_2O \qquad \text{Ec. 1}$$

2. EXPERIMENTAL

2.1 Chemical reactives

All the reactives and solvents used where pro analysis quality: pyrrole and 2-thiophenecarboxaldehyde for synthesis were obtained from Sigma-Aldrich; propionic acid p.a. from Merck; hexane p.a., chloroform p.a., ethanol p.a., methanol p.a., sodium hydroxide p.a., acetone p.a., acetic acid 100% p.a., boric acid, orthophosphoric acid 85%, silica gel 60 230-400 mesh ASTM, 0.04-0.063 mm porosity, for column, cobalt acetate (II), deuterated chloroform and sodium sulfite were from Merck; potassium chloride from Riedel-de-Haen; tetrabutylammonium perchlorate 99% from Across-Organics; silicone oil from Vetec; dichloromethane p.a. from J.T Baker; and ultra pure nitrogen 99.995 from AGA.

2.2 Instruments

Microanalysis was performed on a Fison, Model EA-1108, elemental analyzer. Proton nuclear magnetic resonance spectra (1H-NMR) were registered in a Brucker Advance 400 MHz spectrometer and processed by Mestrec software. UV-visible electronic spectra were registered in a Scinco S-3100 spectrophotometer, which has a diode bridge detector on 1 cm optical pass quartz cell. The equipment is controlled by the LabPro software through an interface. The spectrum window used was 350 to 750 mm. All the measurements were taken in dichloromethane at room temperature. The cyclic voltammograms were measured by a CH Instrument 604C potentiostat, connected to a computer, controlled by CHI software through interface. For pH measurements, it was used a pH-meter (HI 8424 HANNA Instruments).

2.3 Cells and electrodes

Cyclic voltammetry was performed in a pyrex glass three-compartment cell. The modified glassy carbon electrode (GC) goes in the central compartment. A large area platinum wire was the auxiliary electrode. All the potentials were measured taking as a reference an Ag/AgCl/(3M in KCl) electrode.

2.3.1. Synthesis of meso-tetrakis (2-thienyl)porphiryn H_2TTP

The monomer was synthesized according to what is described in literature, Adler Method. (Diagram 1)[24].

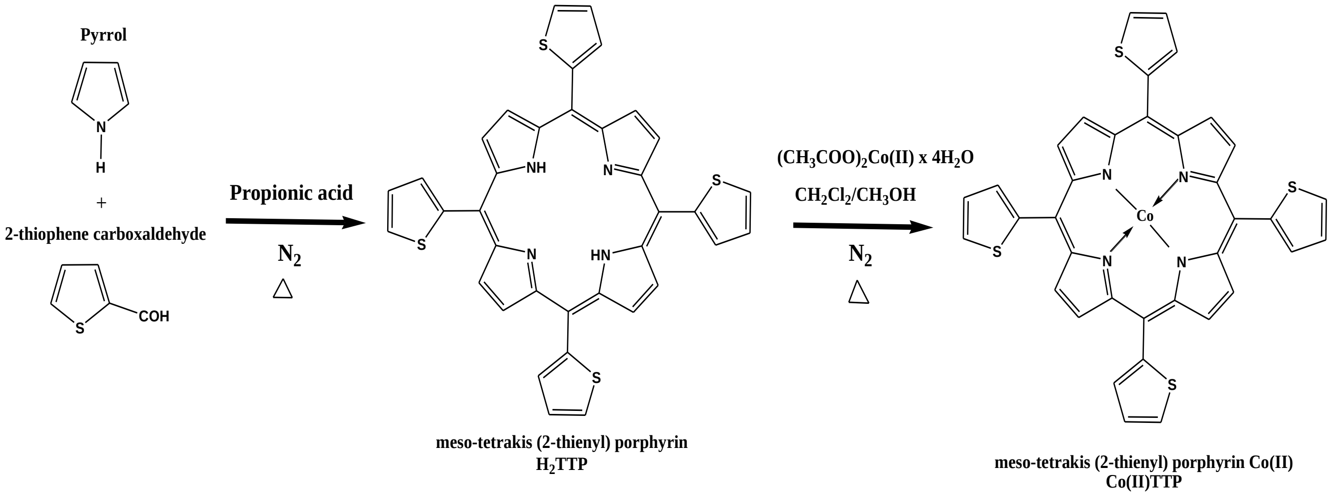


Diagram 1. Synthesis of meso-tetrakis (2-thienyl) porphyrin of Co(II) (Co(II)TTP)

2-thiophenecarboxaldehyde (1.9 mL, 2.1 x 10^{-2} mol) and pyrrole (1.5 mL, 2.1 x 10^{-2} mol) in150 mL of propionic acid were heated by reflux. In about 30 minutes, the formation of a black precipitate was observed. It was cooled at room temperature, and then methanol was added, cooling it by an ice bath at 0ºC during 15 min. Subsequently, it was filtered and the filtrand was washed with distillated water and methanol, dried and later purified by column chromatography (silica/CH_2Cl_2), obtaining a solid and crystalline purple precipitate (21% yield): H_2TTP. Elemental analysis: $C_{36}H_{22}N_4S_4$; calculated: C: 67.71, H: 3.45, N: 8.78; found: C: 67.40, H: 3.48, N: 8.51. ^{1}HNMR (400 MHz, $CDCl_3$) Co(II)TTP : δ 7.19~7.36(6H, thiophene ring hydrogens) , 7.98 (6H, thiophene ring hydrogens), 9.27(8H, porphyrin ring hydrogens) ppm.

2.3.2. Metalation of meso-tetrakis (2-thienyl) porphyrin, (H_2TTP):

H_2TTP (0.047g., 0.073 mol) and cobalt acetate (0,040g., 0,226mmol) in dichloromethane and ethanol (1:1) were placed in a Schlenk reactor to be purged with argon for 5 minutes and later heated by reflux for 6 hours. The obtained violet solution was cooled at room temperature and its organic phase was extracted by dichloromethane and water. The organic phase was dried with sodium sulfate anhydride which was filtered afterwards. The product that contains the metallated porphyrin, was dried before being purified by silica gel column chromatography, and the significant compound was eluted with a mixture of dichloromethane:hexane (3:1). The product obtained is violet colored and has a 74% yield: Co(II)TTP.

Figure 1 shows the UV-visible spectrum of the demetallated macrocycle H_2TTP compared with the response of the metallated macrocycle Co(II)TTP. The absorption spectrum for the ligand shows a Soret band (β) on the 400nm to 430 nm region, and over the 450 nm 4 bands (Q) can be observed. This intense absorption bands are characteristic for porphyrins and are due to π - π^* ligand transitions[25]. On the other hand, cobalt insertion on the porphyrin ring generates an increase of the simmetry (from D2h to D4h), apart from the hypsochromic displacement, Soret band displacement, to lower wavelengths

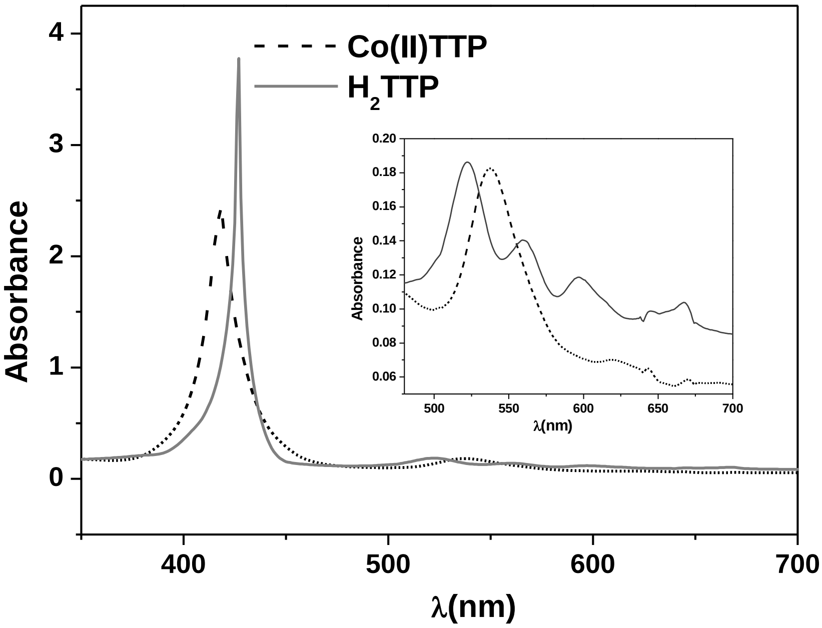


Figure 1. UV-visible spectrum for porphyrin of a) free base H_2TTP and b) metalloporphyrin Co(II)TTP

2.4. Electrochemical characterization of Co(II)TTP

Porphyrin was characterized by cyclic voltammetry of Co(II)TTP in CH_2Cl_2 (see figure 2) where two redox couples can be seen, which are ascribable to electronic transferences from the metallic center (cobalt). They are quasi-reversible processes (ΔE = 0.1V),as it has been observed in other cobalt porphyrins[26].

The first couple corresponds to the couple (Co II/I) where Epa appears at -0.62V and Epc appears at -0.72V at a 0.1V/s. The second couple, attributed to Co(III/II) shows a value of 0.86V for Epa and 0.76V for Epc. At more positive potentials, 1.24V (T/T*), thienyl group oxidation is observed. The couple corresponding to the thienyl group corresponds to a more irreversible process (ΔE = 0.25V).

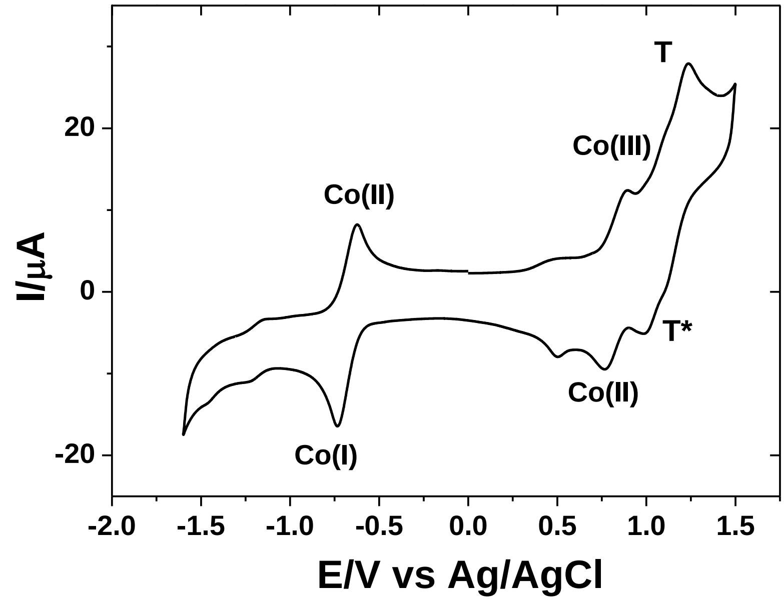


Figure 2. Electrochemical characterization of Co(II)TTP in CH_2Cl_2

2.5 Electropolymerization of Co(II)TTP to form pCo(II)TPP on the glassy carbon.

Co(II)TTP electropolymerization was carried out by cyclic voltammetry of a glassy carbon electrode on a solution of 1 mM [Co(II)TTP] complex and 0.1M tetrabuthyl ammonium perchlorate (TBAP) as supporting electrolyte in dichloromethane (CH_2Cl_2), see Figure 3. The oxidation current increase observed in successive sweeps is ascribed to doping, which occurs simultaneously to the growth of the film due to the electropolymerization. In fact, thienyl groups oxidize becoming radical cations that attack neutral monomers. In figure 3 it is observed also a decrease in the oxidation potential. This change has been attributed to the oligomer chain lengthening, which oxidant potential diminishes due to an increase in the conjugation, and that also gives account for the deposit formation on the glassy carbon electrode[27].

The cathodic and anodic limit potentials were 0.0V and 1.5V respectively. The selected anodic limit potential represents the overpotential that is needed to produce the monomer oxidation and the subsequent polymerization without altering the voltammetric profile. The gradual current increase over 1.3 V represents the oxidation process of thienyl groups[27], and the increase in its value indicates that a certain amount of pCoTTP has been deposited on the electrode. Polymerization occurs in the meso-thienyl groups, especially in position 5[27]. In turn, the oxidation peak inside the 0.9-1.05 V range can be ascribed to the porphyrin ring oxidation[28].

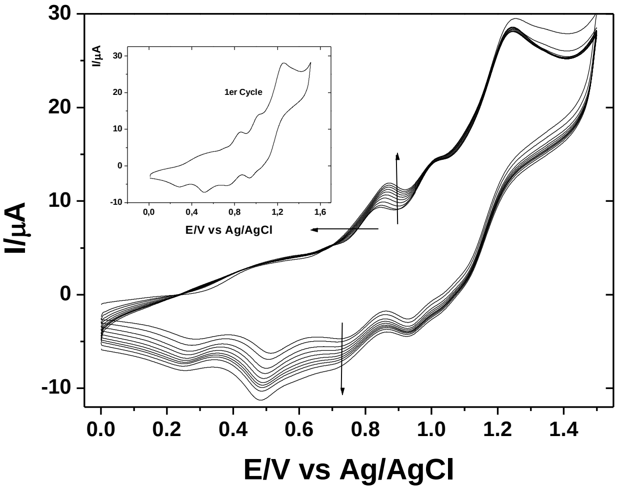


Figure 3. Voltammetric curves of the electrodeposition of Co(II)TTP on glassy carbon in dichloromethane containing 1 mM monomer and 0.1M of TBAP

Once the electrode modified with the polymer is obtained, a characterization in aqueous medium was performed by comparing the voltammetry of the GC electrode and the modified electrode GC/pCo(II)TTP. In the comparison it was observed a redox couple that probably corresponds to Co (III/II)[29] (see Figure 4).

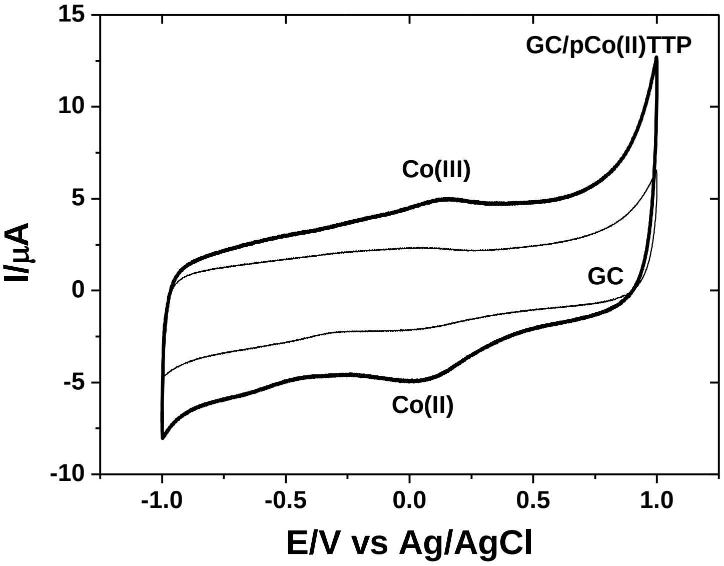


Figure 4. Cyclic voltammetry of GCE glassy carbon (GC) electrode and cyclic voltammetry of the modified electrode GC/pCo(II)TTP in the presence of 0.1M $NaClO_4$ support electrolyte; v = 100 mV/s

In order to obtain and stable and conductive electrode, it is necessary to determine the effect of the polymeric layer thickness on the electrocatalytic properties, what, in this case, was controlled by the number of voltammetric cycles. For that purpose, it was studied the response of modified electrodes obtained by 5, 10, 15, and 20 voltammetric cycles. It is observed that, although there is a direct relation between the number of cycles and the electrocatalytic capacity of the modified electrode, the modified electrodes of more than 10 cycles were not stable in their responses (not shown). Therefore it was used a modified electrode of 10 voltammetric cycles under the conditions mentioned above. The modified electrode is washed first with dichloromethane and then with bidestilated water.

On the other hand, porphyrins behavior mainly depends on pH adding up that this is an important factor in the equilibrium that the sulfite presents at the different molecular forms[8,9]. Then the study of the GC/pCoTTP modified electrode response for different pHs is obtained (see figure 5) where it can be seen that at pH 5.0 it is obtained a high response, but at the same time it is required a very high potential value, and at pH 7.0 the response is still very high and demands much lower potentials. Therefore, this pH value is the most suitable for sulfite determination under the work conditions.

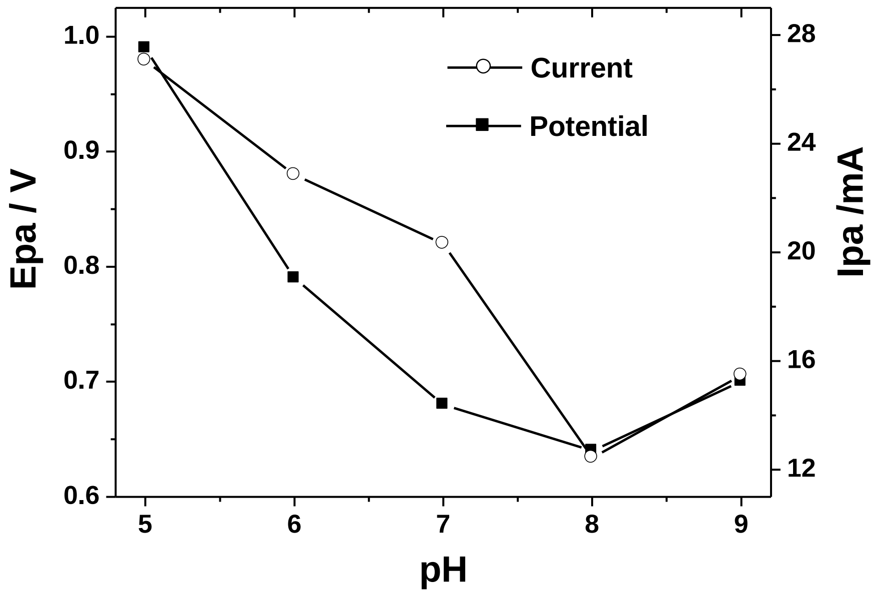


Figure 5. Potential – pH curve, and Current-pH curve of electroxidation of 1.0 mM sulfite GC/pCo(II)TTP at different pHs; v = 100 mV/s^{-1}

GC/pCo(II)TTP chemicall modified electrode has demonstrated its catalytic capacity as it can be seen in figure 6, where the sulfite oxidation is facilitated and catalyzed by the macrocycle presence on the electrode surface, providing it of an alternative reaction site for the sulfite electronic transference processes.

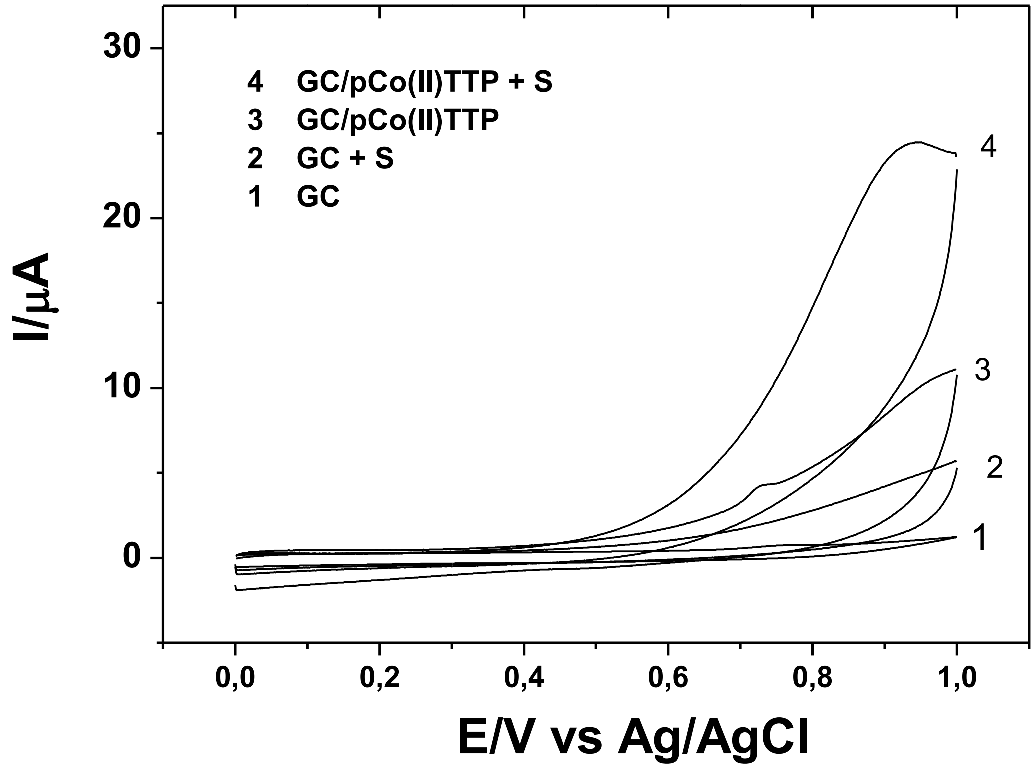
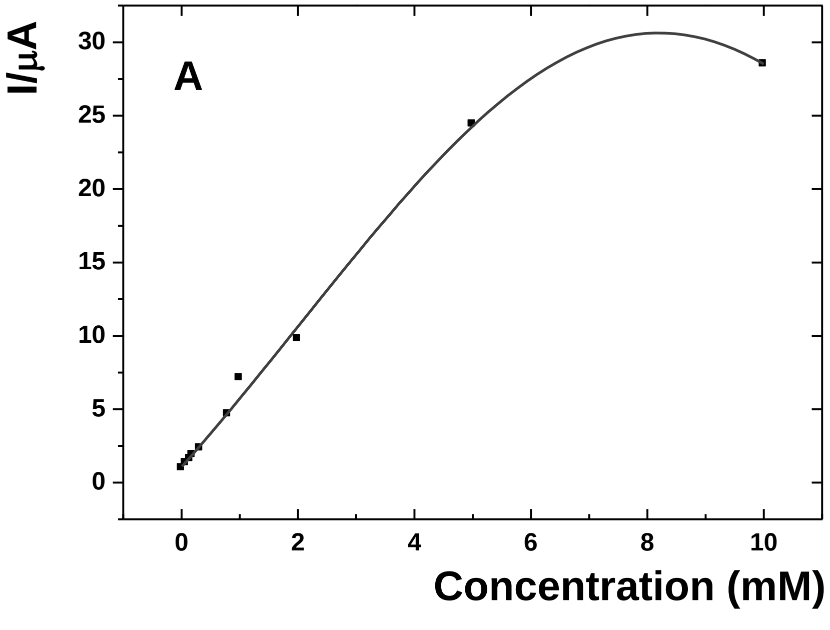


Figure 6. Cyclic voltametric of glassy carbon, GC, glassy carbon in the presence of sulfite (GC + S), GC/pCo(II)TTP and GC/pCo(II)TTP in presence of sulfite, 0.1M $NaClO_4$ + 1mM sodium sulfite a pH 7.0 as electrolyte. v = 100 mV/s.

On the other hand, current at fixed potential of 0.94V vs. concentration shows a linear interval between 1.0 x10^{-7} and 5.0x10^{-3}M of sulfite at pH 7. The relationship between current and concentrations lose linearity for higher concentrations See figure 7.



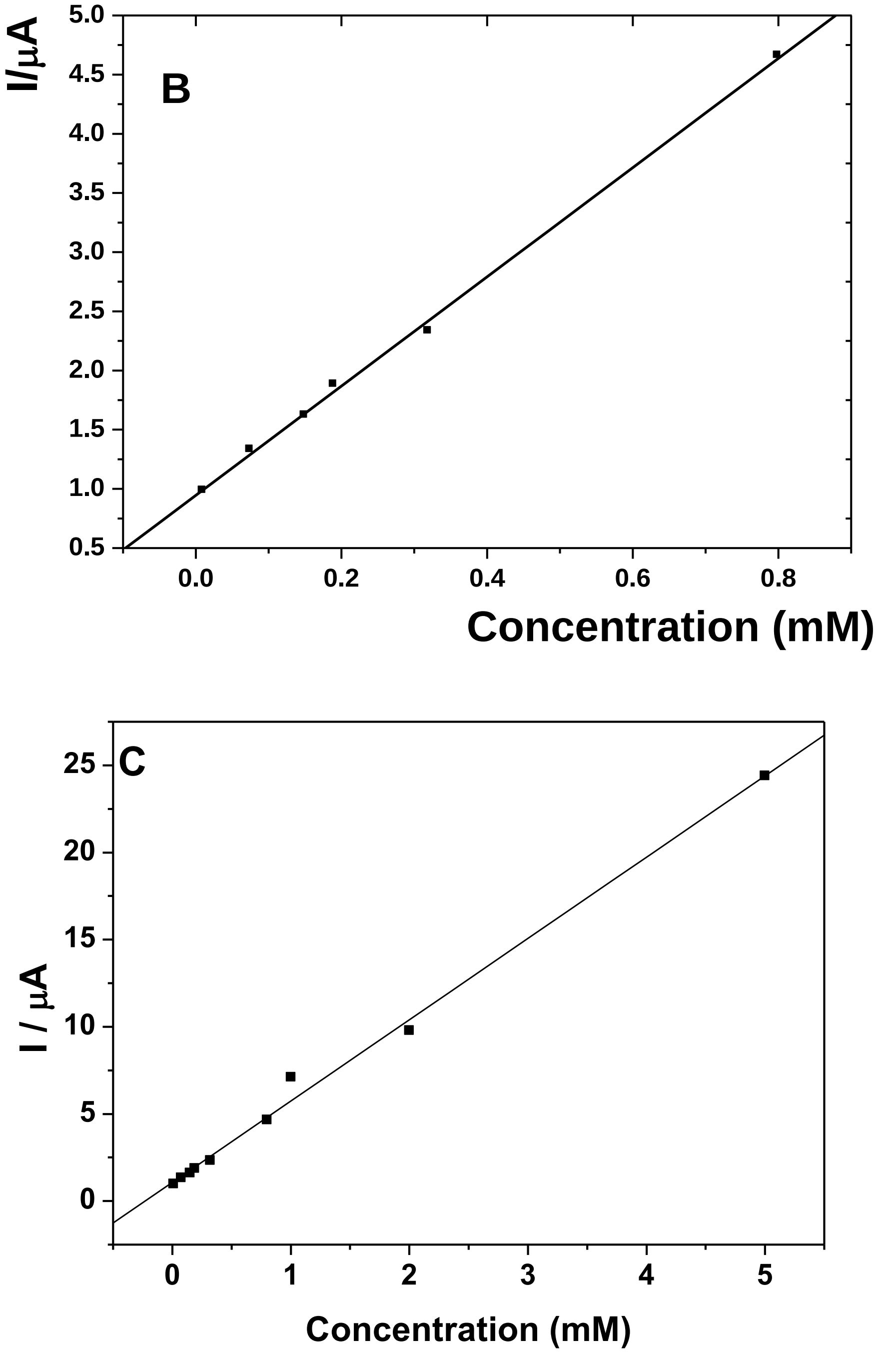


Figure 7. Graphic of current at fixed potential of 0.94V versus concentration of sulfite at pH 7 A) All the range studied, B)high concentration, C) low concentration

As can be seen in Figure 7, the response is very linear (R = 0.9984) in the range of concentrations from 1.0 x10^{-7} to 5.0x10^{-3}M and the slope (0.0047μA/mM) is high enough to use the modified electrode as an amperometric sensor of sulfite in aqueous solutions at pH 7.

Finally is necessary to point out that the electrode is very stable, its response maintains unchanged for more than twenty days exposed to air.

3. CONCLUSIONS

The modified electrode showed here requires a simple preparation and shows a great stability in time, allowing the replication of measurements after three weeks of its preparation. This electrode shows a linear response in a wide range of concentrations, and therefore, it is proposed to be used as amperometric sensor for sulfite in aqueous solutions.

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