

Electrodeposición de vanadio y níquel de los asfaltenos de crudos pesados

V and Ni electrochemical deposition from asphaltenes in heavy oils

Natalia Afanasjeva[§], William H. Lizcano-Valbuena^{**}, Nayeli Aristizabal, Ivone Mañozca

^{*}Departamento de Química, Universidad del Valle, Cali, Colombia

[§]natalia.afanasjeva@correounivalle.edu.co, william.lizcano@correounivalle.edu.co, nay3_21@hotmail.com, ivonne-2212@hotmail.com

Resumen

La presencia de metales en los asfaltenos, especialmente del vanadio y níquel, puede ser una fuente de productos de valor agregado, pero representan una desventaja en las refinerías ya que no solo contaminan los productos sino que envenenan los catalizadores durante el proceso de craqueo catalítico. El objetivo de este proyecto fue el montaje de una celda electroquímica (donde se utilizó una barra de grafito como electrodo de trabajo, un alambre de Pt como contraelectrodo y un electrodo de Ag/AgNO₃ como electrodo de referencia) para la caracterización y electrodeposición de V y Ni contenidos en los extractos resino-asfaltenicos y asfaltenos purificados de los crudos pesados. Los análisis de alta resolución antes y después de la deposición fueron: análisis elemental, FT-IR y absorción atómica. El efecto de las variables electroquímicas como potencial de trabajo, tiempo de reacción y material del electrodo en el proceso de electroreducción se evaluó por voltametría cíclica (VC) y cronoamperometría en dos medios: (I) Tetrahidrofurano y LiClO₄ al 0.02 M, (II) 20% de CH₃OH, 0.5 % de H₃PO₄, 0.1 M de LiClO₄ en acetonitrilo. Los resultados obtenidos se discuten comparándolos con los obtenidos por el método tradicional de desmetalización en ambientes de digestión ácida.

Palabras clave: Asfaltenos, celda electroquímica, crudos pesados, metales V y Ni, voltametría cíclica.

Abstract

Heavy metals are present in porphyrins in oil asphaltenes. High content of V and Ni could be attractive to produce high value metal oxides. These metals are undesirable due to corrosion issues and catalyst contamination in cracking processes. The purpose of this project was to prepare an electrochemical cell, with graphite work electrode, wire Ag counterelectrode and a Ag/AgNO₃ reference electrode, in order to evaluate and make the electrochemical characterization and deposition of V and Ni content in resin asphaltene concentrate and pure asphaltenes obtained from Colombian heavy oils. High resolution analytics before and after the deposition was done: elemental analysis, FT-IR, and atomic absorption.

The variables as work potential, reaction time and electrode materials during the electro-reduction was evaluated by cyclic voltammetry and chronoamperometer in two solutions: (I) Tetrahydrofuran and LiClO₄ at 0.02 M, and (II) 20% CH₃OH, 0.5 % H₃PO₄, 0.1 M LiClO₄ in acetonitrile. Results are discussed compared with traditional method of demetallization by acid digestion.

Keywords: Asphaltenes, electrochemical cell, cyclicvoltametrics, heavy oils, V and Ni metals.

1. Introduction

Light Oil reserves are depleting and needs for transportation fuel liquids poses new problems to Refineries in order to meet the growing demand. Research and development in heavy oils has dramatically raised in last years (Campetrol, 2009) specially focus on resin-asphaltene concentrates (CRA). In Colombia 40 % of the proven reserves corresponds to heavy oils, present in 6 of 16 basins. For example one of these basins Llanos Orientales, counts on 6,806 MMbbl to 319,455 MMbbl probable reserves and actually participate with 73.5 % of the total oil production (Colombia y energía, 2013). Refining the heavy oils in the near future will help to solve production of fuel liquids for transportation.

Nature and structure of both resins and asphaltenes strongly depend on the origin of the oil (Nomura *et al.*, 2005). Heavy oil from same reservoirs can show different properties (Tharanivasan, 2012). ASTM D6560-12, ASTM D3279 and ASTM D4124 are the most used methods for separation and characterization of asphaltenes and resins. Usually research laboratories use the precipitation of these components with aliphatic solvents and extraction with toluene in a Soxhlet reflux system, allowing a good separation of resins from asphaltenes (Aske, 2002). Citations on different models of the asphaltene structure are found, being one of them a model that considers a pillared layers of aromatic structures array (Leyva *et al.*, 2013).

Resins and asphaltenes content in a concentrate type CRA generate industrial and environmental issues because they are highly viscous, high sulfur content, and contains more than 28 metals in form of traces of Pb, V, Ni, Cr, Ti, Fe and Al (Welter *et al.*, 2009), being nickel and vanadium in the porphyrin forms the most important in the heavy cuts. Metal concentration depends on origin of oil. Some authors reports vanadium content 1.0×10^{-7} Kg/L to 1.2×10^{-3} Kg/L, and for Ni 1.5×10^{-4} Kg/L (Ali & Abbas, 2006); Colombian Castilla oil was reported having metal content in asphaltenes 1,686 and 431 μ g/g for V y Ni, (Mogollón, 1997).

Demetallization by electrolysis is a new route that might be used at moderated conditions of temperature in an convenient mix of solvents in a electrolytic solution. An efficiency of 85% is reported in a process of demetallization (Duyck *et al.*, 2006) giving an opportunity to add value extracting the metals present in a heavy oil.

Vanadium and nickel that deactivate hydrocracking catalyst are present in two forms: heterocyclic porphyrins reported by Treibs A. (1936), and in non - porphyrin form with undefined structure (Khuhawaret *et al.*, 2012). Porphyrins are classified as: etioporphyrines (Etio-), deoxofiloeritroetioporphyrin (DPED) observed by Barwise y Roberts (Fish & Wines, 1984) and later cited by Baker and Louda (1988), who discovered tetrahydrobenzoporphyrins, benzo-(rhodo)-etio-, and benzo-(rhodo)porphyrin. Ni in heavy oil is present in form of etioporphyrins (etio III) and are less investigated due to its low concentration compared with Vanadium that is present in form of vanadyl ion ($-VO^{2+}$), axe coordinated to an oxygen and four Nitrogen atoms in structures type vanadyl-deoxofiloeritroetioporphyrin (VODPEP) and in vanadylbenzotioporphyrins (VOB) (Yin *et al.*, 2006) as showed in Figure 1.

Commercial demetallization processes are at high pressures (1500-2500 psi) and temperature (380-450 °C), as demetallization process (Mello *et al.*, 2012) in presence of Hydrogen that reacts with organometallics in the organic matrix (including metallporphyrins). At laboratory level the most common method for determination of V and Ni is the acid digestion with strong organic acids at high temperature generating corrosive vapors.

Clean alternatives of demetallization are electrochemical processes as the one proposed by Welter *et al.* (2009), porphyrines present in asphaltenes, according to this work, ease the demetallization because they are electroactive and redox reactions occur under mild conditions of pressure and temperature. It was reported that metal elimination from a Venezuelan heavy crude oil Ayacucho resulted in a 84% extraction of Vanadium (IV) meso-tetra-phenolporphyrin and

78% V (IV) octa-etioporphyrin (VOHDM-OEP) using commercial porphyrins by electrochemical techniques. With oil porphyrins extractions rates were 66.4% and 64.1% using graphite electrode during 90 minutes and Pt electrode for 120 minutes. (Campero & Espinosa, 1996). The factors that affect this method: electrolytic solution, electrode material, time of reaction and reduction potential.

In this research the electrodeposition was carried out in two solutions evaluating the effect of electrochemical variables by voltammetric determination in the extraction of V and Ni from Castilla heavy crude oil on different electrode materials.

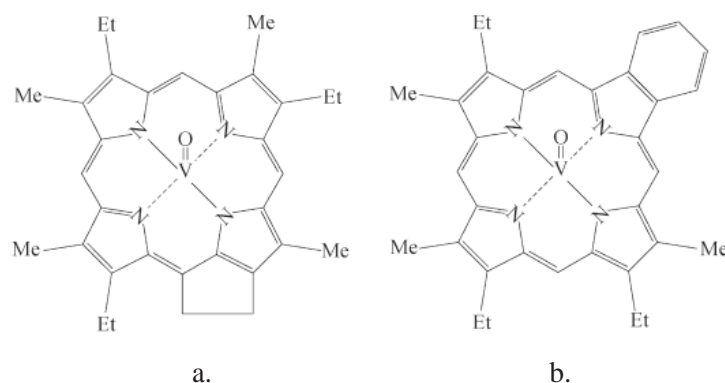


Figure 1. Chemical structure of (a) vanadyl deoxophylloerythroetioporphyrin (VODPEP) and (b) vanadyl benzoetioporphyrin (VOB). (Taken from Fish & Wines, 1984).

2. Methodology

2.1 Characterization of CRA and asphaltene probes.

CRA and asphaltene probes obtained from Castilla crude oil were precipitated with n-heptane and characterized by means of AE, FT-IR techniques and atomic absorption (AAS).

2.1.1 Elemental analysis

Content of carbon, hydrogen, sulfur and nitrogen was determined using 2 mg grinded probe in a FLASHEA 1112 series Analyzer, Thermo ELECTRON CORPORATION at a temperature of 1000°C.

2.1.2 Infrared Spectroscopy with Fourier Transform (FT-IR).

A spectrometer SHIMADZU IR-Affinity 1 was used for this analysis. It was determined the

presence of functional groups and vibration bands assigned to asphaltene, and also the anion V=O band at 1030 cm⁻¹, that is clear signal of the presence of metals in asphaltene.

2.1.3. Quantification of V and Ni in Castilla CRA and asphaltene. Acid wet digestion for metal extraction.

Probes of CRA and asphaltene weight 3.0 ± 0.0001 g were calcined at a temperature 525 °C during 6 hours to eliminate organic material. Digestion procedure is a modification of ASTM D5863 Standard. Digestion was carried out taking an acid mix HNO₃/HCl (2:5). Tubes were sealed and a digest plate type HACH DRB 200 was used. Conditions of wet acid digestion were: temperature = 100 °C for 2 hours followed by hot filtration and weighed with distilled water. Quantification of metals was done in a Spectrometer Perkin Elmer 100, at working conditions shown in Table 1.

Table 1. Conditions for metal analysis by flame atomic absorption of Castilla crude oil.

Element	Current (mA)	Slit	λ (nm)	Relation fuel/oxidant
Vanadium (V)	40	0,7	318,4	Acetylene/ Nitrous oxide
Nickel (Ni)	15	0,2	232,0	Acetylene/ Air

2.2 Electrochemical cell

An electrochemical cell was designed for experiments previous to electrolysis. A second cell with three compartments as seen in figure 2 with a volume probe capacity of 250 ml and a heating jacket with thermostat was built. Working electrode was a graphite bar with a O content 5.1 % and Cl 0.37% (measured by dispersive x-ray spectroscopy, EDX). A SEM analysis was also taken as shown in figure 3. Conterelectrode was built with a Pt wire 0.25 mm thickness. A silver wire 2 cm length immersed in a 0.01 M LiCO_4 and 0.01 M AgNO_3 in CH_3CN solution was used as reference.

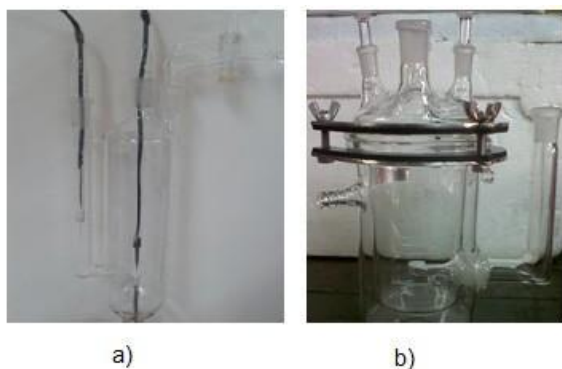


Figure 2. Electrochemical cell a) two compartments and b) three compartments.

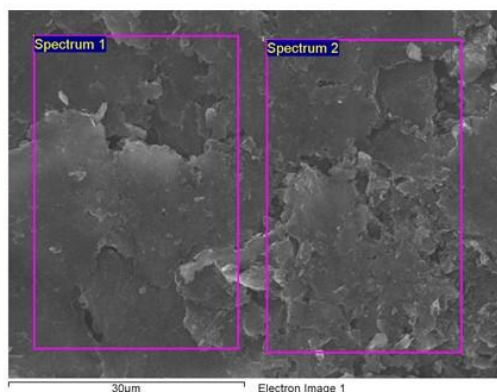


Figure 3. SEM of the graphite bar used as working electrode

2.3 Extraction of V and Ni by electrodeposition

Experiments on a potentiostat Autolab M101 were done to evaluate the effect of electrochemical variables (potential screen, reaction time and electrode materials for the electrodeposition) in the two mentioned electrolytic solution by voltamperometry.

2.4 Cyclic voltammetry electrolytic solution and Castilla crude oil.

Experiments were done at different scanning velocities from 0 to -2000 mV vs. Ag/Ag^+ . 5 g of each product were used for V and Ni electrodeposition. A solution with 90 ml LiClO_4 0.2 M in THF in presence of a protonating agent (mix 70 ml THF and 20 ml CH_3OH) was used. Electrodeposition was carried at conditions that were previously determined. All the experiments were at room temperature and the time of the reaction was 24 hours under agitation.

2.5. Chronoamperometry of Castilla crude oil

To obtain the chronoamperometry for Castilla crude oil 5g were added to a solution with 150ml LiClO_4 0.2 M THF in solution in the presence of the protonating agent CH_3OH . Measurements were done with permanent agitation at a constant potential either -1.0 or -1.7 V. Purge was done every time with Nitrogen during 10 min.

3. Results

Concentrate content (CRA) in Castilla crude oil was determined as 23.21%. Also resin content 2.81 % and 20.04 ± 1.1 % asphaltenes were found, that is according with the classification of this crude oil as heavy oil having an API gravity of 9.6, showing a high resin and asphaltene content.

From the element analysis and the H/C relation, empirical formula and average weight empirical formula (PFEA) were calculated for asphaltenes and CRA concentrate. Empirical formula were $\text{C}_{59}\text{H}_{63}\text{NSO}$ and $\text{C}_{63}\text{H}_{74}\text{NSO}$ for Castilla asphaltenes and CRA respectively. A less content

of C and H in asphaltenes is found due to the resin elimination. The higher relation H/C determines

a less aromatic character in asphaltenes as shown in Table 2.

Table 2. Data on elemental analysis, H/C relation, empirical formula and WFEA of asphaltenes and CRA Castilla crude oil

Sample	Mass (mg)	Element content(%)					Relation H/C	Empirical formula	WFEA(g/mol)
		N	H	C	S	O			
CRA	2.76	1.54	8.15	84.03	4.01	2.25	1.16	C ₆₃ H ₇₄ NSO	892
Asphaltenes	2.45	1.65	7.48	83.66	4.22	2.98	1.07	C ₅₉ H ₆₃ NSO	833

FT-IR spectra for CRA and asphaltenes from Castilla (see figures 4 and 5) showed similarity at the bands in same frequencies. Each one gives absorption bands for aromatic structures at 3010 and 3235 (ν_{CH-Ar}), 1599 and 1615 ($\nu_{C=O}$ aromatic), 861 and 864 (γ_{CH-Ar1}) or ring structures with H alone, 810-808 (γ_{CH-Ar1}) or ring with 2H nearby, 726 and 746 cm^{-1} ($\gamma_{CH-Ar2,3}$) or rings with 4H nearby and vibration bands assigned to aliphatic groups in 2922-2921 ($\nu_{CH_3+CH_2}$) and 1375, 1455 cm^{-1} ($\delta_{CH_3+CH_2}$). Ether signal appears only for asphaltenes at 1029 cm^{-1} and carbonyl signal at 1637 cm^{-1} only for CRA. Both probes give bands associated to a N-H bond.

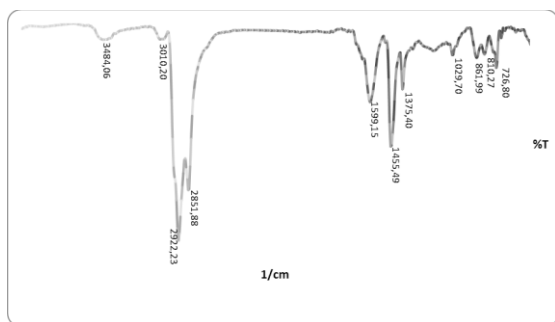


Figure 4. FT-IR of Castilla crude oil asphaltenes

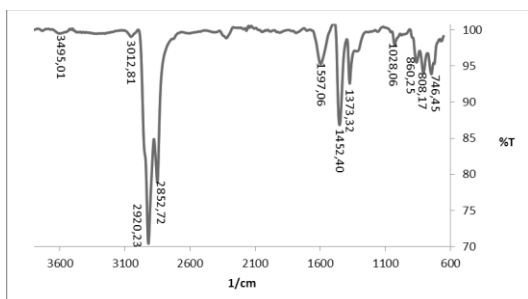


Figure 5. FT-IR of Castilla crude oil CRA

3.1. Results of content quantification for V and Ni in CRA and Asphaltenes by flame atomic absorption

Results for calibration curves for determining V and Ni content (absorbance \pm 0.001) versus concentration is shown in figure 6. Using equation (1) that relates absorbance and metal concentration a content of 4.41×10^{-4} Kg/L of V and 5.86×10^{-5} Kg/L of Ni were found in Castilla crude oil probes. Similar results are reported by the Colombian Oil Institute (ICP): V y Ni content in Castilla crude oil are 1.85×10^{-3} Kg/L y 3.82×10^{-4} Kg/L respectively (Campetrol, 2009).

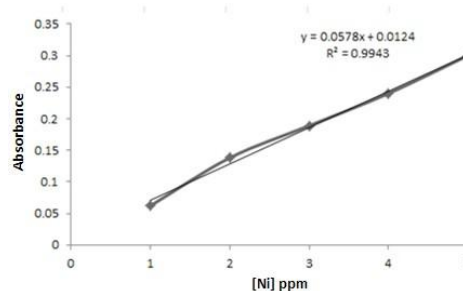
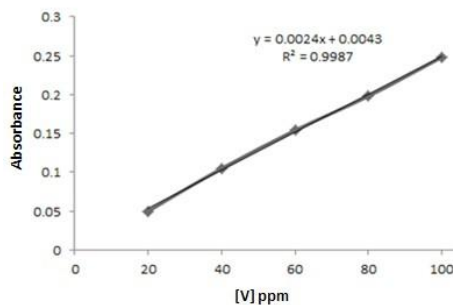


Figure 6. Calibration curves for Castilla crude oil: a) vanadium and b) nickel.

$$[y] = m[x] + b \quad (1)$$

Where:

concentration = $[x]$ = [Kg/L], absorbance = $[y]$ = [dimensionless], tangent = $[m]$ = [L/Kg],

intercept = $[b]$ = [dimensionless]

3.2. Cyclic voltammetry (VC) electrolytic medium and Castilla crude oil.

Effect of electrolytic medium on the metal recuperation by electrochemical way by means of VC was studied. In the figure 7 voltamperogramms at 0 and 2,300 mV vs Ag/AgCl, are shown. Electrolytic medium on Pt does not show associated peaks with reactions on the catalyst in the interval of potential measurements. However, at more negative potential an increase in current densities it is observed, a fact that could be assigned to a medium decomposition as reported in a publication (Márquez *et al.*, 2006).

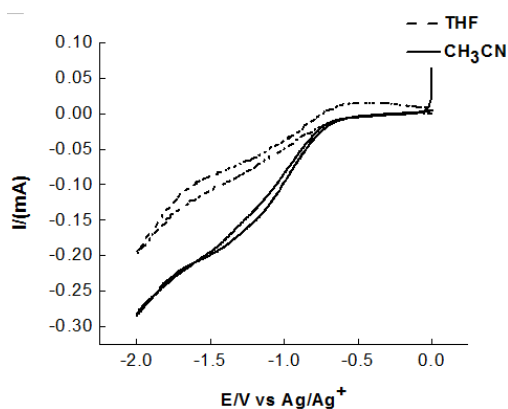


Figure 7. Voltamperogram electrolytic medium THF and CH₃CN on Pt electrode at 100 mV/s.

On the graphite electrode surface as working electrode (figure 8), no peaks were observed in the voltamperometric experiments. That indicates that the chosen potential interval is the adequate.

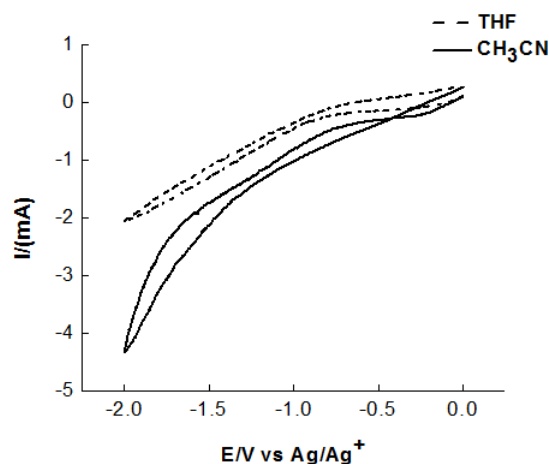
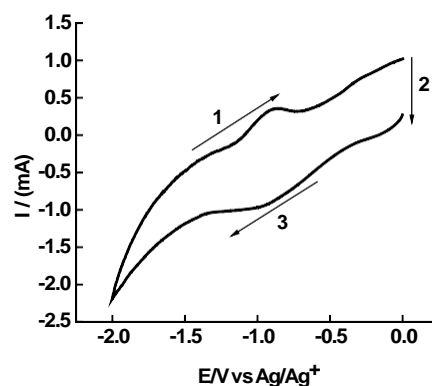
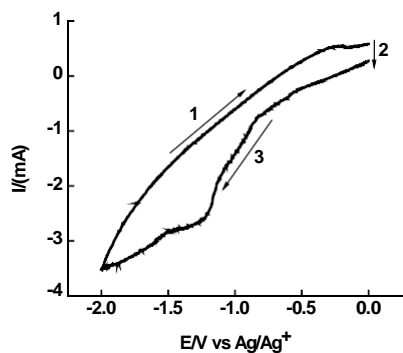


Figure 8. Voltamperogram electrolytic medium THF and CH₃CN on graphite electrode at 100 mV/s.

In figure 9a is shown the voltamperogram of Castilla crude oil in acetonitrile, observing a reduction wave nearby to -1.0 V that could be assigned to the anion radical formation caused by the reduction of the π system in the porphyrinic ring. In figure 9b peak of the radical anion formation appears at -1.2 V, displaced 0.2 V to less negatives potentials due probably to a solvent effect. In this case the effect of THF on the solubility of the petroporphyrins in the solvent (Yin C., 2008).





b.

Figure 9. Voltamperogram electrolytic medium: a) 0.5% $\text{HClO}_4/20\% \text{CH}_3\text{OH} // 0.1\text{M LiClO}_4/\text{CH}_3\text{CN}$ (b) electrolytic medium 0.02 M $\text{LiClO}_4/20\% \text{CH}_3\text{OH} // \text{THF}$ of Castilla crude oil. Scan speed 100 mv/s.

With the purpose to find the reaction time the probe stayed in contact with the working electrode for 15 hours, finding that the peak at -1.0 V (figure 10a) is less remarkable that the same peak but with the electrode at a contact time of 2 hours (figure 10b)

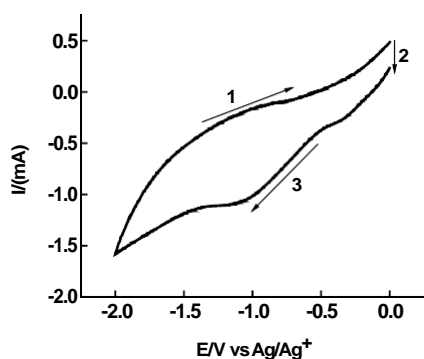
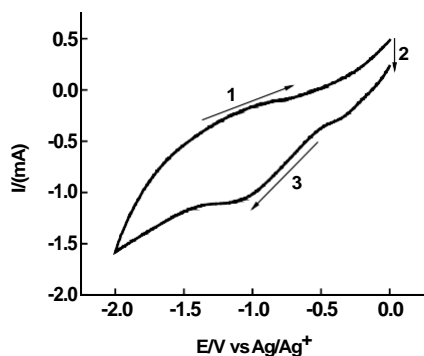


Figure 10. Voltamperogram electrolytic medium 0.02 M $\text{LiClO}_4/20\% \text{CH}_3\text{OH} // \text{THF}$ of Castilla crude oil after (a) 2 hours and (b) 15 hours. Scan speed 100 mv/s.

The conclusion could be that the reaction occurs very slow and other electrochemical parameters must be studied in a more detailed way to diminish time reaction or find a right crude oil concentration to increase the product yield.

3.3. Chronoamperometry Castilla crude oil

Chronoamperometry Castilla crude is shown in figure 11. It can be observed a typical current characteristic, that it means that the species on the electrode surface are slowly diminishing with time. It is remarkable that under constant and mild agitation concentration on electrode active surface can reach a stationary value current. Respecting to V and Ni concentrations the molar relation mM of V:Ni was calculated and resulted in a value of 8:1. With this molar relation and the C charge obtained from the chronoamperometry of Castilla crude the V and Ni mass deposited was calculated as $2,37 \times 10^{-5}$ g.

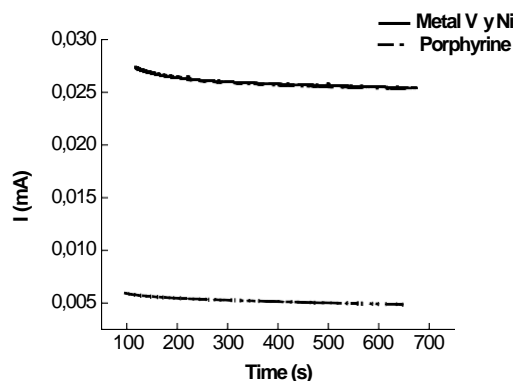


Figure 11. Chronoamperometry electrolytic medium 0.02 M $\text{LiClO}_4/20\% \text{CH}_3\text{OH} // \text{THF}$ of Castilla crude oil

4. Conclusions

Concentration of V and Ni metals determined by atomic absorption in this work was greater in an order of magnitude than the concentrations reported by Colombian Oil Institute for the same probes of Castilla crude oil. (4.4×10^{-4} Kg/L for V and 5.86×10^{-5} Kg/L for Ni). With the experimental data obtained by cyclic voltammetry a potential threshold of 0 to -2,3000 V was determined. In this interval the medium does not present reduction peaks or collateral reactions that could affect

Castilla crude oil probe. Besides, it was possible to find the reaction time for the probe in contact with working electrode as 15 hours, finding the peak at -1.0 V. It was chosen the best graphite material with less impurities for the elaboration of the working electrode referred to SEM technique. Electrodeposition reaction is slow and is affected by electrochemical factors as reaction time and the yield of the process. The low deposition of the metals V and Ni by this electrochemical technique is probably due to the quantity of other metals present in crude oil that interfere, because they form different structures of organic and non organic compounds like Cl and S salts that are known to be in crude oil. Porphyrins containing V, Ni and Fe (III) or Fe (II) are very stable due to the high chelating properties and difficult to go through a reduction process.

5. Acknowledgement

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