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## Poly(3-methylthiophene)- Multi Walled Carbon Nanotubes Composite Electrodes

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### Abstract

Our goal, is focalized in the synthesis of composite film electrodes used in the detection of contaminants from water. Films of poly(3-methylthiophene) (P3MT) were prepared by electropolymerization over glassy carbon electrode ( $\phi = 3\text{mm}$ ) and then impregnated with a thin dispersion of multi wall-carbon nanotubes, (MWCNT). Also, the MWCNT was directly embedded over the glassy carbon electrode. These composite materials P3MT/MWCNT and MWCNT coated onto a glassy carbon electrode (GC) are applied in electrochemical As(III) detection with different supporting electrolytes. The cyclic voltammetry of MWCNT/GC modified electrode in  $\text{NaNO}_3$  or  $\text{Na}_2\text{SO}_4$   $0.1\text{ mol L}^{-1}$  showed As(III) irreversible anodic wave occurring at  $0.9$  to  $1.3\text{ V vs Ag/AgCl}$  range, and lineal conduct up to  $5\text{-}10\text{ mmol L}^{-1}$  As(III), and even reproducible results after it had been used for several times at highest concentrations. The alkaline  $\text{Na}_2\text{HPO}_4$  solution improved the response and resolution this electrode with anodic wave at  $1.1\text{ V vs Ag/AgCl}$ . Performance of modified P3MT/MWCNT/GC electrode, by anodic stripping voltammetry (ASV) in  $0.1\text{ mol L}^{-1}$   $\text{Na}_2\text{HPO}_4$  (pH 10) solution was notable, because the low potential  $0.55\text{ V vs Ag/AgCl}$  by As(III) anodic current peak. The electrolysis of As(III) at constant potential with MWCNT/felt carbon electrode ( $\phi = 8\text{ mm}$ ) produced a 94 % of less toxic As(V) form, which was recovered by liquid phase retention-assisted by polymers (LPR-P) method.

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**Keywords:** Composite electrodes, polymer-multi walled carbon nanotubes, As(III) detection

### 1. Introduction

New nanostructured polymers modified electrodes represent an advantage, because electrocatalysis properties are improved due to major specific area that with a low metallic content exceed that electrode of same bulk metal (B.

Rivas et al. 2009; J. Sanchez et al. 2010). We previously reported about the preparation of noble metals modified electrodes, as Pd polypyrroleQ /glassy carbon, with IrO<sub>2</sub> /glassy carbon, besides their application as electroanalytical sensors and the successful in the quantitative conversion from arsenite to arsenate (B. Rivas et al.2011). Recently, we published the design and use of nanocomposite RuO<sub>2</sub>-polypyrrole quaternized electrode (J.F. Rivera et al.2013). Its design proceed first with electropolymerization of pyrrole –quaternized and subsequent step was the exchange and the capture of RuO<sub>4</sub><sup>2-</sup> by quaternary ammonium groups of polymer and the formation of nanoparticles of RuO<sub>2</sub> with an electrochemical reduction potential. The nanoparticles of 5 nm of RuO<sub>2</sub> distributed on polymer, showed to be an efficient electrocatalyst in the electrochemical oxidation of arsenite and with a low detection potential of 0.5V.

Carbon nanotubes (CNT) modified electrodes have been greatly investigated from Wang et al 2002. Different analytes were studied with glassy carbon electrodes modified with CNT (Y-D. Zhao et al 2003; L.Agüi and C.Peña Farfál et al. 2007; X.Dai et al 2006; C.Hu and S.Hu 2009). These authors showed that these electrodes contribute the benefit of low detection limits (LOD), increasing the sensibility and resistance to fouling of surface, and decreasing of overpotential. The electrocatalytic properties with MWCNT nanocomposites (Z-J Liu et al 2001; G-W. Yang et al.2008) is wide over a wide range of inorganic and organic analytes. The Ag/MWCNT electrode, had a good activity in alkaline media by methanol oxidation (D. J. Guo and H. L. Li 2005) and the nano Pt/MWCNT electrodes showed a reduction peak current of (NO), higher sensitivity than that correspondent to the oxidation (L. Zhang et al. 2008). The CNT modified electrodes also were used by metallic ions determinations in water (G. Zhao et al. 2004; S-H. Shin and H-G.Hong, 2010; V. Sreeja et al. 2011). The nanocomposite Au/MWCNT electrode (L. Xiao et al. 2008), showed to be efficient in the aqueous media arsenite detection via anodic stripping voltammetry (ASV) with a sensibility of (2000  $\mu\text{A} / \mu\text{mol L}^{-1}$ ) and LOD of (0.1  $\mu\text{gL}^{-1}$ ), lower than that permissible limit in tap water of 10  $\mu\text{gL}^{-1}$  by World Health Organization (WHO).

This report informs about the advances in modified electrode building with multiwalled carbon nanotubes (MWCNT), over glassy carbon (GC) and those designed with a nanocomposite of MWCNT contained in a polymeric film (3-methylthiophene) (P3MT). The performance of MWCNT/GC and P3MT/MWCNT/GC modified electrodes in arsenite electrochemical detection by cyclic voltammetry is assayed with inorganic and organic electrolytes at high and media analyte concentrations, observing the changes by pH or ionic strength. Also, the arsenite electrochemical oxidation with electrolysis experiments coupled with the ultrafiltration cells, permitted in the later step to remove arsenic from water. Thus, a new modified MWCNT/felt carbon (FC) electrode promoted the arsenite conversion at constant potential immersed in quaternary ammonium salts polyelectrolyte which acted also as retention agent of arsenate form.

## 2. Experimental procedures

The water-soluble poly[3-methacryloylamine)propyl)trimethyl ammonium chloride, P(CIMP<sub>3</sub>TA), poly[2-(acryloyloxy)ethyl]trimethylammonium chloride, P(CIAETA); and poly[(3-methacryloylamine)propyl]trimethylammonium chloride-co-acrylic acid [P(CIMP<sub>3</sub>TA-co-AA)] were synthesized with method elsewhere descript by us [20-21]. The molecular weight corresponds to the fraction of 100,000 D, after fractioning with ultrafiltration membrane.

MWCNT dispersion was prepared as described by (L. Agüi et al. 2007), with 5 mg MWCNT in 5 mL of de ionized water and 200  $\mu\text{L}$  5% Nafion Solution (Aldrich). The MWCNT, of length 1-5  $\mu\text{m}$  and diameter  $30 \pm 15$  nm, specific area 200-400 $\text{m}^2/\text{g}$  were provide by NanoLab (Waltham, MA. USA), (see Fig. 1). A glassy carbon electrode, diameter ( $\phi = 3$  mm), is impregnated with 20  $\mu\text{L}$  this dispersion preparing thus the MWCNT/GC modified electrode. Besides, a disc of 8 mm diameter and 3 mm thickening of felt carbon was used as support for 50  $\mu\text{L}$  of MWCNT, this modified electrode was labeled as: MWCNT/FC.

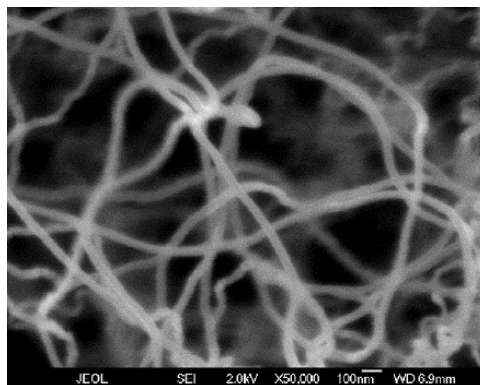


Figure 1. Image SEM of Multi Walled Carbon Nanotubes, with hollow structure.

All experiments were carried out with CHI604C electrochemical analyzer (CH Instruments, Austin, TX, USA). Standard three-electrode cells were used for analytical experiments. Voltages are referenced with respect to the Ag|AgCl in 3 mol L<sup>-1</sup> KCl reference electrode and a platinum wire was used as counter-electrode. The monomer 3-methylthiophene (3MT) (99%) is electropolymerized in acetonitrile and sodium perchlorate mixture solutions. The solution 3-methylthiophene (5 mol L<sup>-1</sup>) + acetonitrile, (3MT+ACN) is 0.1 mol L<sup>-1</sup> and the solution sodium perchlorate + acetonitrile, (SP+ACN) is 0.2 mol L<sup>-1</sup>, and they are mixed in (1:1) volume ratio. The electropolymerization proceeded with 2-3 cycles between the range 0V -1.7 V vs Ag/AgCl, at 50 mVs<sup>-1</sup> onto glassy carbon electrode (diameter (φ) 3mm). The film poly(3-methyl thiopheno) is impregnated with 20 μL of MWCNT dispersion, building the nanocomposite P3MT/MWCNT/GC electrode. The modified MWCNT glassy carbon electrodes and P3MT/MWCNT/GC electrode were used for analytical experiments with As(III). The cyclic voltammetry was applied on potential range 1-1.5 V, at 50 or 10 mV/sec.

Preparative-scale electrolyses of As(III) to As(V) species were performed in air, at room temperature, and under constant stirring of 400 rpm, on a (MWCNT/felt carbon) large area modified electrode, (disc 8 mm diameter). The applied potential for the oxidation of As(III) on modified MWCNT's felt carbon was 1 V. The charge applied is measured during the electrolysis experiment. The total charge for the complete oxidation was calculated by equation (1):  $Q = n [As]F$ , where (n = electron numbers by to pass from As(III) to As(V), [As] = mol arsenite concentration, F = 96.500 C). The NaAsO<sub>2</sub> pattern solution of 20 mmol L<sup>-1</sup> was quantified by atomic absorption spectrometry (AAS). The electrolysis cell was charged with 20 mL of a solution containing the As(III) and a cationic polymer, P(CIMPTA) used as supporting electrolyte and anion removal material. The polymer:As(III) at 20:1 mol ratio, respectively. The procedure and equipment by to remove the arsenate was described by us in (B.Rivas et al.2006; B.Rivas and M.C. Aguirre 2011; M.C.Aguirre et al. 2011) as Retention in Liquid Phase-assisted by polymers, (RFL-P). Before the ultrafiltration the oxidized solution with the anionic species As(V) are complexed with P(CIMPTA) adjusting the pH at 8 with 0.1M NaOH and stirring during 1 h. Resulting solution is kept in ultrafiltration cell, which contain on bottom a polyethersulphone membrane of 10,000 D, and then the washing method proceed at constant ionic strength. It was used a background prepared with the polymer:As(III) 20:1 mol ratio solution, which was not electrochemically oxidized. The results of As(V) consumed are showed systematically as retention percentage R (%) versus filtration factor (Z) (filtrate volume /cell volume).

### 3. Results and Discussion

#### 3.1. Detection of As(III) with modified MWCNT/GC electrode

Performance of modified MWCNT/GC electrode, in the detection of As(III) is showed in Fig. 2. The curve 2a), is the cyclic voltammetry with MWCNT/GC between 0V and 1.6 V at 20mV/sec, in 0.1 mol L<sup>-1</sup> of Na<sub>2</sub>SO<sub>4</sub> aqueous solution without arsenic. The curve 2b), shows in the same aqueous solution a maximum well defined at 0.88 V and 1.30 V due to electro-oxidation of NaAsO<sub>2</sub>, indicating that the oxidation wave of NaAsO<sub>2</sub> is generated by multiwalled carbon nanotubes and they exhibits electroactivity for the electro-oxidation of NaAsO<sub>2</sub> with a 9.55 μAmm<sup>-2</sup> current density by 3 mmol L<sup>-1</sup> As(III). The subsequent addition of As(III) monitored this electrode, determined a current lineal conduct (correlation factor =0.998) up to 4 mmol L<sup>-1</sup> As(III) using the peak at 1.3 V, and sensibility of 22.5 (μA /mmol L<sup>-1</sup>).

The detection of As(III) by modified MWCNT/GC electrode, in the Na<sub>2</sub>HPO<sub>4</sub> 0.1 M solution of pH 10 was given by anodic current peak at 1.15 V, according to CVs of Fig. 3a), with a wide range of stability upon addition of As(III). In the calibration of I<sub>peak</sub> curve vs C<sub>As(III)</sub>, (see inner Fig. 3a) is observed linearity up to concentrations of 10.61 mmolL<sup>-1</sup> of As (III), with a slope I<sub>peak</sub>/C<sub>AsIII</sub> of 14.44 (μA/ mmolL<sup>-1</sup>). In solutions of Na<sub>2</sub>HPO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> of pH 8, the maximum are not well defined at higher As(III) concentrations (see Fig. 3b) and in solutions of Na<sub>2</sub>HPO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> pH 6 was not defined a maximum of oxidation (see Fig. 3c). According to these results, it was concluded that MWCNT/GC are potentially useful electrodes to detect NaAsO<sub>2</sub> in alkaline media.

The literature reports on the efficiency of the composite Au/MWCNT electrode (L.Xiao et al 2008), in the detection of arsenite in aqueous via anodic stripping voltammetry (ASV), but not on the unique effect of the MWCNT. However, it is known (X.Dai et al.2006; Z-J.Liu et al. 2001), that electrocatalytic conduct of carbon nanotubes, occur with only the transfer of 1e<sup>-</sup> which usually happens at the edges of planes or sites which are flaws in the plane of the CNT edges. At these edges, the carbon atoms are either being semiconductor zigzag or planning as armchair in metallic states.

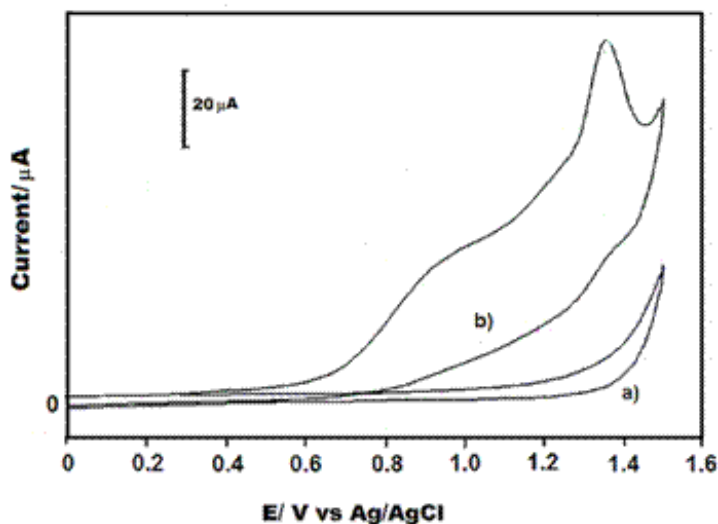


Figure 2. Cyclic voltammetry at 20mVsec<sup>-1</sup>, with modified MWCNT/GC electrode a) 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, y b) in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and 3 mmol L<sup>-1</sup> As(III).

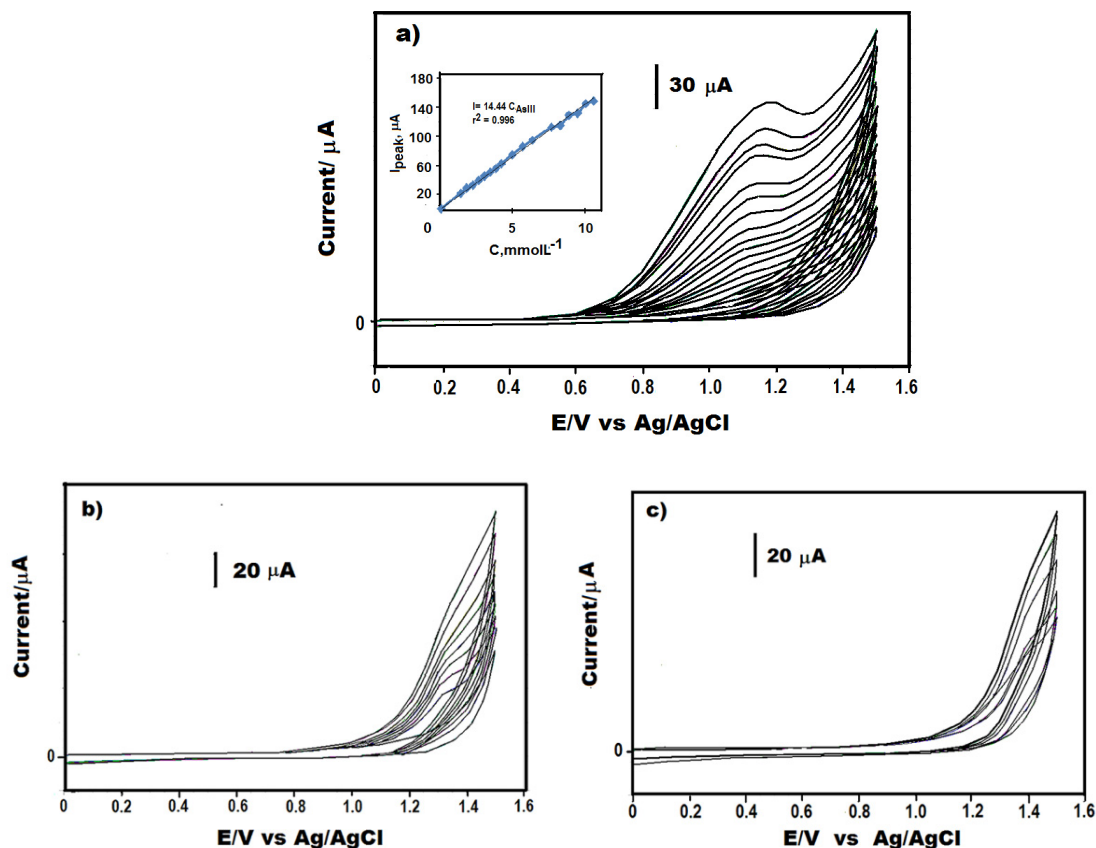


Figure 3. Cyclic voltammetry at  $50\text{mVsec}^{-1}$ , with modified MWCNT/GC electrode and As(III), in  $0.1\text{ mol L}^{-1}\text{ Na}_2\text{HPO}_4 + \text{H}_3\text{PO}_4$  aqueous solution at a) pH 10. Inset calibration curve, b) pH 8 and c) pH 6

An effect of the nature of the electrolyte support on oxidation wave of As(III), guided by changes in the pH and ionic strength of the medium is observed with inorganic aqueous  $0.1\text{ mol L}^{-1}\text{ NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$  (pH 10) solutions. When water-soluble poly[2-(acryloyloxy) ethyl] trimethylammonium chloride, P(CIAETA); poly ([3-methacryloylamine) propyl ] trimethylammonium chloride, P(CIMPTA); and poly ([3 methacryloylamine) propyl] trimethylammonium chloride-*co*-acrylic acid [P(CIMPTA-*co*-AA)] (co-monomer1:1 mol ratio) of acid nature (pH 4.5) were used as electrolytes in the detection of As (III)), they showed a anodic wide wave by As(III) with a maximum at 1.25 V. Fig. 4 shows the behavior of electrode MWCNT/GC in P[CIMPTA-*co*-AA] (pH 5)  $0.01\text{ mol L}^{-1}$  solution, with concentrations up to  $4\text{ mmol L}^{-1}$  As (III). The slope of the calibration curve was  $26.4\text{ (}\mu\text{A}/\text{mmol L}^{-1}\text{)}$  and the correlation factor 0.984.

The stability of modified MW-CNT/GC electrode in different supporting electrolytes as  $0.1\text{ mol L}^{-1}\text{ NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4 / \text{H}_3\text{PO}_4$  (pH 10) and quaternary ammonium salt polyelectrolytes was very good since no significant reduction of the current peak or displacements of the potential were observed after consecutive tests, at highest As (III) concentrations such as  $10\text{ mmol L}^{-1}$ . Confirming in part described by Xiao et al.2008, with a composite Au-CNT electrode, which in the oxidation of As(III) proved to be very stable, with reproducible results even after the experiments were repeated several times for a period of 10 months. The precision of Au-CNT electrode in that period, found that it varied less than 5% within the limit of error. It is presumed that the material

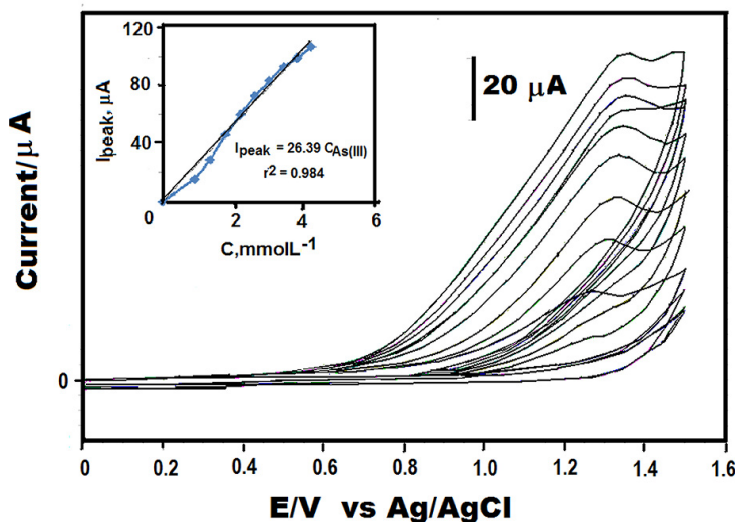


Figure 4. Cyclic voltammetry at 50 mV/sec with MWCNT/GC, in 0.01 mol L<sup>-1</sup> P(CIMPTA-co-AA)(1:1). Inset calibration curve up to 4 mmol L<sup>-1</sup> of As(III).

(MWCNT) and procedures which are in accordance with the various tests is adequate in the field of detection of arsenite, where long periods of storage or immediate use are sometimes necessary.

### 3.2. As(III) detection with the composite P3MT/MWCNT/GC electrode

The modified MWCNT/GC electrodes are stable with the addition of As(III) and with the use in repeated non-destructive testing, however, the high oxidation potential value found (1 V), near organic material oxidation, it motivated us to get new nanocomposite electrodes and modify experimental conditions, thus, to decrease the anodic potential of As(III). The results obtained with new P3MT/ MWCNT/GC electrode by cyclic voltammetry at 10mVsec<sup>-1</sup> in 0.1 M NaOH solution are seen in the Fig. 5. Upon consecutive addition of As(III) the potential was constant at 0.78 V. The calibration curve con I<sub>peak</sub> vs C<sub>As(III)</sub>, calculated a slope value of 15.76 (μA/mmol L<sup>-1</sup>) with a correlation factor of 0.997 (see inside Fig. 5). The sensitivity found by the P3MT/ MWCNT/GC electrode was similar to obtained with MWCNT/GC electrodes in Na<sub>2</sub>HPO<sub>4</sub> (pH 10).

The preparation of a composite P3MTC/MWCNT/GC electrode, as well as the experiment with anodic stripping voltammetry (ASV) were carried out to optimize the conditions of sensitivity and resolution. Measurements by (ASV) to a potential of deposition - 0.6V for 300 seconds, in a solution of pH 10 Na<sub>2</sub>HPO<sub>4</sub>, is shown in Fig. 6. It shows the anodic stripping current of As(III), with a maximum value at 0.55 V. Expected that a time deposition as 300 sec had been long sufficient, for making oxidation currents peaks a constant value, which is independent of the time. Thus the maximum current of the curves obtained in the voltammogram of Fig. 6, should be exclusively an effect of the increase of the As(III) concentration. In them, a sweep rate of 10 mVsec<sup>-1</sup> drew a well-defined maximum at 0.55V, with which built the calibration curve I<sub>peak</sub> vs C<sub>As(III)</sub>, showed inside of Fig. 6. The electrode sensitivity was measured by the value of the slope as 13.04 (μA/mmol L<sup>-1</sup>), whose correlation factor was 0.9952, up to 6 mmol L<sup>-1</sup> of As (III). The P3MT film electro polymerized on glassy carbon (GC) didn't showed activity in the As(III) oxidation.



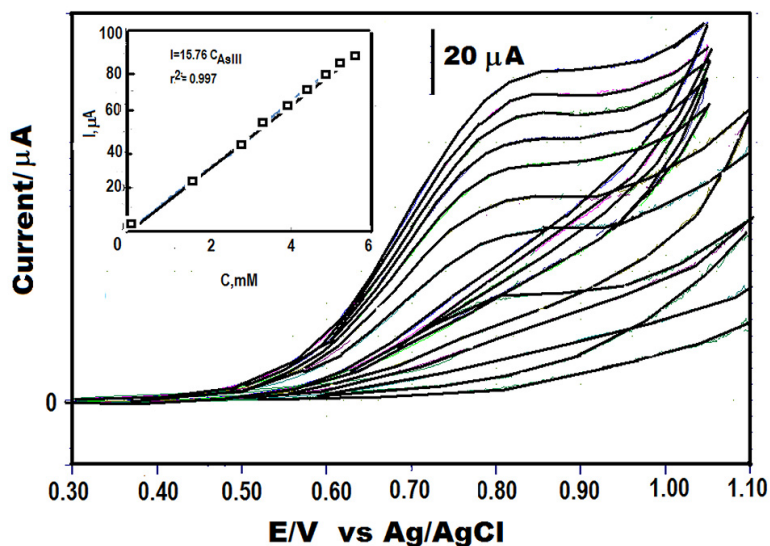


Figure 5. Cyclic voltammetry at  $10\text{mVsec}^{-1}$  with the nanocomposite P3MT/MWCNT/GC electrode in  $0.1\text{ M NaOH}$ , pH 11. Inset  $I_{\text{peak}} \text{ vs } C_{\text{As(III)}}$ , up to  $6\text{ mmol L}^{-1}$  of As(III)

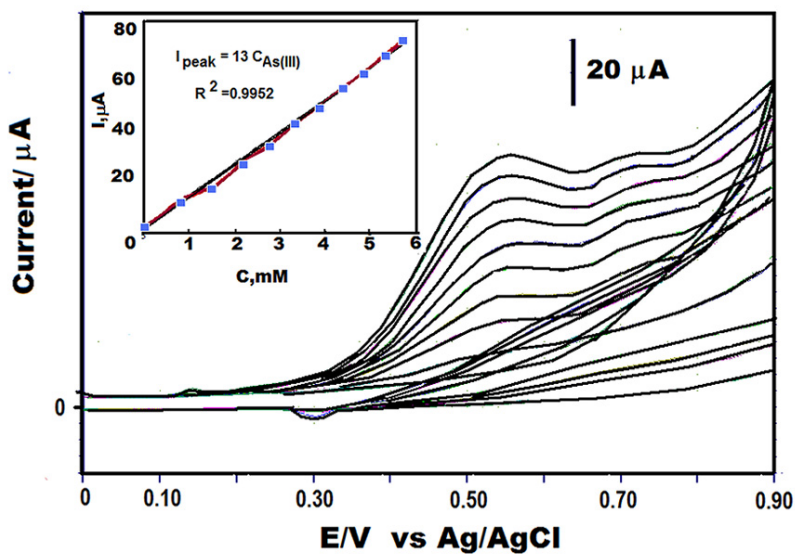


Figure 6. ASV at  $10\text{ mV s}^{-1}$ , with nanocomposite P3MT/ MWCNT/GC electrode, in  $0.1\text{ molL}^{-1}\text{ Na}_2\text{HPO}_4$  of pH 10, Inset the calibration curve,  $I_{\text{peak}} (\mu\text{A})$ , vs As(III) ( $6\text{ mmol L}^{-1}$ ).

### 3.3. Electrolysis of As(III) to As(V) combined with retention phase liquid polymer-assisted

One of the advantages of an electrode built with MWCNT in an electrolytic process is its stability in highly concentrated solutions of As(III), making it feasible to use in monitoring and mass changes with different support electrolytes, as in the case of quaternary ammonium salt polyelectrolytes, which are also a removal agent during the retention phase liquid polymer-assisted. Prior to the electrolysis, is added consecutively As (III) in 0.06 M of P(CIMPETA) monitoring by CV with a modified MWCNT/GC electrode at  $50 \text{ mVsec}^{-1}$ , and it is calculated the calibration curve slope as  $48 (\mu\text{A}/\mu\text{mol L}^{-1})$  with a correlation factor of 0.987 to  $3 \text{ mmol L}^{-1}$  of As (III), (Inset Fig.7a). Furthermore, the As(III) conversion proceeded at controlled potential of 1V with a macro modified MWCNT/FC electrode, ( $\phi = 8\text{mm}$ ). The total theoretical charge calculated as 0.52C by equation (1), was implemented in steps of 0.1C. For this the electrolytic solution was diluted by  $0.13 \text{ mmol L}^{-1}$  of As (III) pH 9, and  $2.69 \text{ mmol L}^{-1}$  of aqueous solution of P(CIMPETA), being later by ionic exchange, the retention agent of the As(V) transformed form. The washing method at pH 8, was used in the retention of As(V) by the polymer (Rivas et al 2006). Retention profile (R%), of As(V) after macro electrooxidation was 94% as is shown in Fig. 7b. It also is showed the profile for As(III) without electro oxidation in the presence of the polymer, noting a sharp fall down due to the non-retention of polymer. The pH decreased in the electrolyte from 9 to 5 during electrolysis, suggesting a mechanism via acid with MWCNT by electronic transfer, during conversion of As(III) to As(V).

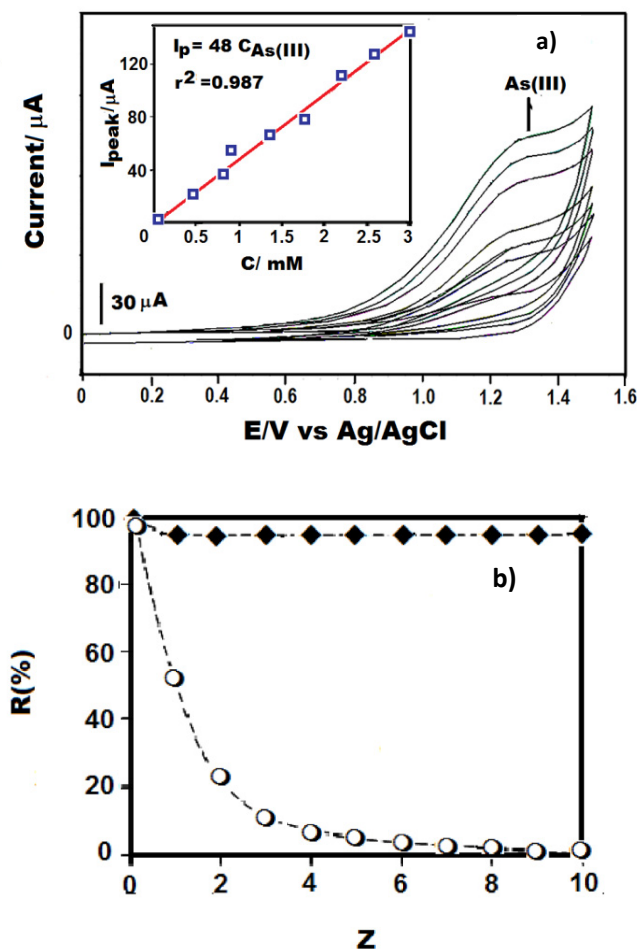


Figure 7. a) the MWCNT/GC electrode in the monitoring of  $3 \text{ mmol L}^{-1}$  As(III), in P(CIMPETA) 0.01 M, b) Retention profile of  $2.69 \text{ mmol L}^{-1}$  P(CIMPETA) with  $0.13 \text{ mmol}$  oxidized As(V) at pH 8; polymer:As(III): ( $\blacklozenge$ )20:1 and background : polymer:As(III) ( $\circ$ ) 20:1 not oxidized



#### 4. Conclusions

The efficiency of the modified MWCNT/GC electrode in the As(III) electrochemical detection at ( $\geq 1V$ ) in inorganic salts, was improved in alkaline media of  $0.1 \text{ molL}^{-1}$  NaOH ( $0.78V$ ) and when built a new composite electrode of a MWCNT/P3MT/GC film. This nanocomposite with the anodic stripping voltammetry (ASV) showed a linear response up to  $6 \text{ mmolL}^{-1}$  As(III) at the lowest  $0.55 \text{ V}$  potential in  $0.1 \text{ mol L}^{-1}$   $\text{Na}_2\text{HPO}_4$  (pH 10). During the electrolysis at potential constant, applying  $0.52C$ , with modified MWCNT/felt carbon electrode, ( $\phi = 8 \text{ mm}$ ) is electrochemically oxidized the arsenite to arsenate in P(CIMPTA)  $2.69 \text{ mol L}^{-1}$  aqueous solution and the subsequent recovery from the aqueous medium by ultra filtration was a 94%. Summary, is effectible to use combined methods as macroelectrooxidation with a modified MWCNT/FC electrode, coupled to a liquid phase retention –assisted by polymers, thus to remove arsenic from aqueous solutions. Besides, the same polyelectrolyte quaternary ammonium salts can be used as supporting electrolyte during the oxidation and retention agent of the oxidized As(V) species, during the LPR-P method.

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