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Electrocatalytic Characteristic of Carbon Nanotubes/Glutamine/Nafion Modified Platinum Electrode in Development of Sensor for Determination of As(III)

Nor Azah Yusof[*], *Nurulhaidah Daud, Tan Wee Tee and Abdul Halim Abdullah*

Chemistry Department, Faculty of Science, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia.
[*]E-mail: azah@science.upm.edu.my

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Electrochemical sensor for As(III) was prepared by using carbon nanotubes/amino acid modified platinum electrode using cyclic voltammetry. Experimental conditions such as pH, supporting electrolyte and scan rate were optimized. It was observed that the modified electrode has significant superior analytical performance in determination of As(III) compared to the unmodified electrode. The determination of As(III) by using modified electrode was reproducible with R.S.D of 7.3%. Determination of As(III) was observed to be free of metal ion interference at pH 4.0 acetate buffer. The electrocatalytic redox peak current of As(III) showed a linear response towards different concentration of As(III) and linear calibration curves were obtained in the range of 0.1×10^{-2} to 50.5×10^{-2} µM. The sensitivity response is 100 µA/µM with limit of detection 3.63×10^{-8} M. This developed method was applied for determination of As(III) in some real samples, such as industrial waste water from wood industry and electroplating industry and a good agreement was obtained between the proposed method and ICP-OES based on the analysis of the waste water samples.

Keywords: As(III) detection, nanohybrid modified electrode, electrocatalytic

1. INTRODUCTION

Arsenic is a highly toxic element and has become one of the major water pollutants in various developing countries [1]. It is a natural component of the Earth's crust, generally found in trace quantities in all rock, soil, water and air. Arsenic can exist in many different chemical forms in combination with other elements. Some forms are inorganic, which do not contain carbon, and others are organic, which always contain carbon. Inorganic arsenic exists in four main chemical forms known as valency or oxidation states. The dominant forms are arsenite, with a valency of +3, and arsenate, with a valency of +5 [2]. Arsenite ions are more soluble in water and approximately 50 times more toxic than the arsenate ions due to their reaction with enzymes in the human respiratory system [3]. EPA has set the arsenic standard for drinking water at 0.010 parts per million (10 parts per billion) to protect consumers served by public water systems from the effects of long-term, chronic exposure to arsenic [4-7].

There are several areas in the world where arsenic-bearing minerals are in contact with groundwater. In such areas, drinking water from underground wells can become heavily contaminated with natural inorganic arsenic, in excess of 1000 µg L^{-1} in some cases. This has been a serious health problem in countries like West Bengal in India, Taiwan, Chile and Mexico and is now a serious problem in Bangladesh [7]. Human exposure to arsenic can cause both short and long term health effects. Non-cancer effects can include thickening and discoloration of the skin, stomach pain, nausea, vomiting; diarrhoea; numbness in hands and feet; partial paralysis; and blindness.

The toxicity of metal ions makes the monitoring of metals in the environment, vital. Current methods of metal ion monitoring involve using classical elemental analysis technique such as atomic absorption spectroscopy (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICPMS), neutron activation analysis, etc [8]. These techniques are reliable but suffer major weaknesses. They require the sample to be transported from the site to a laboratory and sample pre-treatment is inevitable. The challenges are to develop methods for on site measurement of metal ion levels which is simple (requires no pre-treatment), reliable and robust.

Majority of researches in development of detection system for metal ion involve the usage of macrocyclic ligands. In nature however, metal binding is achieved with a high degree of selectivity using peptide rather than macrocyclic ligands. The selectivity of the binding sites of metals in proteins is defined by the sequence of amino acids within the binding site. As a consequence, sensors that use appropriate amino acid sequence as biomimetic ligands for the detection of metal ions could solve some of the difficulties in fabricating sensors using delicate proteins [9].

Electrodes modified with recognition elements of biological origin have advantages over other approaches for detecting metal ions because they have the potential to give an estimate of the bioavailability of heavy metals as distinct from total metal concentration using AAS and ICPMS. Amino acid and peptides represent the simplest biological recognition element for metal binding. Thus the usage of these compounds in metal ion detection is important.

The addition of nanoparticles together with the recognition element has proven to increase the sensitivity of the detection system developed [10]. Carbon nanotubes (CNTs) modified electrodes have shown excellent electrocatalytic activity toward hydrogen peroxide and NADH due to fast electron transfer ability of CNT [11, 12]. CNTs have been found to have the ability to promote electron transfer reactions when they were used to fabricate electrodes for the oxidation of biomolecules including dopamine[12], NADH [13], protein [14]. The CNTs modified electrode has been found to perform much better than other carbon electrodes in terms of reaction rate, reversibility and detection limit [15].

The present study reports the characterization of CNTs/glutamine/Nafion modified Pt electrode for the detection of As(III) using electrochemical technique. Optimized ratio of CNTs/glutamine/Nafion has been identified and used in modification of Pt electrode. The modified electrode has proven to be comparable in detection of As(III) when validated against ICP-OES in real sample application. Detail characterizations in development of electrochemical sensor for As(III) were also discussed.

2. EXPERIMENTAL

2.1. Materials

Multiwall carbon nanotubes (90%) and potassium phosphate monobasic (SigmaUltra, 99.0%) were purchased from Sigma-Aldrich (Sydney, Australia). L-glutamine (98.5-100%) was from Fisher (Japan) while Nafion (117 solution, ~5%) from Fluka (Switzerland). Arsenic trioxide (99.5%), sodium citrate and sodium hydroxide were purchased from Merck (Germany). Nitric acid, boric acid, acetic acid, sodium chloride and potassium chloride were obtained from R&M Chemicals (United Kingdom).

2.2. Instrumentation

All electrochemical measurements were performed with µAutolab (Microchemie) except a BAS: CV50W Voltammetric Analyzer for chronoamperometry and chronocoulometry study. The experiments were carried out in a three-electrode cell at room temperature (25°C).The counter electrode was a platinum wire and Ag/AgCl, 3 M KCl electrode was used as the reference; the modified platinum (Pt) electrode was used as working electrode. Prior to any measurements, the solutions were deoxygenated by bubbling N_2 gas through the solution for 15 min and N_2 gas was allowed to flow freely over the surface of the solution during measurements. The signal of the accumulated modified and unmodified Pt electrode were measured using cyclic voltammetry (CV) by scanning the potential from −1.50 to +1.50 V with a scan rate of 100 mV s^{-1} performed in each solution. All TEM images were taken using a JEOL 2000FX microscope with a tungsten filament as electron source; an acceleration voltage of 200 kV was applied.

2.3. Electrode preparation

Prior to the surface modification, the electrode is polished with 0.3 and 0.05 µm alumina slurry, then rinsed thoroughly with distilled water and ultrasonically agitated. Two milligram of purified multi-walled nanotubes (MWNTs) is dispersed with the aid of ultrasonic agitation in 2.0 mg of amino acid and 1.0 ml Nafion resulting as black dispersion (the ratio for MWNTs and glutamine were studied (not shown) where ratio 1 to 4 is the best). A 20.0 µL of this black dispersion was casted on the electrode surface with a micro-syringe and then evaporated to dryness at room temperature in nitrogen flow overnight. Films formed from Nafion-solubilised MWNTs are more uniform and stable than those cast from organic solvents. Nafion assists the dispersion of MWNTs, and the MWNTs remain well dispersed on prolonged standing [16]. MWNTs sonicated in organic solvents, without Nafion, tend to aggregate after the sonication has stopped.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of the CNTs/glutamine/Nafion modified Pt electrode

The electrochemical properties of the modified electrode were studied in acetate buffer (pH 4.0) by cyclic voltammetry (CV). Based on Figure 1, quasi-reversible redox couple was observed where peak at -0.24 V is attributed to the reduction of As(III) to As(0) and the oxidation peak of As(0) to As(III) was observed at -0.56 V. Anodic peak for oxidation of As(III) to As(V) was observed at + 0.64 V [17, 18]. CV of modified Pt electrode without glutamine (curve B) and bare Pt electrode (curve C) shows a very low redox peaks.

The increase peak current and the decreased of overvoltage of As(III) oxidation confirm that CNTs/glutamine/Nafion nanohybrid has high partitioning-pre-concentration ability for arsenic oxidation simply due to the enhanced partitioning of As(III) in the modified electrode. The anodic peak currents increased with increasing As3+ concentration and cathodic peaks gradually disappeared (figure not shown) [19]. Therefore, CNTs/glutamine/Nafion nanohybrid facilitates electrochemical regeneration following electron exchange with arsenic (Eq. 1).

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2e^- \qquad (1)$$

The glutamine attached carbon nanotubes were characterizes with TEM. Figure 2B showed the attachment of glutamine onto individual carbon nanotubes was successful. Wang and co-worker suggested that the solubilisation action of Nafion is very similar to the other polymeric materials bearing polar side chains, which ‘wrap’ around the CNTs, and the electrocatalytic properties of CNTs are not impaired by Nafion under optimal conditions [19, 20]. On the other hand, dispersing CNTs in 1% Nafion ensures that the amount of CNTs is controllably cast onto platinum electrode and the CNTs still retains its electrocatalytic carbon surface.

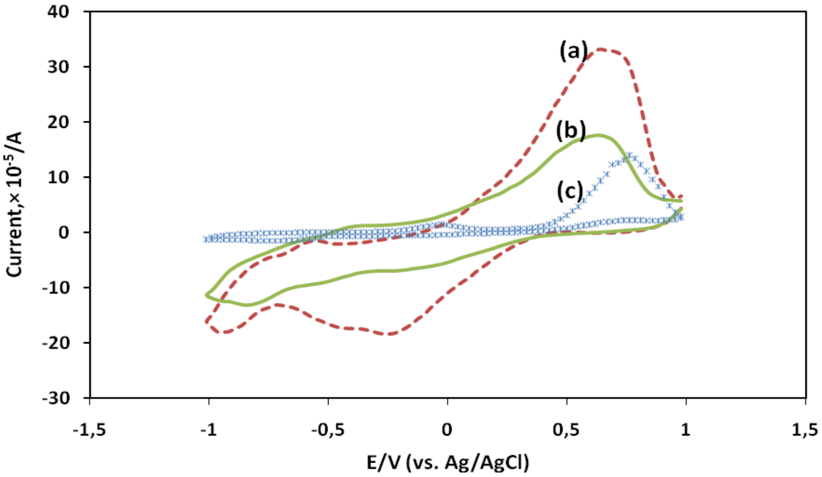
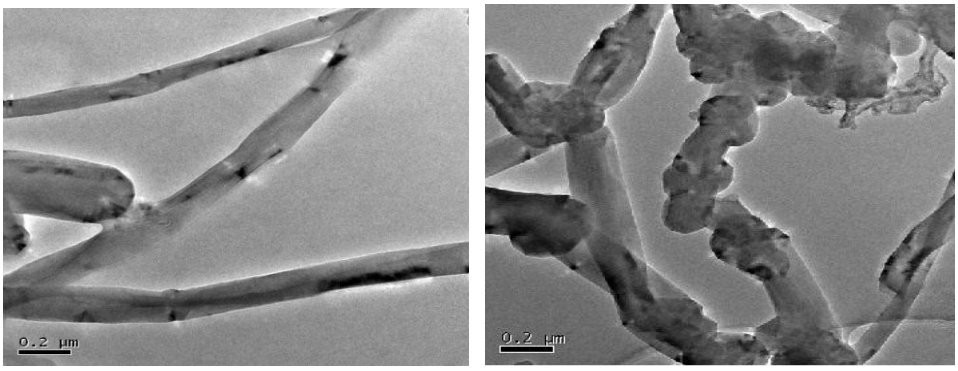


Figure 1. Cyclic voltammograms of 1 mM As(III) solution using **(a)** CNTs/glutamine/Nafion nanoparticles modified Pt electrode **(b)** CNTs/Nafion nanoparticles modified Pt electrode **(c)** bare Pt electrode in the presence of 0.1 M acetate buffer solution (pH 4.0) and at a scan rate of 100 mV s^{-1}.



(a) **(b)**

Figure 2. TEM micrograph of MWNTs (a) before and (b) after attachment of the glutamine molecules.

3.2. Electrochemical Characterization at Different pH Value

The cyclic voltammetry pattern of the modified electrode in different buffer aqueous media (citrate buffer (pH 3), acetate buffer (pH 4.5), phosphate buffer (6.8), and borate buffer (pH 9.5)) showed that the position of redox peaks varies with the nature of supporting electrolyte and the pH of electrolyte (Figure 3). Using CNTs/glutamine/Nafion modified electrode, acetate buffer gave the best oxidation peak of As(III) solution in supporting electrolyte studies where the buffer mechanism makes the effects of a disturbance less than they would otherwise be. A large concentration of H^+ in strongly acidic media brings a large concentration of oxidant that would allow the rate of oxidation and dissolution of As(III) to take place. Otherwise, a lower pH would also bring about a change in diffusion rate affecting the redox reaction.

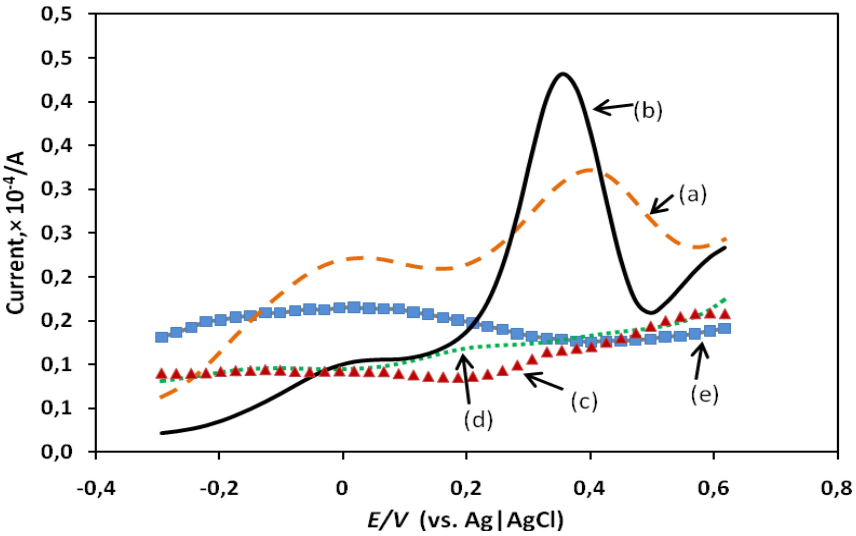


Figure 3: Cyclic voltammograms of CNTs/glutamine/Nafion nanoparticles modified Pt electrode at a scan rate of 100 mV s^{-1} in 1 mM As(III) solution and 0.1 M supporting electrolyte ;**(a)** phosphate buffer,**(b)** acetate buffer, **(c)** borate buffer, **(d)** citrate buffer, and **(e)** without supporting electrolyte.

Effect of different pH on the catalytic oxidation behaviour of the modified electrode was investigated using 0.1 M acetate buffer as the supporting electrolyte with pH variation ranging from 1.0 to 8.0 (Fig. 4). The pH was adjusted using 0.1 M HNO_3 and 0.2 M NaOH.

The cyclic voltammogram of the modified electrode in 1 mM As(III) at different pH values were recorded and showed in Figure 4. From Figure 4, it was observed that the oxidation current increases with an increase in pH from 1 to 4 and started to decrease beyond that. Therefore, an average pH value of 4.0 was chosen in subsequent studies.

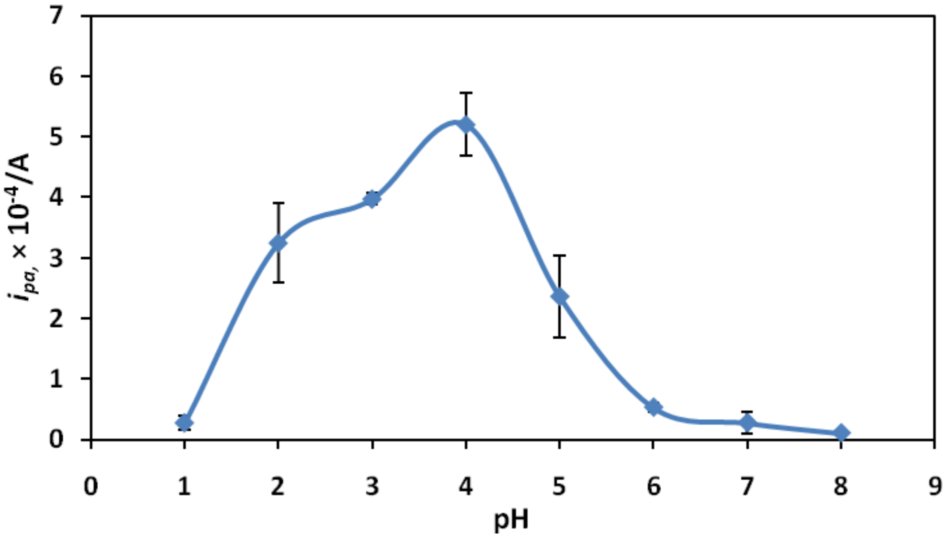


Figure 4. Oxidative current at room temperature of 1 mM As(III) in 0.1 M CH_3COONa as a function of pH using a (40 µL dispersed CNTs/glutamine/Nafion) modified Pt electrode with start potential 1250 mV at a scan rate of 100 mV s^{-1}.

The physicochemical properties of amino acids depend on (a) the presence of functional groups (e.g. amino, carboxy, thiol, phenolic hydroxyl, guanidine and imidazole) (b) the presence or absence of hydrophobic groups (e.g. alkyl, aryl and indole) and (c) the presence or absence of neutral hydrophilic groups (e.g. aliphatic hydroxyl and side chain amide groups). A simple amino acid exists in neutral aqueous solution as a dipolar ion (Zwitterion). The net charge of an amino acid can be altered using the isoelectric point, pI. Isoelectric point for glutamine is 5.65 and at a pH lower than the pI value, glutamine will carry a net positive charge whereas at pH above their pI, glutamine will carry a net negative charge [21]. The positive charge condition of glutamine is preferred due to the negative nature of arsenite ion. Highest peak current of As(III) at pH 4.0 confirms that CNTs/glutamine/Nafion nanohybrid has high electrocatalytic ability when glutamine is in net positive charge.

The reproducibility of the detection system was studied by using 5 similarly constructed modified electrodes as shown in Table 1. Acceptable reproducibility with 7.3% relative standard deviation (R.S.D) was obtained for the determination of 1 mM As(III). Data obtained from repeatability study of the modified electrode is also summarized in Table 1. The repetitive experiments with the same modified electrode lead to current decay. Therefore a freshly prepared electrode needs to be employed in each analytical application.

Table 1. Reproducibility and repeatability study of determination of 1 mM As(III) in 0.1 M CH_3COONa (pH 4) CNTs/glutamine/Nafion modified Pt electrode with start potential 1250 mV at scan rate of 100 mV s^{-1}.

Repeatability		**Reproducibility**	
Number of replicates	Current, $\times 10^{-4}$ A	Number of replicates	Current, $\times 10^{-4}$ A
1	1.31	1	1.31
2	1.30	2	1.22
3	0.89	3	1.20
4	0.63	4	1.25
5	0.41	5	1.07
6	0.23	6	1.10

Figure 5a shows the CV of 1 mM As(III) at different scan rates in acetate buffer solution (0.1 M, pH 4.0). The catalytic oxidation peak potential gradually shifts towards more positive potential with increasing scan rate, suggesting a kinetic limitation for the reaction between the redox site of the glutamine and arsenic.

As the scan rate increased, the kinetics of the electron transfer is not fast enough to maintain (Nernstian) equilibrium. Therefore, we could observe the peaks became broader as the scan rate increases [15].

A plot of log (peak current) and log (scan rate) were plotted for the oxidation peak of arsenic. The slope value of 0.69 from the plotted graph shown in Figure 5b demonstrates this electrochemical electrode process undergoes adsorption-diffusion process [15]. Each curve has the same form but it is apparent that the total current increases with scan rate by considering the size of the diffusion layer and the time taken to record the scan. At slower scan rate, the diffusion layer will grow much further from the electrode in comparison to a faster scan rate. Consequently the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates.

The surface coverage Γ (mol cm^{-2}) of the modified electrode can be estimated using Eq. 2:

$$\Gamma = Q/nFA \qquad (2)$$

Where Q is charge, n is number of electrons (n=2), F is faraday constant and A is electrode area. The Γ value for the modified electrode was calculated to be 1.557×10^{-5} mol/cm^2.

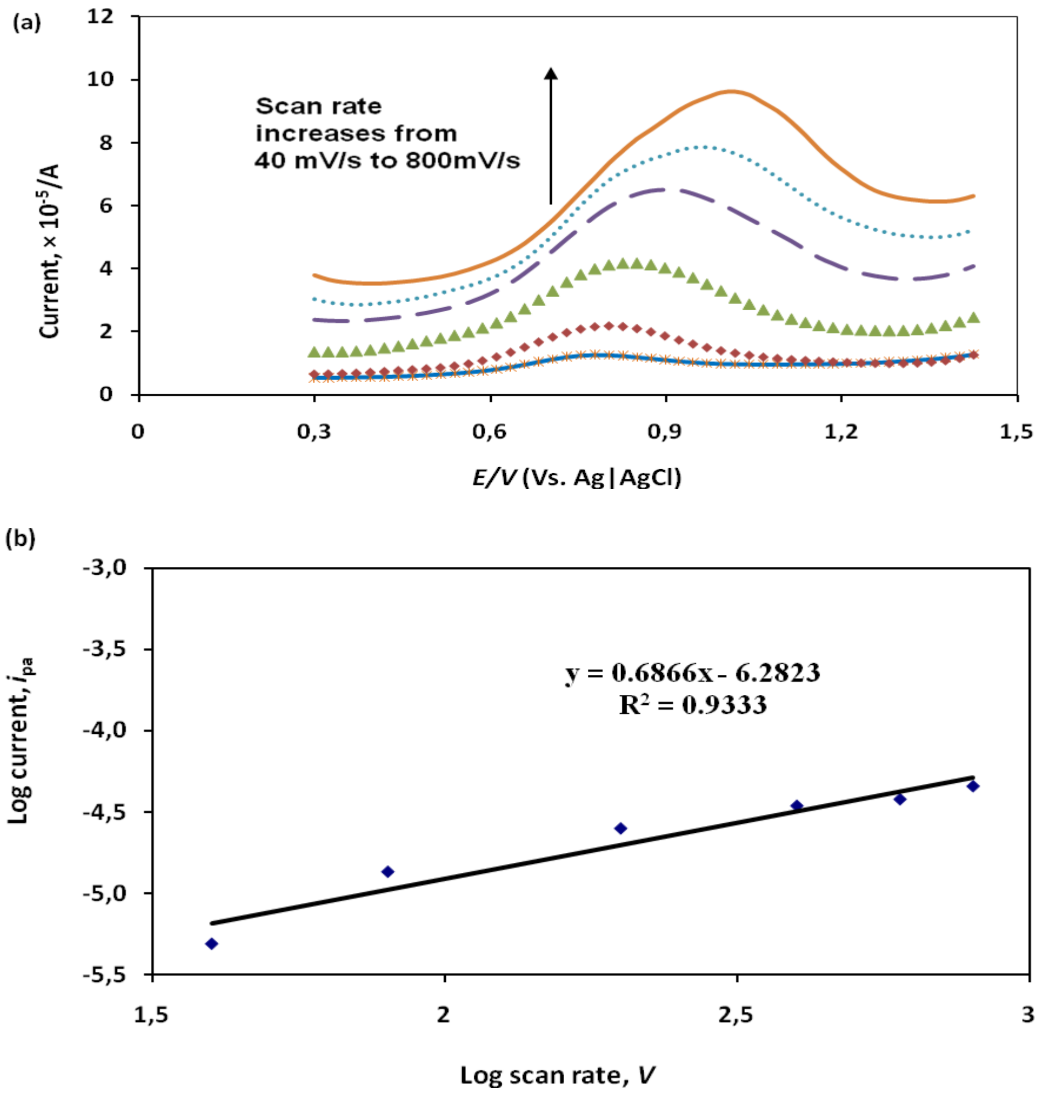


Figure 5: **(a)** Effect of varying scan rate on the cyclic voltammograms of 1 mM As(III) solution, 0.1 M acetate buffer (pH 4.0) using CNTs/glutamine/Nafion nanoparticles modified Pt electrode **(b)** plot of log oxidation current of arsenic versus log scan rate.

3.3. Chronoamperometry and Chronocoulometry Studies

In chronoamperometry, the catalytic oxidation of arsenic at the surface of the CNTs/glutamine was examined using the potential step technique. The current response is described by the Cottrell equation [22]:

$$i\,(t) = nFACD^{1/2}\pi^{-1/2}t^{-1/2} \qquad (3)$$

where, n is number of electrons per molecule (eq/mol), F is Faraday's constant (96500 C/q), A is the electrode area (cm^2), C and D represent the concentration and diffusion coefficient of the electroactive species (mol/cm^3), and t is time in second. Figure 6 shows the monotonous rising and decaying current transient in accordance to the diffusion process.

Surface of the modified electrode was measured in fresh solution of 0.1 mM As(III) in 0.1 M acetate buffer by observing Q-t response. Cottrell's law describes the current corresponding to the electrochemical reaction which is described in Eq. 4[22]:

$$Q = 2nFAC^2D^{1/2}\pi^{-1/2}t^{-1/2} \quad (4)$$

Where Q is charge and the other parameters are as described before. Slope of Q vs. $t^{1/2}$ can be utilized to calculate A using the following equation:

$$A = slope/ (2nFC\ D^{1/2}\pi^{-1/2}) \quad (5)$$

The electroactive area for the modified electrode is 1.92×10^{-4} cm^2 whereas the electroactive area for unmodified electrode is 7.17×10^{-5} cm^2. The chronocoulogram for the modified electrode is shown in Figure 7. The charge density of the modified electrode was calculated to be 14.9 $\mu C/cm^{-2}$.

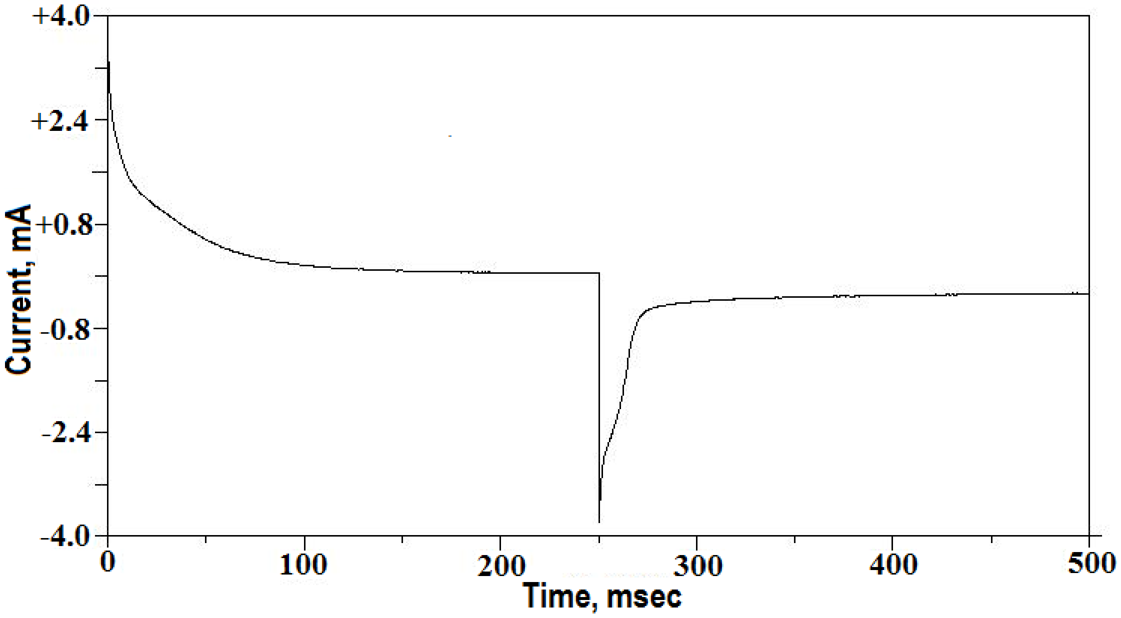


Figure 6. Chronoamperograms of 0.1 mM As(III) in 0.1 M acetate buffer for Pt modified electrode with CNTs/glutamine.

3.4. Interference Study

The effect of various cations and anions for the determination of 0.1 mM of As(III) was studied by using the developed modified electrode. The degree of interference was at 1:1 mole ratio of As(III): foreign ion. The peak potential for arsenic detection at this modified electrode is at less positive potential, which is of advantage since the number of interferences in electrochemical detection increases exponentially with increasing of potentials. The effects of various possible interferences on the electrode response were evaluated by recording CV of the modified electrode in acetate buffer solution (pH 4.0) containing 0.1 mM of As(III) in the absence and presence a specified concentration of interfering substances.

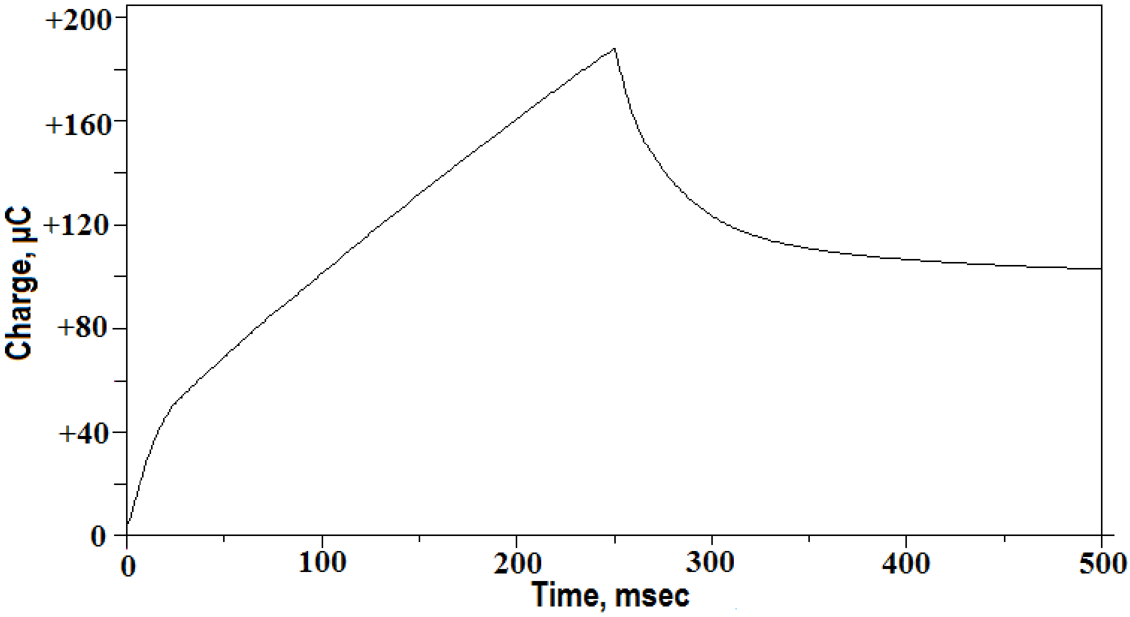


Figure 7. Chronocoulograms of 0.1 mM As(III) in 0.1 M acetate buffer for Pt modified electrode with CNTs/glutamine.

When the concentration of Cd^{2+}, Co^{2+},Cu^{2+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, $Hg^{2+}$and Zn^{2+} coexist in the sample no significant interference could be observed, indicating that these species did not affect the determination of arsenic. The non-significant of interference from other metals can be explained by the optimum pH required for the detection of As(III) in this study. Acidic condition (pH 4.0) is required for detection of As(III) where glutamine is carrying a net positive charge. The positive charge condition of glutamine is preferred due to the negative nature of arsenite ion. However this condition is not favoured by other metal ions due to their positive charges, thus giving this detection system an advantage of free interference from other cations.

3.5. Analytical Application of the Developed Modified Electrode

In order to evaluate the electrocatalytic activity of CNTs/glutamine/Nafion modified electrode, the differential pulse cathodic stripping voltammetry (DPCSV) of the modified electrode in the presence of different concentrations of arsenic were recorded. The As(III) peak appeared at ~ 0.66 V [23] and a linear graph (Figure 8) was observed for the concentration range of 0.1×10^{-2} to 50.5×10^{-2} µM with high value of background current due to the capacitance background. The sensitivity, expressed as the slope of the linear region of the calibration curve was 1×10^{-4} Aµ M^{-1}. The limit of detection (LOD) was calculated as the concentration of As(III) equal to three times the standard deviation of the background signal (3σ). The value of LOD obtained was 3.63×10^{-8} M. Compare to other sensor, Salimi et al., (2008) reported a higher detection limit value. The detection limit (S/N = 3) was 11 nM using a novel cobalt oxide nanoparticles based sensor for the detection of trace amount of As3+ [19].

The limit of quantification (LOQ) defined as ten times standard deviation of the blank was also calculated and the value obtained was 1.19×10^{-4} M. It can be inferred from these results that the presence of CNTs/glutamine nanohybrid on the surface of Pt electrode facilitates the detection of arsenic at low concentration level. This can be explained by a large surface area and higher current density generated by the CNTs. The LOD we report herein is well within the range defined by the WHO regulations [24].

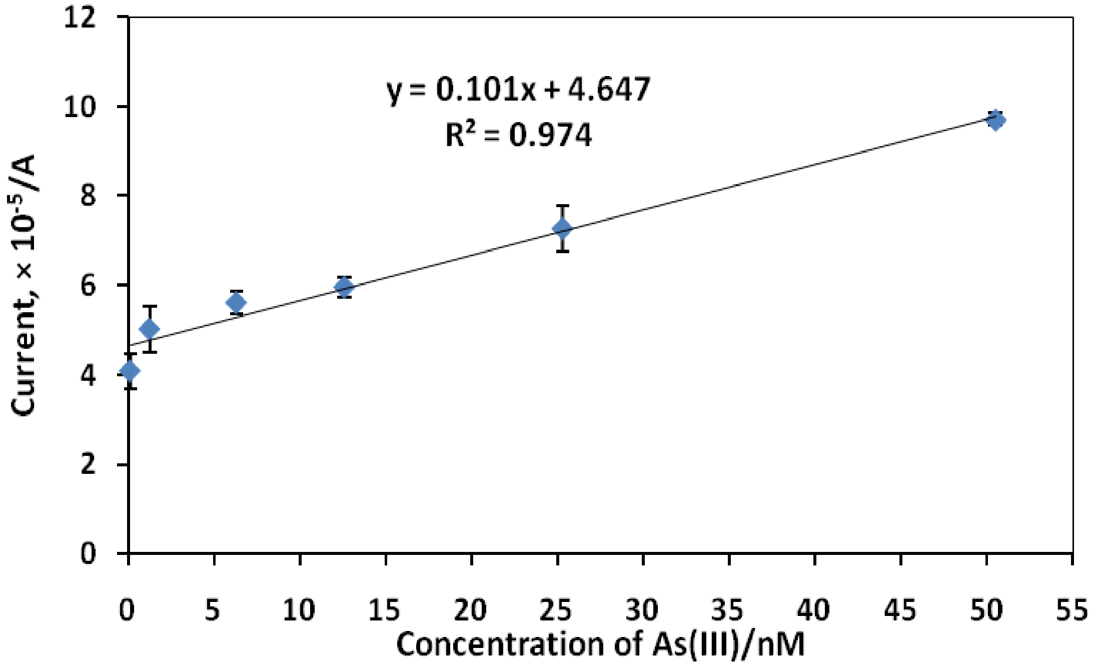


Figure 8. Calibration curve of anodic As(III) solution using CNTs/glutamine.Nafion nanoparticles modified Pt electrode in 0.1 M acetate buffer of pH 4.0.

The applicability of modified electrode for detection of arsenic was tested on real wastewater sample from wood treatment industry and electroplating industry by studying the recovery of spiked As(III) in wastewater samples. The recovery of As(III) from the mixtures prepared by spiking different amount of As(III) in waste water is 97% for wood treatment industry and 116% for electroplating industry.

The developed detection method was validated against Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) method. Good agreement was obtained between the proposed method and ICP-OES based on the analysis of the waste water samples as shown in Table 2.

Table 2: Determination of As(III) in wastewater sample from **(a)** electroplating and **(b)** wood treatment industry.

	Originally present, (ppm)	R.S.D. (%)	Added (ppm)	Found by ICP-OES (ppm)	R.S.D. (%)	Recovery (%)	Found by developed method (ppm)	R.S.D. (%)	Recovery (%)
(a) Electro-plating Industry	0.24	1.39	10	11.9±0.01	0.13	116±0.01	11.9±2	2.81	116±2
(b) Wood Treatment Industry	55.99	0.66	10	62.9±0.01	0.17	95±0.01	63.8±4	2.52	97±3

4. CONCLUSIONS

In this work, we have demonstrated a new CNTs/glutamine/Nafion nanohybrid modified Pt electrode for the determination of As(III). Nafion was used to serve as the electrode binder and also to solubilise the CNTs. Through this procedure, the electrocatalytic activity of CNTs/glutamine modified Pt electrode has been optimized in determination of As(III) and the performance of the resulting modified electrode improved greatly compared to the unmodified electrode. Determination of As(III) was found to be free of metal ion interference of up to 1.5 mM in acetate buffer. The determination of As(III) by using the modified electrode was found to be of good reproducibility (R.S.D=7.3%) and linear at As(III) concentration of sensitivity response of 100 µA/µM and LOD of 3.63×10^{-8} M. The modified electrode has been tested in determination of As(III) in spiked samples of wood and electroplating industrial waste water and found to have a comparable result with ICP-OES.

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