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A Comparative Study: Fast and Direct Voltammetric Measurements of Adenosine and Uric Acid at Copper and Carbon Fiber as Sensors

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Sensitivity of copper sensor (CS) has been tested for the first time using fast scan in direct voltammetric detection of uric acid (UA) and adenosine (ADO). Copper sensor was activated in basic medium, where the stability of the sensor can be achieved as a result of the dissolution of surface layers. Sensitivity of CS (20 μm diameter) was compared to the sensitivity of carbon fiber sensor (CFS) (7 μm diameter) for the determinations of UA and ADO after activation of the sensor surface in 70 mmol L^{-1} phosphate buffer pH 7.4. Good stability and reproducibility of the background current at copper sensor, which was exploited in on-line background subtraction, was observed following electrochemical activation/treatment in the potential window from –0.5 to +0.85V. The stability and reproducibility were strongly dependent on the potential window used for treatment and detection. UA sensitivity was measured at 0.70V (*vs.* SCE). Typical sensitivity for uric acid was 43±6 nA μmol^{-1} L at 100 Vs^{-1} with 100 cycles at copper sensor. More stable responses were observed in a potential range from +0.6 to 0.0V (*vs.* SCE), but with less sensitivities. At CFS, the measured UA sensitivity was 0.043±0.002 nAμmol^{-1} L at 0.3V (*vs.* SCE). Adenosine sensitivity at CS was found to be 0.028±0.003 nAμmol^{-1} L at 0.5V (*vs.* SCE) at 100 V s^{-1} with 100 averaging cycles, while at CFS, the measured ADO sensitivity was 0.150±0.002 at 1.4 V (*vs.* SCE).

Keywords: Copper sensors, Carbon fiber sensors, Fast scan voltammetry, adenosine, Uric acid.

1. INTRODUCTION

The recognition of purines is a necessary and sophisticated issue as these purines involve a large number of biochemical reactions [1]. Previously, several analytical methods were developed for the determination of nucleobases using high-performance liquid chromatography (HPLC) and capillary electrophoresis [2], followed by spectrophotometric detection. Electrochemical detection was shown to be a successful tool for evaluating a huge assortment of analytes in liquid-phase separations since it can be performed without causing sensitivity and selectivity losses. Using amperometry, some purines were identified using ordinary carbon electrodes after HPLC separation [2]. Regrettably, electrooxidation of those compounds requires a moderately high potential for oxidation (ca. +l.1 V vs. Ag/ AgC1), which affected the selectivity [3].

However, a copper sensor can give a hopeful model to reduce impacts of overpotential in conjunction with a highly alkaline condition, since the detection process relies on a mechanism of electrocatalytic oxidation [4-6] and not on the direct electrooxidation of the studied compound. Copper electrode applications was mentioned for the identification of carbohydrates, amino acids and peptide compounds [7-11]. Gold, silver, nickel and copper solid electrodes have been used for the detection of different analytes. The noble metal electrodes can partially compensate for their reduced reactivity and volatility by using pulse amperometric procedures including activation and surface cleaning steps with detection [12-14].

The electrochemistry of copper in basic media has been studied in silent conditions where the production of 'oxide/hydroxide' species is a feature of surface processes, which have implications for electrocatalytic phenomena on this comparatively reactive metal surface [15-19]. In the base medium, where the electrode phase entails the electrochemical formation of high-oxidation metal oxide films, active metal electrodes were used [17]. Even though the mechanisms for the whole process of such films are still not well known, it has recently been suggested that using simple solutions could allow the permanent cleaning of the electrode to create a reproducible surface [20-22].

Copper-purine complexes were tested by anodic redissolution techniques with good detection limits for mercury electrodes [23-26]. Excellent sensitivity was recorded for carbon fiber sensors in biological purine and dopamine measurements [27]. Since they serve as biomarkers to classify such disorders, the precise quantification of biomolecules is critically essential. The study of biomolecules also helps to explain their fundamental physiological functions [28, 29].

The byproduct of purine metabolism is uric acid, which is considered an essential biomarker. Hyperuricemia, Lesch-Nyhan syndrome and gout are caused by its excessive level [30]. In different biological processes, adenosine is alleged to be an effective natural vasodilator that is involved in cerebral and meningeal blood flow control [31]. It is also reported as the most effective neuromodulator in the nervous systems, both central and peripheral [31]

Due to their biological significance, the main aim of this study was to determine for the first time the sensitivities and detection limits for uric acid and adenosine on copper sensors (CSs) using fast scan cyclic voltammetry after copper surface stabilization in basic solutions and to compare the sensitivities with those measured on electrochemically pretreated carbon fiber sensors (CFSs) using background subtraction procedures [32].

2. EXPERIMENTAL

2.1. Materials

All chemicals were obtained from Fisher Scientific (Pittsburgh, PA) and Sigma-Aldrich (St. Louis, MO) and were used as received. Deionized water was used to prepare the working solutions. The pH 7.4 phosphate buffer contained both ($NaH_2PO_4.H_2O$) and (Na_2HPO_4) at a total concentration of 70 mmol L^{-1}. With NaOH or HCl, the pH of the solutions was changed before experiments. Prior to the experiments, adenosine (ADO) and uric acid (UA) were prepared. All CFS determinations were done at 70 mmol L^{-1} phosphate buffer pH 7.4 and CS at 0.10 mol L^{-1} NaOH, respectively. All the measurements were done at room temperature. An analyte's sensitivity was estimated from the slopes of the calibration curves. On three separate electrodes, at least 6 points were obtained for each calibration curve and 3 measurements at each concentration. The measurements acquired at various CFS and CS were pooled. All other measurements have been replicated in triplicate at least. The results recorded indicate the reproducibility of the measurements and of the CFS and CS fabrications.

2.2. Instrumentation

For fast scan cyclic voltammetry (FSCV) The instrumental set up has been described before [32-34]. The details of the instrumental set up is described in the supplementary file. The potential windows used in the analytical measurements of ADO and UA were from 1.0 to 1.5 V in 70 mmol L^{-1} phosphate buffer pH 7.4 at CFS, and from 0 to +0.6 as well as from +0.85 to -0.5 V for ADO and UA, respectively at CS. 250 cycles were used in FSV measurements [32] with a scan rate of 100 Vs^{-1}.

2.3. Sensors

Carbon fibers (7.0 μm diameter) were supplied by Textron Specialties Materials (Lowell, Ma, USA), copper wires 99.99+% (20 μm diameter), from Good fellow Company (London – England), were used in the manufacture of sensors. The fabrication process of such sensors was described before [32]. The details of the sensors manufacture procedures are described in the supplementary file.

2.5. Analytical determinations

ADO and UA were measured by FSV at 100 Vs^{-1} in 70 mmol L^{-1} phosphate buffer pH 7.4 at CFS, and at CS in 0.10 mol L^{-1} NaOH. The average slope of the calibration curve is used to calculate sensitivity using three separate carbon fiber and copper sensors. 6 concentrations and 3 determinations at each concentration, were measured and then data was processed.

3. RESULTS AND DISCUSSION

3.1. Electrochemical pretreatment of CFSs

To obtain a stable, reproductive and active surface, the sensors were electrochemically pre-treated prior to use. Electrochemical pretreatment (ECP) process was explained previously [33, 34]. The CFSs were electrochemically pretreated at 10 Vs^{-1} for 30 min in a 70 mmol L^{-1} phosphate buffer, pH 7.4 Via continuous potential cycling from 1.0 to 1.5 V (vs. SCE) [34]. Methods of electrochemical pretreatment (ECP) [33, 34] are used to etch the surface of the carbon. For UA and ADO determinations at a 500 Vs^{-1} and higher, the pretreatment process was configured earlier [32].

3.2. Electrochemical pretreatment of Copper sensors

Copper sensors were electrochemically pretreated in 70 mmol L^{-1} phosphate buffer, pH 7.4, 0.07 and 0.10 mol L^{-1} NaOH respectively. In the pretreatment process, the electrode potential is continuously cycled at 10 V s^{-1} in a potential window from –0.5 to +1.0V (vs. SCE) for 3000, 4000 and 5000 cycles (Figure 1).

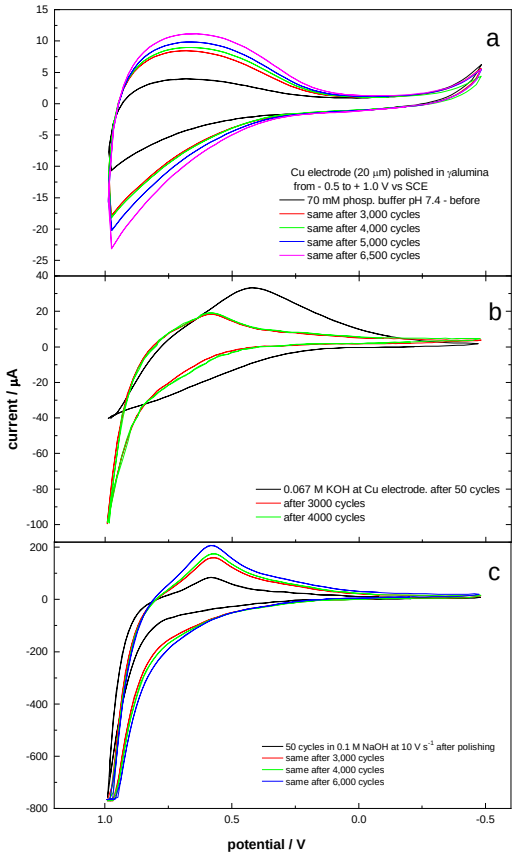


Figure 1. Background currents at 10 Vs^{-1} for different supporting electrolytes after different number of cycles, potential from -0.5 and +1.0 V vs SCE at 20 mm diameter CuS (a) in 70 mmol L^{-1} phosphate buffer pH 7.4 before and after 3000, 4000, 5000 and 6500 cycles respectively, (b) in 0.067 M NaOH after 50, 3000 and 4000 cycles respectively and (c) in 0.1 M NaOH after 50, 3000, 4000 and 5000 cycles respectively.

Figure 1 shows that in 70 mmol L^{-1} phosphate buffer pH 7.4, the increase in current after 5000 continuous cycles indicates that such electrolyte does not produce a stable surface of copper sensor under these conditions. In 0.070 mol L^{-1} NaOH the surface stabilization occurred after 5000 cycles, but with very low current, and consequently poor sensitivity.

Good results were obtained when using 0.10 mol L^{-1} NaOH for electrochemical pretreatment process in the same potential window. The only defect was getting a poor background subtraction as the extension of the potential window up to +1.0 V results in very high background current and consequently leads to poor background subtraction.

Prabhu and Baldwin [35] investigated the influence of NaOH concentration in the amperometric determination of alcohol at +0.48V under hydrodynamic conditions. The authors concluded that for NaOH from 0.050 to 0.20 mol L^{-1} the current is practically constant.

3.3. Potential window influence on the copper sensor response

3.3.1. Influence of Negative Potentials

A positive potential of +0.75V was fixed and the negative potential was changed to –0.5, -1.0 and –1.2 V. Before each measurement the sensor surface was activated by one-minute polishing using 600-grit SiC paper and on a polishing cloth with a γ-alumina suspension of 0.10 μm particle size. Figure 2 shows the background current of 0.1 M NaOH at Copper sensor at different potential windows starting at +0.75 V to -0.5 V, -1.0 V and -1.2 V respectively at 10 Vs^{-1}. The current was measured after 50 cycles in each potential window.

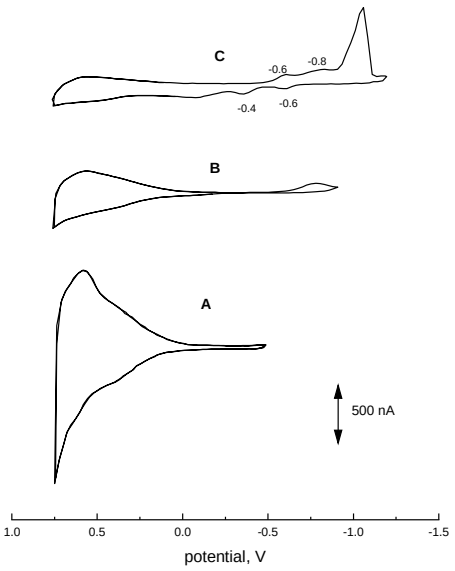


Figure 2. The background current of 0.1 M NaOH at CS at different potential windows starting at +0.75 V to -0.5 V (A), -1.0 V (B) and -1.2 V(C) respectively at 10 Vs^{-1} vs SCE. The current was measured after 50 cycles in each potential window.

From Figure 2, it is obvious that the current measured at +0.75V increases as the negative potential of the potential window increases. the increase in the current resulting in irreproducible background subtractions and consequently low sensitivity of measurements.

By using potential from +0.75 to -0.5 V, the decrease in the background currents after successive cycling, suggests a sensor surface passivation. This process could be related to the formation of inert oxides.

When the potential window is changed from +0.75 to –0.1 V, the peak at –0.75 V suggested a stabilized sensor response, but with loss of sensitivity after 3000 cycles.

For a potential applied from +0.75 to –1.2 V, the peak showed at -1.1 V proposed background subtraction problems.

3.3.2 Influence of positive potentials

Figure 3 shows the effect of using a fixed potential of 0 V and extending the positive potential range to +0.6 V and +1.0 V. The measured current is the average value for 50 cycles at 10 V s^{-1} vs SCE in 0.10 mol L^{-1} NaOH.

The use of potentials between +0.6 and 0 V showed a significant surface stabilization, but with small current, suggesting loss of sensitivity. Extending the potential window up to +1.0 V resulting in an increase in the oxidation peak intensity at this potential and consequently an increase in current is observed even after 5000 cycles, leading to an irreproducible background subtraction. Accordingly, it was necessary to establish an appropriate composition of soluble oxides at the copper surface in order to obtain a balance between sensitivity and reproducibility. Such balance is extremely dependent on the potential window used in the electrode conditioning.

Also, it is necessary to keep the electrode immersed in the NaOH solution after the treatment, submitted to a potential because it was observed that when an electrode is treated in the potential between +0.6 and 0 V and was left in solution for 2 hours without applying any potential the background current changed from 12nA to 150 nA at +0.55V. After 1000 cycles under the same conditions the current was regenerated, but a significant increase in noise was observed, probably due to changes in the oxide layer provoked by dehydration.

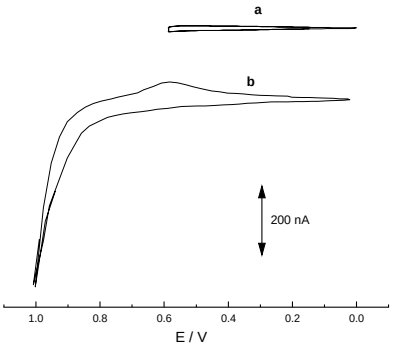


Figure 3. 0.1 mol L^{-1} NaOH background current at copper sensor at potential windows from 0.0 to +0.6 V (a) and to +1.0 V (b) respectively. The measured current is the average value for 50 cycles at 10 V s^{-1} vs SCE.

3.4. Uric acid determination at carbon fiber sensor and copper sensor

The possibilities of the determinations of UA at CFS have been reported previously at scan rates 500 Vs^{-1} and higher [32]. The UA cyclic voltammogram obtained at carbon fiber sensor in 70 mmol L^{-1} phosphate buffer pH 7.4 at 10 V s^{-1} with 100 cycles is represented in Figure 4 A.

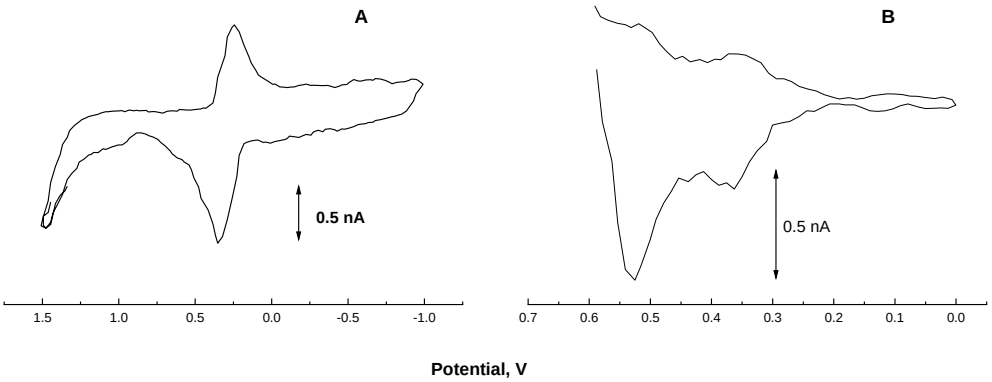
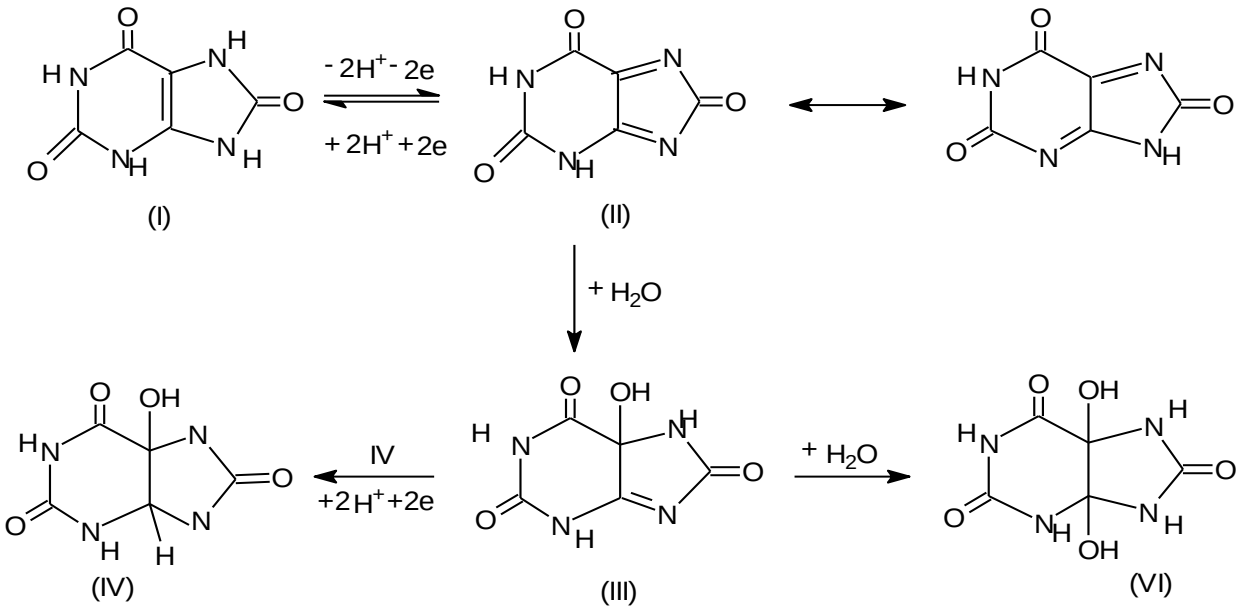


Figure 4. A: Cyclic Voltammogram of 30 mM UA in 70 m mol L^{-1} phosphate buffer pH 7.4, at CFS, scan rate is 100 V s^{-1} vs SCE after 100 cycles. **B:** Cyclic Voltammograms of 10 mM UA in 0.1 M NaOH, at CS, scan rate is 100 Vs^{-1} vs SCE after 100 cycles.

As shown in Figure 4, a well-defined peak of UA appears at +0.3 V in case of CFS (Figure 4A), while two well-defined peaks appear at +0.35 V and +0.55 V for UA in case of CS (Figure 4B). These potential values were used for determining the UA sensitivities at both CFS and CS.

The reversible couple (I/II) around +0.30 V was attributed to the reaction shown in Scheme 1[36].



Scheme (1)

Figure 4 B presents UA cyclic voltammogram at CS in 0.10 mol L^{-1} NaOH after 100 cycles at 100 V s^{-1} in the potential window from +0.85 to –0.5 V (vs. SCE). This potential window has been chosen to prevent any additional treatment of the electrode surface. The electrode has been pretreated at 10Vs^{-1} for 5000 cycles in the same potential window.

From the obtained analytical data representing the relationship between the concentration of UA (μM) and the current produced at CFS (nA) as shown in Figure 5, a sensitivity of 0.043 nA $mol^{-1}L$ is measured with a linear dynamic range from 2.00-20.0 μmol L^{-1}.

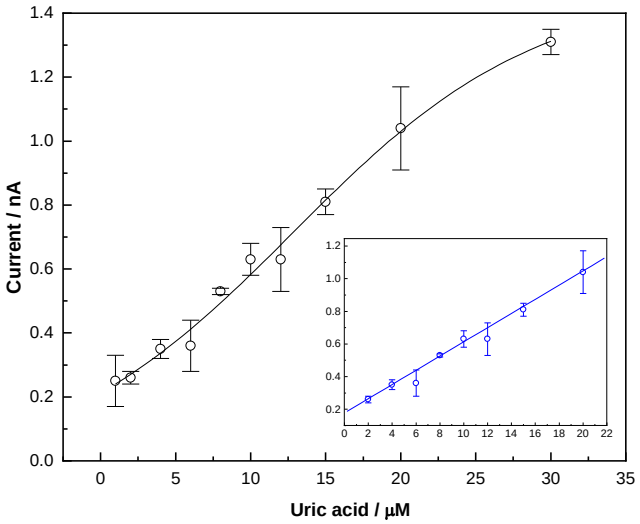


Figure 5. Analytical curve for UA at CFS, in 70 mmol L^{-1} phosphate buffer pH 7.4, at 100 V s^{-1} vs SCE, 100 cycles. Inside Figure represents the LDR.

The Figures of merit for these results are summarized in Table 1.

Table 1. Figures of merit of UA and ADO at CFS and CS

Analyte/ Sensor	**Potential (V)**	**LOD (μmolL^{-1})**	**LDR (μmoL^{-1})**	**R^2**	**Sensitivity (nA μmol^{-1} L)**
UA/CFS[a]	0.30	1	2-20	0.996(n=8)	0.043±0.002
UA/CS[b]	0.55	0.5	0.5-8	0.885(n=5)	43±6.0
	0.35	0.5	0.5-8	0.989(n=5)	33±2.0
ADO/CFS[a]	1.40	3	6-40	0.999(n=8)	0.150±0.002
	0.80	3	6-20	0.994(n=6)	0.093±0.004
ADO/CS[b]	0.53	10	15-100	0.980(n=5)	0.028±0.003

a- 100 V s^{-1}, 100 cycles, 70 mμmol L^{-1} **phosphate buffer pH 7.4**

b- 100 V s^{-1}, 100 cycles, 0.10 mol L^{-1} **NaOH**

From the obtained analytical data representing the relationship between the concentration of UA

(μM) and the current produced at CS (nA), UA currents measured at +0.35 and +0.55 V increased with concentration of UA up to 8 μ mol L^{-1}, then decreased and reached a constant value above the concentration of 20 μ mol L^{-1}. This behavior may be due to a saturation process of the active sites at the electrode surface.

Linear response was observed between 0.5 and 8 μmol L^{-1} for both potentials, but with a certain dispersion of the results. From Table 1, sensitivities of 43 nA μmol^{-1} L measured at +0.55 V and 33 nA μmol^{-1} L measured at +0.35 V were observed. These values are significantly higher than those obtained at the CFSs with the same scan rate (100 Vs^{-1}), and at 500 V s^{-1} (0.1 nA μmol^{-1} L) [37]. LOD at CS is 0.5 μmol L^{-1} which is also better than the LOD obtained at CFS (c.a. 1 μmol L^{-1}).

3.5. Adenosine determination at carbon fiber sensor and copper sensor

ADO was measured at the CFS using different scan rates (10, 100 and 500 Vs^{-1}). Adenosine exhibited two peaks as presented in Figure 6. The peak existed at more negative potential is more sensitive to the scan rate and has been attributed to adenine group oxidation according a voltammogram for adenine under the same conditions [31, 33].

At 500 V s^{-1} the peak appeared at more positive potential is less sensitive to the scan rate, in relation to both potential and current as it may be masked by this more cathodic one.

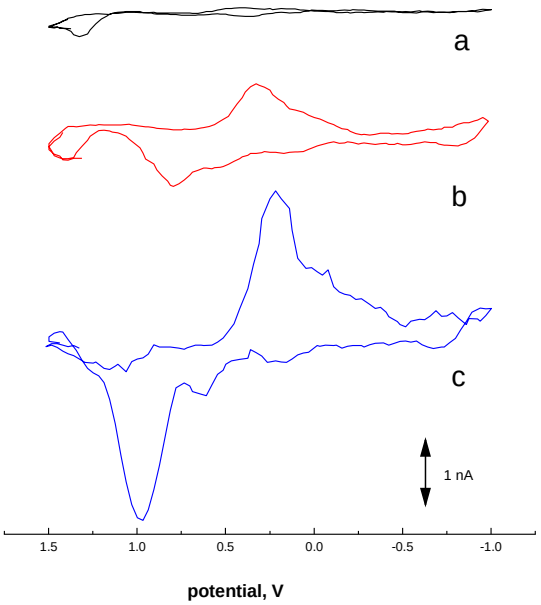


Figure 6. 10 mM adenosine in 70 mmol L^{-1} phosphate buffer pH 7.4 at CFS at different scan rates after 100 cycles: (a) 10 Vs^{-1}; (b) 100 Vs^{-1} and (c) 500 Vs^{-1} vs SCE.

Analytical data for ADO measurements obtained at 100 V s^{-1} in 70 mmol L^{-1} phosphate buffer pH 7.4 at both potentials of maximum current (+0.8 V and +1.4 V) are presented in Figure 7 and results are illustrated in Table 1. The higher sensitivity most sensitive and the larger linear dynamic range was obtained at the more positive peak. Potential (+1.4 V).

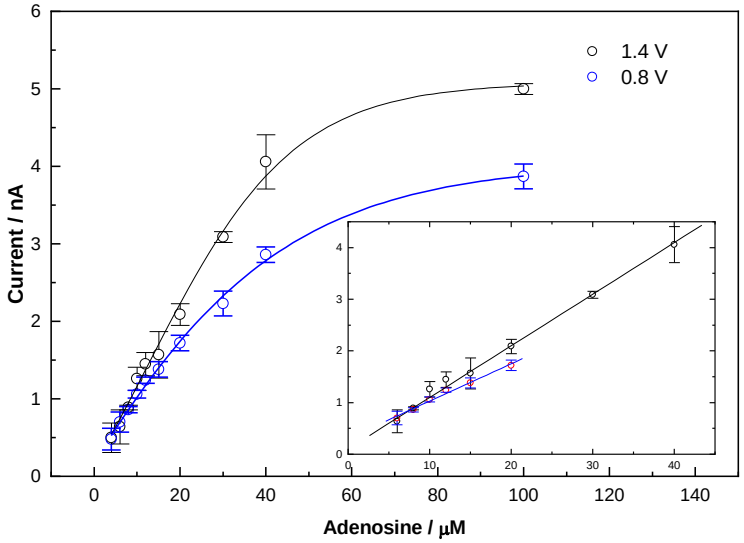


Figure 7. Adenosine calibration curves at CFS in 70 mmol L^{-1} phosphate buffer pH 7.4, measured at +1.4 and +0.8 V with a scan rate of 100 V s^{-1} vs SCE after 100 cycles. Inside Figure shows the linear dynamic range at both potential values (+0.8 V and + 1.4 V).

The cyclic voltammogram of adenosine at CS is shown in Figure 8, at 100 V s^{-1} vs SCE in 0.1mol L^{-1} NaOH after 100 cycles at a potential between +0.6 and 0.0 V. Tests for the potential window +0.85 and –0.5 V, showed problems in the background subtraction due the higher background currents at the positive limit.

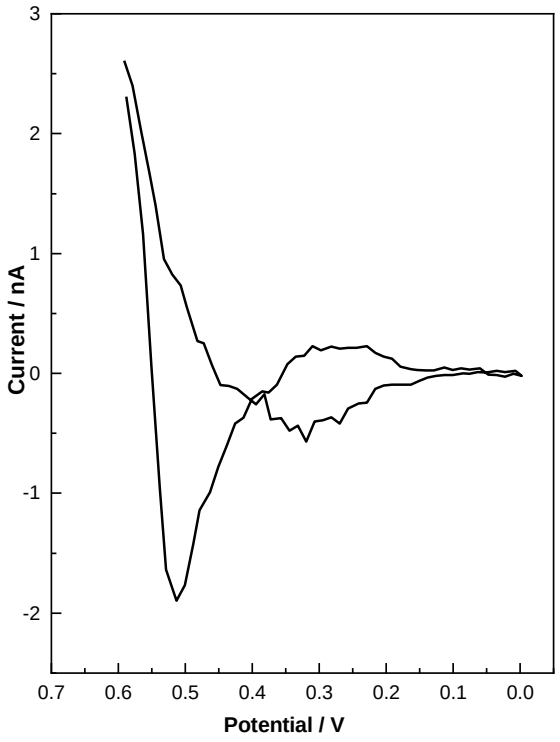


Figure 8. 100 mM adenosine at CS in 0.1mol L^{-1} NaOH, after 100 cycles at 100 V s^{-1} vs SCE.

Adenosine Currents measured at + 0.53 V at CS (Figure 9) showed a linear dynamic range above 15 μmol L^{-1} with sensitivity of 0.028 nA μmol^{-1} L and a limit of detection of 10 μmol L^{-1} (Table 1). The sensitivity is smaller than the observed at the carbon fiber sensors under similar conditions.

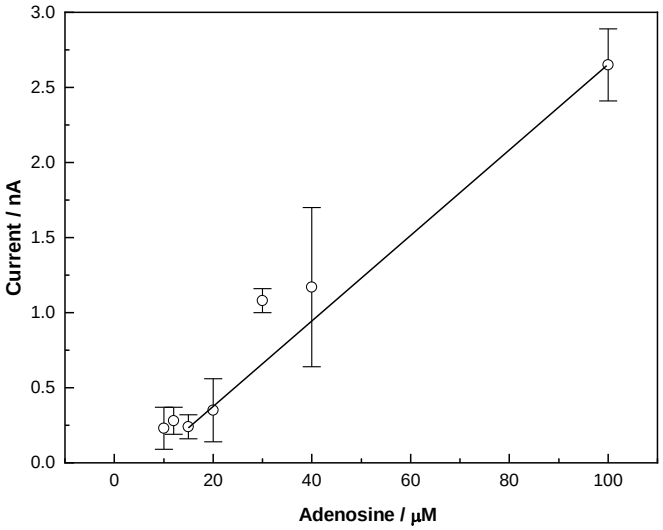


Figure 9. ADO calibration curve at CS after 100 cycles in 0.1mol L^{-1} NaOH, scan rate 100 Vs^{-1}, the potential window is between +0.6 and 0.0 V. Currents measured at + 0.53 V.

3.6. Comparison of the current UA and ADO detection sensors against prior sensors

A comparison between the proposed electrode and other modified electrodes towards detection of UA and ADO is tabulated in Table 2. The results obtained for carbon fiber sensor and copper sensor are comparable with the reported literature results.

Table 2. Summary of the LDR and LOD for UA and ADO using different electrodes

Analyte/ Electrode	LDR (μM)	LOD (μM) (S/N=3)	Reference
UA/ Glassy carbon electrode modified with nanocomposite	5-100	5	38
UA/Pyrolytic graphite electrode	10 - 500	10	39
UA/Nanocomposite modified graphite screen printed electrode	0.75-300	0.57	40
UA/Carbon paste electrode	10 - 200	5	41
UA/CFS	2 - 20	1	This work
UA/CS	0.5 - 8	0.5	This work
ADO/ Modified gold electrode	4 - 10	4	42
ADO/ Modified carbon paste electrode	4 -140	4	43
ADO/CFS	6 - 40	3	This work
ADO/CS	15-100	10	This work

4. CONCLUSIONS

Copper sensors were activated in basic medium using electrochemical activation/treatment in the potential window from –0.5 to +0.85 V. The activated sensors showed good sensitivity in direct voltammetric detection of uric acid and adenosine. The stability and reproducibility of the measurements was strongly dependent on the potential window used for treatment and detection. More stable responses were observed in the potential window from +0.6 to 0V, but with less sensitivities of uric acid and adenosine determinations.

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