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# Electrochemical Redox of $Hg^{2+}$ Mediated by Activated Carbon Modified Glassy Carbon Electrode

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The use of a glassy carbon electrode (GCE) modified by activated carbon (AC) mediates the redox of mercuric chloride ($HgCl_2$) in 0.1 M aqueous solution of potassium chloride (KCl) supporting electrolyte. During cyclic voltammetry, an oxidation and two reduction peaks of $Hg^{2+}$ were appearing at +200, +680 and +100mV respectively, versus Ag/AgCl. The redox current of $Hg^{2+}$ was enhanced by two folds at AC modified GCE and about five folds in acidic media. The oxidation peak of $Hg^{2+}$ was shifted to lower potential by approximately 5mV and for the reduction peak was shifted to 0 mV in acidic solution at AC/GCE. The sensitivity under condition of cyclic voltammetry was significantly dependent on pH, concentration of AA and temperature. Interference with $Hg^{2+}$ was observed in different metal ions, such as $Ca^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Mn^{2+}$ and $Cd^{2+}$. The current enhancement appeared and causes further increase in the reduction peaks of $Hg^{2+}$, in contrast the oxidation current decrease when increase the concentration of the interference metals. Excellent analytical recovery results were observed with using blood sample and seawater. The surface charge determined by chronocoulometry (CC) of $Hg^{2+}$ at AC/GCE in acid solution was more conductive than use of GCE. Diffusion coefficient determined by chronoamperometry (CA) for $Hg^{2+}$ at AC/GCE in presence of AA was promising results.

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**Keywords:** Activated carbon. electrocatalysis. AC/GC electrode. $HgCl_2$. cyclic Voltammetry

## 1. INTRODUCTION

Activated carbons (ACs), which are produced by either thermal activation or chemical activation, have a large surface area, a broad range of pore size distribution and extremely cheap. Activated carbons consist of small hexagonal carbon rings, which are called ‘‘graphene sheets’’. Different size orientation and stacking of these sheets can be achieved by adjusting the carbon preparation method. But, in general, an activated carbon has an amorphous structure and lacks long-range three-dimensional order [1, 2].

Cyclic voltammetric studies of the influence of surface chemistry on the electrochemical behavior of powdered AC electrodes PACE in the presence of selected heavy metal ions $Pb^{2+}$, $Hg^{2+}$, $Cd^{2+}$ in bulk solution and pre-adsorbed on carbon were carried out. Under certain circumstances, the greater current signal obtained by modified carbon electrode has been attributed to the presence of "edge effect" of microparticles of activated carbon. The adsorption capacities of the modified AC samples towards the heavy metal ions were estimated. The mechanisms of adsorption processes of metal species on AC surfaces were extensively studied and described on the basis of their electrochemical behavior [3,4].

The reduction of $Hg^{2+}$ at a GCE in nitrate, perchlorate and sulphate solutions at various pH values has been studied by rotating ring-disk voltammetry and linear sweep voltammetry. The reduction proceeds directly to metallic mercury in a single step, with the take-up of two electrons. Linear sweep voltammetry at a stationary electrode indicates that the reduction of $Hg^{2+}$ behaves reversibly at low sweep rates but irreversibly as the scan speed increases [5].

$Hg^{2+}$, $Pb^{2+}$, $Ag^{+}$ and $Cu^{2+}$ cations have been adsorbed onto a new thick-walled form of mesoporous silica having a minor amount of microporosity and then voltammetrically reduced after the fabrication of a carbon paste-mesoporous silica composite electrode which has been placed in an aqueous acidic electrolyte medium. The following well-defined voltammetric responses are observed for the systems studied: $Hg^{2+}\rightleftarrows e^{-}\text{-}Hg^{+}\rightleftarrows e^{-}\text{-}Hg$ Notable features relative to voltammograms obtained when the metal ions are reduced directly in the solution phase are the stabilization of the $Hg^{+}$ oxidation state, the linear dependence of peak heights on acid concentration in the molar concentration region and the absence of metal stripping characteristics when metal is reoxidised [6].

Mercury reduction and oxidation on ultrathin gold electrodes (Vasjari et. al. 2007) were investigated. The former by simultaneous voltammetry and surface plasmon resonance (SPR). The angle dependencies of SPR signal were analyzed quantitatively. The results indicate partially reversible formation of amalgam with optical properties in between of optical properties of mercury and gold. Up to 12% content of mercury in the gold layer is suggested [7].

Inverse voltammetric signals during $Hg^{2+}$ oxidation-reduction in the presence of potentiated water, lithium chloride, and mercury nitrate were studied by alternating-current inversion voltammetry. Potentiated substances modified oxidation-reduction processes in the electrochemical system. Potentiated solutions of $Hg^{2+}$ increased the effective concentration (activity) of mercury ions. The effect was most significant in the presence of mercury nitrate in homeopathic dilutions $C_6+C_{12}+C_{24}$. The results indicate that potentiated substances specifically modulate kinetic and thermodynamic characteristics of solutions containing the same compounds [8].

AC modified with a liquid anion exchanger (Amberlite LA2) was used for the voltammetric determination of $Hg^{2+}$. Mercury is preconcentrated, as tetrachloromercurateII, on to the surface of the modified electrode only by the ion-exchange effect of the modifier without application of potential. After exchange of the medium the accumulated amount of $Hg^{2+}$ is determined by differential pulse anodic stripping voltammetry in a blank electrolyte solution [9].

In this work, AC modified mediators are fixed on the GC electrode surface by mechanical attachment method to fabricate AC/GCE. Redox peaks of $Hg^{2+}$ have good electrochemical behavior in terms of stability and high sensitivity.

## 2. EXPERIMENTAL PART

### *2.1. Chemicals and materials*

Activated carbon from Fluka at a purity of 98% was used. Other chemicals and organic solvents used were of analar grade and used as received from the manufacturers (KCl, $HgCl_2$, $MnCl_2$, LiOH, HCl, NaOH, $NH_4Cl$, $CdCl_2$, $CuCl_2$ and $MgCl_2$). Distilled water was used for the preparation of aqueous solutions. All solutions had the dissolved oxygen removed with pure nitrogen gas for fifteen minutes prior to making the voltammetric measurements.

### *2.2. Instrumentations and apparatuses.*

Electrochemical workstations of Bioanalytical system (Inc. USA: Models BAS CV 50W) with potentiostat driven by electroanalytical measuring softwares were connected to PC computer to perform cyclic voltammetry CV, CC and CA. An Ag/AgCl (3M NaCl) and platinum wire were used as a reference and a counter electrode, respectively. The working electrode used in this study was 3mm diameter unmodified GC electrode and AC modified GCE using by mechanical method.

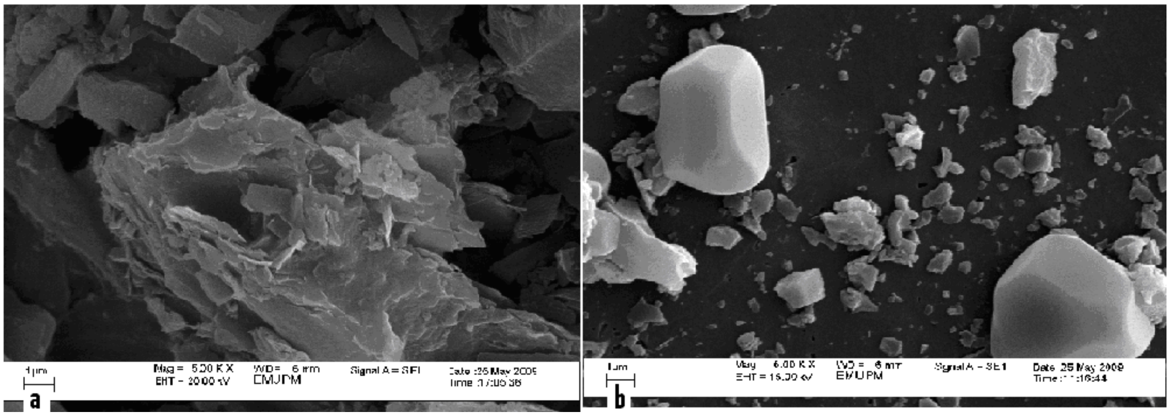


**Figure 1.** Scanning electron micrographs of AC microparticles mechanically attached to a basal plane pyrolitic graphite electrode (a) before and (b) after electroanalysis with $Hg^{2+}$.

### *2.3. Preparing for AC modified GC electrode and SEM.*

A mechanical attachment technique [10,11] used direct use of AC in powder form and and modified GCE by abrasively adhere AC microparticles onto the GC electrode surface. Scanning Electron Microscopy (SEM) was performed to look at the AC microcrystals on a graphite electrode surface. SEM image of AC attached on 5 mm diameter basal plane graphite electrode exhibits an array of microcrystals with sizes ranging from 0.2 µm diameter with the magnification of 5000 times Figure 1a.

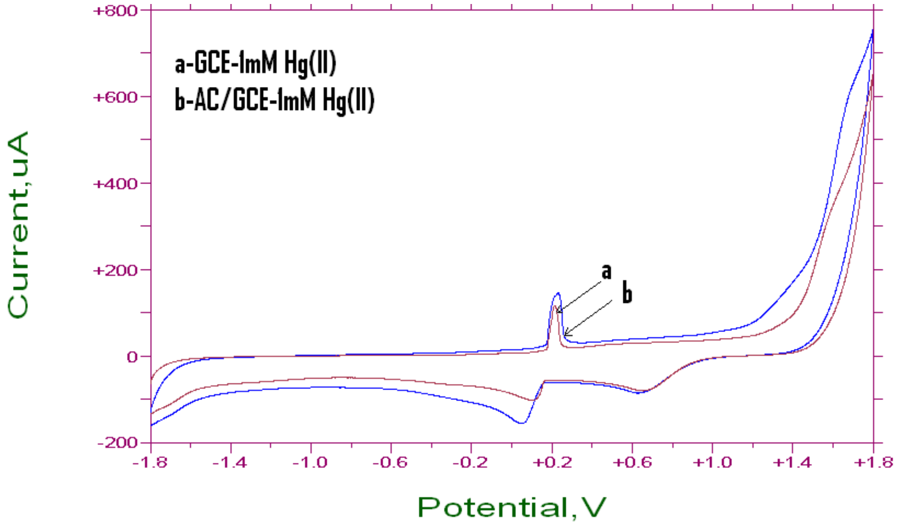
Figure 1b illustrated slightly larger in size than those obtained before electrolysis, with size of ca. 3 µm in diameter indicating the presence of a surface process of solid-solid transformation and attributing to the presence of $Hg^0$, the reduced species of $Hg^+$ and $Hg^{+2}$.

## 3. RESULTS AND DISCUSSION

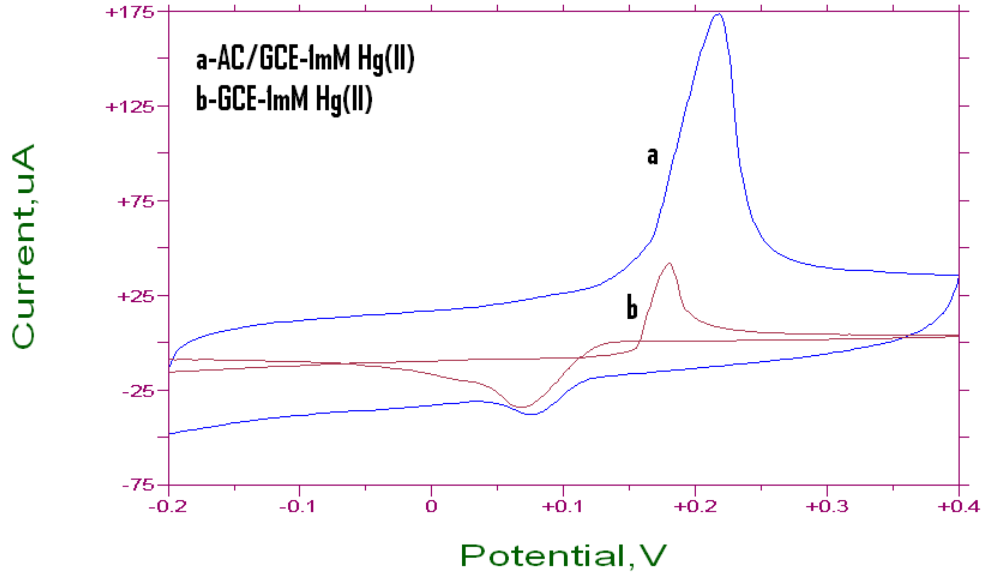
### *3.1. Enhancement studies*

### *3.1.1. Effect of different electrodes*

Figure 2a and 2b show the oxidation and reduction current peaks of $Hg^{2+}$ was considerably enhanced by 2 times with the second reduction peak shifting of about 200 mV towards origin 0mV when AC/GCE was used in comparison with GCE. Evidently degree of sensitivity response increases by modified AC/GCE. The reduction peaks of $Hg^{2+}$ appears more discernable when AC/GC electrode is used as compared with bare GC electrode. Reduction peaks become even more pronounced and enhanced by two times at the electrode surface of AC/GCE. The observation of one oxidation and two reduction peaks appears to be dependent on pH, and temperature conditions.



(A)



(B)

**Figure 2.** (A) cyclic voltammogram of 1mM $Hg^{2+}$ in 0.1M KCl as supporting electrolyte at 100 mV $s^{-1}$ using (a) AC/GCE ( b) GCE, and (B) voltammogram of oxidation-reduction peaks for 1mM $Hg^{2+}$ in 0.1M KCl, pH 3 at 100 mV $s^{-1}$ using (a) AC/GCE ( b) GCE versus Ag/AgC

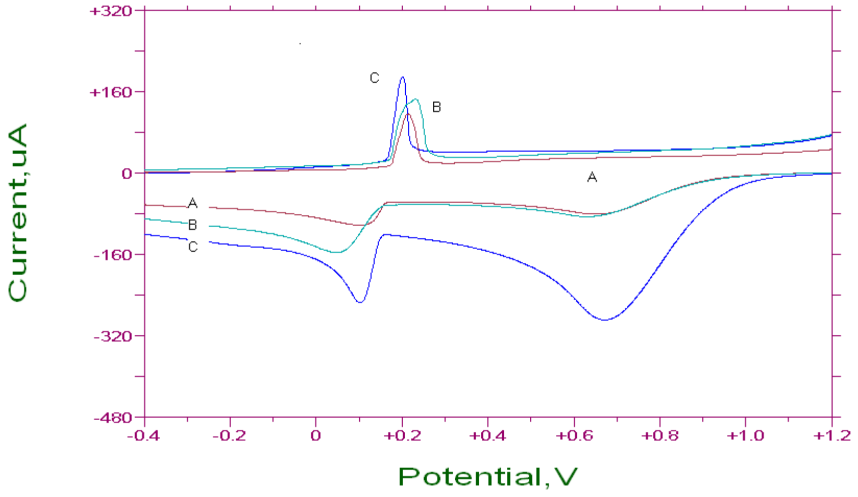


**Figure 3.** Voltammograms for effect of AA in the redox peaks of 1mM $Hg^{2+}$ (A) bare GCE, without AA (B) AC/GCE without AA and (C) AC/GCE with 1mM AA in 0.1M KCl, $100mVs^{-1}$ versus Ag/AgCl.

### *3.1.2. Effect of Ascorbic Acid*

Figure 3 shows the effect for the oxidation and reduction current peaks of $Hg^{2+}$ with and without AA on modified AC/GC electrode using cyclic voltammetry. It was observed that the oxidation peak of $Hg^{2+}$ appeared at +200mV and two others reduction peaks at +650 and +100mV. It was considerably enhanced by 3-4 times in presence of 1mM AA on AC/GCE. Moreover, the second reduction peak of $Hg^{2+}$ appears at +100mV indicate the reduction of mercury ion to mercury metal as a white color precipitated on the modified electrode as in equation 1.

$$Hg^{+} + e^{-} \longrightarrow Hg^{0} \qquad (1)$$

### *3.2. Optimization of conductive effect*

#### *3.2.1. Effect of varying Temperature*

Effect of temperature on the reduction process of $Hg^{2+}$ was studied. The current increases gradually at the temperature of 5 to 80°C. Figure 4 is plot of log (reduction current) of $Hg^{2+}$ versus reciprocal of temperature which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenious equations 2 and 3 [12].

$$\sigma = \sigma^{o} \,\mathrm{Exp}\,(- E_a/ RT) \qquad (2)$$

$$D = D^{o} \,\mathrm{Exp}\,(-E_a/ RT) \qquad (3)$$

Where: σ / D are conductivity / diffusibility and $\sigma^{o}$ /$D^{o}$ are standard conductivity / the initial diffusibility.

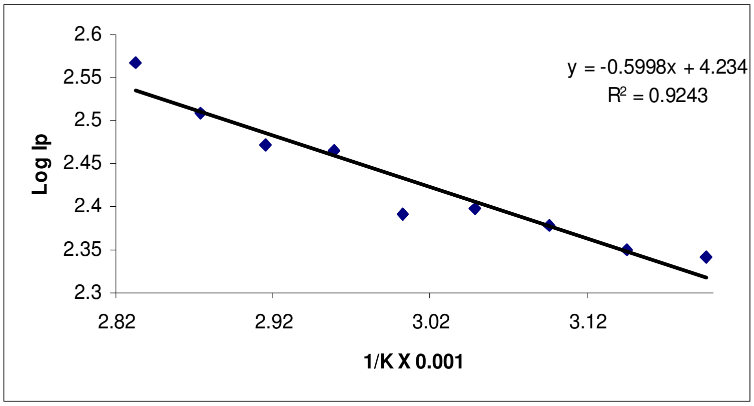


**Figure 4.** Dependence of oxidation current of $Hg^{2+}$ as a function of temperature on AC/GCE.

From slope of linear relation ship the value of activated energy of Hg (II) is Ea =11.5 KJ/mol compared with another works were around Ea=16.30-26.75 KJ/mol [13, 14]. The conductivity of AC/GCE with increasing temperature also plays a significant influence on the activation energy for diffusion of the substrate of interest, Ea. Figure 5 shows that an increase in temperature from 10 to

80°C is accompanied of a sharp increase in current causes shifting of oxidation potential towards higher value and decrease in current of reduction peaks and causes shifting to higher potential. Evidently, simultaneous application of the use of AC/GCE and increase in temperature exert a greater electrocatalyst effect. However, while use at high temperature can give an increase in temperature, in practical sense application need to be continued close to room temperature, 25°C [15].

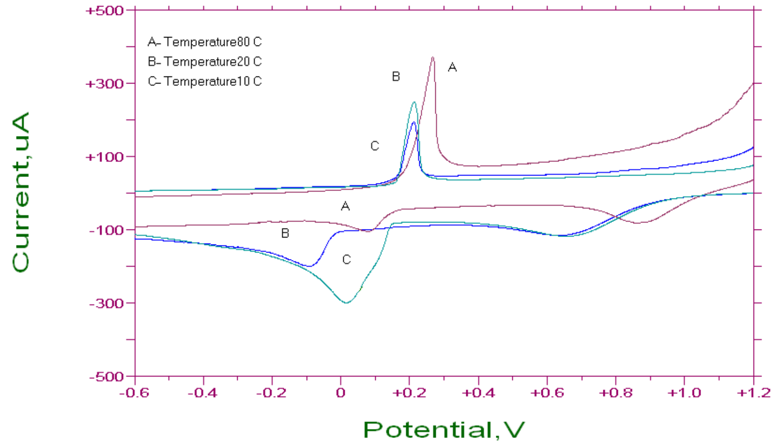


**Figure 5.** Voltammogram for the oxidation and reduction of 1mM $Hg^{2+}$ in 0.1M KCl at AC-GCE at different temperatures (A) 80°C ( B) 20°C and (C) 10°C, $100 mVs^{-1}$ vs. Ag/AgCl.

### *8.3.3.2. Effect of varying pH*

The solution pH was varied from 2 to 12 to determine its effect on the catalytic oxidation-reduction of $Hg^{2+}$ at the AC modified GC electrode. (a) Acidic solution at pH 2 to 6. It was observed that the oxidation current of $Hg^{2+}$ gradually increases linearly with lowering of pH from 6 to 2 accompanied by linear shift in oxidation potential as described by the equations, I(uA)= -23.126 pH + 287.67 with correlation coefficient of $R^2$=0.9941 and E(mV)= - 5.546 pH + 224.09 with $R^2$=09267; the two reduction peaks of $Hg^{2+}$ at +500 and -300mV were shifted to higher potential at +600 and 0mV respectively, with both the current peaks increased by about three times, while the reoxidation peak increased in about two folds and shifting towards origin potential as shows in Figure 6, the mechanism of these reduction process is explained as in the following equations (4 and 5):

$$Hg^{2+} + e^- \longrightarrow 2Hg^+ \qquad E^o = +0.600V \qquad (4)$$

$$Hg^+ + e^- \longrightarrow 2Hg^o \qquad E^o = -0.300V \qquad (5)$$

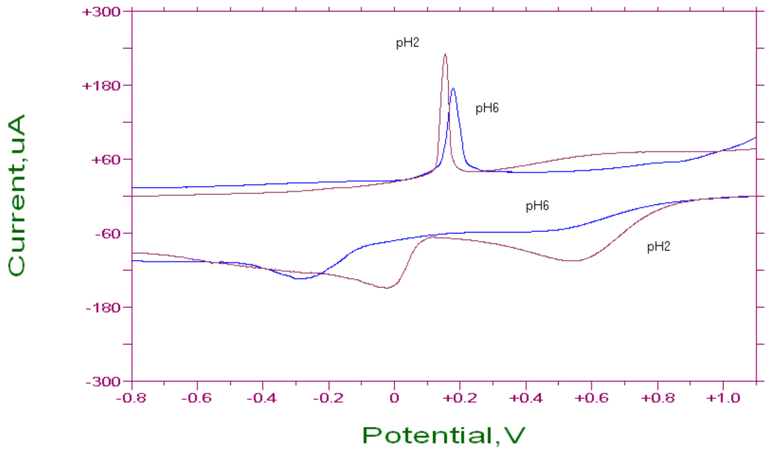


**Figure 6.** Voltammograms for effect different pH ranging from 2-6 for the redox process of 1mM $Hg^{2+}$ in 0.1M KCl vs. Ag/AgCl at AC-GCE, $100mVs^{-1}$.

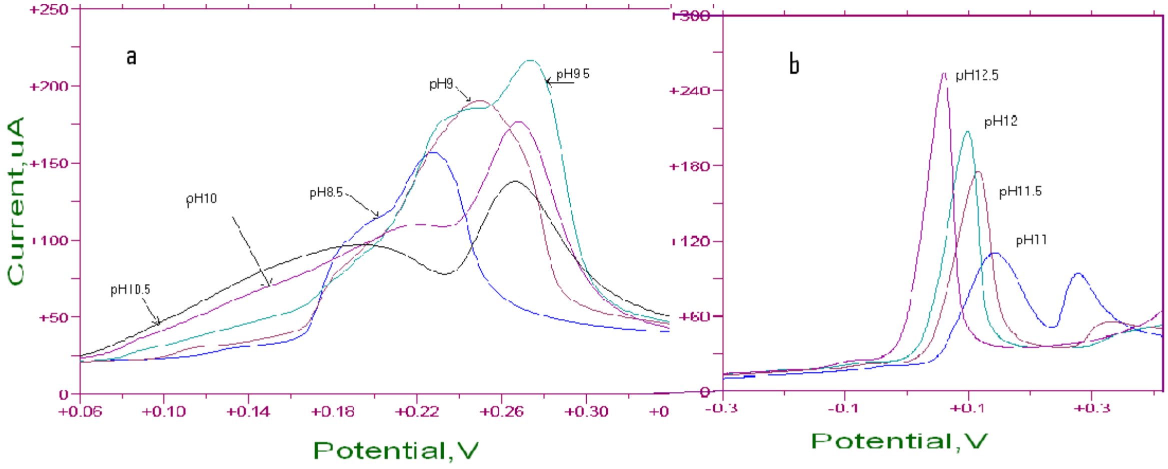


**Figure 7.** The effect pH (a) pH 8.5 – 10.5 (b) pH 11 – 12.5 on the oxidation current peaks of 1mM $Hg^{+2}$ in 0.1M KCl vs. Ag/AgCl at AC/GCE, $100mVs^{-1}$.

(b) Alkaline solution at pH from 8.5 to 12.5, a new phenomena was noted in the oxidation process associated with Hg(II)/Hg(I)/Hg(0) couples in different alkaline solutions. At pH 8.5 to 10.5 the two oxidation peaks instead of the usual one were observed, one with high current and at high potential between +230 to +280mV while the one with lower current situated between +190 to 220mV. In contrast, the properties of split oxidation peak is different at pH 11 to 12.5 as the current peaks changes in magnitude and merge to form one oxidation peak at pH 12.5, with peak potential shifted towards the origin (Figure 7a and 7b). The phenomena can be attributed to the occurrence of two processes during the oxidation of $Hg^{+}$ and $Hg^{o}$ in alkaline solution as in the following equations 6 and 7 [16].

$$\mathrm{Hg}^{+} \quad -\mathrm{e}^{-} \longrightarrow \mathrm{Hg}^{2+} \qquad (6) \qquad \text{Fast reaction}$$

$$\mathrm{Hg}^{0} \quad -2\mathrm{e}^{-} \longrightarrow \mathrm{Hg}^{2+} \qquad (7)$$

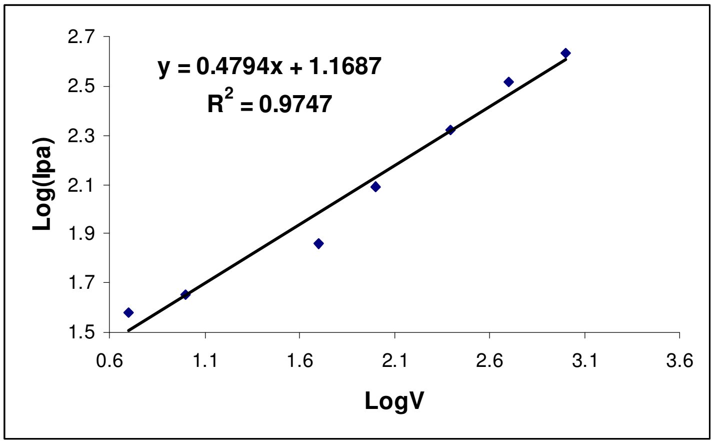


**Figure 8.** Plot of Log (Ipa) reductive current versus LogV scan rate of 1mM $HgCl_2$ in 0.1M KCl using AC/GCE versus Ag/AgCl.

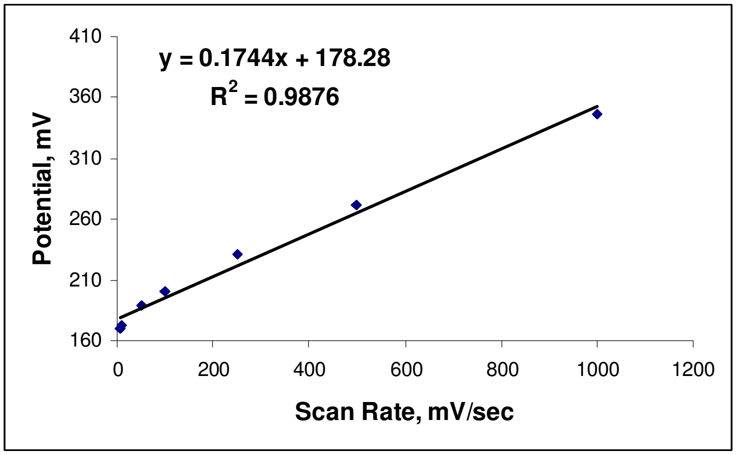


**Figure 9.** Plot of Potential versus scan rate of 1mM $HgCl_2$ in 0.1M KCl using AC/GCE versus Ag/AgCl.

### *3.3.3. Effect of varying scan rate*

A reasonably linear dependence of $Hg^{2+}$ oxidative current on scan rate is described by y=0.4794X – 1.1687, $R^2$ =0.9747. The slope of log Ip (oxidative current) versus log V (scan rate) is 0.48 which is agreed well with the theoretical slope of 0.5 for diffusion controlled process as in Figure 8 indicating the redox currents obtained is predominantly under diffusion controlled.

Figure 9 shows the relationship between oxidative potential and scan rate of $Hg^{2+}$, oxidation peak at 170mV in low scan rate (5mV/sec) is shifted linearly to 307mV at a high scan rate

(1000mV/sec). The linearity can be described by Y=0.1744X+178.28 ($R^2$=0.9876). By extrapolation the linear line towards the origin, the intercept obtained at zero current produces a zero current potential ($E^{0, 1}$) of 170mV for the oxidation of Hg(II) ion at AC/GCE.

### *8.3.4 Calibration Graph*

The calibration plot (Fig. 10) was performed at the AC/GCE in 0.1 mM – 0.6 mM $Hg^{2+}$ solutions with a good linearity of anodic current versus $Hg^{2+}$ described by Y= 90.857X+194.53, $R^2$=0.9792, and excellent sensitivity response of 90.86 mA/mM.

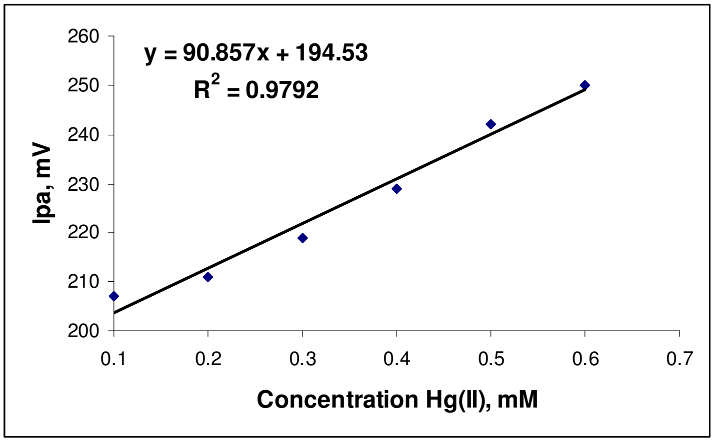


**Figure 10.** Plot of reduction current versus different concentration 0.1-1mM $HgCl_2$ in 0.1M KCl using AC/GCE versus Ag/AgCl.

### *3.5. Interference study*

### *3. 5.1. Effect of heavy metals*

Possible interference of some metals in the voltammetric determination of 1mM $Hg^{2+}$ was studied by addition of the interfering ion to a solution containing 1mM of $Mn^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Ca^{2+}$ using the optimized conditions at pH6. The results in table 1 show positive interference of all ions on the oxidation-reduction peaks of $Hg^{2+}$ by increasing the oxidation-reduction current by 2 to 3 folds and shifting to lower potential except in $Ni^{2+}$ which decreasing the both current oxidation-reduction peaks shifting to higher potential.

**Table 1.** Effect of different heavy metals (1mM) on oxidation and reduction peaks of 1mM $Hg^{2+}$ using AC/GCE.

| Heavy Metals | Ipa, uA | Epa, uA | Ipc(I), uA | Epc(I), mV | Ipc(II), uA | Epc(II),mV |
|---|---|---|---|---|---|---|
| $Hg^{2+}$ only | 150 | +200 | 80 | +700 | 155 | +50 |
| $Hg^{2+}$ +$Mn^{2+}$ | 177 | +156 | 627 | +746 | 263 | +41 |
| $Hg^{2+}$ +$Cd^{2+}$ | 257 | +216 | 298 | +647 | 347 | +57 |
| $Hg^{2+}$ +$Cu^{2+}$ | 192 | +167 | 347 | +636 | 218 | +35 |
| $Hg^{2+}$ +$Cd^{2+}$ | 252 | +193 | 317 | +669 | 332 | +57 |
| $Hg^{2+}$ +$Ni^{2+}$ | 97 | +210 | 74 | +587 | 120 | +134 |

The interfering effects of $Mn^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ on the reduction of $Hg^{2+}$ in 1:1 ratio were investigated using the modified electrode AC/GC during CV. In general, all metal ions except $Ni^{2+}$ under studied pose positive interference as the redox current of Hg(II)/Hg(I)/Hg(0) couples increases further in the presence of these interfering metal ions (Table 1).

### *3.6. Application study*

#### 3.6.1. *Recovery rate of $Hg^{2+}$ in blood*

Calibration of $Hg^{2+}$ in mouse blood was carried out by using blood sample as supporting electrolyte and a known amount of $Hg^{2+}$ was spiked into the blood (Figure 11).

The redox of $Hg^{2+}$ in blood sample as a supporting electrolyte gives a calibration plot of good linearity, Y=19.296X + 34.536 and the correlation coefficient $R^2$=0.9949 with high sensitivity response of 19.20 μAmM$^{-1}$ and good detection limit of $Hg^{2+}$ in blood.

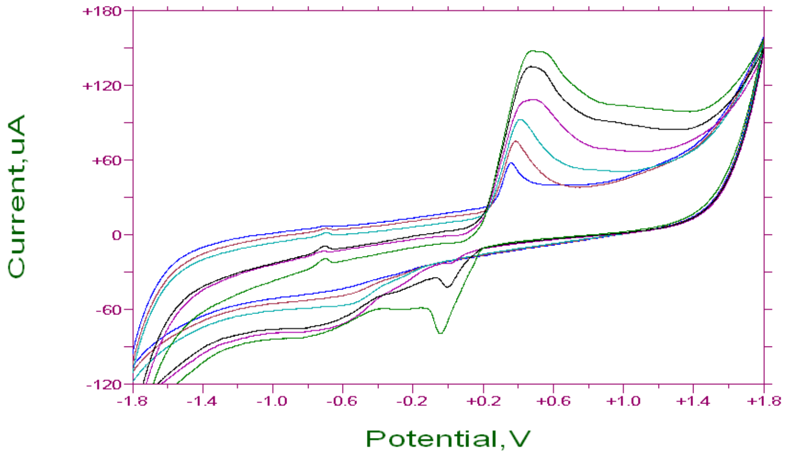


**Figure 11.** Cyclic voltammograms for the effect of blood sample on redox process of different concentration of 0.5-6 mM $Hg^{2+}$ versus Ag/AgCl on AC/GCE; 100 mVs$^{-1}$.

The recovery of 102.75 ± 1.9% was obtained after the addition of 0.9 mM $Hg^{2+}$ in to blood sample as in table 2 while recovery of 95.78 ± 4.9% was obtained after the addition of 4.5 mM $Hg^{2+}$ in to blood sample as in table 3.

**Table 2.** Recovery rate of 0.9mM $Hg^{2+}$ added in to blood samples at AC modified GCE.

| Number of sample Standard | Concentration of $Hg^{2+}$ (mM) | Recovery Rate (%) | Mean Recovery % | Relative Deviation % |
|---|---|---|---|---|
| 1 | 0.97 | 97.0 | | |
| 2 | 0.85 | 85 | | |
| 3 | 0.95 | 106 | | |
| 4 | 1.00 | 111 | 102.75 | 1.9 |

**Table 3.** Recovery rates of 4.5mM $Hg^{2+}$ added in to blood samples at AC modified GCE.

| Number of sample Standard | concentration of $Hg^{2+}$ (mM) | Recovery Rate (%) | Mean Recovery % | Relative Deviation % |
|---|---|---|---|---|
| 1 | 4.5 | 100 | | |
| 2 | 4.0 | 88.9 | | |
| 3 | 4.25 | 94 | | |
| 4 | 4.6 | 101 | | |
| 5 | 4.3 | 95 | 95.78 | 4.9 |

### *3.6.2. Recovery rate of $Hg^{2+}$ in seawater*

Recovery experiments of Hg2+ in seawater were evaluated using direct calibration of Y=37.071X + 214.71, $R^2$=0.9876. The recovery of 95.2± 4.15% was obtained after the addition of 0.5 mM $Hg^{2+}$ in to seawater sample as in table 4.

**Table 4**. Recovery rate of 0.5mM $Hg^{2+}$ added in to seawater sample at AC modified GCE

| Number of sample | concentration of $Hg^{2+}$ | Recovery | Mean | Relative |
|---|---|---|---|---|
| Standard | | | | |
| | (mM) | Rate (%) | Recovery % | Deviation |
| % | | | | |
| 1 | 0.5 | 100 | | |
| 2 | 0.48 | 96 | | |
| 3 | 0.49 | 98 | | |
| 4 | 0.46 | 92 | | |
| 5 | 0.45 | 90 | 95.2 | 4.15 |

### *3.7. Chronoamperomogram (CA) and Chronocoulomogram (CC) studing*

Figure 12 shows the monotonous rising and decaying current transient in accordance to the theoretical expectation of the Cottrell equation [17, 18]. Based on the diffusion process to a planar electrode. Diffusion coefficient (D) of 1.756X$10^{-6}$ $cm^2sec^{-1}$ was determined for $Hg^{2+}$ ion in 0.1 M KCl using AC/GC as a working electrode. It was found that the AC/GCE has a total charge transferred of 46.3μC $m^{-2}$ in AC in the presence of ascorbic acid (AA), while the low charge transferred of 4.0 μ$Cm^{-2}$ in $Hg^{2+}$with out AA. This shows that AC/GCE with attendance of AA is more reducible than its absence as in Figure 13.

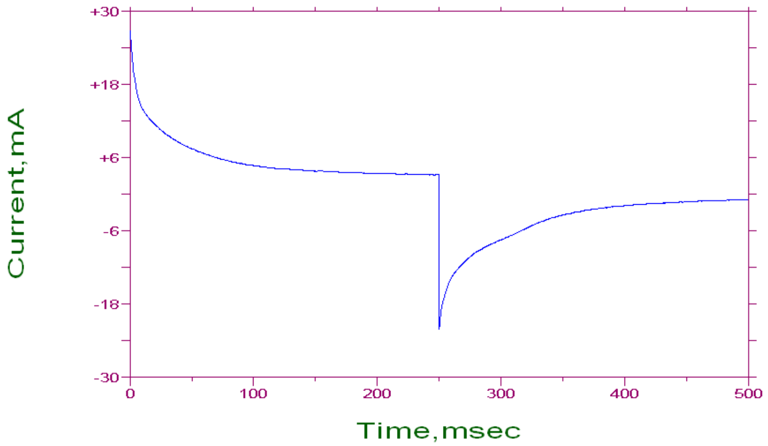


**Figure 12.** CA or Cottrell plot obtained for the redox of 1 mM $Hg^{2+}$ in 1 mM AA in 0.1 M KCl electrolyte at AC/GCE. Potential was scanned in a negative direction from -1800 to +1800 mV with 250 msec. pulse width.

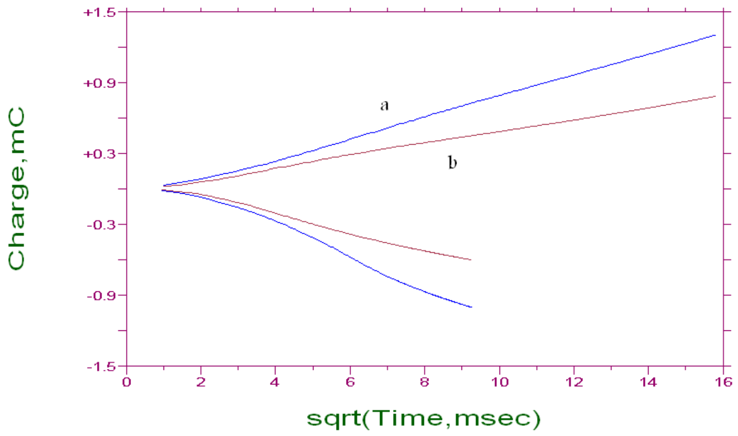


**Figure 13.** CC or Anson plot of charge verses $t^{1/2}$ for redox of 1 mM $Hg^{2+}$ in (a) 1 mM AA at AC/GCE and (b) without AA at bare GCE in 0.1 M KCl vs. Ag/AgCl.

## 4. CONCLUSIONS

AC modified GCE has been successfully fabricated by mechanical attachment method, which is shown to be able to mediate effectively in redox of $Hg^{2+}$ with significant current enhancement. The observed current enhancement can be attributed to the presence of a larger surface area and associated "edge effect" of an array of AC microparticles. The redox peaks of $Hg^{2+}$ was dependent on the concentration AA, pH and temperature. The interference studies with heavy metals $Mn^{2+}$, $Ni^{2+}$, $Cu^{2+}$,$Ca^{2+}$ and $Cd^{2+}$ were promising with the redox current peaks of $Hg^{2+}$. Excellent recovery rates were obtained from the analysis of $Hg^{2+}$ in seawater and mouse blood sample. The magnitude of the surface charge determined by Anson's plot shows that AC/GCE was more conductive (large current transferred) compared with GCE. Diffusion coefficient D has been determined for the redox of $Hg^{2+}$ under the voltammetric conditions mentioned above.

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