INTRODUCTION

Activated carbons (ACs) are high surface area, high porosity carbons made of small hexagonal rings organized into graphene sheets. These sheets can be produced by various processing methods that result in varying pore size distributions and orientations. Activated carbons lack long range order and can therefore be viewed as a mixture of microdomains of ordered graphene sheets. The specific double layer capacitance can be seen as the sum of each microdomain capacitance.

Voltammetric behaviors of Cd(II) ion in the presence of a ligand with glutathione were studied using cyclic voltammetry (CV). The coordination chemistry of reduced glutathione is of great importance as it acts as excellent model system.
for the binding of metal ions. It was observed that an addition of glutathione as ligand to solution containing Cd(II) with sulphate as supporting electrolyte caused an increase in the reduction current of Cd(II) by several factors and also with a slight cathodic shift in the reduction peak potential of Cd(II). Further assessment of the chemical and physical conditions that may favor optimum current enhancement was done by studying the effect of varying pH, supporting electrolyte concentration of ligand and metal ion, interfering ions and scan rate5.

The influence of variables such as the accumulation time, pH solution and apatite loading was tested by square wave voltammetry. The electrochemical response obtained by square wave voltammetry was found to be analytically suitable to develop a method for the determination of cadmium at low concentration levels. The detection limit for cadmium determination was 4.0×10^-9 mol L^-1. The proposed sensor presented good repeatability, evaluated in terms of relative standard deviation (RSD=3.8%) for n = 5 and was applied for cadmium determination in water samples. The average recovery for these samples was 104%6.

A novel method for the simultaneous determination of cadmium(II) and copper(II) during the adsorption process onto Pseudomonas aeruginosa was developed. The concentration of the free metal ions was successfully detected by square wave anodic stripping voltammetry on the mercaptoethane sulfonate modified gold electrode. As the determination of Cd²⁺ and Cu²⁺ was in real time and without pretreatment, the kinetic characteristics of the adsorption process were studied and all the corresponding regression parameters were obtained by fitting the electrochemical experimental data to the pseudo-second-order kinetic model. The proposed electrode system provides excellent platform for the simultaneous determination of trace metals in complex biosorption process7.

Most metals, with the exception of copper, (e.g. Pb, Cd, Tl, In), form binary alloys with bismuth, and hence, display well-defined and undistorted peaks. Such sharp peaks result in high resolution of neighboring signals and permit convenient multi-elemental measurements down to the low ng/l level8. Bismuth film, that was in situ deposited onto glassy carbon electrode, was used to detect zinc content of milk vetch. Variables affecting the response have been evaluated and optimized. Experimental results showed a high response, with a good linearity (between 0.5×10^-6 mol L^-1 and 3×10^-6 mol L^-1) a good precision (R.S.D. = 3.58%) and a low detection limit (9.6×10^-9 mol L^-1 with a 120 s anodic). The anodic stripping performance makes the bismuth film electrode very desirable for measurements of trace nutritive element zinc in milk vetch and should impart possible restrictions on the use of mercury electrode9.

Traces of lead, cadmium, zinc and manganese in copper and copper compounds are determined, in some cases simultaneously, by anodic stripping voltammetry on a hanging mercury drop electrode. The determination limits are about 10^-9 M for lead, 5×10^-10 M for cadmium, 10^-9 M for zinc and 10^-8 M for manganese10.

An automatic system for the in situ determination of dissolved Cu, Zn, Pb and Cd in fresh waters, composed of a filtration unit, a separation and enrichment unit and electrochemical unit for differential-pulse anodic stripping voltammetry, was investigated. The filtration and enrichment units were designed to establish the most effective experimental conditions for the measurement of metal concentration at environmental levels11.

A bismuth-modified carbon nanotube electrode (Bi-CNT electrode) was employed for the determination of trace lead, cadmium and zinc. The peak current response increased linearly with the metal concentration in a range of 2–100 µg/L. The limit of detection was 1.3 µg/L for lead, 0.7 µg/L for cadmium and 12 µg/L for zinc (S/N = 3). The Bi-CNT electrode was successfully applicable to analysis of trace metals in real environments12.

CdS nanoparticles composited with carbon nanotubes not only enhances their electrochemiluminescent intensity but also decreases their ECL starting potential; such a property would promote the application of quantum dots in fabricating sensors for chemical and biochemical analysis13.
The sensitivity and detection limit of the modified electrodes were quantitatively estimated the trace of Cd²⁺ by cyclic voltammetry with different result₁⁴,₁⁵.

**MATERIAL AND METHODS**

**Materials**

AC was obtained from Aldrich, used in powder form. Other chemicals were analytical grade and prepared as aqueous solutions using double distilled water. 1-4 mM of CdCl₂ and AA solutions were prepared before experiment. 1 M concentration of HCl, NaOH solutions were used in dilute pH in acidic and basic respectively.

**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.

**Preparation for AC modified GC electrode**

A mechanical attachment technique₁⁶ used direct use of AC in powder form and modified GCE by doping AC. 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 – 8nm diameter with the magnification of 3000 times Figure 1.

**RESULTS AND DISCUSSION**

**Enhancement studies**

**Effect of different electrodes**

Figure 1a and 1b show the oxidation and reduction current peaks of Cd²⁺ was considerably enhanced by 2 times with about 200mV the second reduction peak shifting 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 Cd²⁺ 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.

**Effect of Ascorbic Acid**

Figure 1a and b show the effect for the oxidation and reduction current peaks of Cd²⁺ with and without AA on modified AC/GCE electrode using cyclic voltammetry. It was observed that the two oxidation peaks of Cd²⁺ appeared at +0.4 and -0.6V and two others reduction peaks at +0.6 and -0.8V. It was considerably enhanced by 3-4 times in present of 1mM AA on AC/GCE. Moreover, the second reduction peak of Cd²⁺ appears at -0.8V indicate the reduction of mercury ion to mercury metal as a white color precipitated on the modified electrode as in the following equations:

\[
\begin{align*}
\text{Cd}^{2+} + e^- & \rightarrow \text{Cd}^+ \quad \text{reduction} \quad (+0.6V) \quad (1) \\
\text{Cd}^+ + e^- & \rightarrow \text{Cd}^0 \quad \text{reduction} \quad (-0.8V) \quad (2) \\
\text{Cd}^0 & \rightarrow \text{Cd}^{2+} + 2e^- \quad \text{oxidation} \quad (-0.6V) \quad (3) \\
\text{Cd}^+ & \rightarrow \text{Cd}^{2+} + e^- \quad \text{oxidation} \quad (+0.4V) \quad (4)
\end{align*}
\]

**Optimization of conductive effect**

**Effect of varying Temperature**

Effect of temperature on the reduction process of Cd²⁺ was studied. The current increases gradually at the temperature of 5 to 70°C. Figure 2 is plot of log (reduction current) of Cd²⁺ versus reciprocal of temperature which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenious equations₁⁷ 2 and 3.

\[
\begin{align*}
\sigma &= \sigma^0 \exp (-E_a / RT) \quad (2) \\
D &= D^0 \exp (-E_a / RT) \quad (3)
\end{align*}
\]

Where \(\sigma/D\) are conductivity/diffusibility and \(\sigma^0/D^0\) are standard conductivity/the initial diffusibility. From slope of linear relationship the value of \(E_a =4.8 \text{ KJ/mol} \). The conductivity of AC with increase temperatures also plays a significant influence on the activation energy for diffusion of the substrate of interest, \(E_a\).
Fig. 1: Cyclic voltammogram of (a) 4mM Cd$^{2+}$ on AC/GCE with 4mM AA (b) 4mM Cd$^{2+}$ on AC/GCE without AA and (c) 4mM Cd$^{2+}$ on GCE with 4mM AA in 0.1M KCl versus Ag/AgCl

Fig. 2: Dependence of reduction current of 4mM Cd$^{2+}$ with 4mM AA as a function of temperature on AC-GCE versus Ag/AgCl in 0.1M KCl

$$y = -0.5766x + 4.2734$$
$$R^2 = 0.9054$$

Fig. 3: Cyclic Voltammogram for effect different scan rate (5-1000 mV/sec.) of 4mM Cd$^{2+}$ with 4mM AA in 0.1M KCl using AC/GCE
Fig. 4: Plot of Log Ipc reductive current versus Log V scan rate (5-1000mV/sec.) of 4mM CdCl\textsubscript{2} with 4mM AA in 0.1M KCl as a supporting electrolyte using AC/GCE versus Ag/AgCl

\[ y = 0.515x + 1.3829 \]
\[ R^2 = 0.9899 \]

Fig. 5: Plot of oxidation current versus different concentration 0.008-0.1mM CdCl\textsubscript{2} with 4mM AA in 0.1M KCl using AC/GCE versus Ag/AgCl

\[ y = 2779.9x - 5.5598 \]
\[ R^2 = 0.9567 \]

Fig. 6: Cyclic Voltammogram for interference of Cd\textsuperscript{2+} with Hg\textsuperscript{2+} using AC/GCE (a)4mM Cd(II) with 4mM AA and 4mM Hg(II) (b)4mM Cd(II) with 4mM AA
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.

Effect of varying pH

The solution pH was varied from 2 to 10 to determine its effect on the catalytic oxidation-reduction of Cd²⁺ at the AC modified GC electrode. (a) acidic solution at pH from 2 to 6 it was observed that the oxidation current of Cd²⁺ gradually and linearly increases with lowering of pH from 6 to 2 accompanied by linear shift in oxidation potential as a linear equation of I(uA) = -144.52 pH + 577.68 with correlation coefficient of R²=0.9681 and E(mV)= - 5.546 pH + 224.09 with correlation coefficient of R²=0.9267, the two reduction peaks of Cd²⁺ at +0.6 and -0.8V which increased the current for both reduction peaks about three times and the oxidation peak increased in about five folds and shifting to origin potential, the mechanism of these oxidation and reduction process is explain as in the equations 1-4.

(b) alkaline solution at pH from 7 to 10, a new phenomena with attendance of AC on GCE in oxidation current peak of Cd²⁺ which notes in different alkaline solution, at pH 7 to 10 the oxidation peak was split in to two high current peaks between +0.2 to 0V. It seems that the oxidation current of Cd²⁺ gradually and linearly increases with increasing of pH from 7 to 10 accompanied by linear shift in oxidation potential as a linear equation of I(uA) = 27.634 pH + 44.623 with correlation coefficient of R²=0.9375.

Effect of varying scan rate

A reasonably linear dependence of Cd²⁺ oxidative current on scan rate is described by y=0.515X – 1.3829, R² =0.9899. The slope of graph Log Ip (oxidative current) versus Log V (scan rate) is 0.5 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process as in Figure 3 indicating presence of a complex.

Fig. 4 shows the relationship between oxidative potential and scan rate of Cd²⁺, oxidation peak at 168mV in low scan rate (5mV/sec) is increased to 1000mV in high scan rate (1000mV/sec).

Calibration Graph

Fig. 5 shows the calibration curve of Cd²⁺ in different concentration (0.008-0.1 mM) in 0.1M KCl with 4mM AA. Linearity of the plot of up to a Cd²⁺ concentration of 8x10⁻³ mM with a current sensitivity of close to 5.56 mV/mM was observed with curvature being detected at a concentration of greater than 8x10⁻³ mM.

The calibration plots were performed at the AC/GCE in the Cd²⁺ with a good linearity of oxidation current versus Cd²⁺ by Y = 2779.9X+5.5598 and the correlation coefficient was R²=0.9567. The oxidation current remarkably, enhanced at the AC surface on GCE which may be attributed to the larger effective surface area and butter electrochemical reacting ability resulting from Cd²⁺.

Interference study

Effect of heavy metals

Possible interference of some heavy metals in the absorptive cyclic voltammetric determination of Cd²⁺ was studied by addition of the interfering ions to a solution containing Cd²⁺ and AA with different concentration of Hg²⁺, Mn²⁺ and Cu²⁺ using the modified electrode AC/GC.

Hg²⁺

As a result, Hg²⁺ has been interference with redox peaks of Cd²⁺, which is shifted to higher potential when mixed in to ratio 1:1 in presence AA and enhancement the current about three folds as shown in Fig. 6.

Mn²⁺

Fig. 7 shows the effect of Mn(II) ions on Cd(II) ions in presence of AA in equal ratio of three ions, it seems that the redox peaks of Cd(II) ions are enhanced in current about five times in oxidation and two times of reduction peaks also, the reduction peak of Mn(II) ions is shifted to lower potential. The interference between Cd(II) and Mn(II) are observed in increasing for both peaks.

Cu²⁺

Fig. 8 shows the effect of Cu(II) ions on the redox peaks of Cd(II) ions which increased the current of redox current about two to four times.
Fig. 7: Cyclic Voltammogram for interference of Cd²⁺ with Mn²⁺ using AC/GCE
(a) 4mM Cd(II) with 4mM AA and 4mM Mn(II) (b) 4mM Cd(II) with 4mM AA

Fig. 8: Cyclic Voltammogram for interference of Cd²⁺ with Cu²⁺ using AC/GCE
(a) 4mM Cd(II) with 4mM AA and 4mM Cu(II) (b) 4mM Cd(II) with 4mM AA

Fig. 9: cyclic voltammogram for the redox peaks of Cd²⁺ (0.1 - 5mM) in Blood sample at scanning rate 100 mv s⁻¹ using AC/GCE
Effect of Blood Sample

The study of effect blood (chose mouse blood) on the Cd$^{2+}$ was carried out by using blood sample as supporting electrolyte and a known amount of Cd$^{2+}$ was spiked in to the blood.

The effect of blood on the oxidation-reduction current peaks of Cd$^{2+}$ is clear as shown in Figure 9 when the oxidation peak of Cd$^{2+}$ appeared with blood samples at -0.8V and reduction current peak appears inconspicuous in the absence of blood providing alternative analytical peak of Cd$^{2+}$, the reduction peak appears at -1.6V, the effect of absence blood at different concentration of Cd$^{2+}$ causes enhancement the current and potential for redox process, blood uses as a catalysis for the redox Cd$^{2+}$ through the modified electrode AC/GCE.

The voltammetric analysis of thus modified glassy electrodes reveals possibilities for driving redox reactions across the AC in the blood. The results suggest a transfer of electrons across the AC mediated through the transitions of Cd$^{2+}$ by presence of blood. The redox of Cd$^{2+}$ in blood sample as a supporting electrolyte gives a good linearity with high sensitivity and good detection limit of Hg$^{2+}$ in blood, $Y=19.296X + 34.536$ and the correlation coefficient $R^2=0.9949$.

Chronoamperomogram CA and Chronocoulomogram CC studying

The monotonous rising and decaying current transient in accordance to the theoretical expectation of the Cottrell equation [19, 20] based on the diffusion process to a planar electrode. Diffusion coefficient ($D$) of Cd$^{2+}$ ion in 0.1 M KCl using AC/GC as a working electrode is $D = 1.501 \times 10^{-6}$ cm$^2$sec$^{-1}$. It was found that the AC/GCE has a total charge transferred of 45.0μC m$^{-2}$ in AC in present AA, while the low charge transferred of 12.0 μCm$^{-2}$ in Hg$^{2+}$ with out AA. This shows that AC/GCE with attendance of AA is more reducible than its absence.

CONCLUSIONS

AC modified GCE has been successfully fabricated by mechanical method, which is shown to be able mediated effectively in redox of Cd$^{2+}$ with significant current enhancement. The redox peaks of Cd$^{2+}$ was dependent on the concentration AA, pH and temperature. The interference studies with heavy metals Mn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$ were promising with the redox current peaks of Cd$^{2+}$. Also, the blood sample is affected on the redox current peaks of Cd$^{2+}$ in current and potential. 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 Cd$^{2+}$ under the voltammetric condition mentioned above.

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