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Electrochemical Characteristic of Biotinyl Somatostatin-14/Nafion Modified Gold Electrode in Development of Sensor for Determination of Hg(II)

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Electrochemical sensor for Hg(II) has been developed using Biotinyl Somatostatin-14 peptide modified gold electrode utilizing nafion as the immobilizing agent. Experimental conditions such as pH, supporting electrolyte and scan rate were optimized. Detection of mercury using Biotinyl Somatostatin-14 peptide/Nafion has been observed to be optimum under acidic conditions. Good relative standard deviation of 3.7% has been obtained indicating reliability of the detection system. A linear calibration plot in the range of 40-170 μgL^{-1} was obtained with sensitivity value of 1×10^{-10} $A\mu M^{-1}$. Limit of detection (LOD) obtained is 0.4 μgL^{-1} which is below the WHO guidelines for drinking water. The scan rate study showed that the process is a complex surface process, mostly involving an adsorption process. This developed method was applied for determination of Hg(II) in actual waste water samples and a good agreement was obtained between the proposed method and ICP-MS based on the analysis of the waste water samples.

Keywords: Hg(II) detection; Modified electrode; Electrochemical Sensor

1. INTRODUCTION

Mercury can accumulate in food chain through gaseous sources, such as coal burning, and from human activities through waste water [1]. [2]. The toxicity of metal ions makes the monitoring of metals in the environment, vital. Current methods of metal ion monitoring involve classical elemental analysis technique which are reliable but suffer major weaknesses. These techniques such as atomic absorption spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectroscopy (ICPMS) 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 ions which is simple, reliable and robust.

Many studies have been utilized for the detection of Hg(II) ions by using anodic stripping voltammetry using modified carbon electrodes [3, 4, 5, 6], screen printed electrodes [7] or metal electrodes such as platinum [8] and gold [9, 10, 11]. There are some reports based on amine, thiol or amine/thiol modified silica gel functionalized carbon electrodes as chemical modifier for electrochemical determination of mercury [12, 13], but most of these methods require functionalization with a sophisticated ligand.

In nature, metal binding is achieved with a high degree of selectivity using peptide. The sequence of amino acids in peptide within the binding site defined the selectivity of the binding sites of metals in proteins. 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 [14]. Electrodes modified with recognition elements of biological origin have advantages over other approaches for detecting metal ions. Amino acid and peptides are known as the simplest biological recognition element for metal binding. Thus the usage of these compounds in metal ion detection is important.

Biotinyl Somatostatin-14 (molecular structure shown in Figure 1) contains two thiol groups which connected to each other through the sulphur ends and serves as a "staple" holding the shape in a more steady position. It also make the immobilization process easier because of it's high affinity towards Hg(II) and the gold electrode [15].

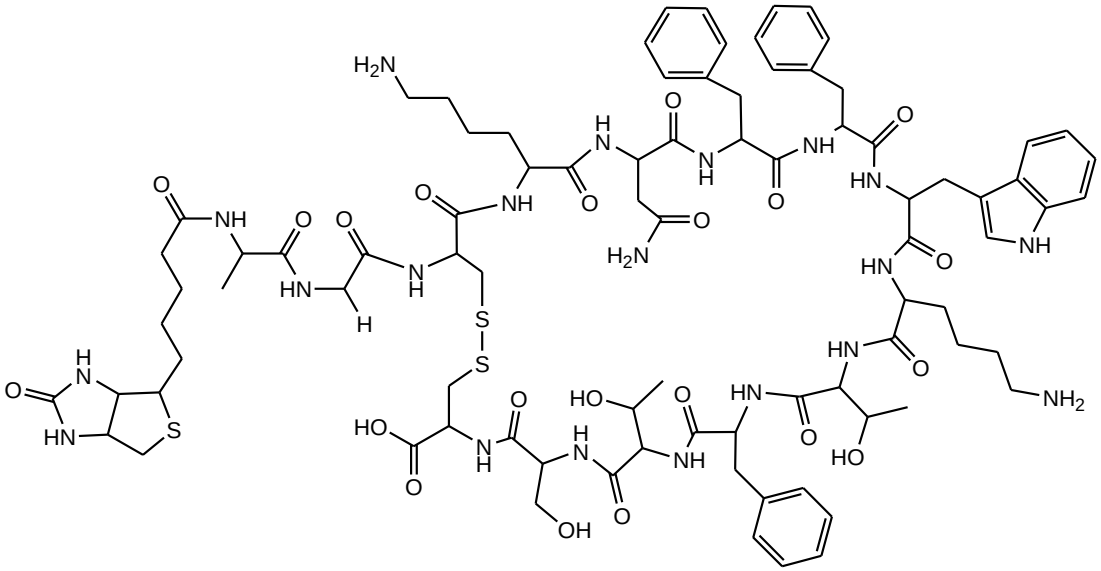

Figure 1. Molecular structure of Biotinyl Somatostatin-14

By using solvent casting method, the biotinylated peptide was adsorbed onto the gold substrate via the cysteine group, which contains a thiol moiety that bind to the gold. The electrode was then coated with Nafion as protective films to decrease the adsorption of non specific substances. Natural environmental samples usually contain complex mixtures of compunds. The effect of surfactant

molecules in decreasing the response of an electrochemical sensor can be diminished by using a protective film [16].

Biotinyl Somatostatin-14 can be used to detect mercury due to the affinity of the mercury with the functional groups present in this peptide. It contain an abundance of oxygen-containing functional groups such as carboxylic structures and amine group, which could possibly form peptide-metal complexes with high stability through ionic, hydrogen and coordinate covalent bonding.

The present study reports the characterization of Biotinyl Somatostatin-14/Nafion modified gold electrode for the detection of Hg(II) using electrochemical technique. Optimized ratio for Biotinyl Somatostatin-14/Nafion (Biotinyl peptide/Nafion) has been identified and used in modification of gold electrode. The modified electrode has proven to be comparable in detection of Hg(II) when validated against ICP-MS in real sample application. Detail characterizations in development of electrochemical sensor for Hg(II) are also discussed.

2. EXPERIMENTAL

All chemicals used were of analytical reagent grade. Aqueous solutions were prepared with deionised water. Nafion (117 solution, ~5%) were purchased from Fluka (Switzerland). Sodium hydroxide was purchased from Merck (Germany). Potassium nitrate from BDH Analar (England) and sodium sulphate hydrate from Fisher Chemical (United Kingdom). Biotinyl Somatostatin-14 was purchased from Bachem (Germany). Hg(II) nitrate were purchased from Aldrich (USA, Germany). $Na_2SO_4.10H_2O$ was purchased from Fisher (United Kingdom) and $CH_3COONa.3H_2O$ from Merck (Germany).

All electrochemical measurements were performed with μAutolab (Type III) (Microchemie) interfaced to a PC using GPES (version 4.9) software for windows. The three-electrode system consists of gold (Au) as working electrode, an Ag/AgCl reference electrode (with 3 M KCl) and platinum wire as auxiliary electrode Supporting electrolyte was purged with high-purity nitrogen for at least twenty minutes prior to experiments and a nitrogen environment was then maintained over solutions in the cell throughout all scans.

The signal of the accumulated modified and unmodified Pt electrode were measured using cyclic voltammetry (CV) by scanning the potential from +1.5 to −1.0 V with a scan rate of 100 mVs^{-1} performed in each solution, unless specified otherwise.

The modified electrode was prepared by immobilization of peptide (disperse in Nafion) layer onto the working electrode. The electrode was polished before immobilization procedure with 0.3 and 0.05 μm alumina slurry. Then it was rinsed thoroughly with distilled water and ultrasonically agitated. 1 mg of peptide was diluted with 30 mL deionised water. About 10 μL of Biotinyl peptide solution and 10 μL of Nafion dispersion were casted on the electrode surface with a micro-syringe and the casting was evaporated to dry at room temperature in the air overnight. All work was performed at room temperature (25 ± 1 °C).

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical characterization of Biotinyl peptide/Nafion modified gold electrode

Voltammogram of Biotinyl peptide/Nafion modified gold electrode and Nafion modified gold electrode was recorded with and without 10 mgL^{-1} Hg(II) immersed in a cell containing 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte As shown in Figure 2, line (c) shows the response of Biotinyl peptide/Nafion modified gold electrode without Hg(II), line (b) shows the response of Nafion modified gold electrode with 10 mgL^{-1} Hg(II) solution and line (a) shows the response of Biotinyl peptide/Nafion modified gold electrode with 10 mgL^{-1} Hg(II) in 0.1 M Na_2SO_4 as supporting electrolyte (pH 3). In line (a), reduction peaks were observed at around +0.79 and +0.02 V corresponding to the reduction of the Hg(II) to Hg(I) and Hg [17] and re-oxidation peaks at 0.69 and 1.21 V corresponding to the oxidation of Hg to Hg(I) and Hg(II) [18], respectively. During the backward anodic potential scan, a double peaks refers to the release of Hg(I) and Hg in the process, in contrast to the counterpart process of reduction which is one electron process (n=1). The recognition mechanism is suggested as below:

[1] Hg^{2+}_{aq} + Biotinyl peptide/Nafion $_{mem}$ ⟶ $[Hg^{2+}$ Biotinyl peptide/Nafion$]_{mem}$

[2] $[Hg^{2+}$ Biotinyl peptide/Nafion$]_{mem} + e^-$ ⟶ Hg^{+}_{mem} + Biotinylpeptide/Nafion

[3] $[Hg^{+}$ Biotinyl peptide/Nafion$]_{mem} + e^-$ ⟶ Hg^{0}_{mem} + Biotinylpeptide/Nafion

[4] Hg^{0}_{mem} ⟶ $Hg_2^{2+} + e^-$

[5] $Hg_2^{2+}{}_{mem}$ ⟶ $Hg^{2+}_{aq} + e^-$

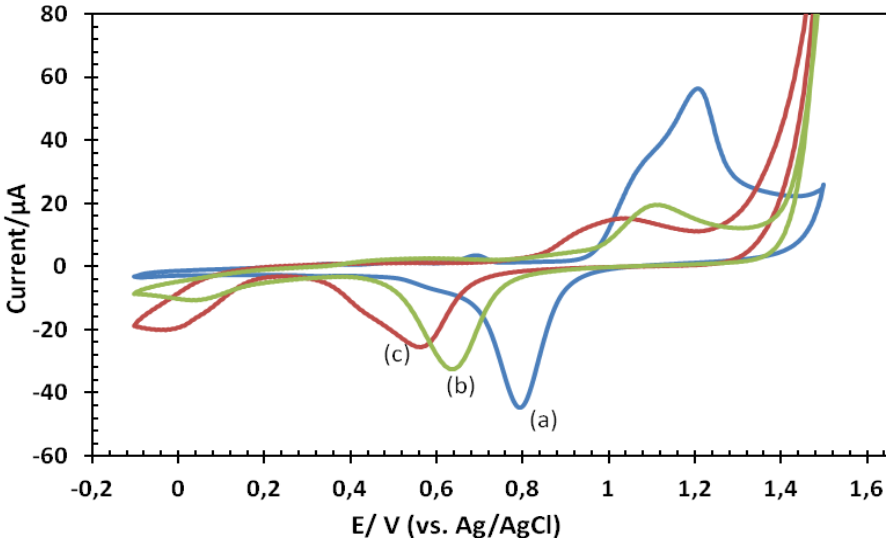

Figure 2. Cyclic voltammetry pattern of (a) Biotinyl peptide/Nafion modified gold electrode in 10 mgL^{-1} Hg(II), (b) Nafion modified gold electrode in 10 mgL^{-1} Hg(II) and (c) Biotinyl peptide/Nafion modified gold electrode without Hg(II) with 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte with potential scanning commenced in negative direction over the range 1.5 to -0.1 V vs Ag/AgCl.

The first process involved the accumulation of metal ions at the modified electrode surface. The process occurs by complexation, involving the properties (physical and chemical) of metal ions and complexing ability of the ligand [19]. The metal ions are then reduced to reductive material and formed a thin film on the electrode surface. The metal ions produced could be either diffused back into solution or complexed (re-adsorbed) on the surface of Biotinyl peptide/Nafion modified gold electrode [19].

In Figure 2(c), with no Hg(II) ion in the solution, the sensitivity of the electrode is at less positive potential, +0.56 V and the response is low compared to modified electrode. If the electrode was modified without the peptide, such that the electrode is only modified with Nafion, the response is low compared to Biotinyl peptide/Nafion modified gold electrode. Line (c) in this figure suggested that the peptide is associated with the interface and Biotinyl peptide/Nafion modified gold electrode can have more sensitive response due to the enhanced partitioning of Hg(II) in the modified electrode.

3.2 Electrochemical Characterization at Different pH Value

The pH of supporting electrolyte were varied from 1 to 12 to determine its effect on the current signal in determination of 10 mgL^{-1} Hg(II). From Figure 3, it was observed that the reduction current increases with an increase in pH from pH 1 to pH 3 [18]. The graph also shows that at pH higher than 3, the peak current decreases. The decreases in the current response of the electrode at higher pH are due to the formation of the hydroxide mercury complexes that inhibit mercury accumulation on the electrode.

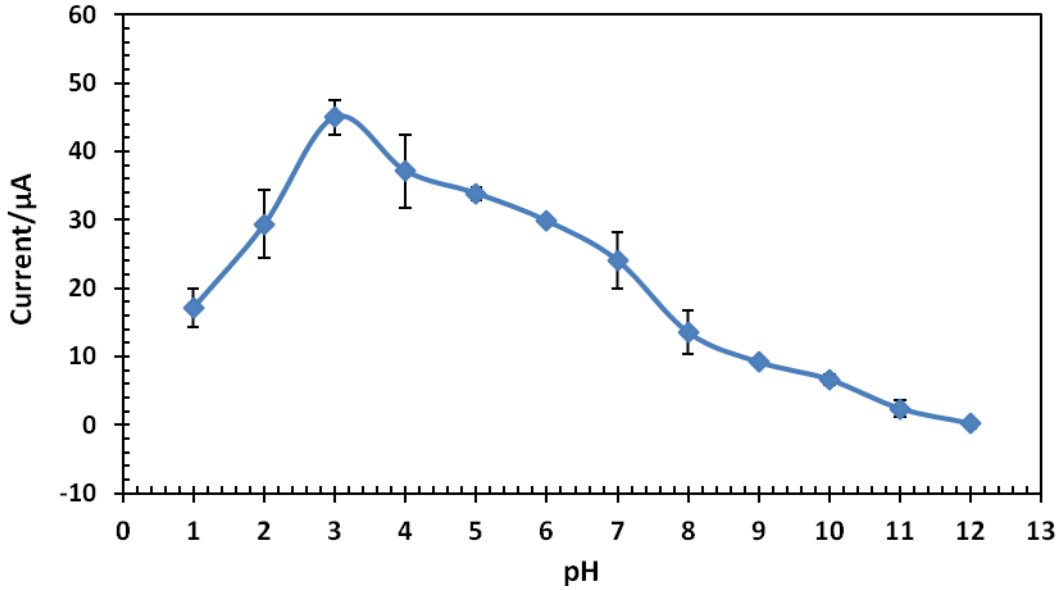

Figure 3. Reduction peak current at 25°C for 10 mgL^{-1} Hg(II) in 0.1 M Na_2SO_4 as supporting electrolyte as a function of pH using Biotinyl peptide/Nafion modified gold electrode. Potential scanning in negative direction from 1.5 to -0.1 V vs Ag/AgCl at a scan rate 100 mVs^{-1}.

Conversely, low peak current at low pH values is because the protonation of the weakly basic coordinating groups at the surface of the modified electrode [20]. If the mechanism of accumulation of

the mercury onto the electrode surface is through ion exchange, acidic media is not suitable because protons compete with mercury for the negative charged of the carboxylic groups. Hence, less metal cation will be adsorbed onto the surface of Biotinyl peptide/Nafion modified gold electrode, resulting in a decreased peak current response. Therefore, an average pH value of 3 was chosen in subsequent studies.

In Table 1, the reproducibility was evaluated by the precision obtained for a series of six repetitions (n=6), with 10 mgL^{-1} Hg(II) using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte . Reproducibility was studied due to constructional variation which could arise from different thickness of the immobilized peptide on the surface of the electrode and the uneven distribution of Hg(II) solution on it. A good relative standard deviation of 3.7% was obtained indicating a reproducible and reliable signal of the developed detection system.

Table 1. Reproducibility study for determination of 10 mgL^{-1} Hg(II) using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. Potential scanning in negative direction from 1.5 to -0.25 V vs Ag/AgCl at a scan rate 100 mVs^{-1}.

Replicates	Current, µA
1	-43.98
2	-44.51
3	-45.00
4	-41.71
5	-41.13
6	-42.57

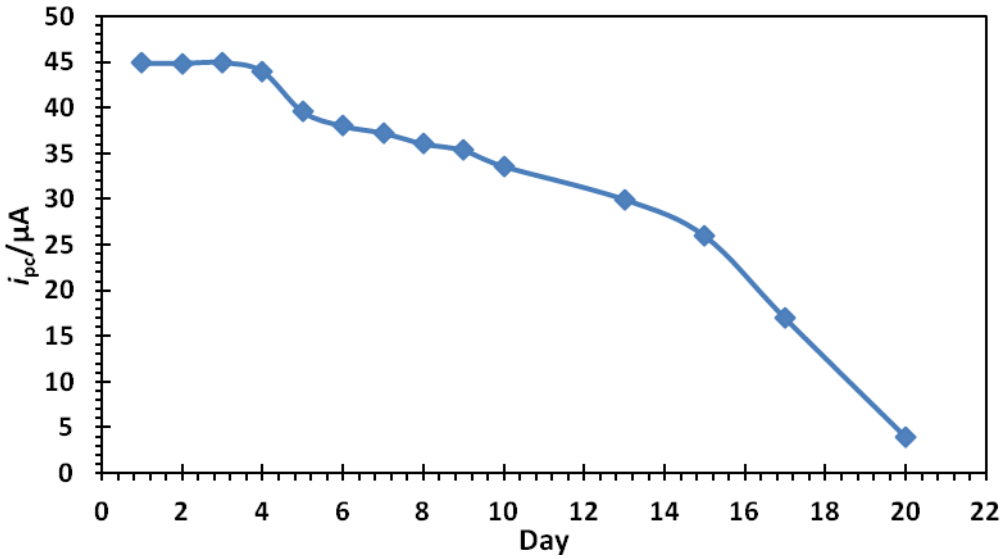

Figure 4. A graph of stability study for determination of 10 mgL^{-1} Hg(II) using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 7) as supporting electrolyte. Potential scanning in negative direction from 0.9 to 0.2 V vs Ag/AgCl at a scan rate 100 mVs^{-1}.

The storage stability of the Biotinyl peptide/Nafion modified gold electrode system was investigated by storing an electrode in dry condition and was electrochemically studied everyday for 20 days in different solution of 10 mgL^{-1} Hg(II) with 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. By the fifth day, peak current in Figure 4 was found to decrease to less than 10 % of their initial values.

Result obtained from multiple cycling in Figure 5 showed that the reduction peaks continuously decay after each 5 cycles indicates that the modified electrode is not stable for repeated usage and only suitable for disposable basis [21].

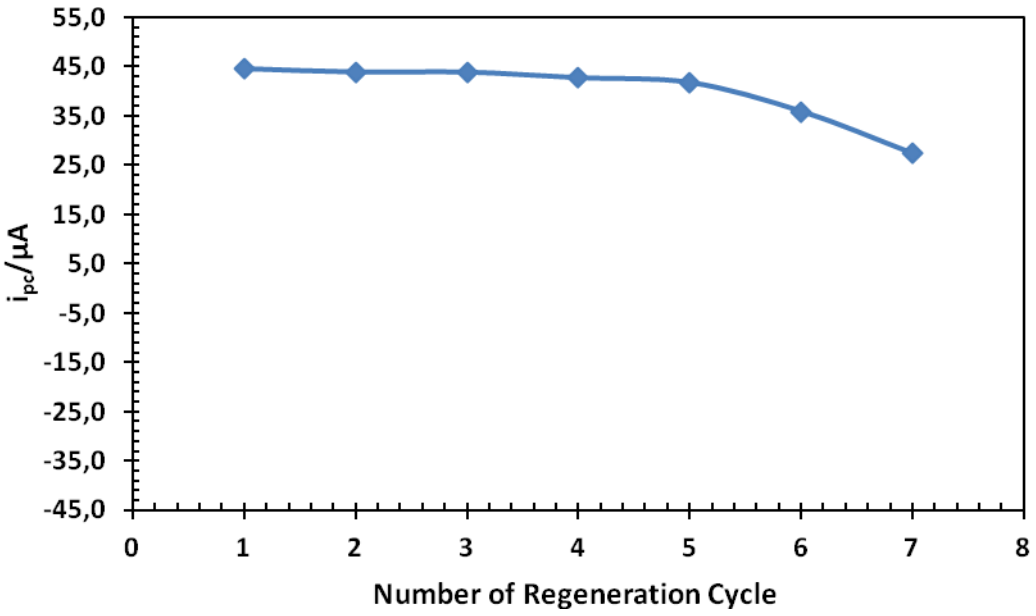

Figure 5. A graph of repeatability study for determination of 10 mgL^{-1} Hg(II) using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. Potential scanning in negative direction from 1.5 to -0.25 V vs Ag/AgCl at a scan rate 100 mVs^{-1}.

3.3. Effect of Varying Scan Rate

Figure 6 shows cyclic voltammogram of 10 mgL^{-1} Hg(II) using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte in a range of scan rate 20 to 1000 mVs^{-1}. The increase of potential scan rate promoted an increase of current peak in anodic and cathodic reactions. The current of the cathodic wave increases and the peak potentials shifted to less positive value with the increasing of scan rates. The changes in peak potential indicated that the electron transfer of Hg(II) with the Biotinyl peptide/Nafion modified gold electrode is a typical surface controlled electrochemical process [22].

The mode of transport can be accomplished by varying the scan rate and the relationship between peak current and scan rate is given by two equations; Randles-Sevcik equation for diffusion-controlled reaction (Equation 1.1) and Laviron equation for adsorption-controlled reaction (Equation 1.2) [7].

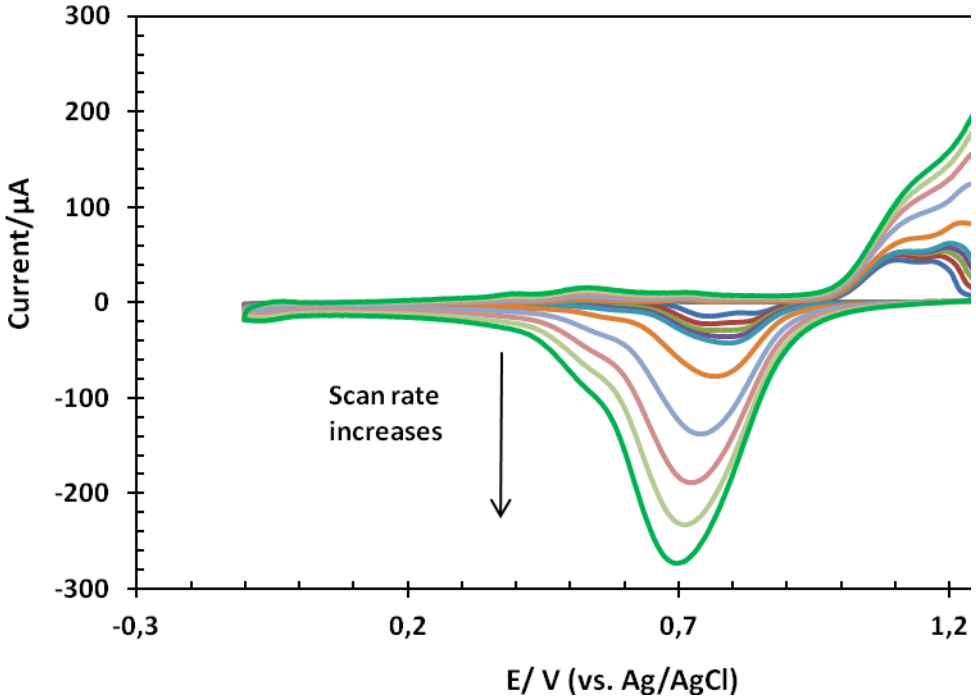

Figure 6. Effect of varying the scan rate on the cyclic voltammogram of Biotinyl peptide/Nafion modified gold electrode in 10 mgL^{-1} Hg(II) and 0.1 M Na_2SO_4 as supporting electrolyte (pH 3). Potential scanning commenced in negative direction over the range 1.5 to -0.25 V vs Ag/AgCl at a scan rate 20 to 1000 mVs^{-1}.

$$i_p = (2.69 \times 10^5) n^{3/2} \mathrm{ACD}^{1/2} v^{1/2} \qquad (1.1)$$

$$i_p = \left(\frac{n^2 F^2}{4RT}\right) A\Gamma v \qquad (1.2)$$

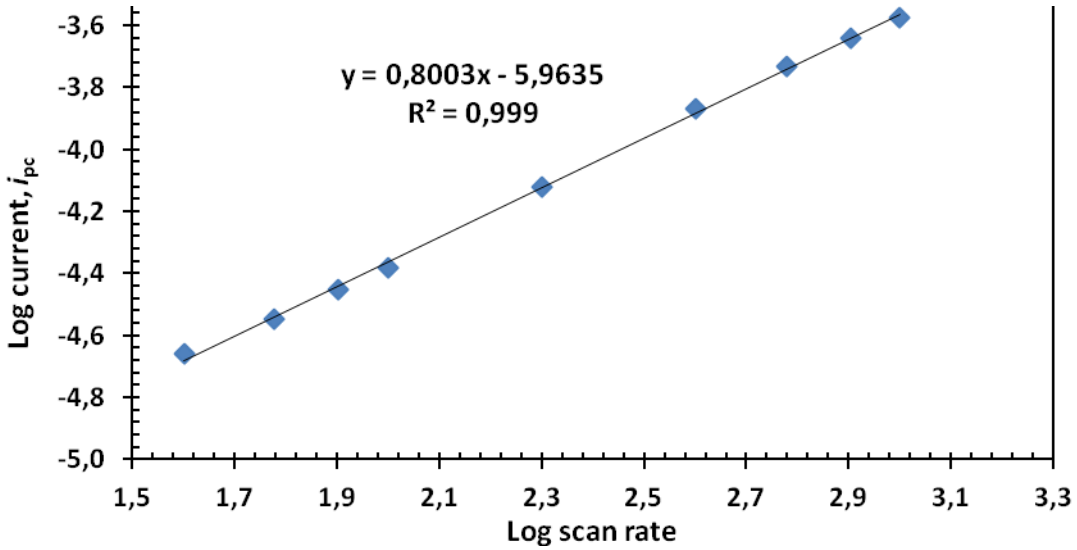

Figure 7. Dependence of log cathodic current on log scan rate for Biotinyl peptide/Nafion modified gold electrode in 10 mgL^{-1} Hg(II) and 0.1 M Na_2SO_4 as supporting electrolyte (pH 3) with potential scanning commenced in negative direction over the range 1.5 to -0.25 V vs Ag/AgCl at a scan rate of 10 to 1000 mVs^{-1}.

Consistent with both equations, if the peak current (i_p) is proportional to $v^{1/2}$ then the process involved is diffusion-controlled reactions whereas if peak current is proportional to v then the process involved adsorption-controlled process. Since a major (and measurable/controllable) difference between equations 1.5 and 1.6 is the exponent of the scan rate, the factors can be removed by plotting a graph of log i_p (y-axis) versus log v (x-axis) [7].

A graph of log current versus log scan rate was plotted for the reduction peak of 10 mgL^{-1} Hg(II). The peak current is proportional to log scan rate as indicated in Figure 7 and the slope value of 0.80 from the plotted graph suggest that the process is a complex surface process, mostly involving an adsorption process, as indicated theoretically [23, 24, 25].

3.4. Chronocoulometry Studies

A double step chronocoulometric experiment was carried out for 0.5 mgL^{-1} Hg(II) in 0.1 M Na_2SO_4 (pH 3) supporting electrolyte. Initial potential step is from 0.07 to 0.17 V vs Ag/AgCl. The charge-time (Q-t) (the Anson equation, 1.4) is obtained by integrating the Cottrell Equation 1.3.

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2} + Q_{dl} + nFA\Gamma \qquad (1.3)$$

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2} \qquad (1.4)$$

An Anson coulometric plot is illustrated in Figure 8 and shows that during the reduction of mercury there is an initial rapid increase in charge with time. However, during the re-oxidation step there is an absence of electroactivity, as is evident because its charge versus square root of time coincides with the background line.

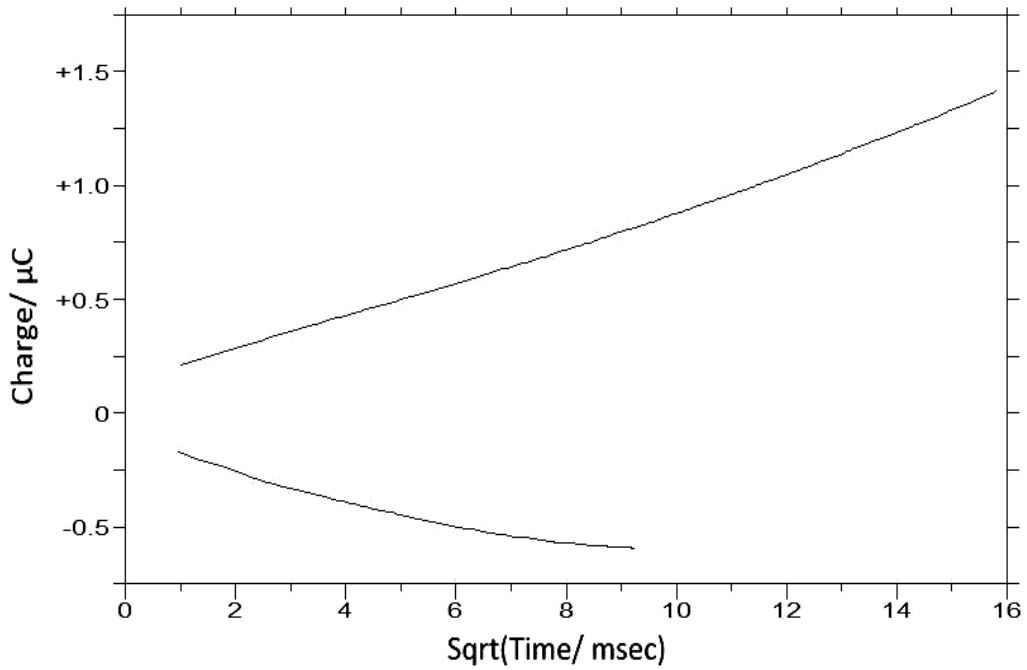

Figure 8. Charge versus square root of time of double step chronocoulograms of 0.5 mgL^{-1} Hg(II) using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3), potential scanning from 0.07 to 0.17 V vs Ag/AgCl.

With electrode area value (0.07 cm^2), the diffusion coefficient of Biotinyl peptide/Nafion modified gold electrode was calculated to be 1.49×10^{-7} cm^2s^{-1}. The surface coverage for Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) is 4.93×10^{-11} $molcm^{-2}$ whereas for Nafion modified gold electrode is 4.14×10^{-12} $molcm^{-2}$. The charge density of Biotinyl peptide/Nafion modified gold electrode was calculated to be 4.71 μCcm^{-2} and Nafion modified gold electrode is 0.43 μCcm^{-2}.

3.5. Interference Study

The effect of various metals and organic compounds (known or expected to give a voltammetric response with a gold electrode, or with a chance of either interacting with Hg(II) or might reasonably be expected to exhibit redox activity in roughly the same potential range as Hg(II)) were studied in order to evaluate their interfering effect on detection of Hg(II).

The interference study was carried out using 1:1, 1:2 and 2:1 ratio of each metal ions with 60 $\mu g\ L^{-1}$ Hg(II). The ions chosen for the study were As(III), Cr(III), Cu(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(II)and Zn(II). In Figure 9, a significant effect was observed for As(III) and Cr(III) but the percentage of interference is less than 10%. Other metals had no significant percentage of interference on the determination of 60 μgL^{-1} Hg(II) except for a small suppression (strong chelates probably do not release Hg(II) ions even in acidic solution and the bound fraction of mercury is not accessible to determination).

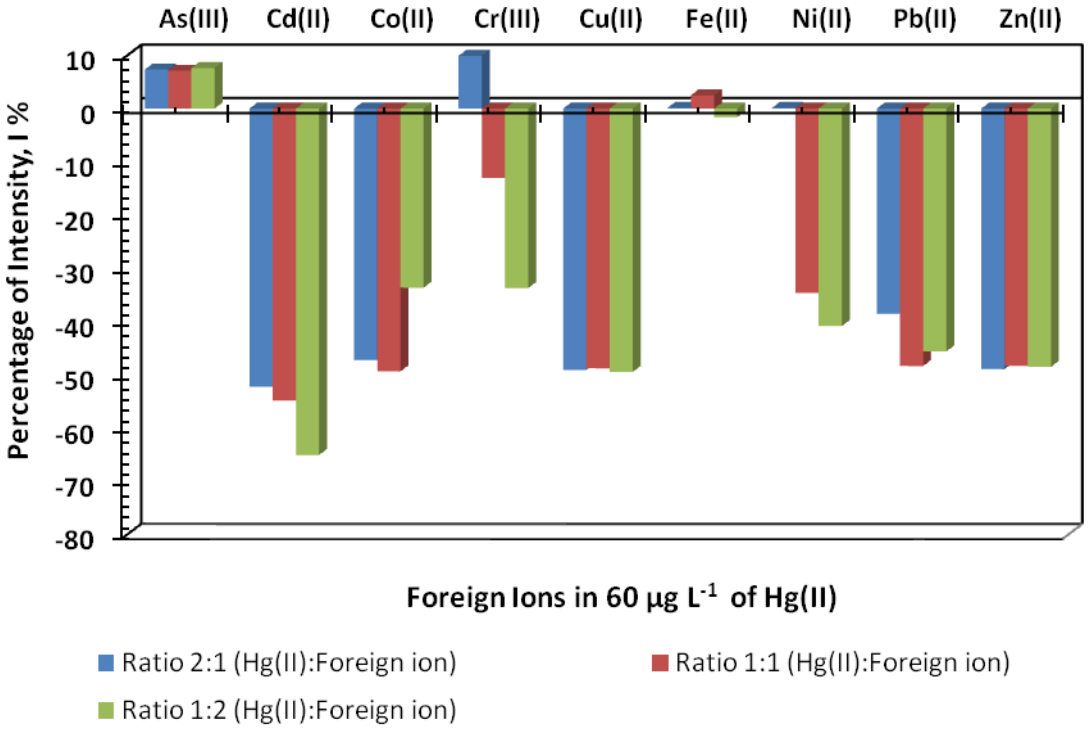

Figure 9. Effect of foreign metal ions using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. Potential scanning in negative direction from 1.5 to -0.25 V vs Ag/AgCl at a scan rate 100 mVs^{-1}.

3.6 Analytical Application of the Developed Modified Electrode

A calibration graph for the determination of Hg(II) was prepared from graph in Figure 10 (study on effect of different concentration of Hg(II) according to the general procedure under the optimum conditions developed above using DPV). Concentration as low as 40 μgL^{-1} Hg(II) can be detected using this method.

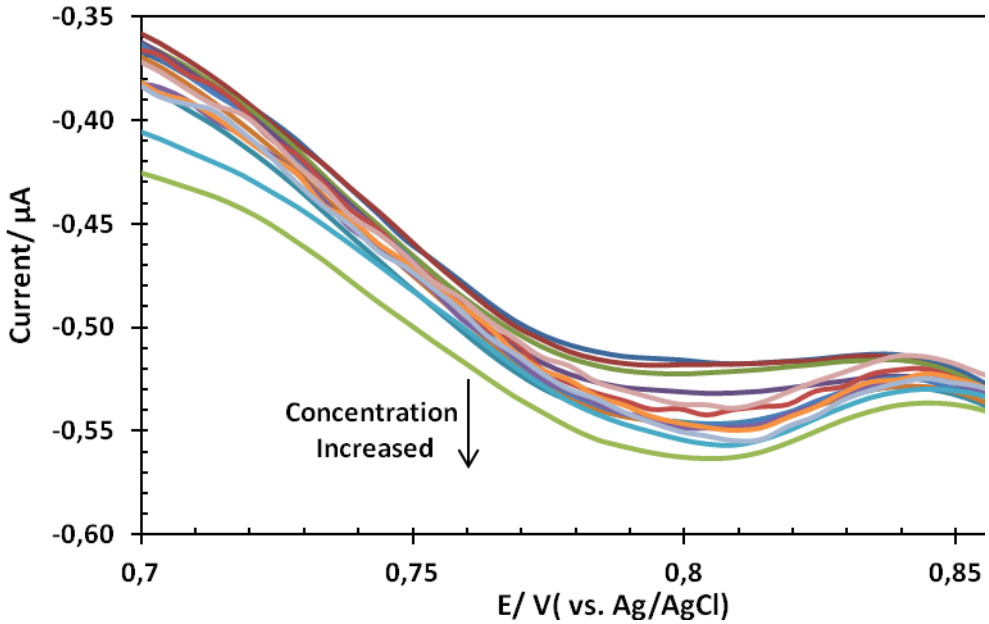

Figure 10. Voltammograms of Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) supporting electrolyte with different concentration of Hg(II). Potential scanning in negative direction from 0.95 to 0.6 V vs Ag/AgCl.

In Figure 11, the current, i_{pc}, is linearly proportional to the concentrations of Hg(II) observed in potential range of 0.95 to 0.6 V with a correlation coefficient of 0.991. The concentration of Hg(II) is in the range of 40 to 170 μgL^{-1} in a mixture of 0.1 M Na_2SO_4 (pH 3) solution with preconcentration time of 60s. The sensitivity, expressed as the slope of the linear region of the calibration curve is 1×10^{-10} $A\mu M^{-1}$. The value of LOD obtained is 0.4 μgL^{-1} which is below the WHO guidelines for drinking water of 2 µg/litre (WHO, 2004). The presence of Cys as a chelating ligand which is able to form much more stable complex with Hg(II) than with other metal ions is very important for increase selectivity toward Hg(II) [26, 27].

This detection limit is similar or lower than the LOD obtained with other gold electrode. For instance, the detection limit for the determination of Hg(II) using gold modified electrode with screen-printed electrodes modified with thiol-modified magnetic particles by Mandil is 1.5 µgL-1 [28]. In other modifications of electrode for mercury determination, the detection limit obtained is in the range of 1.0×10−8 and 1.0×10−7 molL−1 [29, 30, 31] which is almost in the same range as current work.

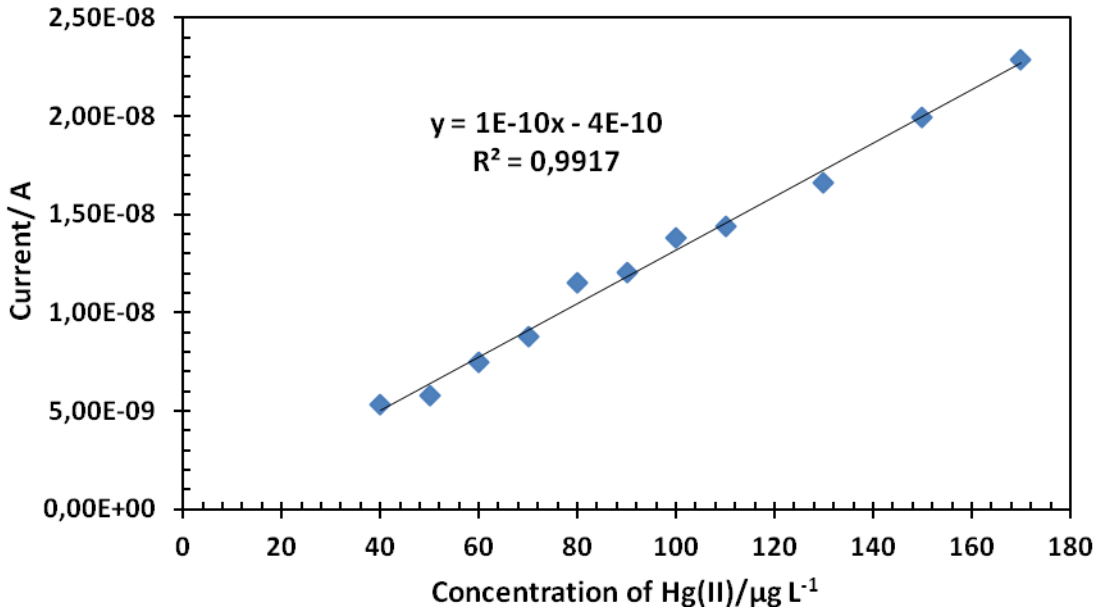

Figure 11. Calibration plot of current intensity versus concentration of Hg(II) concentration using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. Potential scanning in negative direction from 0.95 to 0.6 V vs Ag/AgCl.

The determination of Hg(II) concentration in waste water samples were carried out using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3). The determinations were carried out using spiked waste water samples. No pretreatment of samples was carried out.

The developed methods was applied for determination of Hg(II) in some real waste water samples (industrial waste water from wood industry and electroplating industry). Four different waste water samples from two sources were spiked with 60 and 90 μgL^{-1} of Hg(II) and the percentage of recoveries were calculated. Percentage of recovery was evaluated using direct calibration based on Figure 11 and the result is summarized in Table 2.

Table 2. Recovery data for detection of Hg(II) in waste water samples using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. Potential scanning in negative direction from 0.95 to 0.6 V vs Ag/AgCl.

Waste water samples	Originally present, μgL^{-1}	Added, μgL^{-1}	Recovered	Recovery, %
Wood Treatment Industry	18.1±0.2	60	76.2±3.0	99
	18.1±0.2	90	110.9±12.2	103
Electroplating Industry	16.7±3.0	60	85.1±13.1	111
	16.7±3.0	90	112.7±6.4	106

The original samples were also analysed using inductively coupled plasma mass spectrophotometer (ICP-MS) and the percentages of different with the developed method were

calculated. The percentage of error for wood treatment industry is 9.0% and 16.8% for electroplating industry. The results were summarized in Table 3. These observations and results confirmed that the Biotinyl peptide/Nafion modified gold electrode can be used for practical analysis.

Table 3. Percentage of error between inductively coupled plasma mass spectrophotometer method and developed method using Biotinyl peptide/Nafion modified gold electrode in 0.1 M Na_2SO_4 (pH 3) as supporting electrolyte. Potential scanning in negative direction from 0.95 to 0.6 V vs Ag/AgCl.

Wastewater Samples	Detected by ICP-MS, ($\mu g\ L^{-1}$)	Detected by developed method, ($\mu g\ L^{-1}$)	% Error
Wood Treatment Industry	16.6±0.9	18.1±0.2	9.0
Electroplating Industry	14.3±1.1	16.7±3.0	16.8

4. CONCLUSION

The used of Biotinyl somastostatin-14 modified electrode has been successfully applied in detection of Hg(II) in aqueous environment. Through this procedure, the electrochemical activity of Biotinyl somastostatin-14/Nafion modified gold electrode has been optimized in determination of Hg(II) and the performance of the resulting modified electrode improved greatly compared to the unmodified electrode. Modification of electrode was done by self assembly of peptide via the cysteine group, which contains a thiol moiety that binds to gold. The assembled peptides can facilitate electron transfer between analyte and electrode surface. A good RSD value of 3.7% was obtained. Sensitivity obtained was 1×10^{-10} AμM^{-1}, with LOD value 0.4 μgL^{-1}. The modified electrode has been tested in determination of Hg(II) in spiked samples of wood and electroplating industrial waste water and found to have a comparable result with ICP-MS.

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References

1. N.E. Selin, E.M. Sunderland, C.D. Knightes and R.P. Mason, *Environ. Health Perspect,* 118 (2010) 137-143.
2. J. Mutter, A. Curth, J. Naumann, R. Deth and H. Walach, *Journal of Alzheimer's Disease,* 22 (2010) 357-374.

3. O. Abollino, A. Giacomino, M. Malandrino, G. Piscionieri and E. Mentasti, *Electroanalysis*, 20 (2008) 75-83.
4. J. Gong, T. Zhou, D. Song, L. Zhang and X. Hu, *Anal. Chem.*, 82 (2010) 567-573.
5. F. Wang, X. Wei, C. Wang, S. Zhang and B. Ye, *Talanta*, 80 (2010) 1198-1204.
6. L. Liu, H.N.L. Do, J. Wang and F. Zhou, *Electroanalysis*, 22 (2010) 1476-1482.
7. V. Somerset, J. Leaner, R. Mason, E. Iwuoha and A. Morrin, *Electrochimica Acta*, 55 (2010) 4240-4246.
8. A. Uhlig, U. Schnakenberg and R. Hintsche, *Electroanalysis*, 9 (1997) 125-129.
9. B.K. Jena and C.R. Raj, *Anal. Chem.*, 80 (2008) 4836-4844.
10. O. Ordeig, C.E. Banks, J. Del Campo, F.X. Muñoz and R.G. Compton, *Electroanalysis*, 18 (2006) 573-578.
11. Z. Zhu, Y. Su, J. Li, D. Li, J. Zhang, S. Song, Y. Zhao, G. Li and C. Fan, *Anal. Chem.*, 81 (2009) 7660-7666.
12. I. Cesarino and É.T.G. Cavalheiro, *Electroanalysis*, 20 (2008) 2301-2309.
13. E. Şar, H. Berber, B. Aşçi and H. Cankurtaran, *Electroanalysis*, 20 (2008) 1533-1541.
14. Y. Wenrong, J.J. Gooding and D.B. Hibbert, *Journal of Electroanalytical Chemistry*, 516 (2001) 10-16.
15. E. Chow and J.J. Gooding, *Electroanalysis*, 18 (2006) 1437-1448.
16. C. Gouveia-Caridade, R. Pauliukaite and C.M.A. Brett., *Electroanalysis*, 18 (2006) 854-861.
17. A. Manivannan, M.S. Seehra, D.A. Tryk and A. Fujishima, *Analytical Letters*, 35 (2002) 355-368.
18. N.L. Dias Filho and D.R. do Carmo, *Talanta, 68 (*2006) 919-927.
19. J. Lu, X. He, X. Zeng, Q. Wan and Z. Zhang, *Talanta*, 59 (2003) 553-560.
20. E.E. Mojica, F.E. Merca and J.R.L. Micor, *Philippine Journal of Crop Science, 27 (*2002) 37-42.
21. K.C. Honeychurch, J.P. Hart, D.C. Cowell and D.W.M. Arrigan, *Sens. Actuators. B:Chemical*, 77 (2001) 642-652.
22. S.F. Wang, T. Chen, Z.I. Zhang, X.C. Shen, Z.X. Lu and D.W. Pang, *Langmuir*, 21 (2005) 9260-9266.
23. R.G. Compton and C.E. Banks, World Scientific Publishing Co Pte Ltd.: Singapore, 2007.
24. N.P. Shetti, L.V. Sampangi, R.N. Hegde and S.T. Nandibewoo, *Int. J. Electrochem. Sci.*, 4 (2009) 104 -121.
25. M.H. Yaacob, A.R.M. Yusoff and R. Ahamad, *Malaysian Journal of Chemistry*, 12 (2010) 9- 14.
26. C.J. Yu and E.L. Tseng, *Langmuir*, 24 (2008) 12717-12722.
27. Y. Kim, R.C. Johnson and J.T. Hupp, *Nano Letters*, 1 (2001) 165-167
28. A. Mandil, L. Idrissi and A. Amine, *Microchimica Acta*, 170 (2010) 299-305.
29. H.M. Dong, L. Lin, H. Zheng, G. Zhao and B. Ye, *Electroanalysis*, 18 (2006) 1202-1207.
30. A.A. Ensafi and M. A Fouladgar, *Sensors and Actuators B*, 136 (2009) 326-331.
31. C. Dridi, M.B. Ali and F. Vocanson, *Materials Science and Engineering C*, 28 (2008) 765-770.