American Journal of Applied Sciences 7 (3): 395-401, 2010
ISSN 1546-9239

Voltammetric Detection of Mn(II) in Blood Sample at C_{60} and MWCNT Modified Glassy Carbon Electrodes

Muhammed Mizher Radhi, Wee Tee Tan, Mohamad Zaki B. Ab Rahman and Anuar Bin Kassim
Department of Chemistry, Faculty of Science, University Putra Malaysia,
43400, UPM Serdang, Selangor, Malaysia

Abstract: Problem statement: Glassy carbon electrode GCE was modified with different microparticles to increase the efficiency of analysis Mn^{2+} in blood samples by cyclic voltammetry and applied for the detection of trace Mn(II) by oxidation process. **Approach:** The structure and composition of the modified GCE processed by using Carbon Nanotubes CNT and C_{60} to produce two modified electrodes CNT/GCE and C_{60}/GCE, to detect a trace Mn^{2+} by cyclic voltammetry for mouse blood with comparison the best modified electrode for detection the ion by the sensitivity and values of Relative Standard Deviation (RSD) in calibration curve. **Results:** A wide linear range and good repeatability were obtained for Mn^{2+} detection by CNT/GCE in aqueous KCl as supporting electrolyte at different ratio of KCl: Blood using CNT/GCE and C_{60}/GCE, the relative standard deviation of two modified electrodes are good on CNT/GCE than C_{60}/GCE. **Conclusion:** The two modified electrodes CNT/GCE and C_{60}/GCE depending on the redox current of Mn(II) ions were evaluated by the determination of low concentration of Mn(II) in blood samples by cyclic voltammetric method, the most modified electrode to detect the Mn(II) in blood is CNT/GCE.

Key words: CNT/GC electrode, C_{60}/GC electrode, blood sample, Mn(II), cyclic voltammetry

INTRODUCTION

The fabrication of CNTs-based films using the multilayer MWCNTs films has gained interest because of its simplicity and the wide choice of micromaterials using on GCE in electroanalysis studies esp. cyclic voltammetry (Agui *et al*., 2008).

Also the reduction of electrodes coated with C_{60}-fullerene is used in acetonitrile solution containing a wide variety of supporting electrolytes. Electrochemical intercalation is observed that the electron-transfer reactions at electrodes modified can be passed with chemical reversibility (Compton *et al*., 1993).

CNTs-modified electrodes were also used for the stripping analysis of drugs as simvastatin (Zhang *et al*., 2005), reserpine (Zhang and Wu, 2005), theophyilline (Zhu *et al*., 2005), lyncomicin (Zhu *et al*., 2006), piroxicam (Abbaspour and Mirzajani, 2007), procaine (Wu *et al*., 2006a), phenylephrine (Wu *et al*., 2006b) and urapidil (Zheng and Song, 2007). Other applications involve determination of the herbicide amitrole (Chicharro *et al*., 2005), flavonoid compounds such as quercetin (He *et al*., 2005; Xu and Kim, 2006; Zeng *et al*., 2006; Xiao *et al*., 2007) and rutin (Zeng *et al*., 2006) and dopamine in serum (Wang *et al*., 2006).

Voltammetric determination of chloride and bromide ions in serum blood was made using a one-body type Ag electrode. This determination was based on measurement of the charge of the reduction wave of silver halide formed on the Ag electrode surface in a halide ion solution during a cathodic potential sweep. Linear concentration ranges were shown in good resolution for both chloride and bromide ions. The correlation coefficient was 0.999 in each case and relative standard deviation for chloride and bromide ions was obtained at a relatively high concentration (Arai *et al*., 1996).

Detection of blood cholesterol is of great clinical significance. Multiwall carbon Nanotubes (MWNTs), vertically aligned on a silicon platform, promote heterogeneous electron transfer between the enzyme and the working electrode. The fabricated working electrodes showed a linear relationship between cholesterol concentration and the output signal. The efficacy of the multiwall carbon nanotubes in promoting heterogeneous electron transfer was evident by distinct electrochemical peaks and higher signal-to-noise ratio as compared to the Au electrode with identical enzyme immobilization protocol. The selectivity of the cholesterol sensor in the presence of

Corresponding Author: Muhammed Mizher Radhi, Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia

common interferents present in human blood, e.g., uric acid, ascorbic acid and glucose (Roy *et al*., 2006).

Cyclic Voltammetry (CV) is a new method for evaluating the antioxidant capacity of plasma in Low Molecular Weight Antioxidants (LMWA) and the severity of oxidative stress exerted on the plasma. It is based on the reducing properties of these molecules. CV has been proven to be a simple, sensitive and reliable method (Chevion *et al*., 1997).

Cyclic Voltammetry (CV) on a bare Glassy Carbon Electrode (GCE) has been applied to measure human and horse plasma antioxidant activity. The CV response of human plasma consisted of two broad voltammetric peaks observed in the potential range from 0.2-0.6 V and from 0.6-0.9 V. Horse plasma showed no voltammetric response on the non-activated GCE. Electrochemical activation in 0.5 H2SO4 induced a response similar to that in human plasma. Parameters that indicate the Antioxidant Capacity (AC) of the samples, i.e., the peak potential Ep, the peak current density ip and the charge Q below voltammetric waves were calculated for both waves (Martinez *et al*., 2006; Psotova *et al*., 2001).

In this work, CNT and C_{60} were modified GCE by mechanical and solution evaporation methods to resulting composites modified electrodes were successfully applied to detect trace Mn^{2+} by cyclic voltammetry with an application to determine the Mn^{2+} ion in blood samples.

MATERIALS AND METHODS

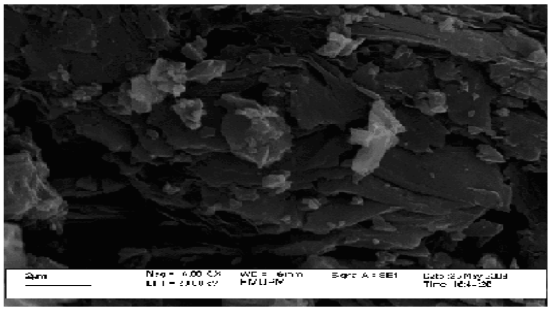
C_{60} (Fluka, 98%) and CNT (Fluka, 98%): Blood samples were used from healthy mice. Other chemicals and solvents were of annular grade and used as received from the manufacturer. Distilled water was used for the preparation of aqueous solutions. All solutions were deaerated with oxygen free nitrogen gas for 15 min prior to making the measurement.

Instruments: Electrochemical workstations of Bioanalytical system Inc. USA: Models BAS CV 50W with potetiostate driven by electroanalytical measuring softwares was connected to PC computer to perform Cyclic Voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire (1 mm diameter) was used as a reference and counter electrode respectively. The working electrodes used in this study were modified CNT by doping GCE with CNT by mechanical method, also the C_{60} evaporated on the GC electrode.

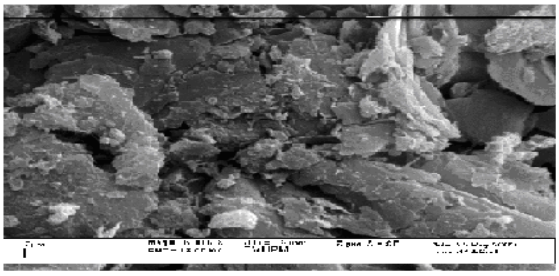
Preparation of CNT and C_{60} modified GC electrodes:

- A Mechanical Attachment technique (MA) was used which involved the pressing of a clean GC electrode surface onto a few mg of CNT powder placed on a filter paper
- Solution evaporation technique: This method includes application of a 2 μL of saturated C_{60} in acetonitrile and subsequently dried by hot air blower before placing in voltammetric cell

Scanning electron microscopy: SEM the Fractured surfaces of the nanocomposites were studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20-30 kV. The scanning electron photographs were recorded at a magnification of 1000-6000X depending on the nature of the sample. SEM analysis was carried out to investigate microcrystals. Samples were dehydrated for 45 min before being coated with goal particle using SEM coating unit baltec SC030 sputter Coater. Scanning Electron Microscopy (SEM) was used to examine the morphology of CNT and C_{60} microcrystals by mechanical attached and evaporated technique on a graphite electrode surface before and after electrolysis with Mn(II) by cyclic voltammetry. Figure 1a and 2a are SEM of CNT and C_{60} attached and evaporated on to 6 mm diameter basal plane graphite electrode which exhibits an array of microcrystals with 0.1-2 μm diameter.

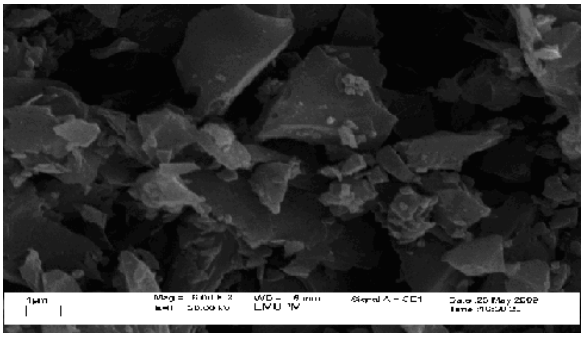


(a)

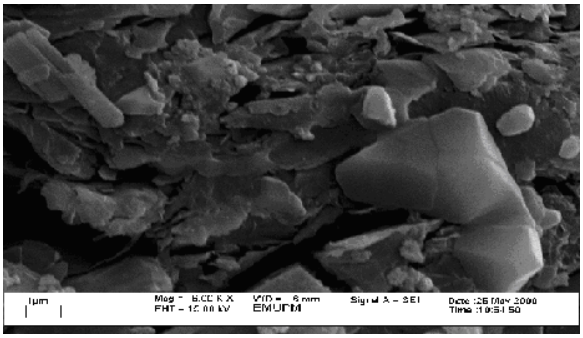


(b)

Fig. 1: Scanning electron micrographs of CNT microparticles mechanically attached to a basal plane pyrolitic graphite electrode (a) before and (b) after electroanalysis with Mn^{2+}



(a)



(b)

Fig. 2: Scanning Electron Microscopy (SEM) was used to look at the morphology of the C_{60} microcrystal on a graphite electrode. (a) SEM of C_{60} attached via solvent cast on to 5mm diameter basal plane graphite electrode exhibits an array of microcrystal. (b) SEM of C_{60} after electrolysis of Mn(II) by cyclic voltammetry

Figure 1b and 2b are SEM of CNT and C_{60} after electrolysis with Mn^{2+} using cyclic voltammetry on to 5 mm diameter basal plane graphic electrode with slightly enlarged size range of 0.2-5 μm diameter indicating presence of solid to solid conversion and that the film appears stable even after 10 potential cycling.

RESULTS

The following effects on the CV of Mn(II) in blood sample were carried out:

Effect of varying modified electrodes: Figure 3 shows the redox peaks of Mn^{2+} in different modified electrodes.

Effect of blood on redox reaction of Mn(II) using CNT/GCE and C_{60}/GCE redox: The study on the effect of blood (chose mouse blood) on the redox reaction of Mn^{2+} was carried out by using different volume ratio of mouse blood to 0.1 M KCl in the presence of a known amount, 0.05 and 0.2 mM of Mn^{2+} (Table 1 and 2 Fig. 4). The detection limit and sensitivity of

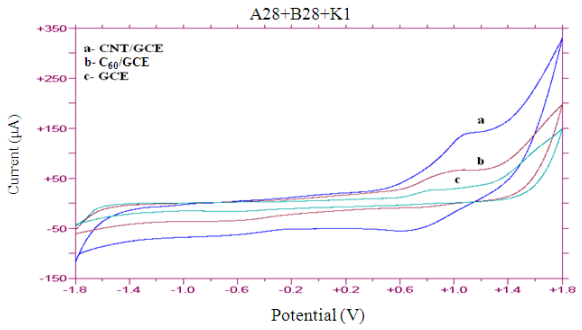


Fig. 3: Cyclic voltammogram of 0.5 mM Mn^{2+} in blood sample as supporting electrolyte at scanning rate 100 mV sec^{-1} using (a) CNT/GCE (b) C_{60}/GCE and (c) GCE versus Ag/AgCl

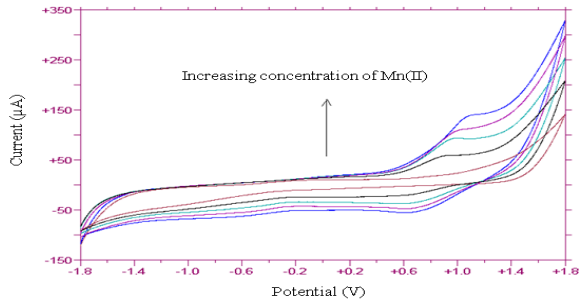


Fig. 4: Cyclic voltammogram for the redox peaks of Mn^{2+} (different concentration 0.1-3 mM) in blood sample at scanning rate 100 mv sec^{-1} using CNT/GCE versus Ag/AgCl

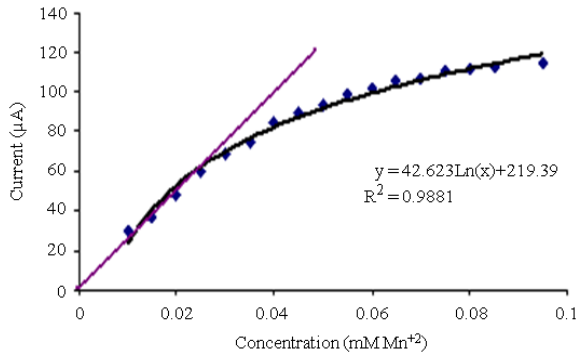


Fig. 5a: Plot of oxidation current versus different concentration 0.01-0.1 mM $MnCl_2$ in blood sample at scan rate 100 mV sec^{-1} using CNT/GCE versus Ag/AgCl

Mn(II) ions in blood samples was determined from the relationship between redox current peaks and the concentration using CNT/GCE as shown in Fig. 5a and 5b.

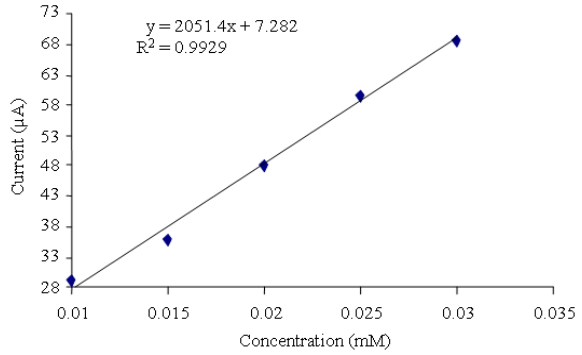


Fig. 5b: Plot of oxidation current versus different concentration 0.01-0.03 mM $MnCl_2$ in blood sample at scan rate 100 mV sec^{-1} using CNT/GCE versus Ag/AgCl

Table 1: Effect of different ratio (Blood: 0.1 M KCl) 0n the redox current and potential of 0.05 mM Mn^{2+} at a scan rate of 100 mV sec^{-1} using CNT/GCE versus Ag/AgCl

Ratio (by volume in mL)		Current/uA		Potential/mV	
Blood	0.1 M KCl	Ipc	Ipa	Epc	Epa
1:	9	Nd	Nd	Nd	Nd
1:	4	-65.38	80.77	860.4	947.8
3:	7	-33.33	61.54	811.2	833.1
2:	3	61.54	102.6	811.2	980.6
1:	1	Nd	35.38	Nd	783.9
3:	2	-45.13	88.21	811.2	9953.3
7:	3	-30.77	71.79	778.5	849.5
4:	1	-38.97	Nd	811.2	Nd
9:	1	-26.67	43.08	833.1	833.1

Table 2: Effect of different ratio (Blood: 0.1 M KCl) on the redox current and potential of 0.2 mM Mn^{2+} at a scan rate of 100 mV sec^{-1} using CNT/GCE versus Ag/AgCl

Ratio (by volume in mL)		I (µA)		Ep (mV)	
Blood	0.1M KCI	Ipc	Ipa	Epc (red.)	Epa (ox.)
1:	9	-28.21	41.03	696.5	625.5
1:	4	-46.15	Nd	871.3	Nd
3:	7	-53.85	92.31	854.9	936.9
2:	3	-65.38	107.7	844.0	975.1
1:	1	10.26	36.92	833.1	794.8
3:	2	-61.54	112.8	816.7	1013.4
7:	3	30.77	71.79	805.8	893.2
4:	1	47.18	86.15	827.6	1073.4
9:	1	22.56	43.08	838.5	816.7

Effect of blood on Mn(II) using C_{60}/GCE: The study on the effect of blood on the redox reaction of Mn^{2+} was carried out by using different volume ratio of mouse blood to 0.1 M KCl in the presence of a known amount, 0.05 and 0.1 mM of Mn^{2+} (Table 3 and 4 Fig. 6).

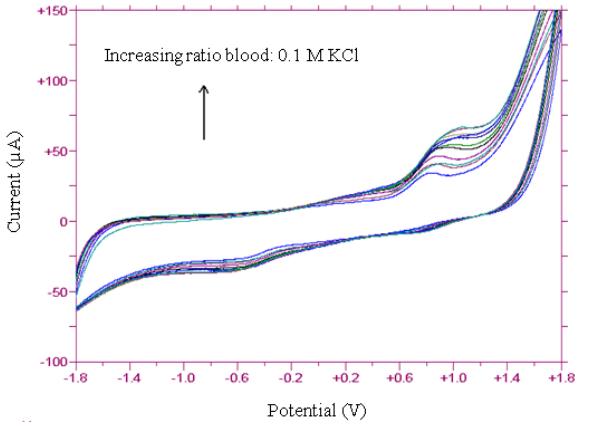


Fig. 6: Cyclic voltammogram of 0.05 mM Mn^{2+} in different ratio of blood sample and 0.1 mM KCl as a supporting electrolyte at scanning rate 100 mv sec^{-1} using C_{60}/GCE versus Ag/AgCl

Table 3: Effect of different ratio (Blood: 0.1 M KCl) 0n the redox current and potential of 0.1 mM Mn^{2+} at scan rate 100 mV sec^{-1} using C_{60}/GCE versus Ag/AgCl

Ratio in 10 mL		1 (µA)		E(mV)	
Blood	0.1 M KCl	Ipa	Ipc	Epa	Epc
1:	9	227	Nd	1161.0	Nd
1:	4	49	-28.7	745.7	844
1:	1	65	-28	870.0	810
4:	1	47	-14.3	860.0	696.5
9:	1	35	10.2	844.0	533

Table 4: Effect of different ratio (Blood: 0.1 M KCl) 0n the redox current and potential of 0.05 mM Mn^{2+} at scan rate 100 mV sec^{-1} using C_{60}/GCE versus Ag/AgCl

Ratio in 10 mL	I(uA)		E(mV)	
(Blood: 0.1 M KCl)	Ipa	Ipc	Epa	Epc
1:9	185.0	Nd	1185.0	Nd
1:4	49.2	-22.5	784.0	827.6
1:1	65.6	-28.7	876.8	816.7
4:1	51.5	-15.4	871.0	636.5
9:1	31.3	Nd	855.0	Nd

Table 5: Recovery rate of 0.02 mM Mn^{2+} added in to blood at scan rate 100 mV sec^{-1} using CNT/GCE

No. of sample	Concentration of Mn^{2+} (mM)	Recovery rate (%)	Mean recovery (%)	Relative SD (%)
1	0.0205	102.5		
2	0.0199	99.5		
3	0.0198	99.0		
4	0.0195	97.5	99.6	2.09

Application studies: The recovery of Mn(II) in blood matrix at 0.02 and 0.03 mM was investigated at C_{60}/GCE and CNT/GCE. Excellent recovery of 99.0-99.6% with R.S.D. of less than 3% was obtained at both the modified GC electrodes (Table 5-8).

Table 6: Recovery rate of 0.03 mM Mn^{2+} added in to blood at scan rate 100 mV sec^{-1} using CNT/GCE

No. of sample	Concentration of Mn^{2+} (mM)	Recovery rate (%)	Mean recovery (%)	Relative SD (%)
1	0.0305	101.6		
2	0.0290	96.6		
3	0.0295	98.3		
4	0.0299	99.6	99.025	2.1

Table 7: Recovery rate of 0.02 mM Mn^{2+} added in to blood at scan rate 100 mV sec^{-1} using C_{60}/GCE

No. of sample	Concentration of Mn^{2+} (mM)	Recovery rate (%)	Mean recovery (%)	Relative SD (%)
1	0.0205	102.5		
2	0.0199	99.5		
3	0.0198	99.0		
4	0.0195	97.5	99.6	2.09

Table 8: Recovery rate of 0.03 mM Mn^{2+} added in to blood at scan rate 100 mV sec^{-1} using C_{60}/GCE

No. of sample	Concentration of Mn^{2+} (mM)	Recovery rate (%)	Mean recovery (%)	Relative SD (%)
1	0.0305	101.6		
2	0.0290	96.6		
3	0.0295	98.3		
4	0.0299	99.6	99.025	2.1

DISCUSSION

Effect of varying modified electrodes: Figure 3 shows that the redox peaks of Mn^{2+} was considerably enhanced by 4-5 times with about 400mV peak shifting towards a higher potential when CNT/GCE and blood as supporting electrolyte were used in comparison with C_{60}/GCE and GCE. Evidently, in blood, degree of sensitivity response towards the redox reaction of Mn(II) increases in the order of:

$$CNT/GCE > C_{60}/GCE > GCE$$

The redox peaks of Mn^{2+} appears more discernable when modified electrode is used as compared with bare GC electrode. The observation of the oxidation peak of Mn(II) in blood appears to be dependent on the volume ratio of 0.1M KCl as supporting electrolyte in relationship with the blood.

Effect of blood on redox Mn(II) using CNT/GCE: The effect of blood (mouse blood) on the redox reaction of Mn^{2+} was carried out by using different volume ratio of mouse blood to 0.1 M KCl in the presence of a known amount of Mn^{2+} .

The amount of blood presence appears to have an effect on the redox processes of Mn^{2+} as is evident when cv of 0.05 and 0.2 mM Mn^{2+} were studied in blood/KCl mixtures in the ratio of 1:9, 1:4, 3:7, 2:3, 1:1, 3:2, 7:3, 4:1 and 9:1 by 10 mL volume of blood to 0.1M KCl respectively. The oxidation peak of Mn^{2+} was undetectable in pure KCl and became detectable and more pronounced at +800 to +1000 mV in the presence of increasing amount of blood providing an alternative analytical peak of Mn^{2+}(see calibration study). It is noted that the increase in current was not proportional to the amount of blood presence (Table 1). There was a corresponding reduction peak appear in the range of +700 and +800 mV (Table 1). Based on the results summarized in Table 1 and 2, it shows the effect of blood on the redox processes of 0.05 and 0.2 mM Mn(II) by causing the oxidation peak of Mn(II) to increase significantly and peak shifting, It is therefore evident that the mouse blood appears to also exert an electrocatalytic activity on the reduction of Mn^{2+} through the modified electrode CNT/GC.

The voltammetric analysis of thus modified glassy electrodes reveals possibilities for driving redox reactions across the CNT in the blood and KCl electrolyte. The results suggest a transfer of electrons across the CNT mediated through the transitions of Mn^{2+} by presence of blood. The redox of Mn^{2+} in blood sample as a supporting electrolyte gives a good results as shown in Fig. 4. The more oxidizable species of Mn(II), most probably in the form of Mn(II)-L complex species could be due to the interaction of Mn(II) with the functional groups (L), such as those presence in hemoglobin,, complex amino acids, hormone of the blood.

The detection limit of the method based on CNT modified glassy carbon electrode for the determination Mn^{2+} solution was found from 0.01-0.1 mM as in Fig. 5.

Figure 6 shows the calibration curve of current vs. Mn^{2+} concentration ranging from 0.01-0.03 mM in the blood sample produces a good linearity with R^2 = 0.9929 of high sensitivity response.

Effect of blood on Mn(II) using C_{60}/GCE: The study on the effect of blood (mouse blood) on the redox reaction of Mn^{2+} was carried out by using different ratio of mouse blood to 0.1M KCl (V:V) and a known amount of Mn^{2+} was spiked in to the solution.

The effect of blood on the oxidation and reduction of Mn^{2+} is clear when added 0.1 and 0.05 mM Mn^{2+} on different ratio of blood/KCl mixtures of (1:9, 1:4, 3:7, 2:3, 1:1, 3:2, 7:3, 4:1 and 9:1), (Table 3,4) similar CV behaviors of Mn^{2+} in the presence of varing amount of blood is also observed at C_{60}/GCE as those reported at CNT/GCE. In this case, C_{60} and blood appears to exist electrocatalytic effects on the redox reaction of Mn^{2+} especially the oxidation process as show in Fig. 7.

Application studies:

Analysis of Mn(II) in blood Sample using CNT/GCE: The determination of Mn^{2+} concentration in Blood samples using modified GC electrode with CNT for oxidation peak as show in Fig. 4. Recoveries experiment were evaluated using direct calibration based on Fig. 5a and 5b.

The recovery of 99.6± 2.09% was obtained after the addition of 0.02 mM Mn^{+2} in to Blood sample as in Table 5 while recovery of 99.025±2.1% was obtained after the addition of 0.03 mM Mn^{+2} in to Blood sample as in Table 6.

Analysis of Mn(II) in blood sample using C_{60}/GCE: The determination of Mn^{2+} concentration in blood samples (mouse blood) using modified GC electrode with C_{60} for oxidation peak of Mn^{2+}. Recoveries experiment were evaluated using direct calibration of 99.6± 2.09% was obtained after the addition of 0.02 mM Mn^{+2} in to Blood sample as in Table 7 while recovery of 99.025±2.1% was obtained after the addition of 0.03 mM Mn^{+2} in to blood sample as in Table 8.

CONCLUSION

Voltammetric determination of Mn(II) ions in blood sample was studied using different modified glassy carbon electrode, whose surface was covered with microparticles of CNT and C_{60}. This determination was based on measurement of the charge of the redox peaks of Mn(II) ions formed on modified electrode surface in a KCl solution during a cyclic voltammetric analysis. In this method, depending on the redox current was evaluated the determination of low concentration of Mn(II) in blood samples. Here, the method was used CNT/GCE to determine the Mn(II) ions in blood with good results.

AKNOWLEDGEMENT

The authors wish to thank University Putra Malaysia and MOSTI for the provision of facilities and financial assistance.

REFERENCES

Abbaspour, A. and R. Mirzajani, 2007. A capillary zone electrophoretic method for simultaneous determination of 7th drugs in pharmaceuticals and in human urine. J. Pharm. Biomed. Anal., 44: 41-48.

Agui, L., P.Y. Seden and J.M. Pingarro, 2008. Role of carbon nanotubes in electroanalytical chemistry. Anal. Chim. Acta, 622: 11-47.

Arai K., F. Kusu, N. Noguchi, K. Takamura and H. Osawa, 1996. Selective determination of chloride and bromide ions in serum by cyclic voltammetry. Anal. Biochem., 240: 109-113.

Chevion, S., E.M. Berry, N. Kitrossky and R. Kohen, 1997. Evaluation of plasma low molecular weight antioxidant capacity by cyclic voltammetry. Free Radic. Biol. Med., 22: 411-421.

Chicharro, M., E. Bermejo, M. Moreno, A. Sanchez, A. Zapardiel and G. Rivas, 2005. Adsorptive stripping voltammetric determination of amitrole at a multi-wall carbon nanotubes paste electdrode. Electroanalysis, 17: 476-482.

Compton, R.G., R.A. Compton, D.J. Spackman, R.G. Riley and J.C. Wellington *et al*., 1993. Voltammetry at C_{60}-modified electrodes. Electroanal. Chem., 344: 235-247.

He, J.B., X.Q. Lin and J. Pan, 2005. Multi-wall carbon nanotube paste electrode for adsorptive stripping determination of quercetin: A Comparison with graphite paste electrode via voltammetry and chronopotentiometry. Electroanalysis, 17: 1681-1687.

Martinez, S., L. Valek, J. Rešetić and D.F. Ruzic, 2006. Cyclic voltammetry study of plasma antioxidant capacity: Comparison with the DPPH and TAS spectrophotometric methods. J. Electroanal. Chem., 588: 68-73.

Psotova J., J. Zahalková, J. Hrbac, V. Simanek and J. Bartek, 2001. Determination of total antioxidant capacity in plasma by cyclic voltammetry two case reports. J. Pharm. Biomed., 145: 81-83.

Roy, S., H. Vedala and W. Choi, 2006. Vertically aligned carbon nanotube probes for monitoring blood cholesterol. Nanotechnology, 17: S14-S18.

Wang, H.S., T.H. Li, W.L. Jia and H.Y. Xu, 2006. Highly selective and sensitive determination of dopamine using a Nafion/carbon nanotubes coated poly (3-methylthiophene) modified electrode. Biosens. Bioelect., 22: 664-669.

Wu, K., H. Wang, F. Chen and S. Hu, 2006a. Electrochemistry and voltammetry of procaine using a carbon nanotube film coated electrode. Bioelectrochemistry, 68: 144-149.

Wu, Y., S. Ye and S. Hu, 2006b. Electrochemical study of lincomycin on a multi-wall carbon nanotubes modified glassy carbon electrode and its determination in tablets. J. Pharm. Biomed. Anal., 41: 820-824.

Xiao, P., F. Zhao and B. Zeng, 2007. Voltammetric determination of quercetin at a multi-walled carbon nanotubes paste electrode. Microchem. J., 85: 244-249.

Xu, G.R. and S. Kim, 2006. Selective determination of quercetin using carbon nanotube-modified electrodes. Electroanalysis, 18: 1786-1792.

Zeng, B., S. Wei, F. Xiao and F. Zhao, 2006. Voltammetric behavior and determination of rutin at a single-walled carbon nanotubes modified gold electrode. Sens. Actuators B: Chemical., 115: 240-246.

Zhang, H. and K. Wu, 2005. Sensitive adsorption stripping voltammetric determination of reserpine by a glassy carbon electrode modified with multi-wall carbon nanotubes. Microchim. Acta, 149: 73-78.

Zhang, H., C. Hu, S. Wu and S. Hu, 2005. Enhanced oxidation of simvastatin at a multi-walled carbon nanotubes-dihexadecyl hydrogen phosphate composite modified glassy carbon electrode and the application in determining Simvastatin in pharmaceutical dosage forms. Electroanalysis, 17: 749-754.

Zheng, L. and J. Song, 2007. Voltammetric behavior of urapidil and its determination at multi-wall carbon nanotube paste electrode. Talanta, 73: 943-947.

Zhu, Y.H., Z.L. Zhang and D.W. Pang, 2005. Electrochemical oxidation of theophylline at multi-wall carbon nanotube modified glassy carbon electrodes. J. Electroanal. Chem., 581: 303-309.

Zhu, Y.H., Z.L. Zhang, W. Zhao and D.W. Pang, 2006. Voltammetric behavior and determination of phenylephrine at a glassy carbon electrode modified with multi-wall carbon nanotubes. Actuators B, 119: 308-314.