Int. J. Electrochem. Sci., 7 **(2012)** 7797 - 7808

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Sensor for Cobalt(II) by Modified Carbon Paste Electrode with Zn/Al-2(3-Chlorophenoxy)Propionate Nanocomposite

Illyas Md Isa[1,*], *Siti Nur Athirah Dahlan*[1], *Norhayati Hashim*[1], *Mustaffa Ahmad*[1], *Sazelli A. Ghani*[2]

[1]Department of Chemistry, Faculty of Sciences and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tg. Malim, Perak, Malaysia.
[2]Department of Mathematics, Faculty of Sciences and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tg. Malim, Perak, Malaysia.
[*]E-mail: illyas@fsmt.upsi.edu.my

Received: 18 July 2012 / *Accepted:* 14 August 2012 / *Published:* 1 September 2012

A new pencil-based renewable carbon paste electrode modified with Zn/Al-2(3-chlorophenoxy)propionate (Zn/Al-CPPA) nanocomposite was developed for the voltammetric determination of cobalt(II). The best voltammetric response was reached for an electrode composition of 7.5% Zn/Al-CPPA nanocomposite in the paste, 0.1 M sodium acetate of pH 8.0 and scan rate 100 mVs^{-1} in the voltammetric measurement. Under optimized conditions, a linear response to cobalt(II) was found in the ranges of $1x10^{-3}$ M - $1x10^{-8}$ M and detection limit of 1.26 $x10^{-8}$ M. High sensitivity and reproducibility, together with the ease of preparation and regeneration of the electrode surface by simple polishing, make the electrode very suitable for the voltammetric determination of cobalt(II) in water samples.

Keywords: Cyclic voltammetry, chemically modified electrode, Zn/Al-CPPA nanocomposite, cobalt(II)

1. INTRODUCTION

The quantitative determination of trace amounts of cobalt plays an important role in the field of environmental analysis, process control and medicine [1-3]. Moreover, food and drinking water are the largest sources of exposure to cobalt for the general population. Toxicological effects of cobalt include vasodilation, flushing and cardiomyopathy in humans and animals [4]. Since the concentration of cobalt is extremely low in various natural samples [5], a sufficiently sensitive and selective analytical procedure for the determination of cobalt would be of great interest. In the determination of trace cobalt, various methods including modern instrumental methods such as flame atomic absorption spectrometry (FAAS) [6-9], electrothermal atomic absorption spectrometry (ETAAS) [10,11], graphite furnace atomic absorption spectrometry (GFAAS) [12], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [13,14], inductively coupled plasma-mass spectrometry (ICP-MS) [15-17], spectrophotometric [18-21], ion selective electrode [22,23] and flow injection analysis (FIA) [24] have been used for the determination of metal ion in various media. However, most of these methods are time consuming and have high maintenance costs. In most common procedures for the determination of low concentrations of cobalt such as GFAAS, a preconcentration step is required. This technique usually involves the risk of sample contamination and loss of analyte during the several sample preparation steps involved [5,18].

A number of studies on the use of the chemically modified electrodes (CMEs) for analytical determinations of cobalt ions by voltammetric measurements have been reported such as adsorptive stripping by using hanging mercury drop electrode (HMDE) [25,26], adsorptive stripping by using carbon paste electrodes (CPE) [27], catalytic adsorptive stripping by using HMDE [28,5], catalytic-adsorptive differential pulse by using HMDE [29], adsorptive stripping by using integrated planar metal-film electrode [30] and adsorptive stripping by using bismuth film electrode [31].

However, most of these methods are mercury-based electrode which has negative environmental benefit. Among the studies made for the determination of cobalt, there has not been any work presented about the successful usage of the pencil-based renewable CME for cyclic voltammetry analysis.

The aim of the present investigation was to develop a new pencil-based renewable chemically modified electrode with Zn/Al-CPPA nanocomposite (Figure 1) as a mediator. The surface morphology of Zn/Al-CPPA shows an agglomerate and non porous structure in which the presence of the intercalated anion in the interlayer did not very much influence the morphology of the resulting materials.

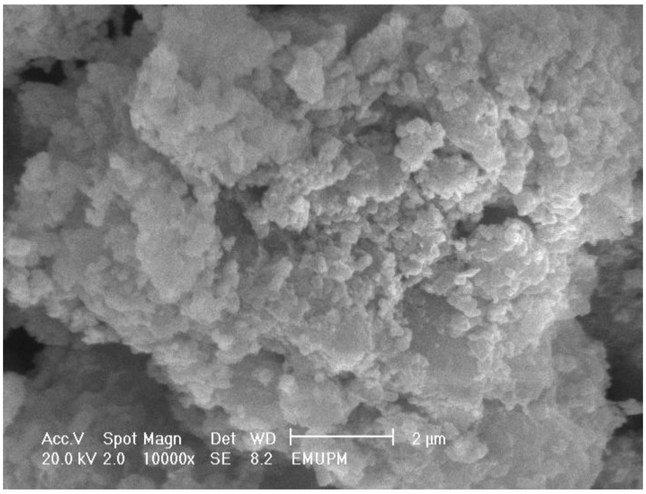

Figure 1. Scanning electron micrographs for Zn/Al-2(3-chlorophenoxy)propionate nanocomposite at magnification of 10 000 X

2. EXPERIMENTAL

2.1. Reagents and chemicals

A pencil lead, Noris 2B was obtained from Staedtler (Germany). Paraffin oil and acetic acid were obtained from Merck (Germany) without purification. Analytical grade of sodium acetate, sodium hydroxide and cobalt(II) chloride hexahydrate were obtained from Sigma-Aldrich (Switzerland). All other reagents and chemicals were of analytical grade reagent. The pHs of the solutions were adjusted to the desired value by adding acetic acid or sodium hydroxide. Distilled deionized water from EASYpure LF, Barnstead (USA) was used for preparing all of the solutions and throughout the experiments. The complex Zn/Al-CPPA nanocomposite was synthesized and purified as reported previously [32].

2.2. Apparatus and procedures

Cyclic voltammetry (CV) was performed with a Gamry Potentiostat Series- G750. All the experiments were carried out in a one compartment electrochemical cell with a carbon-paste working electrode (unmodified and modified), a saturated Ag/AgCl reference electrode and a Pt wire as the counter electrode. The three-electrode configuration was immersed in 25 ml buffer solution of different pH (as a supporting electrolyte) and known amount of Co(II) solution served as the measurement cell. The pH value was determined by using Orion, 915600, Mass. (USA) glass-pH electrode. Prior to any measurement, the solutions were deoxygenated by bubbling nitrogen gas purged through the solution for 30 min to remove the interfering oxygen gas during measurement.

2.3. Electrode preparation

A pencil lead was obtained by completely removing the wooden outer part. The pencil lead was transferred into a cellulose thimble and then placed into a soxhlet extractor for 24 h continuous reflux in methanol. Subsequently, the solid phase extracted pencil lead was washed by 0.1 M HCI and then thoroughly rinsed with water prior to 10 min ultrasonic cleansing. The pencil lead was later dried and grinded with mortar until fine. The modified carbon paste electrodes were prepared by substituting corresponding amounts of pencil lead powder (2.5%, 5.0%, 7.5%, and 10%) by Zn/Al-CPPA nanocomposite and then mixing with appropriate amount of paraffin oil and thoroughly hand-mixing in a mortar and pestle. The unmodified carbon paste electrode was prepared by adding graphite powder and paraffin oil (~75:25, w/w). Both modified and unmodified carbon paste electrodes were packed firmly into the Teflon rod with a hole at one end. Electrical contact was made with a copper wire through the centre of the rod. Before measurement the electrode was smoothened on a piece of weighing paper to get a smooth, uniform and fresh surface.

3. RESULTS AND DISCUSSION

3.1. Voltammetric behaviour of cobalt(II) on Zn/Al-CPPA nanocomposite modified CPEs

Cyclic voltammetry (CV) were performed to elucidate the catalytic activity of Zn/Al-CPPA nanocomposite modified electrode toward Co(II). Cyclic voltammograms were obtained at freshly prepared unmodified and modified pencil-based CPEs in 0.1 M sodium acetate buffer of pH 8.0 as shown in Figure 2.

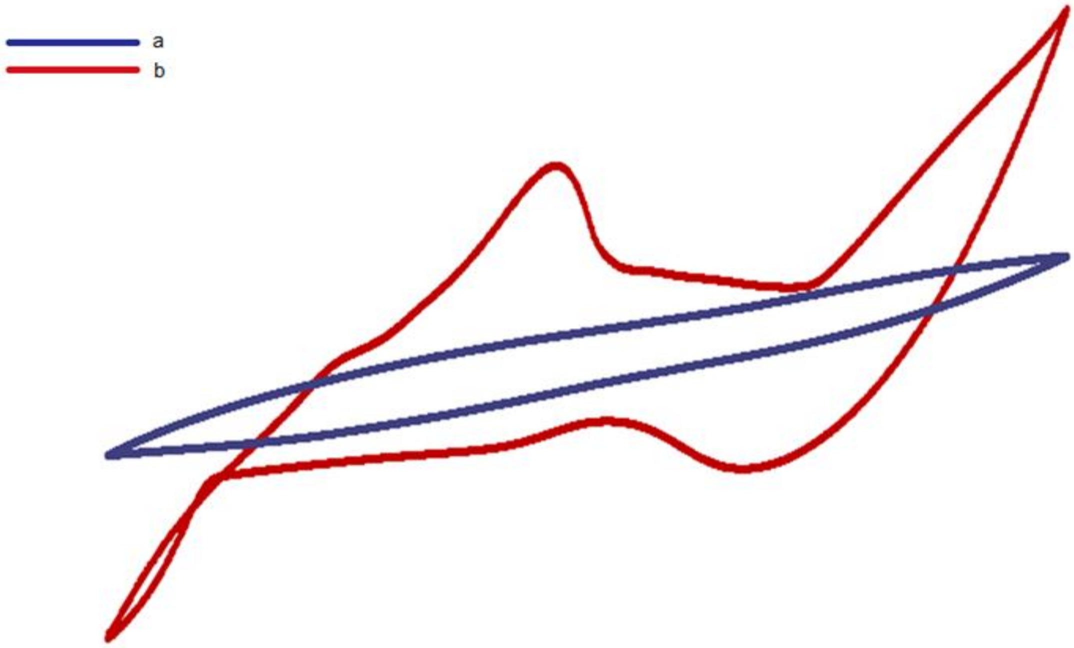

Figure 2. Cyclic voltammograms of (curve a) Zn/Al-CPPA nanocomposite modified carbon paste electrode (curve b) unmodified carbon paste electrode. Cobalt(II) concentration: 1 x 10^{-7} M; Potential range: -1.5 V to +1.5 V; Scan rate: 100 mV/s; Supporting electrolyte was 0.1 M sodium acetate buffer solution with pH 8.0

Owing to the complex properties [33,34] and the sluggishness of the kinetics of the electrode process [35], the CV of the unmodified electrode did not show any wave in the potential range used which result in weak responses because of large activation over potential. However, the voltammetric response is apparently improved at Zn/Al-CPPA nanocomposite modified electrode, reflected by the enlargement of the peak currents (i_p) on both cathodic and anodic peaks at -349.9 mV and 204.0 mV. On the basis of these observations, it can be postulated that the addition of Zn/Al-CPPA to the matrix of CPE exhibits an effective catalytic fashion in the electrochemical. The CV was run starting from -1.5 V to 1.5 V and back. The catalytic rule of the modifier causes the anodic over potential to be lowered and enhancement of the anodic peak current in the electrode process [35]. Based on the results obtained on the electrochemical behavior of Co(II) at the surface of Zn/Al-CPPA nanocomposite modified electrode, the following mechanism is represented for the electrocatalytic oxidation of Co(II) at the surface of modified electrode:

$$(Co^{2+})_{sol.} + (Zn/Al\text{-}CPPA)_{surf.} \longrightarrow (Co^{2+} - Zn/Al\text{-}CPPA)_{adsorb.}$$
$$(Co^{2+} - Zn/Al\text{-}CPPA)_{adsorb.} + 2e^{-} \longrightarrow (Co^{0}, Zn/Al\text{-}CPPA)_{adsorb.}$$
$$(Co^{0}, Zn/Al\text{-}CPPA)_{adsorb.} - 2e^{-} \longrightarrow (Zn/Al\text{-}CPPA)_{surf.} + (Co^{2+})_{sol./surf.}$$

3.2. Improvement of the electrode quality of CPE with the modification of CPPA nanocomposite

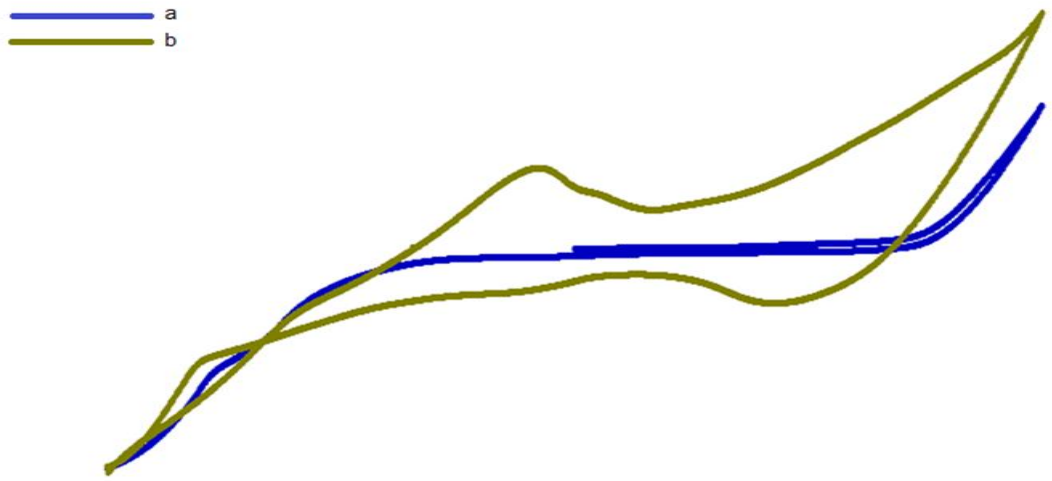

Figure 3. Cyclic voltammograms of (curve a) unmodified carbon paste electrode and Zn/Al-CPPA nanocomposite modified electrode (curve b) in blank supporting electrolyte at scan rate 100 mV s^{-1}

Figure 3 shows the cyclic voltammogram of Co(II) at modified and unmodified pencil-based CPEs in the blank supporting electrolyte. The result showed no anodic and cathodic peaks were observed at unmodified CPE. In contrast to the Zn/Al-CPPA nanocomposite modified CPE, the electrochemical signal on Co(II) showed low current response. This indicates that the surface property of the modified electrode has been significantly changed [33]. The separation of the peak potentials, $\Delta E = E_{pa} - E_{pc}$ increases, which is a characteristic for a quasi-reversible behaviour [36].

3.3. Effect of Zn/Al-CPPA nanocomposite modified CPE composition

The amount of Zn/Al-CPPA nanocomposite in the carbon paste had a significant influence on the voltammetric response, depending on the character of the modifying agent and its capability of forming enough active sites in modified paste group [37]. The anodic and cathodic peaks of cobalt have increased with Zn/Al-CPPA nanocomposite modified CPEs. This obviously indicates that the voltammetric response results from the accumulation of Co(II) at these electrodes by means of the complex formation reaction between the metal ion, Co(II), and the modifier, Zn/Al-CPPA nanocomposite. Four different modified carbon pastes (2.5%, 5%, 7.5%, and 10% Zn/Al-CPPA nanocomposite) were tested for their voltammetric signals under identical conditions (Figure 4). The sensitivity of pencil-based CPE was improved when the Zn/Al-CPPA nanocomposite composition in the paste was 7.5%, reflected by the higher peak current. Higher amount of Zn/Al-CPPA (>7.5%) decreased the peak current significantly. This is presumably due to the reduction of conductive area (carbon particles) at the electrode surface [38-42], leading to an unsuitable electrode for analytical uses. Therefore, an electrode containing 7.5% Zn/Al-CPPA nanocomposite was employed in all subsequent experiments.

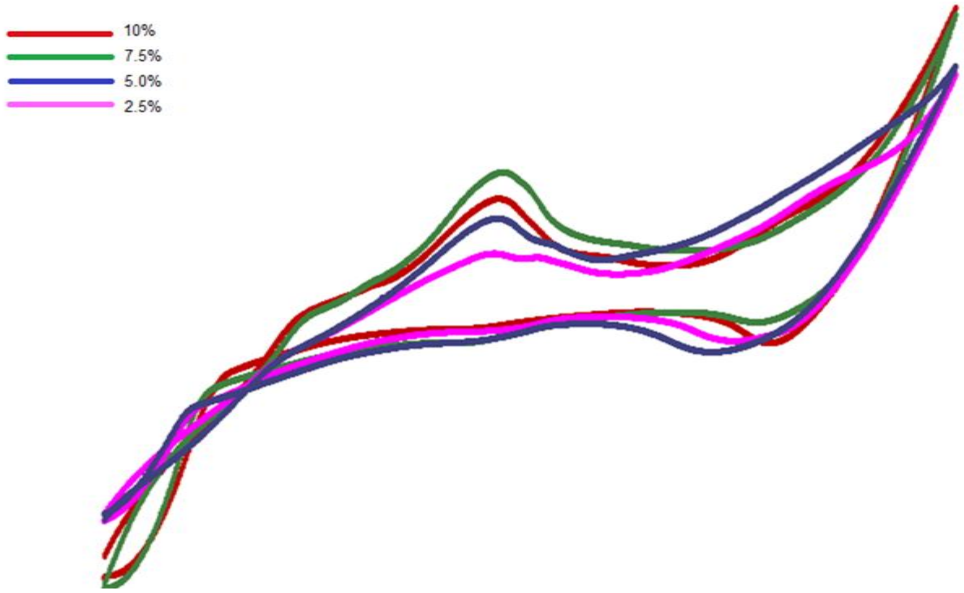

Figure 4. Cyclic voltammograms of four different modified carbon pastes (2.5%, 5%, 7.5%, and 10% Zn/Al-CPPA nanocomposite) at scan rate 100 mV s^{-1}.

3.4. Effect of regeneration of the Zn/Al-CPPA nanocomposite modified CPE

Table 1. The regeneration conditions of Zn/Al-CPPA nanocomposite modified CPE

Regeneration Condition	i_p (Co)/µA		i_p loss (%)^a
	Before regeneration	After regeneration	
Mechanical polishing	922.5	922.5	0
HCl	922.5	802.9	12.96
NaCl	922.5	791.7	14.18
H_2O	922.5	412.0	55.34
$NaNO_3$	922.5	406.7	55.91

[a] i_p loss (%) = $\frac{i_p \text{(before)} - i_p \text{(after)}}{\text{(before)}}$ 100

The regeneration of the electrode surface was tested with several cleaning solutions and mechanical polishing to renew the electrode after electrochemical measurement. The efficiency of the cleaning methods decreased in order as, mechanical polishing, HCl, NaCl, $NaNO_3$, H_2O, respectively (Table 1).

HCl solution regenerated the electrode surface, but the peak current of Co(II) decreased after regeneration. This is presumably due to the change of the surface properties of the electrode with acid solution. The regenerated electrode surface was saturated with excess of H^+ ions. Therefore, they prevented the effective preconcentration of Co^{2+} onto the electrode surface [43]. Other cleaning solutions did not clean the electrode surface completely and gave memory effects. The best cleaning efficiency and reproducibility were obtained with mechanical polishing without any memory effect. Under normal conditions, the electrode can be used for about 8 weeks.

3.5 Effect of pH and supporting electrolyte

The effect of the pH and type of supporting electrolyte on cyclic voltammetric signals of Co(II) was investigated. The influence of pH of the supporting electrolyte was studied by varying the pH in the range of 4.5-11.0. The Co(II) peak current as a function of pH is shown in Figure 5. The peak current increased gradually with increasing pH until the peak current reached a maximum value at pH 8.0 and then remained constant in the pH range of 8.5-10.0.

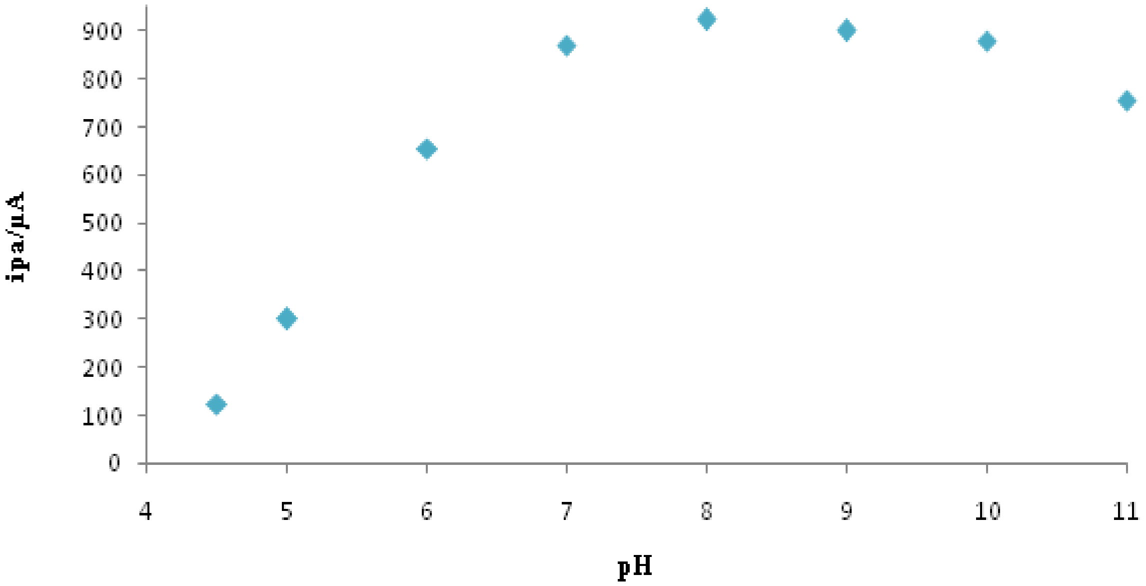

Figure 5. Effect of pH of supporting electrolyte on the peak current. Supporting electrolyte 0.1 M sodium acetate at scan rate 100 mV s^{-1}

The continuous increase of pH led to a decrease of peak current. This is due to the increasing complex formation of cobalt(II) with Zn/Al-CPPA nanocomposite at the electrode surface with increasing pH and the completion of complex formation at higher pH (>8) [44]. Thus, a pH of 8 was adopted for further studies. The effect of different type of supporting electrolyte such as potassium chloride, potassium nitrate, and lithium chloride on the modified CPE was investigated. The sensitivity and stability of the voltammetric responses showed a considerable decrease in all tested supporting electrolyte. The highest peak current and the best peak shape for oxidation of Co(II) complex were observed using sodium acetate (Figure 6). Therefore, 0.1 M sodium acetate of pH 8.0 was used for voltammetric measurement, respectively.

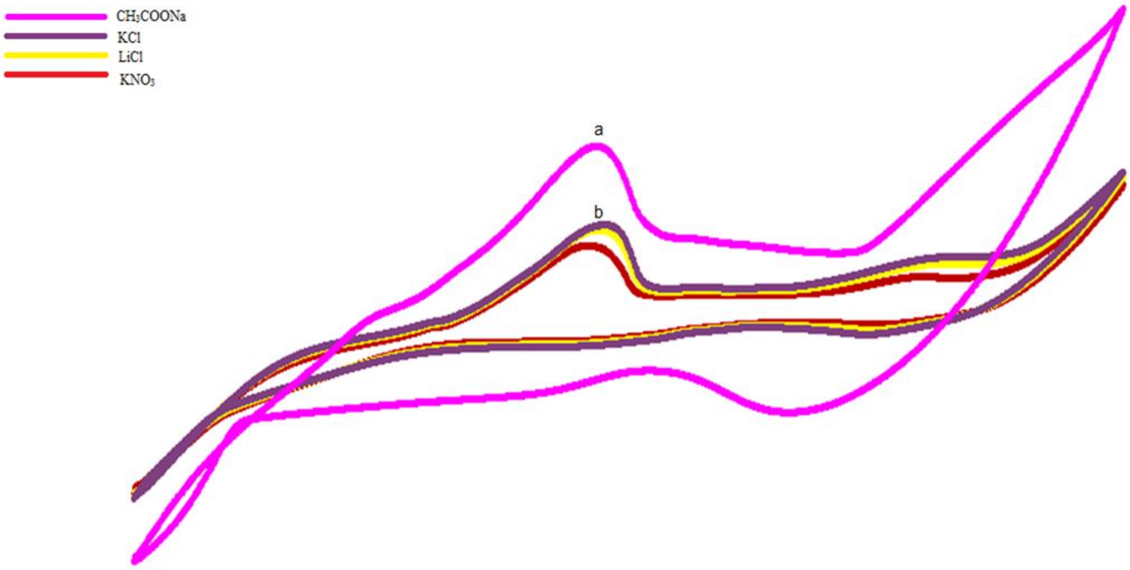

Figure 6. Cyclic voltammograms of 7.5% Zn/Al-CPPA nanocmposite modified electrode (a) in 0.1 M sodium acetate and (b) in 0.1 M potassium chloride, 0.1 M potassium nitrate, and 0.1 M lithium chloride at scan rate 100 mV s^{-1}

The effect of the concentration of sodium acetate, as a supporting electrolyte, was also studied in the range of 0.1-0.5 M keeping the pH at 8.0. When the measurements were performed in this supporting electrolyte, a smaller peak height and current were obtained when increasing the concentration of sodium acetate. This is presumably due to the fact that acetate ions form weak complexes with Co(II) [45] and therefore decreases the accumulation of Co(II) as a Zn/Al-CPPA nanocomposite complex at the electrode surface. The maximum and reproducible peak current of Co(II) was observed in a 0.1 M sodium acetate solution.

3.6 Effect of varying scan rates

The scan rate plays an important role on the sensitivity of the analysis. The variation of the potential scan rate showed that the anodic peak current increased linearly with the scan rate in the range of 10-100 mV/s. The plot of anodic peak currents vs. the scan rate (*v*) showed a very good correlation ($R^2 = 0.994$) as shown in Figure 7, which, indicates that the electron transfer is controlled by catalytic adsorption mechanism [46-48] and this is due to an enhancement of the mass-transfer rates of the metal ions to the electrode surface [49]. Such a behaviour is in agreement with the results reported for the electrocatalytic oxidation of sulfhydryl compounds on the surface of modified CPEs by phthalocyanine and schiff base complexes of cobalt [50,51]. The optimum condition conditions obtained are summarized in Table 2.

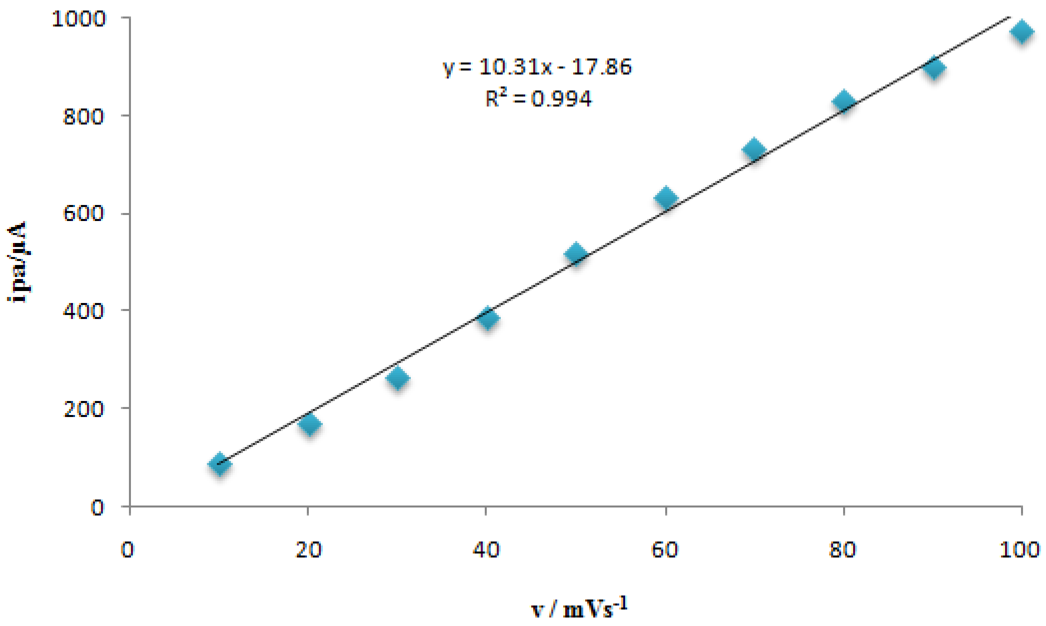

Figure 7. Effect of varying scan rates for carbon paste modified with Zn/Al-CPPA nanocomposite in 0.1 M sodium acetate buffer of pH 8.0

Table 2. Optimization of the experimental conditions of the CV method for the determination of Co(II)

Parameter	Parameter examined	Optimized parameter
Renewal of electrode	HCl, NaCl, H_2O, $NaNO_3$, Mechanical polishing	Mechanical polishing
Composition of CPPA nanocomposite modified CPE	2.5%, 5.0%, 7.5%, 10%	7.5%
Type of supporting electrolyte	CH_3COONa, KCl, KNO_3, LiCl	CH_3COONa
pH of supporting electrolyte	pH 4.5 - pH 11.0	pH 8.0
Concentration of supporting electrolyte	0.1 M - 0.5 M	0.1 M
Scan rate	10 to 100 mV/s	100 mV/s

3.7 Calibration curve

The effect of different concentrations of Co(II) was investigated in order to obtain the calibration curve. Standard solution containing different concentrations of Co(II) were prepared in pH

8.0 solutions. A linear calibration graph was obtained in the concentration range of 1x10^{-3} M - 1x10^{-8} M (R^2 = 0.989) as shown in Figure 8. The detection limit was found to be 1.26 x10^{-8} M. The effects of electrochemical method and working electrode used were investigated and summarized in Table 3. The results obtained compared favourably if not better than many other reported electrodes.

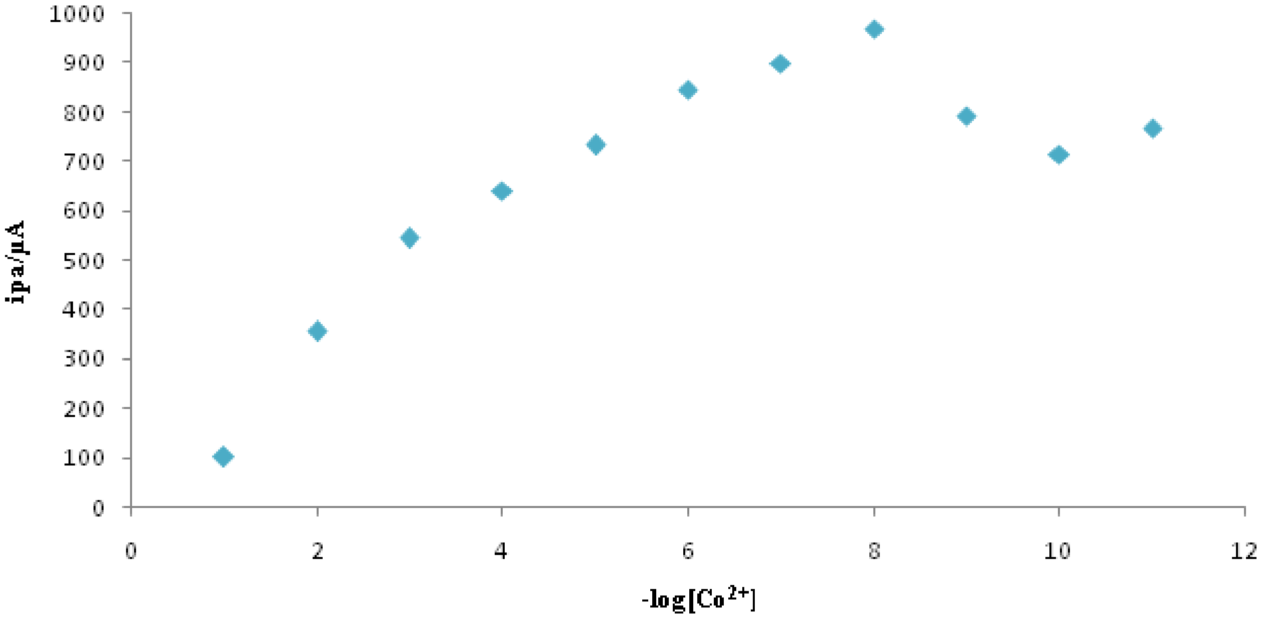

Figure 8. Plot of the anodic peak currents vs. Co(II) concentration

Table 3. Comparison of the proposed electrode with the reported electrodes

Reference number	Working Electrode	Concentration Range (M)	Detection Limit (M)	Electrochemical Method	Type of electrode
This work	Pencil-based renewable Zn/Al-CPPA nanocomposite electrode	1.0 x 10^{-3} - 1.0 x 10^{-8}	1.26 x10^{-8}	Cyclic voltammetry	Mercury-free electrode
52	Nitroso-S complex carbon paste electrode	1.871 x 10^{-4} - 3.3 x10^{-6}	1.8 x 10^{-6}	Adsorptive stripping voltammetry	Mercury-free electrode
53	Hanging mercury drop electrode	-	7.0 x 10^{-9}	Adsorptive stripping voltammetry	Mercury-based elecrode
54	Hanging mercury drop electrode	-	7.0 x 10^{-9}	Catalytic adsorptive stripping voltammetry	Mercury-based elecrode
26	Hanging mercury drop electrode	3.0 x 10^{-9} - 5.0 x 10^{-11}	1.7 x 10^{-11}	Adsorptive stripping voltammetry	Mercury-based electrode

3.8 Real samples analysis

The proposed method was applied to determine the presence of Co(II) in drinking water, mineral water and tap water samples (Table 4). The developed method was also validated with ICP-OES (Agilent 720 Axial, Australia) and the results obtained from the developed method were observed to be comparable with the ICP-OES method.

Table 4. Analysis of cobalt(II) in water samples by the proposed electrode and the ICP- OES (*n=3*)

Samples	**Cobalt(II)**	
	Proposed Zn/Al-CPPA nanocomposite modified electrode (ppb)	ICP-OES (ppb)
	40.1±0.3	41.5±0.3
	63.3±0.3	62.4±0.3
	22.1±0.3	21.8±0.2

4. CONCLUSIONS

A new pencil-based renewable chemically modified CPE has been developed using Zn/Al-CPPA nanocomposite for the determination of Co(II) by cyclic voltammetry. The modified electrode shows excellent sensitivity, low detection limit, broad working range together with non-toxic character. The proposed method was applied for the determination of Co(II) in various water samples and the result obtained were comparable with the ICP-OES method. Therefore, the electrode can be considered as an efficient voltammetric sensor for simultaneous determination of Co(II) in biological compound and water samples.

ACKNOWLEDGEMENT
The authors would like to thank the Universiti Pendidikan Sultan Idris for financial support (Grant No: 2011-0064-102-01).

References

1. M. Korolczuk, A. Moroziewicz, M. Grabarczyk, *Anal. Bioanal. Chem*. 382 (2005) 1678
2. M. Haij, S. Dadfarnia, K. Dehghan, *Talanta* 59 (2003) 719
3. A. Mohadesi, E. Teimoori, M.A. Taher, H. Beitollah, *Int. J. Electrochem. Sci*. 6 (2011) 301
4. S.R. Yousefi, S.J. Ahmadi, *Microchim. Acta*. 172 (2011) 75
5. A. Safavi, E. Shams, *Talanta* 51 (2000) 1117
6. N. Pourreza, M.R. Fathi, Z. Ardan, *J. Iran. Chem. Soc.,* 7 (2010) 965
7. M. Soylak, U. Divrikli, S. Saracoglu, *Environ. Monit. Assess* 127 (2007) 169
8. E. Kenduzler, A.R. Turker, *Int. J. Environ. Anal. Chem*. 86 (2006) 843
9. J. Chen, K.C. Teo, *Anal. Chim. Acta* 450 (2001) 215
10. N. Todorovska, I. Karadjova, S. Arpadjan, T. Stafilov, *Acta Pharm.* 53 (2003) 83
11. T. Stafilov, D. Zendelovska, *Acta Chim. Slov.* 47 (2000) 381
12. T. Minami, K. Atsumi, J. Ueda, *Anal. Sci.* 19 (2003) 313

13. M. Zougagh, P.C. Rudner, A.G. de Torres, J.M. Cano Pavon, *Anal. Bioanal. Chem.* 378 (2004) 423
14. K. Sreenivasa Rao, T. Balaji, T.P. Rao, Y. Babu, G.R.K. Naidu, *Spectrochim. Acta B* 57 (2002) 1333
15. L. Yang, Q. Wang, Z. Zhao, C. Yang, B. Huang, K. Tsunoda, H. Akaiwa, *Anal. Sci.* 17 (2001) 1105
16. A. Sarmiento Gonzalez, J.M. Marchante Gayon, J.M. Tejerina Lobo, J. Paz Jimenez, A. Sanz Medel, *Anal. Bioanal. Chem.* 391 (2008) 2583
17. T. Tanaka, Y. Ando, T. Saitoh, M. Hiraide, *J. Anal. At. Spectrom.* 17 (2002) 1556
18. E.K. Paleologos, M.I. Prodromidis, D.L. Giokas, A.Ch. Pappas, M.I. Karayannis, *Anal. Chim. Acta* 467 (2002) 205
19. B.R. Reddy, P. Radhika, J.R. Kumar, D.N. Priya, K. Rajgopal, *Anal. Sci.* 20 (2004) 2
20. G. A. Shar, G.A. Soomro, *The Nucleus* 41 (2004) 77
21. S.G. Prabhulkar, R.M. Patil, *Int. J. Chem. Sci.* 6 (2008) 1480
22. I.M. Isa, S. Mustafar, M. Ahmad, N. Hashim, S.A. Ghani, *Talanta* 87 (2011) 230
23. V.K. Gupta, A.K. Jain, M. Al-Khayat, S.K. Bhargava, J.R. Raisoni, *Electrochim. Acta* 53 (2008) 5409
24. J.M. Ruedas Rama, A. Ruiz Medina, A. Molina Diaz, *Anal. Bioanal. Chem.* 376 (2003) 527
25. P. Kajic, I. Milosev, B. Pihlar, V. Pisot, *J. Trace Elem. Med. Biol.* 17 (2003) 153
26. M. Korolczuk, A. Moroziewicz, M. Grabarczyk, K. Paluszek, *Talanta* 65 (2005) 1003
27. A. Mohadesi, E. Teimoori, M.A. Taher, H. Beitollah, *Int. J. Electrochem. Sci.* 6 (2011) 301
28. L. Husakova, A. Bobrowski, J. Sramkova, A. Krolicka, K. Vytras, *Talanta* 66 (2005) 999
29. Z. Gao, K.S. Siow, L. Yeo, *Anal. Chem. Acta* 320 (1996) 229
30. C. Kokkinos, A. Economou, M. Koupparis, *Talanta* 77 (2009) 1137
31. M. Korolczuk, A. Moroziewicz, M. Grabarczyk, *Anal. Bioanal. Chem* 382 (2005) 1678
32. M.Z. Hussein, N. Hashim, A.H Yahaya, Z. Zainal, *J. Exp. Nanosci.* 5:6 (2010) 548
33. E. Niranjana, B.E Kumara Swamy, R. Raghavendra Naik, B.S. Sherigara, H. Jayadevappa, *J. Electroanal. Chem.* 631 (2009) 129
34. J-B. Raoof, R. Ojani, H. Beitollahi, *Int. J. Electrochem. Sci.* 2 (2007) 534
35. S. Shahrokhian, L. Fotouhi, *Sens. Actuators, B* 123 (2007) 942
36. C.A. Borgo, R.T. Ferrari, L.M.S. Colpini, C.M.M. Costa, M.L. Baesso, A.C. Bento, *Anal. Chim. Acta* 385 (1999) 103
37. I. Svancara, K. Vytras, J. Barek, J. Zima, *Crit. Rev. Anal. Chem.* 31(4) (2001) 311
38. W. Huang, W. Hu, J. Song, *Talanta* 61 (2003) 411
39. S. Shahrokhian, M. Ghalkhani, M.K. Amini, *Sens. Actuators, B* 137 (2009) 669
40. G. Marino, M.F. Bergamini, M.F.S. Teixeira, E.T.G. Cavalheiro, *Talanta* 59 (2003) 1021.
41. C. Hu, K. Wu, X. Dai, S. Hu, *Talanta* 60 (2003) 17
42. K. Fanta, B.S. Chandravanshi, *Electroanalysis* 13 (2001) 484
43. S. Kilinc Alpat, U. Yuksel, H. Akcay, *Electrochem. Commun.* 7 (2005) 130
44. H. Alemu, B.S. Chandravanshi, *Anal. Chim. Acta* 368 (1998) 165
45. E. Shams, R. Torabi, *Sens. Actuators, B* 117 (2006) 86
46. G.A.M. Mersal, M.M. Ibrahim, *Int. J. Electrochem. Sci.* 6 (2011) 761
47. S. Chitravathi, B.E. Kumara Swamy, Umesh Chandra, G.P. Mamatha, B.S. Sherigara, *J. Anal. Chem.* 645 (2010) 10
48. S. Shahrokhian, Z. Kamalzadeh, A. Bezaatpour, D.M. Boghaei, *Sens. Actuators, B* 133 (2008) 599
49. S. Chuanuwatanakul, W. Dungchai, O. Chailapakul, S. Motomizu, *Anal. Sci.* 24 (2008) 589
50. S. Shahrokhian, A. Souri, H. Khajehsharifi, *J. Electroanal, Chem.* 565 (2004) 95
51. M.K. Halbert, R.P. Baldwin, *Anal. Chem.* 57 (1985) 591
52. A. Mohadesi, E. Teimoori, M.A. Taher, H. Beitollah, *Int. J. Electrochem. Sci.* 6 (2011) 301
53. P. Kajic, I. Milosev, B. Pihlar, V. Pisot, *J. Trace Elem. Med. Biol.* 17 (2003) 153
54. L. Husakova, A. Bobrowski, J. Sramkova, A. Krolicka, K. Vytras, *Talanta* 66 (2005) 999