Determination of Lead Using a Feather-Modified Carbon Paste Electrode by Anodic Stripping Voltammetry

[1]Elmer-Rico E. Mojica, [2]Jose H. Santos and [1]Jose Rene L. Micor

[1]Institute of Chemistry, University of the Philippines Los Baños, College, Laguna, 4031, The Philippines
[2]Department of Chemistry, University of Brunei Darussalam,
Bandar Seri Begawan, BE 1410, Brunei Darussalam

Abstract: A feather-modified carbon paste electrode has been examined for its ability to preconcentrate and determine trace levels of lead (II) in aqueous samples. The lead ions are preconcentrated on the modified electrode surface and then reduced and stripped off from the electrode surface. Different conditions like supporting electrolyte, pH, amount of feathers, preconcentration time, deposition time and deposition potential were optimized. The peak current was linearly dependent on the concentration of lead ions from 0.5 to 5 mg L^{-1}. The detection limit was determined to be 0.121 mg L^{-1} using optimized conditions.

Key words: Feather . electroanalysis . lead . carbon paste electrode

INTRODUCTION

Lead is one of the most common heavy metal ions in the environment. The determination of trace levels of lead in the environment is important because of its toxic effects on human health. Some of the methods used for the determination of lead are Atomic Absorption Spectrometry (AAS), Mass Spectrometry (MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). These methods have the advantages of excellent sensitivity, good selectivity and wide range of linearity. However, they also have drawbacks since longer waiting times and expensive instruments are required.

Chemically Modified Electrodes (CME) have been developed in recent years [1-3]. These electrodes have been used for electroanalysis of different analytes [3] because of their fast response, high selectivity, low detection limit and low cost. Carbon Paste Electrode (CPE) is one example of CME and was invented by Adams in 1958 [4]. This is prepared by mixing carbon powder with a suitable pasting (binding) liquid and a material known as modifier that improves the selectivity of the prepared electrode. Some of the modifiers used in carbon paste electrodes that have been developed for the determination of the lead ions includes alginic acid [5], poly (calyx [4] arene) [6] and

dibenzo-18-crown-6-ether [7] and moss [8]. These materials were used as modifiers because of the functional groups that they have which can serve as binding sites for lead ions.

Poultry chicken feathers representing about 6% of the total weight of a mature chicken are generated in huge quantities as a waste byproduct at commercial poultry plants that sometimes lead to environmental problems [9, 10]. Feathers are valuable protein source since it is the most abundant keratinous biomass in the world [11] and contain high amounts of water-insoluble fiber proteins known as keratin. Although feathers are deficient in certain essential amino acids [12], they contain other essential amino acids such as arginine and threonine [13, 14]. Feather waste has been used as feedstuff for poultry and livestock. In addition, chicken feathers have been used for the removal of heavy metals in wastewater [15] and industrial water [16]. Keratin was previously reported to be an effective modifier in a carbon paste electrode format for the detection of silver ions [17]. A preliminary study had shown that chicken feathers has been successfully used as component of a sensor called feathertrode to determine trace amounts of lead ions [18]. In this study, an improved version of a carbon paste electrode using chicken feathers as modifier was developed and applied to environmental samples.

Corresponding Author: Jose Rene L. Micor, Institute of Chemistry, University of the Philippines Los Baños, College, Laguna, 4031, The Philippines

MATERIALS AND METHODS

Reagents: Deionized distilled water obtained through a Barnstead E-Pure Deionizer was used all throughout the xperiment in the preparation of all solutions. The 1000 mg L^{-1} stock standard solutions of lead (Pb), an AAS-standard purchased from AJAX chemicals was used to prepare solutions of different concentrations.

Deactivated carbon powder and mineral oil were obtained from Sigma. Analytical grade hydrochloric acid, sodium chloride and sodium hydroxide pellets, all obtained from Ajax Chemicals were used for the preparation of supporting electrolytes (0.01 M HCl, 0.01 M NaCl and 0.01 M NaOH). Acetic acid (J.T Baker), sodium acetate (Merck), sodium phosphate (Ajax) and sodium biphosphate (Ajax Chemicals) were used in preparation of buffers with different pH.

Preparation of modifier: Poultry feathers were collected from a market in Blumentritt, Manila. The samples were washed with tap water, sun-dried and ground using a laboratory mill (Model 4). Ground samples were then oven-dried at 95°C to constant weight. The modified carbon paste electrodes were prepared by hand mixing graphite powder with the ground feathers and mineral oil until a paste is formed. A portion of the modified carbon paste was packed from the end of a plastic tube (diameter 2.5 mm) where a copper rod (2.5 mm diameter) was inserted to establish electrical contact.

Procedure: Most experiments were done using the preconcentration/medium exchange/voltammetry/ regeneration scheme. In the preconcentration step, the feather-modified electrode was immersed in the stirred sample solution for a given time at open circuit. The electrode was then placed in the three-electrode system containing supporting electrolyte for voltammetric measurement.

Voltammetric measurements were carried out in a three-electrode cell connected to a Metrohm 693VA processor. The three-electrode cell is consisted of Ag/AgCl as reference electrode, platinum as auxiliary electrode and the modified electrode as working electrode The processor was interfaced to a personal computer via a RS232 connection which converts the generated data into an ASCII format. The data obtained were then exported into the Microcal Origin version 5.

Cyclic Voltammetry (CV) was performed with both bare CPE and feather-modified CPE in a 0.01 M HCl solution. Optimization of parameters like supporting electrolyte, amount of modifier, pH, preconcentration time, deposition time and deposition potential was done using Differential Pulse Anodic Stripping Voltammetry (DPASV) analysis. During DPASV, the modified electrode was pre-concentrated under open circuit, rinsed with deionized distilled water and then connected to Metrohm 693VA processor for voltammetric measurements.

Multiple stripping was also performed by successive stripping of the electrode to see if the electrode surface can be stripped off of bound lead ions. The regeneration of the electrodes was also tested by soaking the used electrode in a 0.01 M EDTA. The time required to regenerate the electrode in EDTA was noted.

RESULTS AND DISCUSSION

The cyclic voltammograms of both the unmodified and feather modified Carbon Paste Electrodes (CPE) are shown in Fig. 1. The two cyclic voltammograms
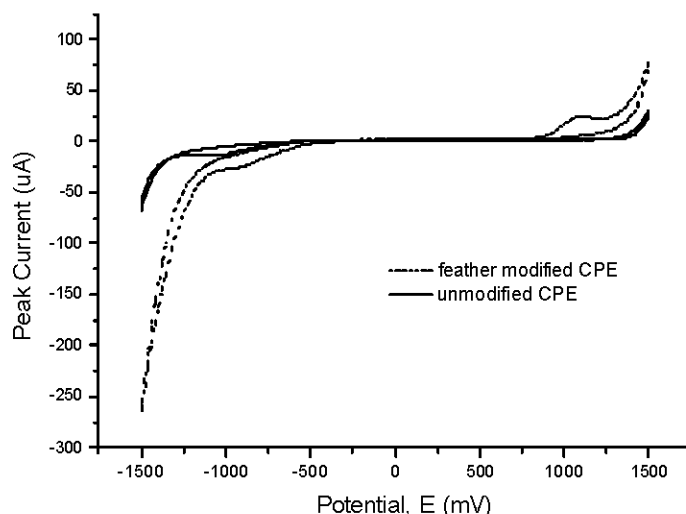

Fig. 1: Cyclic voltammograms of unmodified carbon paste electrode and feather-modified carbon paste electrode at potential ramp of-1500 mV to +1500 mV and scan rate of 100 mV s^{-1}
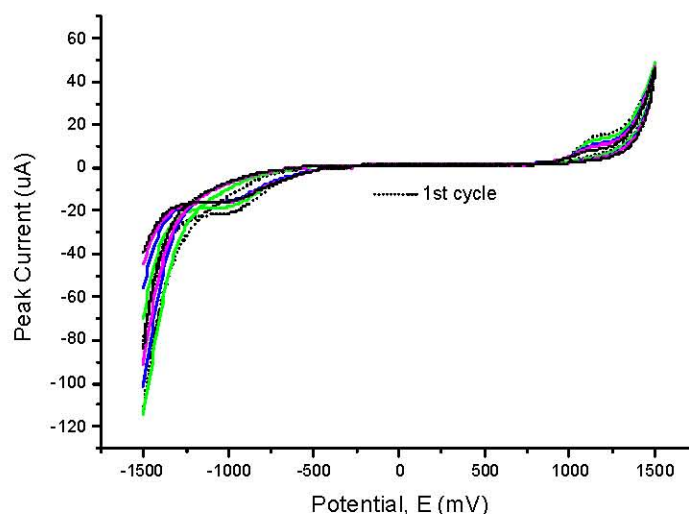
Fig. 2: Multiple cyclic voltammogram of a 15% (w/w) modifier at potential ramp of-1500mV to +1500 mV and scan rate of 100 mV s^{-1}
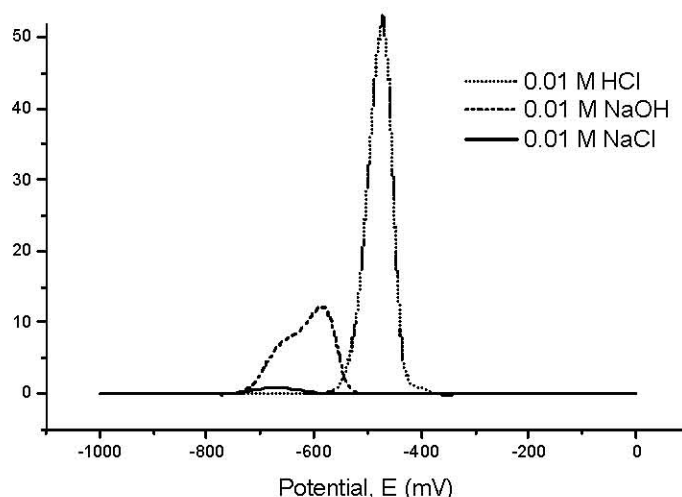

Fig. 3: Effect of different supporting electrolyte

showed that both electrodes are electroinactive at a reasonably broad potential range of approximately-1500 mV to +1500 mV and-900 mV to +1000 mV for unmodified and feather-modified CPE, respectively. There was also some indication that the modifier had undergone a slight redox reaction as exhibited by the broadening of the cyclic voltammogram and appearance of a small anodic peak at around +1100 mV and small cathodic peak at around-900 mV. It may be inferred that any current signal observed between-900 mV and +1000 mV during voltammetric analysis of an aqueous sample using feather-modified CPE can be attributed solely to the analyte of interest undergoing a redox reaction within this potential range.

Multiple cyclic voltammogram of a feather modified CPE is shown in Fig. 2. It shows a significant decrease in the charging current after a series of cycles. This observation could be attributed to the continuous removal of undefined water-soluble substances present on the electrode surface. Multiple cyclic voltammetry is very useful since it could increase the surface area of the binding site for the analyte by removing any impurities present in the modifier so as to eliminate any unnecessary matter adhering on the electrode surface. Thus, multiple cyclic voltammetry can be used as an effective preconditioning step to improve the current response of the modified electrode towards the analyte, which was brought about by the reaction of the analyte itself.
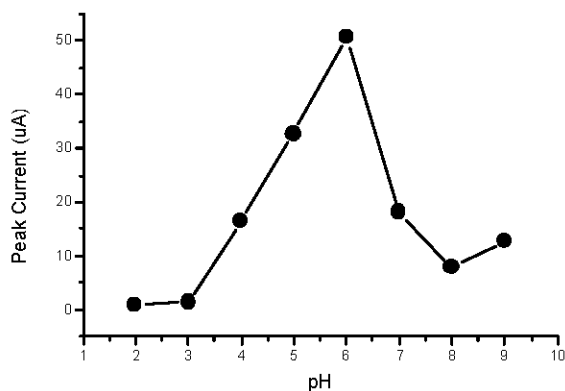
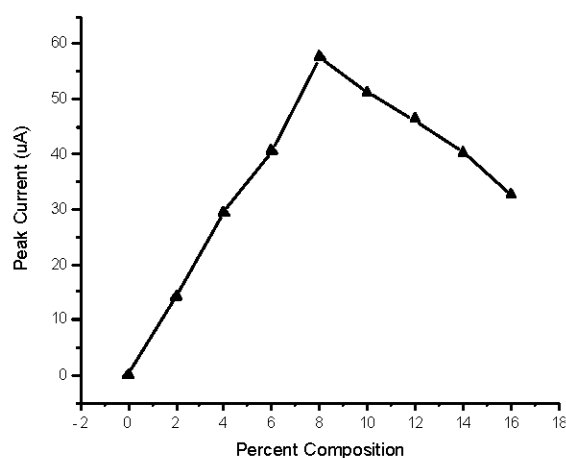Fig. 4: Effect of pH on peak current

Fig. 5: Effect of percent modifier

Anodic stripping voltammetry in differential pulse mode was then performed for the voltammetric analysis of lead ions. The effect of various supporting electrolytes on the voltammetric analysis of Pb (II) is shown in Fig. 3. The highest peak can be observed in 0.01 M HCl followed by 0.01 M NaOH and then by 0.01 M NaCl. Previous study made use of NaOH as supporting electrolyte [18]. Broad signal and poor sensitivity were observed using NaOH in comparison to those obtained using HCl. NaCl also exhibits very poor sensitivity as observed from the peak current response. HCl gave sharp and reproducible analytical signals for anodic stripping of Pb (II). This could be due to the presence of Cl⁻ion. Electrolytes containing acidic Cl⁻ion gave sharper and well defined peaks because acidic chloride ions are classified as better ligand for Pb (II) as compared to other ions [19]. The more acidic chloride ions in the solution, the more suitable is the supporting electrolyte.

pH: The effect of pH (adjusted using different buffers) on the preconcentration solution is shown in Fig. 4.
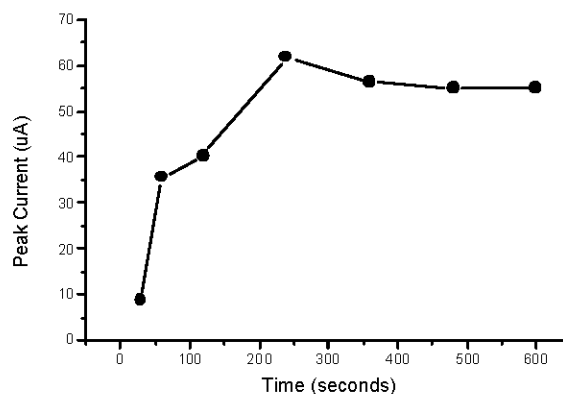

Fig. 6: Effect of preconcentration time on peak current using feather-modified carbon paste electrode

Results showed that the current peak decreased above pH 6 which could be due to the inability of the proton in the thiol group to dissociate making the complexation between Pb (II) and sulfur difficult. An increase in pH led to an increase in peak current up to pH 6.0. This is also the same with a study [20] which demonstrated that lead belongs to the first class of metals where metal ions can tightly bind and is rapidly bound at pH$\geq$5.0. Arrigan [3] also classified lead (II) as among those that are tightly bound at pH greater than or equal to 5 and not bound to pH values of 2 and below. This is also in agreement with the previous study using feathertrode and in addition to this, the present study have higher signals compare to the previous one.

Modifier concentration: The peak current increased upon increasing the amount of feather up to 8% (Fig. 5). The increase in peak current is due to the increase in the amount of modifier which provides additional sites for binding of lead ions. An increase in the amount of feather after 8% resulted to a decrease in current response since the amount of carbon was decreased, thus, sensitivity and conductivity of the modified carbon paste electrode also decreased.

Preconcentration time: The effect of varying the preconcentration time on the peak current response of the feather modified CPE is shown in Fig. 6. For short preconcentration times, the peak current increases linearly with increasing preconcentration time while for long preconcentration times, in this case above 8-10 minutes, it is expected that the peak currents will level off and attain a constant value because the electrode surface is already saturated with the metal. Prolonged period of stirring during the preconcentration process may also cause the surface to be agitated and this could cause the electrode surface to be damaged, which could result to an inconsistent peak current response.
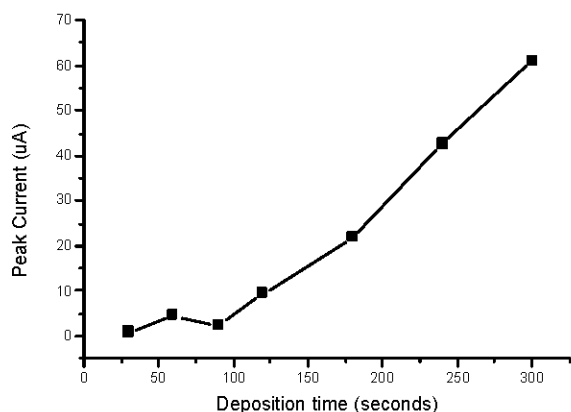
Fig. 7: Effect of increasing deposition time on peak current

Fig. 8: Effect of deposition potential on peak current

Deposition time: Deposition time is the amount of time required to convert or reduce Pb^{2+} to $Pb°$. The effect of deposition time on peak current is shown in Fig. 7. It shows that the peak current increases as the deposition time increases. This is because longer deposition time ensures maximum amount of the accumulated analyte that are reduced to its elemental form, consequently giving higher peak current response.

Deposition potential: The deposition potential is the value of negative potential that is applied into the electrochemical cell at which the accumulated metal on the electrode surface is deposited or reduced. It is the potential that is applied on the working electrode. Figure 8 shows the effect of deposition potential on the peak current response. The voltammogram shows an increase in peak current as the deposition potential is varied from-500 mV to-1500 mV. The peak current increases as more negative potential are applied. It is the expected trend for the analysis of the effect of deposition potential on peak current because more lead ions, Pb^{2+} are reduced to its original metallic form, Pb^{0}.

Regeneration: It is important to determine the extent by which electrodes can be re-used after analysis. Regeneration of the modified electrodes are typically done using cleaning agents such as HCl and EDTA and by electrochemical means such as multiple anodic stripping to remove bound metal ions. Results in Fig. 9 shows after five strippings, no peak was observed which means that no significant amount of lead ions are attached on the electrode surface. This would indicate that multiple stripping would be an appropriate regeneration method to allow the re-use of the electrodes. In addition, regeneration seems to enhance the performance of the electrode as higher signal were obtained after the first and second regeneration. A cleaning reagent (0.1 M EDTA solution) was also used
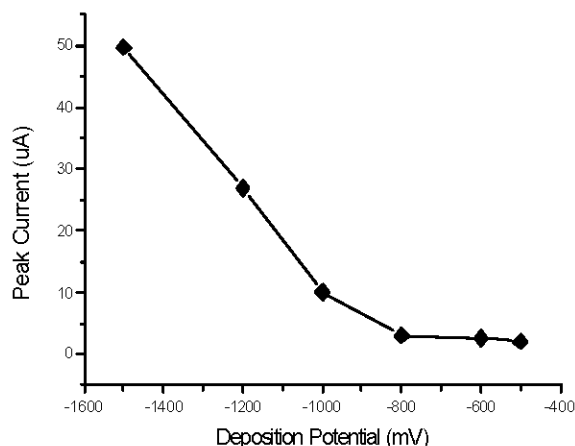
and it showed that the metal ions are removed after soaking the electrode for at least 20 minutes in the cleaning solution (data not shown).

Calibration curve: The calibration graph of peak current vs lead concentration in the range 0.5-10.0 mg L^{-1} is shown in Fig. 10. The calibration graph was linear over the range 0.5-5.0 mg L^{-1} Pb (II) and obeys the straight-line equation: I (uA) = 1.9617 [Pb (II)]+0.7791 with a correlation coefficient of 0.995. The plot shows non-linear behavior between 6.0-10.0 mg L^{-1}.

Reproducibility was illustrated by the precision obtained from a series of 10 readings using 1 mg L^{-1}. The mean peak current obtained was 2.77 μA with a range of 2.55-2.94 μA and a relative standard deviation of 4.45%. The detection limit was found to be 0.227 mg L^{-1}, a much improved one in comparison to the earlier feathertrode which have an LOD = 0.59 mg L^{-1}.

Interferences: Several other metal ions were examined for their possible interference in lead (II) analysis using the prepared electrode. The determination of a 10 mg L^{-1} Pb (II) using the optimized conditions was not affected by the presence of up to 100 mg L^{-1} of Cr (III), Cd (II), Zn (II), Co (II), Ni (II) Ca (II), Mg (II), Mn (II), Al (II) and Fe (III). However, the presence of Hg (II), Ag (I) and Cu (II) at 100 mg L^{-1} reduced the Pb(II) peak by 43.27%, 54.37% and 24.93%, respectively. No Pb (II) peak was observed when 300 mg L^{-1} of Hg (II) and 250 mg L^{-1} Ag(I) was used. From these results, the application of the modified electrode without interference is dependent on the sample matrix. However, these interferences can be eliminated by the use of masking reagents like KSCN and KCN [21].
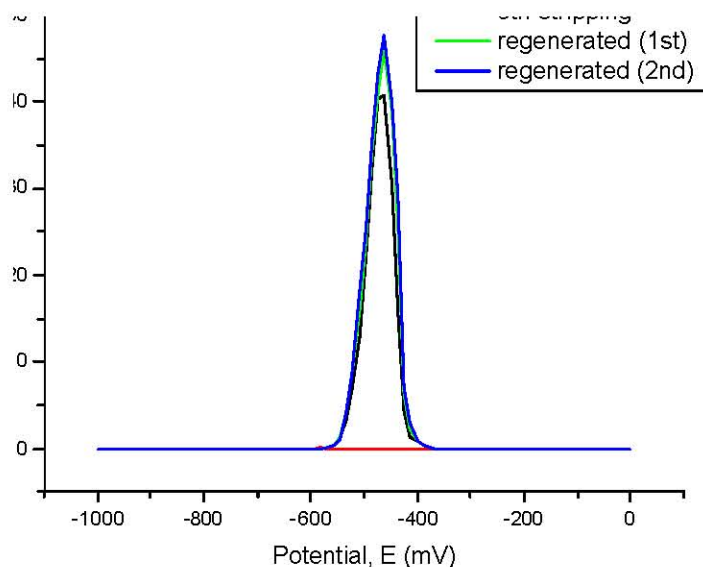
Fig. 9: Regeneration of feather-modified carbon paste electrode surface using multiple stripping
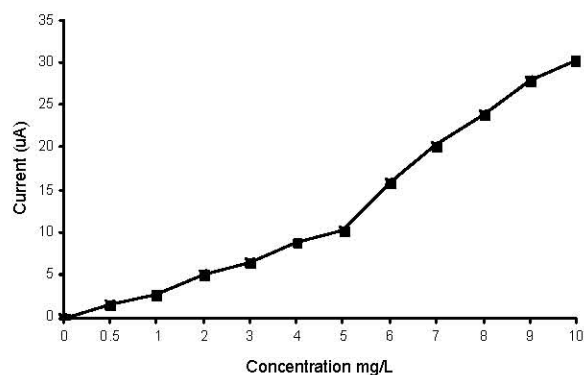

Fig. 10: Calibration graph of current versus lead concentration using optimized conditions

Fig. 11: Performance of feather modified CPE stored in different conditions

Application to lead ion determination: The determination of Pb (II) was carried out in both laboratory waste samples and river water samples. No pretreatment of samples to remove any matrix component was carried out in the analysis for lead content employing the feather modified CPE at optimized conditions. The determination was carried out in "spiked" samples (standard addition technique). Laboratory waste samples were found contain 26.64 ± 0.41 mg l^{-1}. Analysis of the same samples by graphite furnace AAS gave an average lead content of 27.83 ± 0.01 mg L^{-1}. The discrepancy could be due to the presence of other compounds in the samples. These compounds might also bind with the feather in the electrode and thus compete with the lead ions for the binding sites in the electrode.
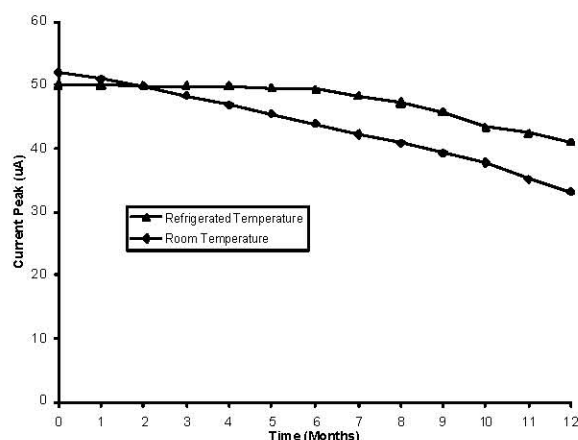
On the other hand, the river samples were found not to contain any lead ions using the feather modified CPE. This was confirmed by the results obtained using AAS. When these samples were spiked with 10 mg L^{-1} lead ions, the feather modified CPE gave a $9.85 + 0.15$ or 98.5% recovery while the AAS gave $100.2 + 0.01$ or 100.2% recovery. The agreement between the above results confirms the validity of the method for lead analysis in water samples.

Lifetime of bioelectrode: The shelf-life of the feather modified CPE was determined by storing in two conditions: one set in refrigerator and another set in a room temperature condition. The electrodes stored in refrigerator have the same signal (less than 1% change)

as newly constructed ones after five months of storage while for electrodes stored at room temperature, the performance of the electrodes began to deteriorate by more than 5% just after three months (Fig. 11). After a year of storage, the signal generated by the electrodes stored in room temperature is 36% less than the original. This is twice the signal loss by the other set of electrodes stored in refrigerator. This could be due to the denaturation of the modifier due to the effect of the other components present in the modifier mixture or due to temperature effect. The insolubility of feather in water may also be the reason for the stability of the electrodes. Unlike the other protein based modifier used [22], the protein in feathers are not dissolved either in the preconcentration solution or supporting electrolyte thus giving longer stability on the fabricated electrode.

REFERENCES

1. Urbaniczky, C. and K. Lundstrom, 1984. Voltammetric studies on carbon paste electrodes: The influence of paste composition on electrode capacity and kinetics. J. Electroanal. Chem., 176: 169-182.
2. Baldwin, R.P., J.K. Christensen and L. Kryger, 1986. Voltammetric determination of traces of nickel (II) at a chemically modified electrode based on dimethylglyoxime-containing carbon paste. Anal. Chem., 58: 1790-1798.
3. Arrigan, D.W.M., 1994. Voltammetric determination of trace metals and organics after accumulation at modified electrodes. Analyst., 119: 1953-1966.
4. Adams, R.N., 1958. Carbon paste electrodes. Anal. Chem., 30: 1576.
5. Wang, J., Z. Taha and N. Naser, 1991. Electroanalysis at modified carbon-paste electrodes containing natural ionic polysaccharides. Talanta, 38: 81-88
6. Arrigan, D.W.M., G. Svehla, S.J. Harris and M.A. McKervey, 1994. Use of calixarenes as modifiers of carbon paste electrodes for voltammetric analysis. Electroanal., 6: 97-106.
7. Prabhu, S.V., R.P. Baldwin and L. Kryger, 1987. Chemical preconcentration and determination of copper at a chemically modified carbon-paste electrode containing 2, 9-dimethyl-1, 10-phenanthroline. Anal. Chem., 59: 1074-1078.
8. Ramos, J.A., E. Bermejo, A. Zapardiel, J.A. Perez and I. Hernandez, 1993. Direct determination of lead by bioaccumulation at a moss-modified carbon paste electrode. Anal. Chim. Acta, 273: 219-227.
9. Dalev, P.G., 1994. Utiliziation of waste feathers from poultry slaughter for production of a protein concentrate. Bioresource. Technol., 48: 265-267.
10. Mohamedin, A.H., 1999. Isolation, identification and some cultural condition s of a protease producing thermophilic Streptomyces strain graon on chicken feather as a substrate. Intl. Biodeterioration. Biodegrad., 43: 13-21.
11. Onifade, A.A., N.A. Al-Sane, A.A. Al-Musallam and S. Al-Zarban, 1998. A review, potential for biotechnological applications of keratin-degrading microorganisms and their enzymes for nutritional improvement of feathers and other keratins of livestock feed resources. Bioresour. Technol., 66: 1-11.
12. Papadopoulos, M.C., A.R. El-Boushy and E.H. Ketelaars, 1985. Effect of different processing conditions on amino acid digestibility of feather meal determined by chicken assay. Poult. Sci., 64: 1729-1741.
13. Eggum, B.O., 1970. Evaluation of protein quality of feather meal under different treatments. Acta Agric. Scand., 20: 230-234.
14. Latshaw, J.D., N. Musharaff and R. Retrum, 1994. Processing of feather meal to maximize its nutritional value for poultry. Anim. Feed Sci. Technol., 47: 179-188.
15. Al-Asheh, S., F. Banat and D. Al-Rousan, 2003. Beneficial reuse of chicken feathers in removal of heavy metals from wastewater. J. Cleaner Prod., 11: 321-326.
16. Sayed, S.A., S.M. Saleh and E.E. Hasan, 2005. Removal of some polluting metals from industrial water using chicken feathers. Desalination, 181: 243-255.
17. Sugawara, K., H. Matsui, S. Hoshi and K. Akatsuka, 1998. Voltammetric detection of silver(I) using a carbon paste electrode modified with keratin. Analyst., 123: 2013-2016.
18. Mojica, E.R.E., A.B. Tocino, J.R.L. Micor and C.C. Deocaris, 2005. A feather-trode sensor for detecting lead ions. Philipp. J. Sci., 134: 51-56.
19. Bartlett, P.N., G. Denuarret and M.F.B. Souza. A study of the preconcentration and stripping voltammetry of Pb (II) at carbon electrodes. Analyst., 125: 1135-1138.
20. Gardea-Torresday, J., D. Darnall and J. Wang, 1988. Bioaccumulation and measurement of copper at an alga-modified carbon paste electrode. Anal. Chem., 60: 72-76.
21. Molina-Holgado, T., J.M. Pinilla-Macias and L. Hernandez-Hernandez, 1995. Voltammetric determination of lead with a chemically modified carbon paste electrode with diphenylthiocarbazone. Anal. Chim. Acta, 309: 117-122.
22. Mojica, E.R.E., S.P. Gomez, J.R.L. Micor and C.C. Deocaris, 2006. Lead detection using a pineapple bioelectrode. Philipp. Agric. Sci., 89: 134-140.