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Voltammetric Determination of Lead (II) Ions at Carbon Paste Electrode Modified with Banana Tissue

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Abstract: Banana tissue contains materials with functional groups which have the ability to form complexes with metal ions. With this property, banana tissue was used as modifier of carbon paste electrode for voltammetric determination of lead ions in aqueous samples. The use of 0.01 M HCl as supporting electrolyte and 20% (w/w) modifier gave an optimum current response for lead (II) solution. Accumulation time of 6 min, accumulating solution of pH 5, deposition time of 300 sec and deposition potential of -1500 mV were found to give the best results in the analysis of lead (II). Multiple stripping of the used electrode successfully removed lead ions for the regeneration of the electrode. The banana modified carbon paste electrode exhibited a sensitivity of 2.81 $\mu\text{A}/\text{ppm}$ and a limit of detection (LOD) of 0.10 mg L^{-1} .

Key words: Carbon paste electrode, banana tissue, lead, modifier

INTRODUCTION

Lead pollution is one of the most serious environmental problems because of its stability in contaminated site and complexity of mechanism in biological toxicity. Once absorbed by the body, lead can be accumulated and greatly threaten human health (Agusa *et al.*, 2006). Several sensitive methods for lead determination in trace amount have received much attention and many techniques have been employed for lead determination. The most commonly used methods for the determination of various metal ions are atomic absorption spectrophotometry (AAS) (Mhaske *et al.*, 2006), atomic emission spectrometry (AES) (Xu *et al.*, 2007) and mass spectrometry (MS). However, these techniques have some disadvantages such as complicated operation, high cost of maintenance, expensive apparatus and requiring well-controlled experimental conditions.

Electrochemical method is one of the most favorable techniques for the determination of heavy metal ions including lead (II) because of its low cost, high sensitivity, easy operation and the ability of analyzing element speciation. Stripping voltammetry at the mercury electrode is a well established technique for the determination at low levels of different metal ions. However, mercury electrodes have the disadvantage of being mechanically unstable during various steps of the assay procedure, thus they are less desirable than solid-state sensors in routine field applications (Wang *et al.*,

1995, 1997). In addition, mercury-based electrodes have issues related to the use and disposal of toxic mercury.

On the other hand, in adsorptive stripping voltammetry (AdSV), preconcentration at an electrode modified with functional ligands uses the specific binding properties of the ligand (towards the target metal ions) to accumulate the metal ions via ion exchange or chelation onto the electrode without applying any potential. In addition to being solid-state and mercury-free, this technique has several advantages: (1) it can preconcentrate metal ions that cannot be reductively accumulated (2) electrolytes are not required in the preconcentration solution, thus reduces the risk of introduction of contaminants or competing ligands and (3) with the appropriate ligand, the overall selectivity of the analysis for the targeted metal is greatly enhanced. There have been many studies that made use of plant tissues as source of ligands (Chen and Tan, 1995; Wang and Lin, 1988). The use of tissue slices as catalytic layers is very attractive because of their high stability, high level of activity and low cost compared to the use of isolated enzymes. Tissue based electrodes are usually prepared by physically retaining the biocatalysts with a support membrane. Plant tissues such as banana, potato, apple, (Sidwell and Reichnitz, 1985; Wang and Lin, 1988; Chen and Tan, 1995; Li *et al.*, 2004) have been used in tissue based electrodes for the determination of dopamine. In this study, banana tissue was used as source of ligands to modify the surface of carbon paste electrode with the main goal of using it as a binding

material of modifier for the heavy metal lead. Banana tissue was mixed with carbon powder and packed in a plastic tube and used as a working electrode for the voltammetric determination of lead in aqueous samples similar to the study reported by Mojica *et al.* (2006) where in pineapple peelings were used instead.

MATERIALS AND METHODS

Place and date of study: The study was conducted at the Institute of Chemistry, University of the Philippines Los Baños, College, Laguna, Philippines. Preliminary studies were done starting May 2004. The validation and application studies were done by the last quarter of 2006.

Reagents: Deionized distilled water was used all throughout the experiment. The 1000 ppm stock standard solutions of Pb, an AAS-standard purchased from AJAX chemicals was used to prepare the solutions. Deactivated carbon powder, mineral oil and sodium acetate were obtained from Sigma Aldrich Co. (St. Louis, Mo., USA). Analytical grade of hydrochloric acid, sodium chloride and sodium hydroxide, sodium phosphate and sodium biphosphate were from Ajax Chemicals. Acetic acid was purchased from J.T Baker.

Preparation of banana modified carbon paste electrode: The modified carbon paste electrode (CPE) was prepared by making a homogenous paste with various amounts of banana tissue and carbon powder (100 mg). Twenty microliter of mineral oil was added as binder. The paste mixture was firmly packed inside a 3 mm polyethylene tube, which is in contact to a copper wire.

Voltammetry: All voltammetric measurements were done on the Metrohm 693 VA Processor. The Metrohm is connected to a three-electrode system which was made up of the working electrode (modified CPE), the auxiliary electrode (platinum wire) and the reference electrode (Ag/AgCl electrode). The voltammetric data processed on the Metrohm are displayed on the computer via the RS232 interface. The computer has 693 VA back up software compatible with the Metrohm output data.

Experiments were done using the accumulation/medium exchange/voltammetry/regeneration scheme. In the accumulation step, the modified CPE was immersed in a stirred lead ion solution for a given time at open circuit. The electrode was then placed in the three-electrode system containing supporting electrolyte for voltammetric measurement. Cyclic voltammetry was performed with both unmodified CPE and the banana modified CPE in a

0.1 M HCl solution. A potential range of -1500 to 1500 mV was applied and reversed. Scan rate of 100 mV/s was used in the analysis.

For differential pulse anodic stripping voltammetric (DPASV) analysis, the banana modified CPE was pre-concentrated under open circuit, rinsed with deionized distilled water and then connected to Metrohm 693VA processor. Optimization of parameters like electrode composition, supporting electrolyte, pH, accumulation time, deposition time and deposition potential was done by DPASV analysis. The regeneration of the modified CPE for possible reuse of the electrodes was performed by multiple stripping or continuous stripping of used electrode. Determination of figure of merits such as limit of detection, sensitivity, repeatability and reproducibility was also performed.

Application to real samples: Application of banana-modified CPE in real samples for the determination of Pb (II) content by DPASV was conducted using water samples from a lake, Laguna de Bay. Four sites of the lake namely Cabuyao, Los Baños, Sta. Cruz in Laguna province and Binangonan, Rizal serve as sampling sites. The four represents the north, west, south and east side of the lake. In addition to this, laboratory waste sample was also analyzed for lead ion content.

RESULTS AND DISCUSSION

Cyclic voltammetry: The first step in any electrochemical study involving characterization of a modified CPE is cyclic voltammetry (CV). CV is usually used to determine the potential window of the modified CPE. A modified CPE can only be utilized for analysis in a potential region that exhibits a constant or minimal current response (Gosser, 1993). The modified electrode must exhibit inertness in the potential region to make it useful in evaluating electroactive species.

Results of the CV conducted comparing an unmodified CPE with banana-modified CPE is showed broadening of the cyclic voltammogram in modified CPE (Fig. 1). This could be due to an inherent redox reaction occurring at a minimal in the modifier. Figure 2 showed the cyclic voltammogram of banana-modified CPE spiked with 1000 ppm of Pb²⁺. The anodic peak observed at approximately 500 mV was more defined than the cathodic, or the backward scan peak. This implied that differential pulse stripping voltammetry would give a better response if done through anodic scan. Differential pulse anodic stripping voltammetry (DPASV) confirmed that lead can be detected using the banana modified CPE and was used for the optimization of different parameters.

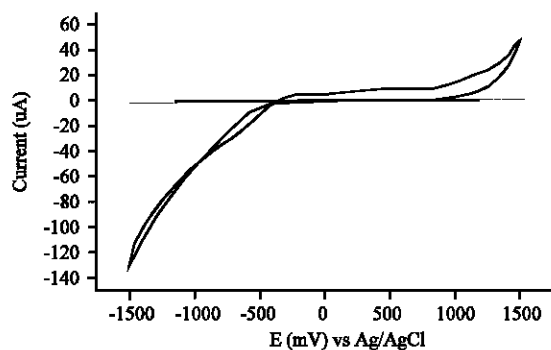


Fig. 1: Cyclic voltammogram of unmodified and banana modified-carbon paste electrode in 0.01 M HCl supporting electrolyte at a scan rate of 100 mV/s

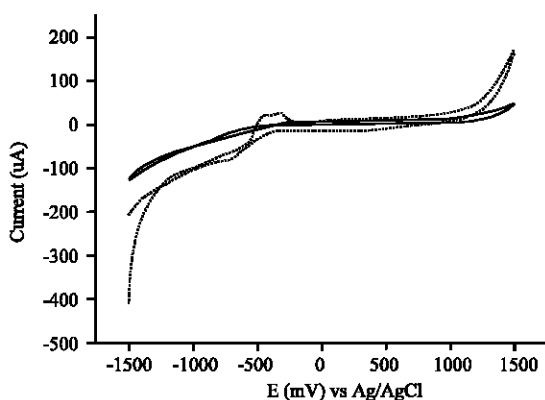


Fig. 2: Cyclic voltammogram of banana-modified CPE spiked with 1000 ppm Pb^{2+} with 0.01 M HCl as the supporting electrolyte

These results only showed that banana tissues contain materials modified the electrode surface and allowed the accumulation of Pb^{2+} . Banana was known to contain polyphenol oxidase, a copper-containing enzyme that had Cys-His linkage. Metals like lead might likely bind to SH functional group present in cysteine. It was also possible that the affinity of lead to banana tissues was due to other materials like other proteins aside from polyphenol oxidase. These proteins could contain amino acids or peptides that could serve as ligand for lead since they contain a great number of potential donor atoms through a peptide backbone and amino acid side chains (Gooding *et al.*, 2001).

Optimization: Supporting electrolyte. The supporting electrolyte or stripping solution serves to facilitate electrical conduction in solution. They are used to decrease the resistance of the solution, to eliminate electromigration effects and to maintain a constant ionic strength in controlled potential experiments (Wang, 1994). Supporting electrolyte usually influences mass transfer,

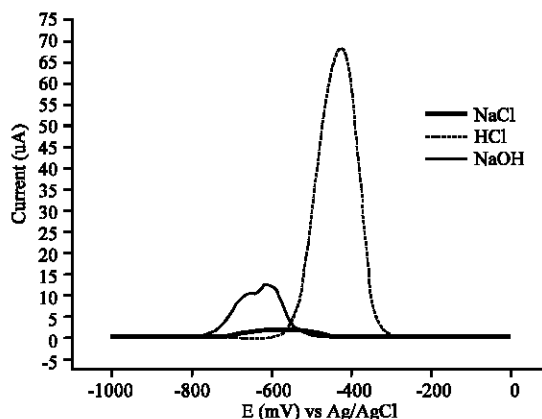


Fig. 3: Effect of 0.01 M supporting electrolytes on the voltammetric analysis of 100 ppm Pb (II) using banana-modified CPE at 2 min accumulation time

electrode reaction and chemical reactions for electron transfer (Vassos and Ewing, 1983). Electrochemical inertness, electrical conductivity, good solvent power, chemical inertness and convenient liquid range must be considered in choosing the appropriate supporting electrolyte (Fry, 1996). It must be carefully selected in order to avoid unwanted interferences during voltammetric runs.

Different supporting electrolytes (acid, base and salt solutions) were used in determining the appropriate supporting electrolyte. Low concentration (0.01 M) was used to avoid possible formation of complexes with the desired analyte. Results in Fig. 3 showed that HCl gave the best result among the three supporting electrolytes used. This electrolyte gave sharper and well-defined peak compared to NaOH and NaCl. This may be due to the characteristic of acidic chloride ions as better ligand for Pb (II) compared to OH^- ions. HCl has the ability to enhance the current due to the complexation reaction between Pb (II) and chloride giving an extra driving force for the oxidation. This was confirmed by a study done by Bartlett *et al.* (2000) involving the use of chloride media such as NH_4Cl and HCl in determining trace amount of heavy metals, the presence of species capable of complexing the metal ion formed during the anodic scan favors the oxidation reaction. This is in contrast to NaOH and NaCl, where the positive inert species, Na^+ , might compete in carrying the current (can also be oxidized or stripped) that could result to interferences. HCl was also found to be the best supporting electrolyte for the voltammetric determination of lead using CPE modified with orange peel essential oil (Elviña and Mojica, 2005) and pineapple peelings (Mojica *et al.*, 2006).

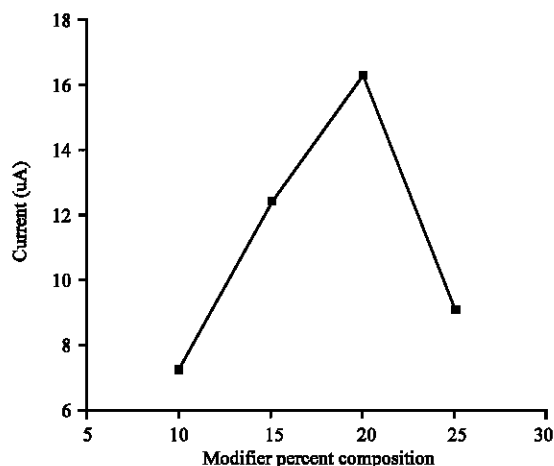


Fig. 4: Electrode composition. Scan rate of 40 mV/s and accumulation time of 2 min was employed. Deposition time and deposition potential employed were 30 sec and -1000 mV, respectively

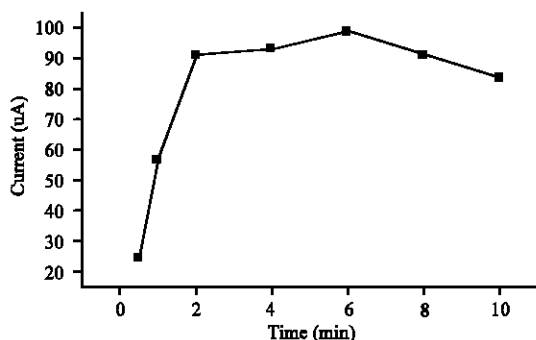


Fig. 5: Effect of increasing accumulation time on the electrode response of bananatrode

Electrode composition: The effect of banana to carbon powder ratio on the electrode response of banana-modified CPE was investigated using 10 to 25% (w/w) modifier. Figure 4 showed an increasing current response from 10 to 20% modifier by mass. This is due to a greater number of sites available for cation exchange with Pb (II) ions. The decrease in current peak observed using 25% of banana on the other hand is caused by less conductivity at the surface of the CPE since there is a larger amount of the modifier.

Accumulation time: The length of time that the electrode is exposed to the analyte solution to allow transport of lead ions towards the electrode is an important parameter. Linear relationship was observed initially till 5 min of accumulation time (Fig. 5). Afterwards, peak current started to decrease and this can be attributed to the saturation of the binding sites in the electrode surface

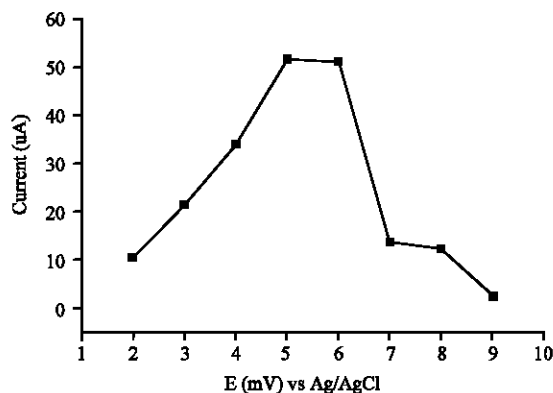


Fig. 6: Effect of pH of accumulating solution on the electrode response of bananatrode

with Pb (II) ions. In addition, longer accumulation time could also cause damages to the electrode surface that worsen the sensitivity and reproducibility of the measurements taken.

pH of the accumulating solution: The effect of pH on the electrode response of banana-modified CPE was determined using acetate and phosphate buffers. Figure 6 showed the ability of banana tissue to accumulate lead as a function of pH. It can be observed that peak current increases from pH 2 to 5 and decreases at pH higher than 5. Thus, optimum metal accumulation occurred at pH 5.0. Such behavior could be explained by postulating a lead adsorption process due to ionic exchange. Lead competed with protons for the negative charges of the carboxylic groups and hydroxyl groups present in polyphenol oxidase. pH values higher than 6 caused a decrease in peak current due to formation of hydroxylic lead complexes that prevent lead from incorporation to the electrode (Ramos *et al.*, 1993). On the other hand, an acidic pH resulted in an increase in peak current, since the protons' ability to displace lead from the binding positions is added to the ability of acetate to form complexes with lead. According to the analysis of Gardea-Torresdey *et al.* (1988), lead belonged to the first class of metal ions that are tightly and rapidly bound at pH greater than or equal to pH 5.0 and can be stripped at pH less than or equal to 2.0. Ions like Cu(II), Cd(II), Cr(III), Co(II), Al(III), Zn(II), Fe(III) and $UO_2(VI)$ also belonged to this class.

Deposition time: Deposition time is defined as the period of time needed to reduce Pb (II) ions back to its metallic state. The reduction takes place at the electrode while it is immersed in the supporting electrolyte. Figure 7 showed the dependence of peak current on deposition

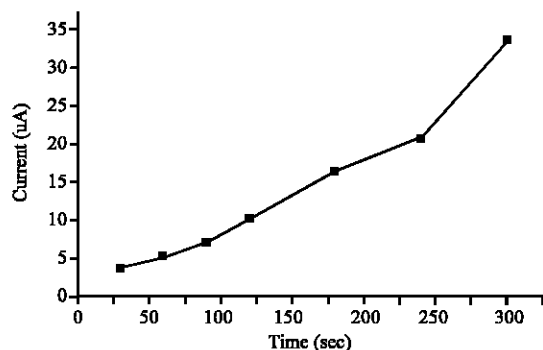


Fig. 7: Effect of deposition time on peak current response of banana electrode

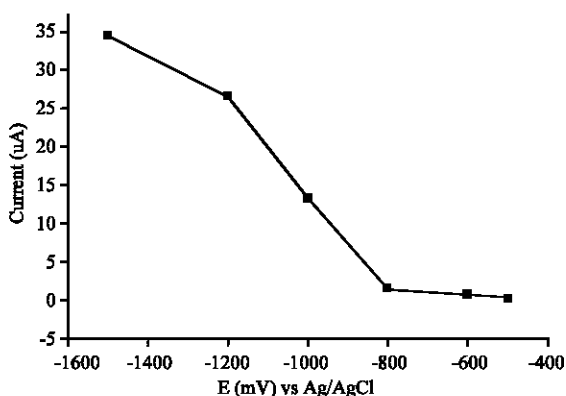


Fig. 8: Effect of deposition potential on peak current response of banana electrode

time of Pb (II). An increase in peak current was observed as the deposition time was increased. Increasing the deposition time would mean more time for the deposition of Pb (II) ions on the surface of the electrode.

Deposition potential: Deposition potential is the applied potential at which the accumulated metal on the electrode surface is deposited or reduced. A more negative potential was expected to give a higher current response because during deposition more lead ions, Pb^{2+} are reduced to its metallic form, Pb^0 . Figure 8 confirmed this trend as the most negative potential gave the highest peak current.

Regeneration of the electrode surface: One of the numerous problems of electroanalytical chemistry is the problem of forming the electrode surface, which possesses the required and reproducible properties (Brainina and Neyaman, 1993). The ability of the banana-modified CPE to be reused or regenerated was investigated by multiple stripping. Results showed that there is a gradual decrease in peak current height as the number of stripping increased (Fig. 9). The modified CPE

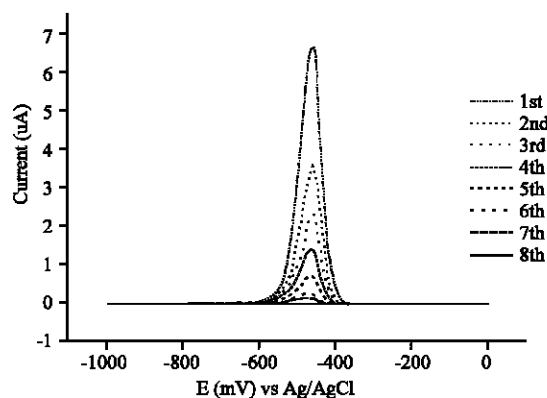


Fig. 9: Effect of multiple stripping on the electrode response of banana electrode

was successfully regenerated because Pb (II) ions bound to the electrode were removed from the electrode surface by successive stripping.

Figure of merits: The relationship between the peak current and the concentration was studied. The peak current was directly proportional to the concentration of lead ions in the range 1 to 20 ppm ($R = 0.9803$). Limit of detection (LOD) calculated based on signal-to-noise ratio (S/N) of 3:1, was found to be 0.10 ppm. This is much better than the LOD obtained from carbon paste electrode modified by feathers (0.59 ppm) (Mojica *et al.*, 2005) although higher than the one obtained using mercury film deposited on wax impregnated carbon paste electrode (1.12 ppb) (Sherigara *et al.*, 2007). The sensitivity of banana-modified carbon paste electrode, given by the slope of the concentration versus peak current response, was $2.81 \mu A \text{ ppm}^{-1}$. The coefficient of variation using 1 mg L^{-1} lead solution was calculated to be 6.7% ($n = 10$).

Application to real samples: The banana-modified CPE was applied to real aqueous samples using DPASV. The calculated Pb (II) concentration of water obtained from Cabuyao, Los Baños, Sta. Cruz and Binangonan was 0.78, 0.15, 0.51 and 0.53 ppm, respectively. Among the four sampling sites, sample from Cabuyao have the highest amount of lead. This is due to the presence of industrial plants near the sampling site. The results observed in other sites were also consistent with the presence of industrial plants near the sampling site. The sample from Los Baños gave the lowest lead content since this sampling site has the least number of industrial plants of the four sites sampled. On the other hand, the calculated Pb (II) concentration of the laboratory waste sample was found to be 3.61 ppm.

These results were compared with that obtained using atomic absorption spectroscopy (AAS). All the water samples from the lake were found to have a Pb (II) concentration of <0.01 ppm using the AAS method. There was a difference in the values obtained using the two different methods and this can be attributed to two methods having different sensitivities. However, the result on the laboratory waste sample using AAS method was 52.27 ppm, higher than that obtained using the modified electrode. The differences could be accounted on the nature of the method used. AAS has higher Pb (II) concentration since it determines the total lead content in a sample while DPASV determines only Pb (II) ions. In addition, the laboratory waste sample analyzed might contain several heavy metals that can compete with the lead thus reducing its peak current. Agraz *et al.* (1993) reported that the presence of other metals either enhances or decreases the peak currents of a certain metal present in the analyte.

CONCLUSIONS

Banana tissue was successfully used as modifier of carbon paste electrode (CPE). The banana-modified CPE was able to detect lead (II) ions in aqueous samples using DPASV. Optimization of parameters like supporting electrolyte, modifier concentration, pH of accumulation solution, accumulation time, deposition time and deposition potential was performed. Using the optimized parameters, the modified CPE was found to be linear in the range of 1 to 20 ppm and used to determine lead in real aqueous samples.

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