CHAPTER 4

DISCUSSION AND CONCLUSION

This work has illustrated the utility of treated-*Pennisetum* as surface modifiers for the determination of lead(II) by bioaccumulation at treated-*Pennisetum* modified carbon paste electrode. *Pennisetum setosum* was selected as an electrode modifier because of its strong affinity towards lead(II). By using chemical modifications, it can enhance the sorption capacity of *Pennisetum setosum*. Peak currents and slope of calibration curves were increased when treated-*Pennisetum* modified carbon paste was used as a working electrode. Ability of treated-*Pennisetum* to accumulate lead(II) was evaluated by atomic absorption spectrophotometry. The results indicate that treated-*Pennisetum* has strong affinity towards lead(II). Cyclic voltammetry was used to preliminary study of voltammetric properties of lead(II) on the electrode surface. It was seen a well-defined anodic wave between –0.600 to –0.450 volt and no peaks were observed upon subsequent scans. Therefore the anodic peak was chosen for lead(II) determination.

The effect of varying the electrolyte pH on peak current for determination of lead(II) at treated-*Pennisetum* modified (15% w/w) carbon paste electrode was studied by varying the pH of electrolyte solution in the range of 3.5-70. The results obtained are shown in Figure 3.4. The maximum peak current was obtained when the pH of electrolyte solution is 5.0. The variation in response is most likely due to the wide range of ligands and binding sites present in each treated-*Pennisetum*. The functional group most likely to be involved in binding is cellulose xanthate ($-CH_2OCS_2Na$). A rapid increase of the lead(II) response is observed upon increasing the pH between 3.5-5.0, reflecting the proton competition for active binding sites. At pH values higher than 5.0 cause a decrease in peak current due to formation of lead(II) hydroxy species that prevent lead(II) incorporation to the electrode.

The effect of varying the preconcentration time for 0.05, 0.1 and 1 ppm lead(II) solutions at the treated-*Pennisetum* modified (15% w/w) carbon paste electrode was studied by varying the preconcentration time in the range of 1-10 min. The results obtained are shown in Table 3.3 and Figure 3.5. A linear dependence of peak current on preconcentration time is established for all lead(II) concentrations. Short preconcentration times yield well-defined peaks for lead(II) at part per million (ppm) concentration level. The longer the preconcentration time, the more lead(II) is collected, and the larger the peak current is obtained. A leveling off was observed about 6 min for a 1 ppm lead(II) solution. Long preconcentration time permit lead(II) measurements down to the microgram concentration level.

The effect of various ionic strength on peak current for determination of 0.05 ppm lead(II) at treated-*Pennisetum* modified (15% w/w) carbon paste electrode was studied by varying the ionic strength of electrolyte solution in measurement cell over the range of 0.2-1.0. The results obtained are shown in Table 3.4 and Figure 3.6. The difference in peak current is due to the fact that, acetate in electrolyte solution forms weak complexes with lead(II), facilitating lead(II) dissolution from the electrode surface. In view of this result, acetate buffer with ionic strength of 0.60 was chosen as a supporting electrolyte, in order to obtain the highest analytical signal.

The effect of various paste composition on the peak current for determination of 0.05 ppm lead(II) at treated-*Pennisetum* modified carbon paste electrode was studied by varying the percentage of treated-*Pennisetum* in the range of 0-20 % (w/w). The results show that the best analytical response was obtained with the one containing 10 % (w/w) of treated-*Pennisetum*. A decrease in the signal at larger amount of treated-*Pennisetum* is probably due to the lowering of electrical conductivity. In addition lower percentages cause reduce of peak current. This behavior is probably due to a decrease of treated-*Pennisetum* on the surface of electrode.

The effect of various modulation amplitude on peak current for determination of 0.05 ppm lead(II) at treated-*Pennisetum* modified (10% w/w) carbon paste electrode was

studied by varying the modulation amplitude in the range of 20-160 mV. The results indicate that high peak current was obtained when modulation amplitude is 120 mV

The effect of various scan rate on the peak current for determination of 0.05 ppm lead(II) at treated-*Pennisetum* modified carbon paste electrode was studied by varying the scan rate in the range of 1-20 mV/s. The results show that the maximum peak current can be attained at the higher scan rate. Unfortunately, peak profile was not smooth when scan rate was high. Therefore the scan rate of 10 mV/sec was selected for the remainder of the experiments as the best compromise between the resulting signal and the peak profile.

The effect of various interference ions present in mineral waters was studied. A 0.05 ppm lead(II) solution was used for the preconcentration step, with increasing concentration of the interference until the usual concentrations in mineral water were reached. The preconcentration time was 5 min. The results show that cations of low concentration do not interfere. Such examples of those cations are iron(III) (1 ppm), copper(II) (0.05 ppm), mercury(II) (0.50 ppm), barium (II) (1 ppm), sodium (1 ppm) and potassium (5 ppm) do not interfere. However, cations of higher concentration could interfere the lead(II) signal because they are potentially competing for the binding sites with lead(II) ion. Therefore the peak current obtained from the lead(II) accumulated on the electrode is reduced.

For the measurement step, the best condition was acetate buffer pH, 5.0; ionic strength, 0.60; percentages of treated-*Pennisetum* on paste composition,10 % (w/w); scan rate, 10 mV/sec; modulation amplitude, 120 mV and preconcentration time, 5 min. The electrode surface can be regenerated by immersion the modified electrode in 0.05 M hydrochloric acid for 2 min. A calibration curve was linear over the range of 0.02-0.08 ppm lead(II) solution. The linear portion for treated-*Pennisetum* modified carbon paste electrode is characterized by a slope of 305.14 μA / ppm and correlation coefficient of 0.9975. By contrast, the linear portion for untreated-*Pennisetum* modified carbon paste electrode is characterized by a slope of 185.32 μA / ppm, and correlation coefficient of 0.9966. The relative standard deviation for treated-*Pennisetum* modified carbon paste

electrode was 5.39 % for a series of 16 measurements of 0.05 ppm lead(II) solution. The detection limit was 5 ng/ml (5 min preconcentration time). Long preconcentration time permit convenient measurements down to the microgram concentration level.

The method has been applied to determine lead(II) in mineral waters by standard addition method. To certify the correctness of the analytical method, mineral water samples were spiked with 0.05 ppm lead(II) standard solution and it was analyzed by the described method and by atomic absorption spectrophotometry. Agreement between both methods is achieved. This confirms the validity of the described method for lead(II) analysis in water samples.

In conclusion, the above results prove the feasibility of exploiting treated-*Pennisetum* for bioaccumulation of lead(II) solution. Such a use of treated-*Pennisetum* as a modifier in carbon paste matrix in connection with preconcentration/voltammetric measurement schemes provides an attractive analytical method for the determination of lead(II) in samples of mineral waters. Low detection limit and high selectivity are achieved. Besides, convenient operation and possible automation are expected utilizing an appropriate flow system. In addition, this concept could be extended to other plant-material/analyse system.