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Electrochemical Determination of Mercury at Trace Levels Using *Eichhornia Crassipes* Modified Carbon Paste Electrode

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A new carbon paste electrode modified with water hyacinth (Eichhornia Crassipes) was developed for the determination of mercury in aqueous sample using differential pulse anodic stripping voltammetry. First mercury was adsorbed on electrode surface at open circuit, following this the adsorbed mercury was determined by anodic stripping voltammetric scan from -0.5 to 0.5 V. Factors affecting sensitivity and precision of the electrodes, including amount of modifier, supporting electrolyte, accumulating solvent, pH of the accumulating solvent, accumulation time and scan rate were investigated. Optimized working conditions are defined as 5 % water hyacinth biomass of graphite powder, sodium hydroxide as supporting electrolyte, acetate buffer of pH 3 as an accumulating solvent and scan rate 50 mV/S. Linear calibration curves were obtained in the concentration range 400 μgL^{-1} to 800 μgL^{-1} of mercury for accumulation time of 10 min with limit of detection 195 μgL^{-1}. This technique does not use mercury and therefore, has a positive environmental benefit.

Keywords: Modified carbon paste electrode, mercury, anodic stripping voltammetry, water hyacinth

1. INTRODUCTION

Mercury one of the most important endocrine disrupters has been reported as poisonous to human body. Mercury can impair the human senses because it is a potent nerve toxin. Mercury evaporates readily and travels long distances in the atmosphere causing local and global pollution. Therefore knowledge of the mercury content in various matrixes, together with the development of fast, reliable and sensitive analytical methods for determination at trace level are mandatory[1].

The analytical techniques which are frequently used for the determination of mercury includes chromatography, spectro-photometry, cold vapor atomic absorption spectrometry, cold vapor atomic florescence spectrometry, inductively coupled plasma mass spectrometry [2-5]. Compared with the expensive optical detection method, electrochemical methods, particularly stripping voltammetry, have many advantages such as simple, economical and rapid for the practical trace analysis and suitable for onsite monitoring [6].

Generally mercury electrode is used in stripping voltammetry for the determination of trace levels of metal ions. However, mercury electrodes have the disadvantage of being mechanically unstable during various steps of the assay procedure. In addition, mercury based electrodes have issues related to the use and the disposal of mercury [7]. Hence, the electrochemical determination of heavy metals at low concentration with the use of modified electrodes has been in great demand. In recent years the construction and the application of modified electrodes have remarkable development. A common approach to modify an electrode is to attach host molecules which selectively interact with specific guest molecules [8]. Such type of electrodes utilizes chemical and biological modifying moieties such as tissues, extracts, ligands, redox mediators, algae and enzymes that can accumulate or complex metal ions. A few articles discuss the determination of mercury ion by modified electrodes [9-12].

Water hyacinth is an aquatic plant. Water hyacinth received considerable attention in metal removal because of its potential to remove the pollutants, when used as a biological filtration system [13]. Accordingly, the usefulness of the biomass of non-living water hyacinth in removing metal ions from solution was investigated recently[14,15]. On the basis of its high adsorption behavior shown by water hyacinth biomass it is assumed that it can be used as a modifier for preparation of carbon paste electrodes. In continuation of our work on plant modified carbon paste electrodes for metal determination [16] water hyacinth leaves were used as a modifier for preparation of the modified electrode for determination of mercury in aqueous sample.

2. EXPERIMENTAL

2.1 Materials

All chemicals were of analytical reagent grade. Carbon powder (< 20 µm) and mineral oil (light, density- 0.838) were purchased from Aldrich. 1000 mgL^{-1} stock solution of mercury was prepared by dissolving the appropriate amounts of nitrate salt (Merck). Working standards were daily prepared by suitable dilutions from the stock solution. Triply distilled water (Elga mili Q ultra pure, R=18 MΩ) was used throughout the experiment. Potassium chloride, acetic acid, sodium acetate, nitric acid, sulfuric acid, perchloric acid were purchased from Merck.

2.2. Instrumentation

Electrochemical experiments were performed using a µ Autolab Type III potentiostat (Ecochemie, Utrecht, Netherlands) controlled by a PC using the NOVA 1.7 software. A three-electrode system containing the metal sensor (constituted by mineral oil, graphite powder and water-hyacinth biomass), an Ag/AgCl (3.0 molL^{-1} KCl) and a platinum wire as working, reference and auxiliary electrodes respectively were used. Voltammetric measurements were carried out in an electrochemical cell of 50 ml capacity. Differential pulse voltammetry in anodic mode was used for metal estimation.

2.3. Preparation of biomass

Water hyacinth leaves were collected form Keetham Lake, situated at the west side of Agra, Uttar-Pradesh, India. Leaves were washed with water, chopped, dried at room temperature and grinded. Powdered material was passed through the sieve. The fraction of particle with size less than 150 µm was selected for electrode preparation. Prior to any experimentation, the ground water-hyacinth biomass was washed two times with 0.01 M hydrochloric acid to remove any metals that may be present on the biomass. The biomass was then washed two times again with deionized (DI) water to remove the acid prior to any further experimentation.

2.4. Modified Carbon Paste electrodes preparation

Unmodified carbon paste electrode (CPE) was prepared by mixing 100 µL mineral oil to 0.3 g carbon powder. Water hyacinth biomass modified carbon paste electrodes (WBMCPE) were prepared by substituting corresponding amounts of the carbon powder (2%, 3%, 4%, 5%, 6%, 7% and 8 % w/w) by the water hyacinth biomass followed by addition of the mineral oil and thoroughly hand-mixed in a mortar and pestle. The homogenized paste was packed in a glass tube (id 3mm) where a copper wire was inserted for electrical contact. The electrode surface was renewed by squeezing out a small amount of paste and polishing the tip on a photo paper to get the surface smoothed. All the prepared electrodes were stored in a desiccator and then used for analysis. Further they were kept in refrigerator.

3. RESULT AND DISCUSSION

3.1 Characterization of Modified electrode

Atomic force microscopic (AFM) images of unmodified CPE and WBMCPE are given in the figure 1a) and b). It is clear from the AFM data that WBMCPE surface is smoother then unmodified CPE. Surface of the WBMCPE is free from any structural defects. Average roughness data of the bare CPE and WBMCPE are given in the table 1.

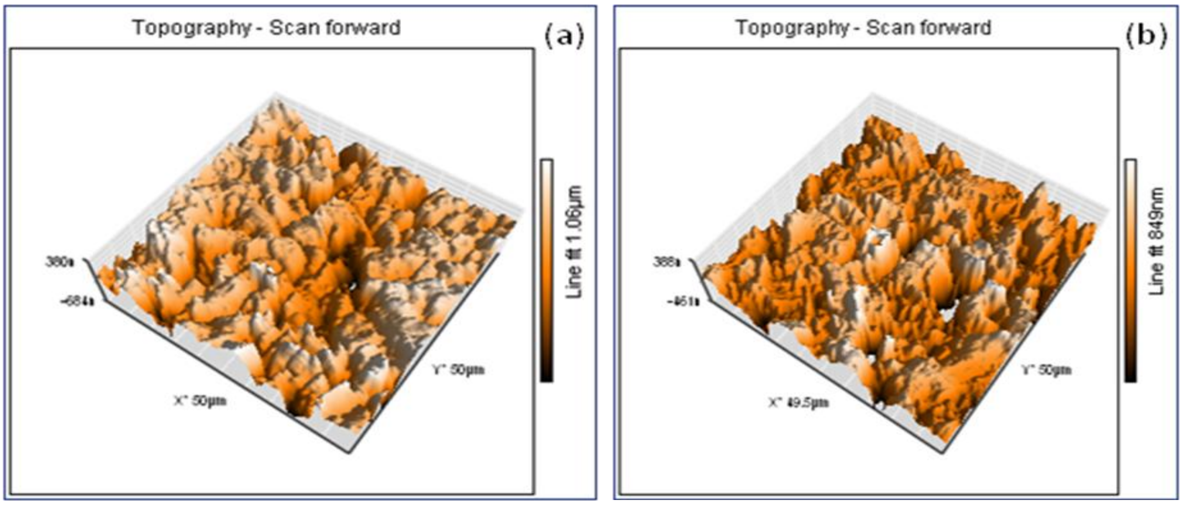


Figure 1. AFM images of unmodified carbon paste electrode a) and water hyacinth biomass modified carbon paste electrodes b)

Table 1. Average roughness of bare and modified CPE measured by AFM

	Unmodified CPE	Modified CPE
Average Roughness	195.79	160.36

3.2. Electrochemical characterization of WBMCPE

Cyclic voltammetry and Electrochemical impedance analysis was carried out to check the changes of the electrode behavior after modification. The experiment confirmed that the water hyacinth biomass was successfully assembled on electrode surface. Fig 2 shows CVs of unmodified and modified electrode in the solution of 5.0 mM $K_3[Fe(CN)_6]$.

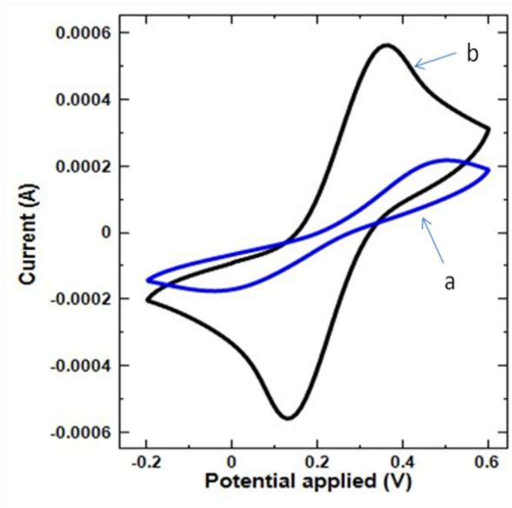


Figure 2. Cyclic voltammograms of unmodified a) and modified electrode b) in 5 mM $K_3[Fe(CN)_6]$ solution.

After modification the electrode, the current values of redox system were increased and the peak potentials difference decreased remarkably. Results of impedance analysis are also in accordance (Fig 3). Decrease in the resistance value was observed after modification of the electrode.

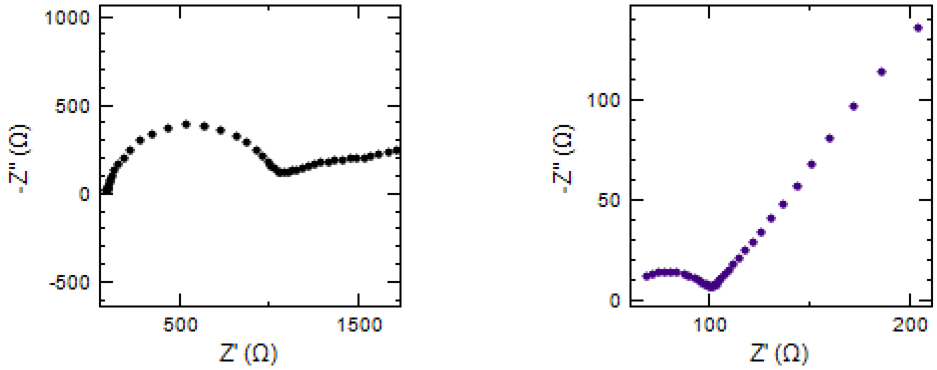


Figure 3. Nyquist plot of unmodified and modified electrodes in 5 mM $K_3[Fe(CN)_6]$ solution using electrochemical impedance spectroscopy.

Observed enhancement in the current value was due to the increase in the effective surface area. The effective surface area of the electrodes was estimated according to the Randles-Sevcik equation. $Ip = 2.69 \times 10^5 AD^{1/2} n^{3/2} \gamma^{½} C$ [17]

Where n is the number of electrons participating in the redox reaction, A is the area of the electrode (cm^2), D is the diffusion coefficient of the molecule in solution ($cm^2\ s^{-1}$), C is the concentration of the probe molecule in the bulk solution ($mol\ cm^{-3}$), and γ is the scan rate of the potential perturbation ($V\ ^{s-1}$). The effective surface areas of unmodified electrode and water hyacinth modified electrode employed in the present work were calculated to be 0.144 cm^2 and 0.226 cm^2 in $K_3[Fe(CN)_6]$ solution, respectively.

3.3. Electrochemical behavior of mercury on modified electrode

The electrochemical behavior of mercury on WBMCPE was evaluated using cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) and the results are shown in Figure 4 and 5. CV was used to determine the potential window and to investigate the extent of mercury uptake by the surface confined water hyacinth biomass at the modified carbon paste electrode (MCPE) after the accumulation of mercury at open circuit. The CV curves recorded in 0.1 M HCl didn't show any peak without accumulation within the range -0.8 V to + 1V whereas, after the accumulation well defined oxidation peaks relevant to the electrochemical oxidation of mercury proving the mercury uptake by the WBMCPE (Fig. 4). Further on, the oxidation peak heights of the CV curves recorded in multi run mode was decreasing with increasing number of cycles, which suggests that the mercury get oxidized and stripped out from the electrode.

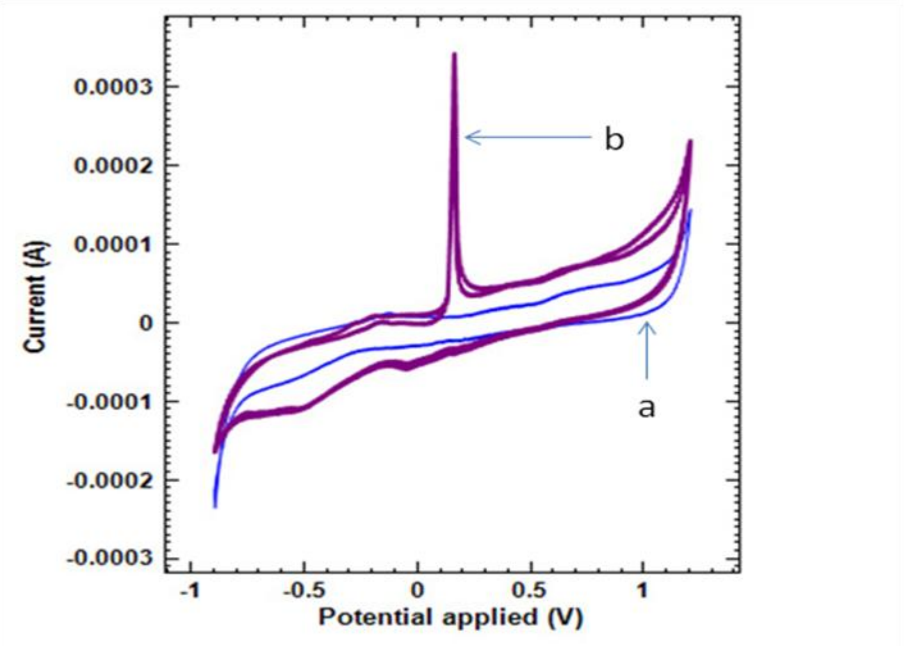


Figure 4. Cyclic voltammograms of WBMCPE in 0.1 M HCl without accumulation a) after 10 minute accumulation of mercury b) at scan rate: 50 mV s–1.

Based on the CV results differential pulse voltammetry scan in anodic direction from -0.5 V to 0.5 V was carried out. As shown in figure 5 stripping peak was appeared at - 0.11 V. Therefore, differential pulse was employed in the present work for the anodic stripping voltammetric determination of mercury using WBMCPE.

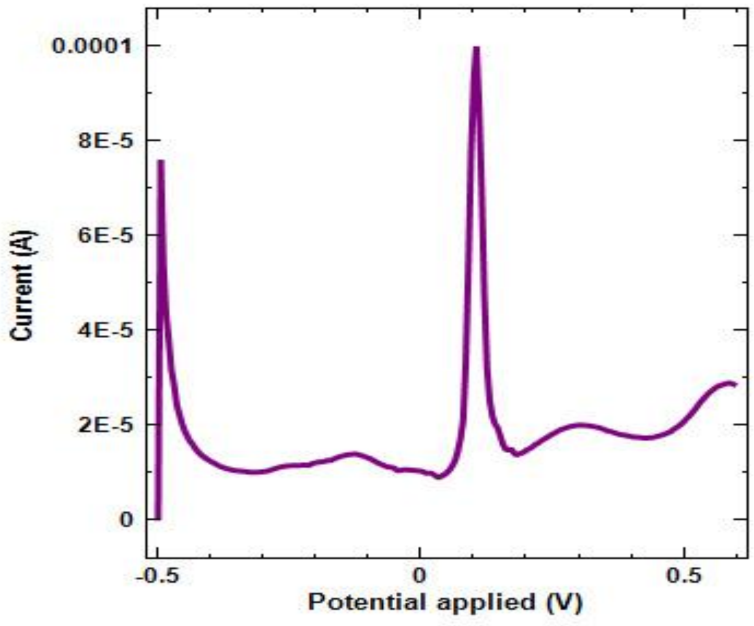


Figure 5. DPASV for determination of mercury after 10 min accumulation [supporting electrolyte: HCl].

3.4. Optimization of parameters

Voltammetric behavior of the modified CPE was evaluated in terms of the influence of accumulation and stripping parameters such as the effect of amount of modifier, supporting electrolyte, accumulation time, pH of the accumulation medium and scan rate. Finally, the calibration curves were plotted and the influence of various substances as potential interference compounds on the determination of foregoing ions was studied under the optimum conditions.

3.4.1. Amount of water hyacinth biomass

The effect of the ratio of biomass to graphite powder was evaluated within the range of 2 % to 8% (w/w). Figure 6 shows an increase in the peak current from 2% to 5% of modifier to graphite powder ratio. Current value increases due to greater number of sites available for adsorption of mercury at the electrode surface. At greater than 5 % of water hyacinth biomass, decrease in the conductivity leads to the decrease in the peak current value.

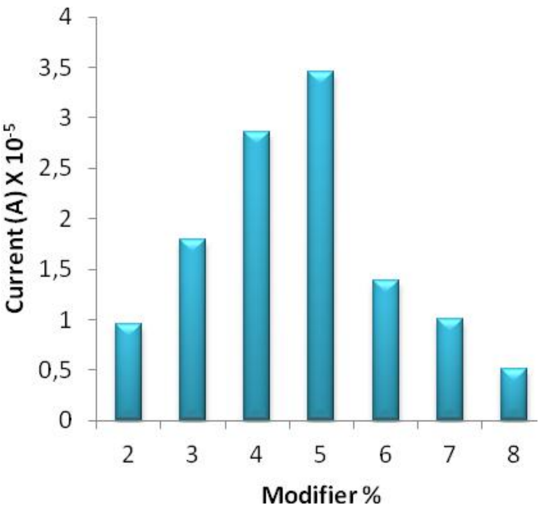


Figure 6. DPASV current response of 1 µg/ml Mercury using different percentage of water hyacinth biomass, 0.1 M HCl as supporting electrolyte. The accumulation time is 10 min at open circuit; scan rate is 50 mV/Sec and pulse amplitude 25 mV.

3.4.2. Accumulation time

Accumulation time was varied from 1 min to 60 min and the corresponding current value was measured, using two concentrations of mercury solution. It is clear from figure 7 that initially the current value increase linearly with accumulation time which indicates that the mercury ions get adsorbed at the electrode surface rapidly while further prolonged accumulation time did not improve the peak height and a plateau was observed. A pre-concentration time of 10 min was selected as a compromise between length of analysis time and sensitivity. In addition, longer accumulation time could also damage the electrode surface that worsens the sensitivity and reproducibility of measurements taken.

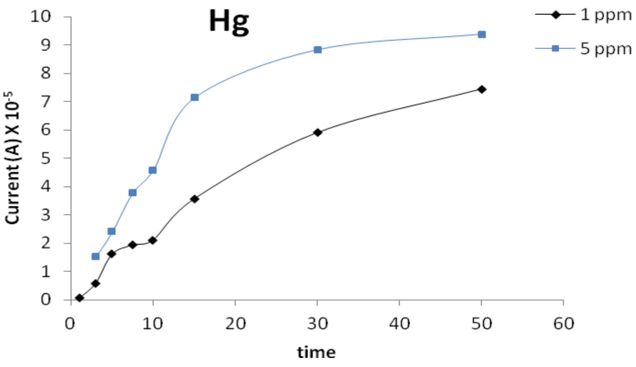
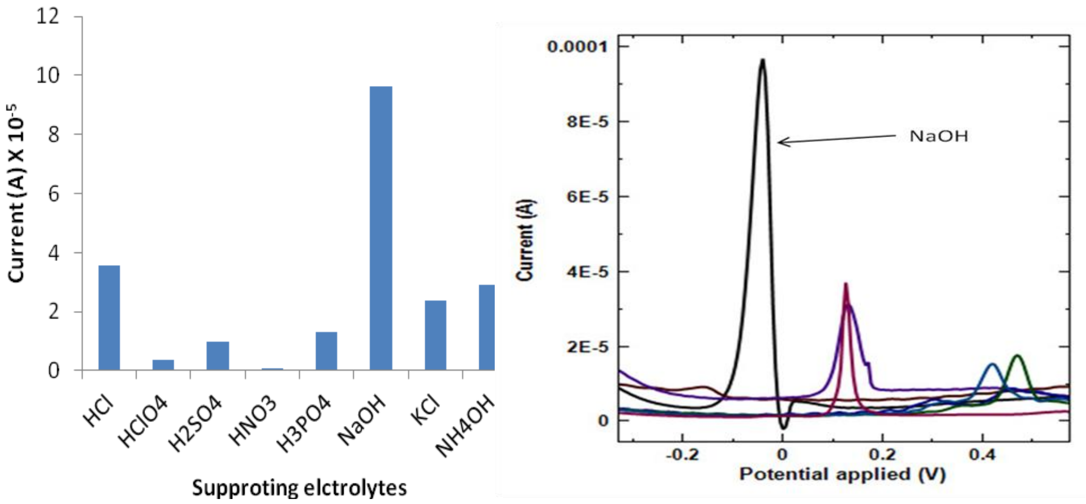


Figure 7. Dependence of DPASV current response on accumulation time for 1 µg/ml and 5 µg/ml of mercury. The supporting electrolyte is HCl, scan rate is 50 mV/Sec and pulse amplitude 25 mV.

3.4.3 Supporting electrolytes

The influence of the nature of supporting electrolyte on the shape, position and current of stripping peaks of mercury was investigated. Different solutions hydrochloric acid, nitric acid, sulfuric acid, perchloric acid, phosphoric acid, sodium hydroxide, ammonium hydroxide, sodium chloride and potassium chloride were used as supporting electrolyte. The peak position and the peak height were greatly influenced with the stripping media. Results in figure 8 a) and b) shows that maximum peak current was observed for sodium hydroxide and it is found to be the most suitable supporting electrolyte for mercury determination which is according to the previously reported literature [18]. The shift in the peak position was varied up-to 500 mV.

The effect of the supporting electrolyte concentration was also studied by varying the concentration within in the range 0.01 M to 1 M NaOH. Optimum current response was observed at 0.1 M NaOH for mercury as shown in figure 8 C).



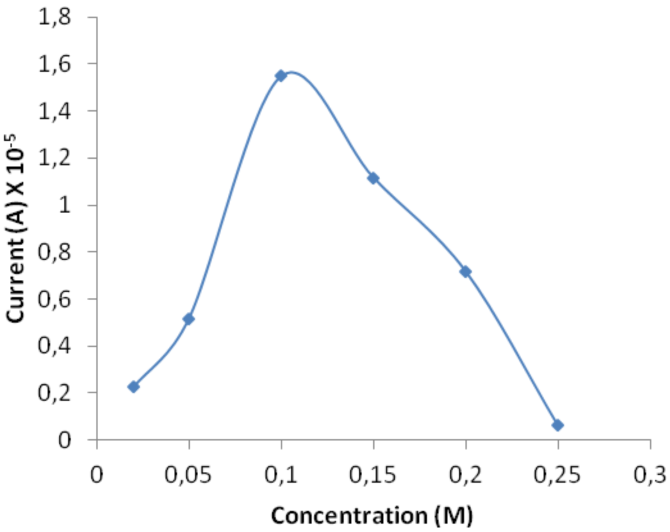


Figure 8. Effect of different supporting electrolytes on DPASV current response of the WBMCPE for 1 µg/ml mercury for 10 min accumulation time a) and their corresponding differential pulse anodic stripping voltammograms b) Effect of concentration of NaOH c) other parameters are same as Fig 4.

3.4.4. Accumulation solvent

The metal ions get accumulated at the electrode surface at different functional groups. When we dip the electrode in accumulating solvent then the organic functional groups present at the biomass on electrode surface gets ionized. Ionization of these groups in aqueous solution enables them to participate in metal binding. The ionization of functional groups on the biomass surface depends on pH of the solution: at pH > pKa, most of these functional groups are mainly in an ionized form and can exchange H+ with the metal ions in solution. The effect of the accumulation solution pH on the stripping signal was accessed in order to find the right pH value. It was previously concluded from the researchers that the acidic media in comparison to the basic media is good for accumulation of mercury [19,20]. A high H^+ concentration was avoided in order to minimize protonation. Accumulation of mercury was examined in supporting electrolytes such as acetate buffer, phosphate buffer and Britton-Robinson buffer. Voltammetric peaks were observed in most of these electrolytes, however, in acetate buffer solution the anodic peak current was higher and better defined peak shape was observed. The base line for the determination of mercury in acetate buffer is comparatively low, suggests acetate buffer as the best accumulating media, therefore acetate buffer was used in further studies.

The effect of pH on the voltammetric response of the WBMCPE was studied in a pH range 3.0 to 6.0 in a solution containing mercury. The anodic peak current for mercury was decreased as the pH is changed from 3.0 to 6.0. The results show that the maximum binding of mercury ions on the electrode surface occurs at pH 3. The concentration of acetate buffer was also varied from 0.1 mM to 100 mM. The maximum current value was obtained for 1 mM acetate buffer.

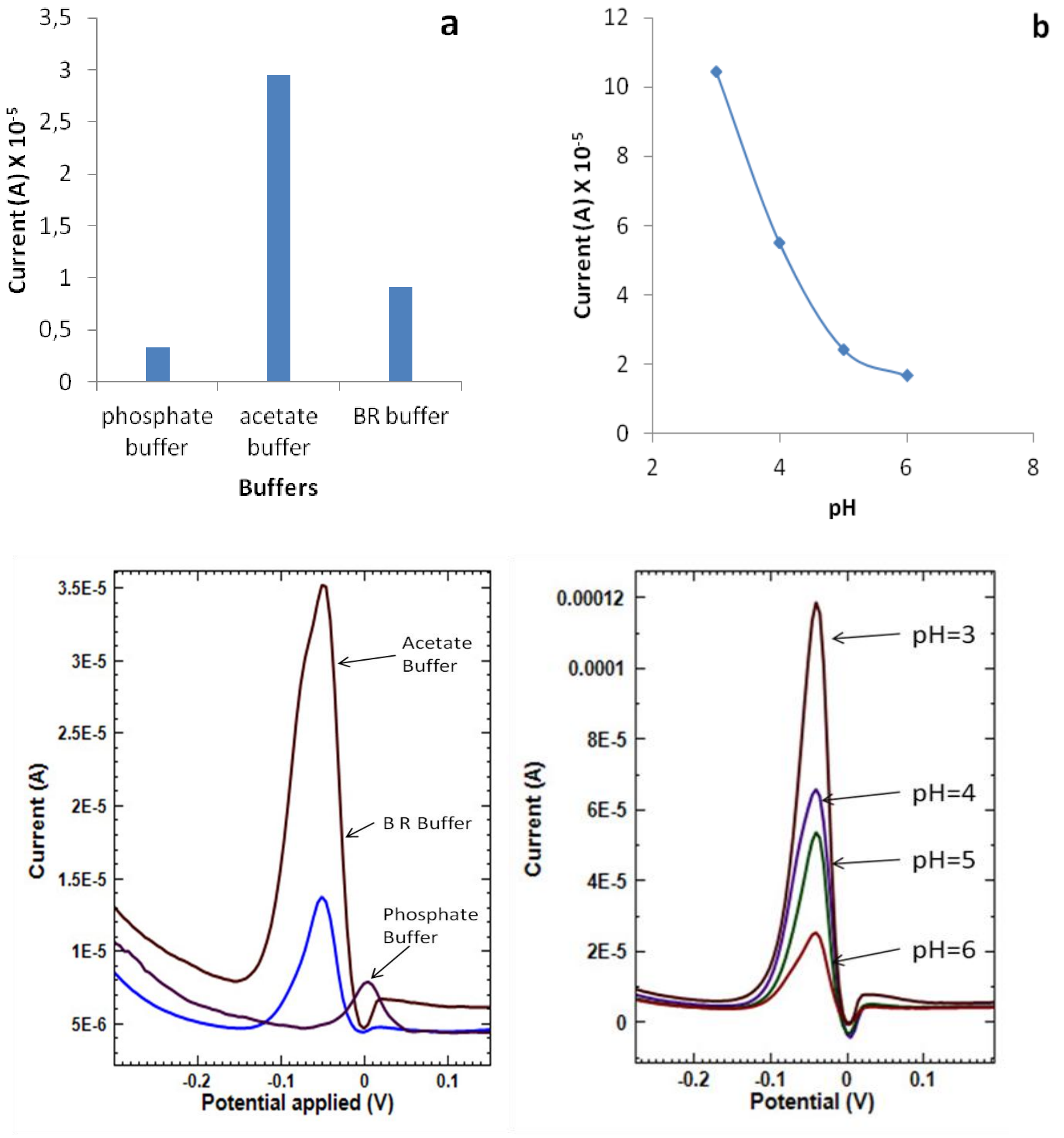


Figure 9. Effect of different accumulating solvents and the pH of accumulating solvent on DPASV current response for the WBMCPE of 1μg/ml mercury for 10 min in 0.1 M NaOH a) and b) and their corresponding differential pulse voltammograms.

3.4.5. Instrumental parameters

All the instrumental parameters involved in the analytical procedure were submitted to optimization. This study was performed in 0.1 mol L^{-1} sodium hydroxide solution after accumulation of 1 μg/ml mercury for 10 min. The parameters optimized are scan rate and pulse amplitude. Optimized values are given in the table.

Table 2. Optimized values of the differential pulse parameters scan rate and pulse amplitude.

Parameter	Optimized Value
Scan rate	50 mV/Sec
Pulse amplitude	25 mV

3.5. Interference study

The influence of the other metal ions present in the solution on the anodic peak current of mercury was evaluated. Different interfering ions used for the study are lead, cadmium, nickel, copper and chromium. For the determination of mercury no effect was observed up to 15 fold of lead, 25 fold of cadmium, 5 fold of copper, 15 fold of nickle and 25 fold of Cr(VI).

3.6. Reproducibility and stability

The reproducibility of the proposed method was studied by repeated determination of mercury 10 times in a day (intra-day precision), whereas inter-day precision was tested by triplicate quantifications for 4 days. The results are in good precisions with standard deviation (RSD) of the peak current less than 1.5 % (Intra-day precision) and lower than 2.0 % (inter-day precision). The results indicate that the proposed method has good precision for both qualitative and quantitative studies.

The stripping voltammograms at the same modified electrode with interval of one week, over a month were also recorded, and the maximum deviation obtained was 3.5 %. The results indicate that the water hyacinth biomass modified carbon paste electrode has good reproducibility and long-time stability.

3.7. Determination of metals in the presence of surfactants

The surfactants differ in their effect on the electrode process, according to the type of surfactant, electrode and electro-active species. Thus, the characterization of the electrode behavior in the presence of surfactants is an extremely complex undertaking. Triton X-100, SDS and CTAB were selected as representatives of nonionic, anionic, and cationic surfactants. The effect of these surfactants was studied for determination of mercury using WBMCPE.

Typical voltammograms in the presence of increasing amounts of each surfactant was recorded and the effect of surfactant on current value was presented in figure 10. It was also observed that in solutions containing surfactants, no variation in the peak potential value was observed. The increase in the current value was observed for mercury determination with increase in the amount of SDS where as decrease was observed for CTAB, for Triton X-100 no significant change in the current value was observed. These results also prove the electrostatic attraction in binding of mercury at modified electrode surface.

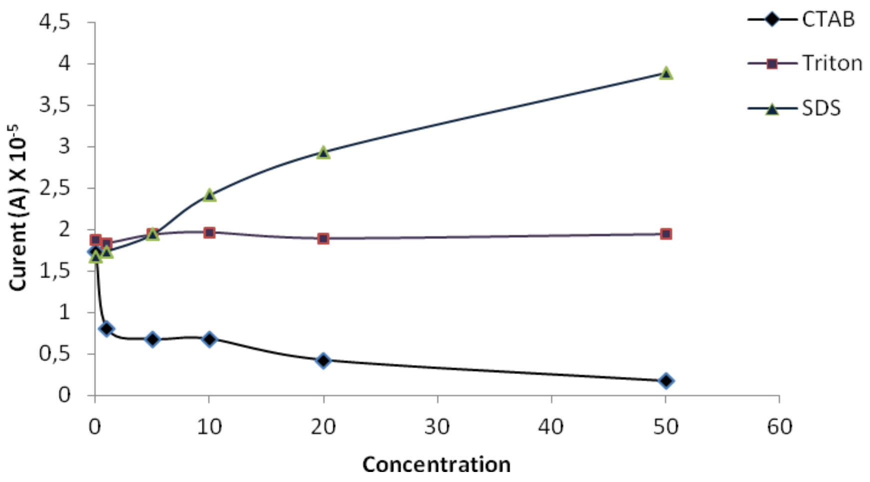


Figure 10. Effect of increasing amount of surfactants on DPASV current response of 1µg/ml mercury using WBMCPE for 10 min accumulation and NaOH as supporting electrolyte.

3.8. Analytical characteristics and method validation

Analytical performance of the WBMCPE was evaluated with different concentrations of mercury under the optimum conditions determined above. The voltammetric response of the WBMCPE for determination of mercury is shown in figure 11. Linear relationship was observed between the analytical signal and concentration ranging from 400 µgL^{-1} to 800 µgL^{-1} with a correlation coefficient of 0.998.

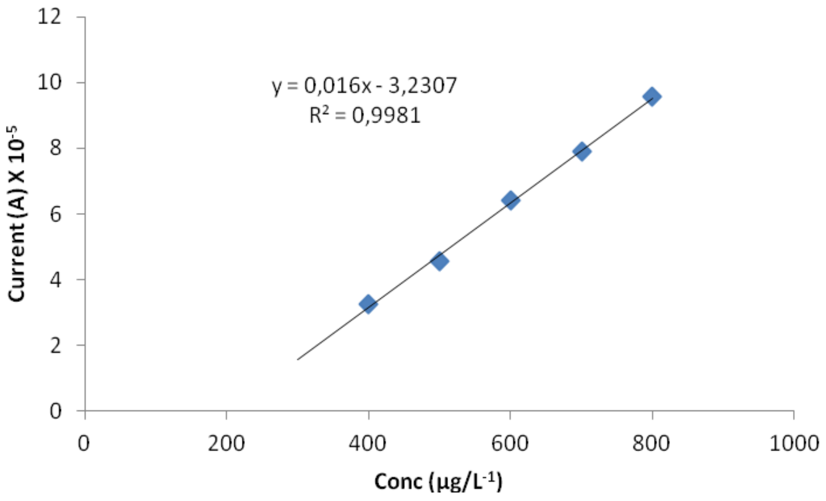


Figure 11. Standard addition curve for determination of mercury obtained with a pre-concentration time of 10 min and under the optimized conditions described in the text.

The detection limit is evaluated to be about 195 μgL^{-1} (S/N = 3) after 10 min accumulation time. Nevertheless, low concentration detection can be realized conveniently by increasing the accumulation time. The results are according to the previously reported literature [21-23].

4. CONCLUSION

In this study, carbon paste electrode modified with water hyacinth biomass was prepared. CV measurements indicated that the modified electrode could be used in the measurement of mercury in aqueous solutions. Differential pulse anodic stripping voltammetry was used to optimize the conditions for the determination of mercury. Maximum sensitivity of WBMCPE was obtained from the pre-concentration conducted in solution with the acetate buffer of pH=3 for 10 min and the sodium hydroxide as the supporting electrolyte. Despite of some mutual interference effects, mercury can be reliably determined when the standard addition procedure is used, with low detection limits. The utilization of mercury-free electrodes for stripping voltammetry is an attempt to perform environment friendly electro-analysis and hence practically addresses global health concerns.

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References

1. P. Richter, M. I. Toral, B. Abbott, *Electroanalysis*, 14(18), (2002) 1288–1293.
2. G. Jarzynska and Jerzy Falandysz, *J. Environ. Sci. and Health: A*, 46(6), (2011) 569-573.
3. P. E. Koulouridakis and N. G. Kallithrakas-Kontos, *Anal. Chem.*, 76(15), (2004) 4315–4319.
4. M. Jeoung and H. Choi, *Bull. Korean Chem. Soc*., 25 (12) (2004), 1877-1880.
5. E Gao and J. Liu, *Anal Sci*., 27(6) (2011) 637-41.
6. B. Chen, L. Wang, X. Huang and P. Wu, *Microchim. acta* 172(3-4) (2011), 335-341.
7. E. E. Mojica, J. M. Vidal, A. B. Pelegrina and J. L. Micor, *J. Applied Sci., 7: 1286-1292.*
8. D. S. Rajawat and S P Satsangee, *Res. J. Chem. Environ*. 15(3) (2011) 55-59.
9. N. L. Dias Filho, D. R. do Carmo, L Caetano and A H Rosa, *Anal Sci.* 21(11) (2005) 1359-63.
10. U. Tamer, T. Oymak and N. Ertaş, *Electroanalysis* 19(24) (2007) 2565–2570.
11. A. Samphao, H. Rerkchai, J. Jitcharoen, D. Nacapricha and K. Kalcher, *Int. J. Electrochem. Sci.*, 7 (2012) 1001 – 1010.
12. J. Singh, S. K. Mittal, *Sensors Actuat B: Chem* 165(1), (2012), 48–52.
13. B. Dhir, *Int. J. Environmental Engeniering*. 2(1)-3/2010.
14. C. Mahamadi, *Afr J Environ Sci Technol* 5(13), (2011) 1137-1145, 29.
15. Z. Ismail and A. M. Beddri. *Water Air Soil Pollut.* 199(1-4) (2009), 57-65
16. D. S. Rajawat, A. Kardam, S. Srivastava and S. P. Satsangee. *Environ Sci Pollut Res*, DOI 10.1007/s11356-012-1194-4).
17. B Rezaei and S Damiri. *Sensors*, 8(9):1523-1529

18. E E Mojica, F E Merca. *J Appl Sci*. 5(8) (2005), 1461-1465.
19. F Wang, J Liu, Y Wu, Y Gao and X Huang. *J. Chin. Chem. Soc.* 56(4) 2009, 778-784
20. M. N. Abbas and G. A. E. Mustafa. *Analytica Chimia Acta*. 478(23) (2003), 329-335.
21. M. Javanbakht, H. Khushsafar, M. R. Ganjali, A Dadiei, P Norouzi and A Hasheminasab. *Current Analytical chemistry*, 5, (2009), 35-41.
22. J. R. Micor, E. E. Mojica, J.H. Santos and C.Deocaris. *Philippines Nuclear Journal*, 14,(2005), 78-80.
23. J.H Santos, S R Ward. *Chemicke Listy Journal*, 102, (2008), 448-449.