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Modified Electrode Used For Detection of Heavy Metals

A. Vimala [1], C. Vedhi [2]

[12] Department of Chemistry, V.O.Chidambaram College, Tuticorin – 628 008, Tamilnadu, India.

Abstract: - Electroanalysis more advantages due to high sensitivity, reduction in sample consumption, high-speed analysis, low operating cost and high scan rate in all cases. Surface modification by multiwalled carbon nanotubes (MWCNTs) on a glassy carbon electrode (GCE) was employed in the present study to determine metal traces (Pb, Cu, Cr, and As). The multiwalled carbon nanotubes modified glassy carbon electrode (MWCNTs/GCE) exhibits superior performance in comparison to the bare glassy carbon electrode and yielded a higher electrochemical response. After optimization of the experimental and voltammetric conditions, the best voltammetric responses were obtained in pH 7.0 with -1.2 V initial scanning potential, 0.004 V scan increment, 0.075 V pulse amplitude and 0.1 s pulse width. A straight line with good correlation was obtained from the plot of peak current vs. concentration. From the straight line plot, R2 values were obtained to be 0.990 (Pb), 0.995 (Cu), 0.988 (Cr), and 0.989 (As). With the MWCNTs/GCE as the working electrode there is a noticeable shift in the peak potential. This may be due to the increase of the electrochemically active surface. The results compared with Inductively coupled plasma optical emission spectroscopy (ICP-OES) and found to be in good agreement. Crystalline nature of the sample was represented by the sharp X-ray diffraction (XRD) peaks.

Keywords
Heavy metals, ICP-OES, MWCNTs/GCE, XRD.

I. INTRODUCTION

Increased knowledge about eco-toxicological effects as well as increased legal requirements for reductions in industrial emissions necessitates research and development in the area of seawater treatment. In this context, the contamination of the environment with toxic heavy metals is a significant problem. Industrial effluents are considered to be the major sources of heavy metal contamination. Because of heavy metal accumulation in the food chain and their persistence in nature, it is necessary to remove toxic heavy metals from seawater. Conventional technologies for the removal of heavy metals such as chemical precipitation, ion exchange, or electrochemical processes are often neither effective nor economical, especially when used for the reduction of heavy metal ions to low concentrations [1]. New separation methods are required that reduce heavy metal concentrations to environmentally acceptable levels at affordable cost. Bio removal has the potential contribute to the achievement of this goal [2]. The ability of microorganisms to remove heavy metals from aqueous solution has been known for some decades. Algae, bacteria, fungi, and yeast have proved to be potential heavy metal sorbents [3], [4]. Algae, primarily marine macro algae, play an important role in the research and development of new biosorption materials due to their high capacities, similar to commercial ion-exchange resins and their availability in nearly unlimited amounts from the ocean [5]-[7]. The cell wall of algae consists of a variety of polysaccharides and proteins, some of which contain anionic carboxyl, sulfate, or phosphate groups. Crist et al. [8], [9] considered carboxyl and sulfate groups as binding sites for the metals by the algae Vaucheria by displacing either an existing metal (ion exchange) or a proton (proton displacement), depending on the pH. Gardea-Torresdey et al. [10] described the importance of the carboxylate anion for the biosorption of copper (II) and aluminum(III) by five algae strains. Studies of the removal of cadmium(II) and lead(II) with the algae Sargassum fluitans [11] and copper(II), strontium(II), cadmium(II), and lead(II) with the plant Datura innoxia [12], [13] from aqueous solution have also demonstrated the great influence of anionic sitesat the cell wall on the biosorption. Following these results, recent investigations [14]-[17] have described the increase of metal capacities of the biosorbents due to the successful introduction of additional functional groups into the biomass cell wall.

Although there are methods with adequate sensitivity for the determination of heavy metals such as atomic absorption, atomic emission spectrometry and inductively coupled plasma mass spectrometry (ICP-MS), electrochemical methods are one of the most favorable techniques for determination of heavy metal ions because of their low cost and high sensitivity [18], [19]. In recent years, applications of chemically modified electrodes have great interest in various areas of research and development, such as material corrosion and inhibition, electrocatalysis, electronics, biosensors and electroanalysis [20]-[24]. For the analysis of trace metals, modified electrodes have shown some advantages over other analytical methods and have been employed as powerful tools for concentration determination and surface structure identification [25], [26].

Figure 1. Photograph of Syringodium isoetifolium

2.2. Inductive Coupled Plasma Optical Emission Spectroscopic studies (ICP-OES)

Inductively coupled plasma optical emission spectrometer (ICP-OES, Thermoscientific 6100 Series) was used to determine the metals at trace level concentrations. Multi elements were analyzed in a single run. Metals were determined by emission of a light at a precise wavelength. From the intensity of the emitted light the concentration of the metals in the seaweed were determined.

2.3. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) pattern of the powdered sample was obtained by employing XPERT-PRO diffractometer in the scanning range of 10-80º (2θ) using Cu Kα radiation having wavelength of 1.54060Aº. The diffractometer was operated at 40kV and 30mA.

2.4. Electrochemical methods

Electrochemical experiments were performed using CHI 650C electrochemical workstation. A three-electrode system was used consisting of a glassy carbon electrode as a working electrode, an Ag/AgCl as a reference electrode and a Pt-wire as an auxiliary electrode. Metal concentration was measured by CV, LSV, DPAV, and SWAV. The anodic scan was initialised at -1.2V and stopped at 1.2V.

III. RESULTS AND DISCUSSION

3.1. Inductive Coupled Plasma Optical Emission Spectroscopic studies (ICP-OES)

ICP-OES study of Syringodium isoetifolium revealed the presence of seven heavy metals in the order of Cd < Co < As < Cu < Zn < Pb < Fe.

Syringodium isoetifolium has a cadmium concentration of 0.95 mg L-1. The sample was found to possess 9.76 mg L-1 of cobalt. The As content was found to be 24.71 mg L-1. 30 mg L-1 concentration of copper was analyzed in the sample. The concentration of zinc in the studied sample was analysed to be 32.48 mg L-1. The sample attempts to reveal the very high concentrations of lead (97.55 mg L-1) and iron (358.6 mg L-1).

There were no regulatory limits by WHO [27] for cobalt content in drinking water. After comparison, metal limits in the sample with those proposed by WHO we found that studied sample have metals above the permissible limits set by WHO (2004) [27] and WHO (2008) [28].

3.2. X-ray diffraction (XRD) analysis

XRD pattern of Syringodium isoetifolium is presented in Fig. 2. Five diffraction peaks are observed at 29.8865°, 31.7986°, 45.4708°, 56.6251°, and 75.3700° corresponding to the relative intensities of 16.62%, 100%, 57.95%, 16.53%, and 16.53%, respectively. Crystalline nature of the sample was represented by the sharp peaks. (010), (100), (001), (101), and (011) are the sets of lattice planes calculated from the peaks of 29.8865°, 31.7986°, 45.4708°, 56.6251°, and 75.3700°, respectively.

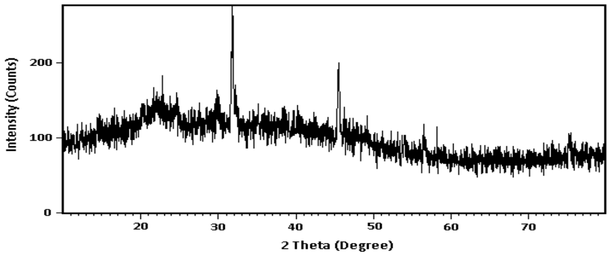


Figure 2. XRD pattern of Syringodium isoetifolium

3.3. Electrochemical analysis

3.3.1. Effect of pH

The effect of pH was studied from 1.0 to 13.0 by voltammetrically. The potentials and currents were measured for the oxidation peaks and correlated with pH (Fig. 3) to understand the influence of pH. The peak potential was around 0.1V and 0.9V that may be oxidation of heavy metals of copper (Cu) and arsenic (As). From the curve the maximum peak current was obtained at pH 7.0. This may be due to faster electron transfer rate at neutral medium pH 7.0 and this indicates that the rate of the reaction is controlled only by electron transfer. Thus, pH 7.0 was chosen as the optimized pH value to carry out quantitative determination of heavy metals.

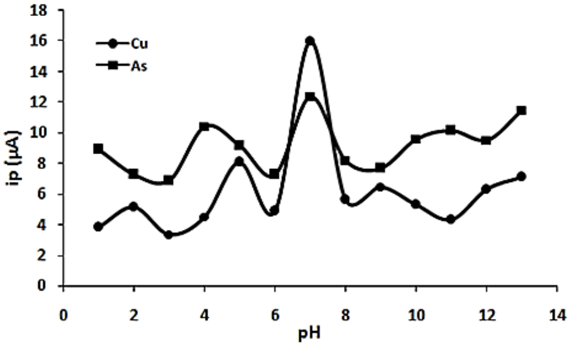


Figure 3. Plots of ip vs pH solution (pH 1 to pH 13) for lead and arsenic in 3125 mg L-1 of the sample by cyclic voltammetry; scan rate of 50 mV s-1

3.3.2. Cyclic voltammetric (CV) studies on MWCNTs modified GCE

The CV response of the MWCNTs/GCE in 3 mL buffer solution (pH 7.0) displays no any redox peaks at 50 mV s-1. After addition of the sample to the same buffer solution two anodic oxidation peaks were obtained. CV signals on the MWCNTs / GCE (Fig. 4) shows two oxidation peaks: a peak at +0.0669V(Cu) and a more positive oxidation peak at +0.4321V(As) with sharper outlines. As for the uniformly distributed MWCNTs, it increases the active sites of the GCE surface and effectively prevents the GCE sheets from restacking and reaggregating, which results in the increase of specific surface area and the enhancement of sensing property. Thus the modified electrode yield better currents for Cu (18.39 µA) and As (2.984 µA).

The peak current get increased with scan rate. Fig. 5(a) reveals the plot of peak current versus scan rate resulted in a straight line with R-squared values of 0.979 (Cu) and 0.985 (As). Fig. 5(b) exhibits the plot of peak current versus square root of scan rate led to a curved line. Fig. 5(c) shows the logarithmic plot of peak current versus scan rate was also linear with slope values 0.559 (Cu) and 0.502 (As). All these factors reveal that the reaction is adsorption controlled. The oxidation peak current increases with the concentration range of 2000 to 3125 mg L-1 at a constant scan rate of 50 mV s-1 (inset of Fig. 4).

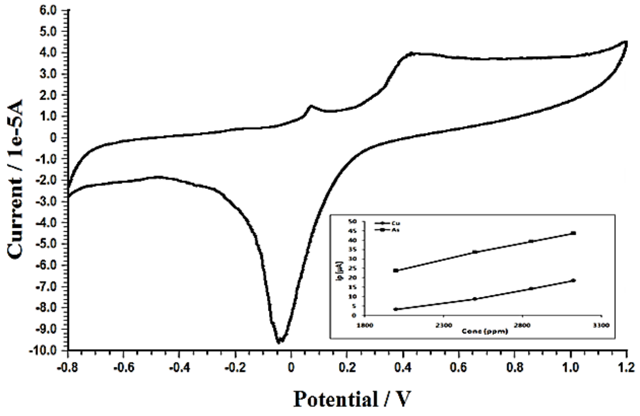


Figure 4. CV of 3125 mg L-1 Syringodium isoetifolium on MWCNTs modified GCE at pH 7.0; scan rate 50 mV s-1; Inset: Plot of concentration vs. peak current at 50 mV s-1.

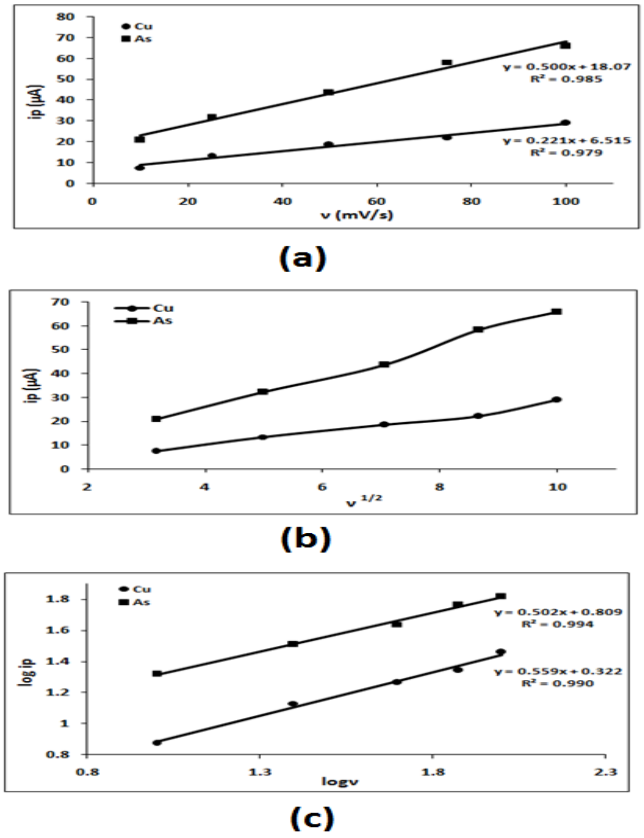
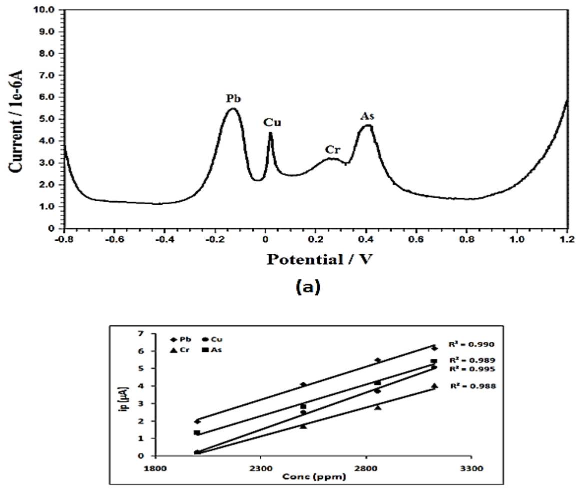


Figure 5. (a) Plot of peak current vs. scan rate. (b) Plot of peak current vs. square root of scan rate. (c) Plot of log peak current vs. log scan rate for 3125 ppm of Syringodium isoetifolium at pH 7.0 using MWCNTs modified GCE by Cyclic Voltammetry

3.3.3. Differerential pulse anodic voltammetric (DPAV) analysis on MWCNTs modified GCE

Differential pulse voltammetric technique was used for the deposition of the analyte on the working electrode surface as this procedure facilitates detection at very low concentrations. DPAV was performed to examine the relationship between the oxidation peak current and concentration of seagrass under the optimal conditions on account of its low background current and high sensitivity.

The reproducibility and stability of MWCNTs/GCE were investigated to ensure the precision of the method proposed in our work. Fig. 6(a) reveal that, the MWCNTs/GCE sensor produced the best current responses of heavy metals. The peak potential values were found to be -0.1338V (Pb), +0.0138V (Cu), +0.2499V (Cr), and +0.4006V (As). On comparison the peak current signal of Pb (6.144 µA) is higher for the MWCNTs/GCE than Cu (5.099 µA), Cr (4.053 µA), and As (5.44 µA). Moreover an appreciable peak currents were obtained for all the four aforementioned metals. This may be due to the increase of the electrochemically active surface together with the synergistic effect of MWCNTs. The linear dependence of peak current with concentration was understood from the straight line with good correlation as shown in Fig. 6(b). A peak shift to positive and negative potentials was observed at higher concentrations of seagrass which could be explained by some interaction between the analyte and the electrode surface, however this problem did not affect peak height. Compared with the reported modified electrodes MWCNTs/GCE exhibits comparable properties in linear range in metal detection. Thus, the electrochemical sensor for sensitive and rapid detection of metals is finally attained.



(a)

(b)

Figure 6. (a) DPAV behaviour of 3125 mg L-1 Syringodium isoetifolium on MWCNTs modified GCE at pH 7.0. (b) Plot of concentrations vs. peak current

IV. CONCLUSIONS

ICP-OES recorded all the heavy metals (Fe, Pb, Zn, Cu, As, Co, and Cd) in Syringodium isoetifolium. From XRD pattern, the sets of lattice planes were calculated from the sharp peaks. From voltammetric behavior, pH 7.0 was selected as optimum pH for further electrochemical studies of heavy metals in the seagrass. Straight line plot of peak current versus scan rate by CV for MWCNTs modified glassy carbon electrode suggested that the overall reaction was adsorption controlled. The MWCNTs modified electrode yield better reproducibility for Pb, Cu, Cr and As due to the increase of the electrochemically active surface by DPAV. This made the system promising to be used in routine analytical applications. To the best of our knowledge, this work is the first attempt to elucidate the electrochemical oxidation mechanism of the compound in seagrass.

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REFERENCES

[1] E.W. Wilde, J.R. Beneman, Bioremoval of heavy metals by the use of microalgae, Biotechnol. Adv. 11 (1993) 781-812.

[2] B. Volesky, Advances in biosorption of metals: selection of biomass types, FEMS Microbiol. Rev. 14(4) (1994) 291-302.

[3] B. Volesky, Z.R. Holan, Biosorption of Heavy Metals, Biotechnol. Prog. 11 (1995) 235-250.

[4] F. Veglio, F. Beolchini, Removal of metals by biosorption-a review, Hydrometallurgy 44 (1997) 301-316.

[5] G.W. Garnham, The use of algae as metal biosorbents, In Biosorbents for metal ions: J. Wase, C. Forster (Eds.), Taylor and Francis, London, 1997, pp. 11-39.

[6] R.P. DeCarvalho, K.H. Chong, B. Volesky, Evaluation of the Cd, Cu, and Zn Biosorption in Two-Metal Systems Using an Algal Biosorbent, Biotechnol. Prog. 11 (1995) 39-44.

[7] A. Leusch, Z.R. Holan, B. Volesky, Biosorption of heavy metals in water supplies production of oil industry, J. Chem. Technol. Biotechnol. 62 (1995) 279-288.

[8] R.H. Crist, K. Oberholser, J. McGarrity, D.R. Crist, J.K. Johnson, J.M. Brittsan, Interactions of metals

and protons with algae. 4. Ion exchange vs. adsorption models and a reassessment of scatchard plots; Ion-exchange rates and equilibria compared with calcium alginate, Environ. Sci. Technol. 28 (1994) 496-502.

[9] R.H. Crist, J.R. Martin, D.R. Crist, Interaction of Metal Ions with Acid Sites of Biosorbents Peat Moss and Vaucheria and Model Substances Alginic and Humic Acids, Environ. Sci. Technol. 33 (1999) 2252-2256.

[10] J.L. Gardea-Torresdey, M.K. Becker-Hapak, J.M. Hosea, D.W. Darnall, Effect of chemical modification of algae carboxyl groups on metal ion binding, Environ. Sci. Technol. 24 (1990) 1372-1378.

[11] E. Fourest, B. Volesky, Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of Sargassum fluitans, Environ. Sci. Technol. 30 (1996) 277-282.

[12] S. Lin, G.D. Rayson, Impact of surface modification on binding affinity distribution of Datura innoxia biomass to metal ions, Environ. Sci. Technol. 32 (1998) 1488-1493.

[13] L.R. Drake, S. Lin, G.D. Rayson, Chemical modification and metal binding studies of Datura innoxia, Environ. Sci. Technol. 30 (1996) 110-114.

[14] H.U. Meisch, J. Gauer, Schwermetalle binden mit Holz und Chitin, Nachr. Chem. Technol. Lab. 46 (1998) 948-951.

[15] J.Z. Xie, H.L. Chang, J.J. Kilbane II, Removal and recovery of metal ions from Wastewater using biosorbents and chemically modified biosorbents, Bioresour. Technol. 57 (1996) 127-136.

[16] W.E. Marshall, L.H. Wartelle, D.E. Boler, M.M. Johns, C.A. Toles, Enhanced metal adsorption by soybean hulls modified with citric acid, Bioresour. Technol. 69 (1999) 263-268.

[17] M. Kraemer, H.U. Meisch, New metal-binding ethyldiamino- and dicarboxy- products from Aspergillus niger industrial wastes, Biometals 12 (1999) 241-246.

[18] F. Arduini, J. Quintana, A. Amine, G. Palleschi, D. Moscone, Bismuth-modified electrodes for lead detection (review), Trends Analyt Chem 29 (2010) 1295.

[19] Linyuan Cao, Jianbo Jia, Zhenhui Wang, Sensitive determination of Cd and Pb by differential pulse stripping voltammetry with in situ bismuth-modified zeolite doped carbon paste electrodes, Electrochim. Acta 53 (2008) 2177.

[20] H.D. Abruna, Coordination chemistry in two dimensions: chemically modified electrodes, Coord Chem Rev 86 (1988) 135-189.

[21] R.W. Murray, Chemically modified electrodes, Acc Chem Res 13 (1980) 135-141.

[22] W. Kutner, J. Wang, M. L'her, B.P. Buck, Analytical aspects of chemically modified electrodes: Classification, critical evaluation and recommendations (IUPAC Recommendations 1998), Pure Appl Chem 70 (1998) 1301-1318.

[23] D.W. Arrigan, Tutorial review. Voltammetric determination of trace metals and organics after accumulation at modified electrodes, Analyst 119 (1994) 1953-1966.

[24] K. Kalcher, Chemically modified carbon paste electrodes in voltammetric Analysis, Electroanalysis 2 (1990) 419-433.

[25] S.K. Cha, H.D. Abruna, Determination of copper at electrodes modified with ligands of varying coordination strength: a preamble to speciation studies, Anal Chem 62 (1990) 274-278.

[26] J. Labuda, V. Plaskoni, Determination of mercury ions on a diphenylcarbazone bulk modified graphite electrode, Anal Chem Acta 228 (1990) 259-263.

[27]. J. Bala Chennaiah, M.A. Rasheed, D.J. Patil, Concentration of heavy metals in drinking water with emphasis on human health, International Journal of Plant, Animal and Environmental sciences 4(2) (2014) 205-214.

[28]. Chaitali V. Mohod, Jayashree Dhote, Review of heavy metals in drinking water and their effect on human health, International Journal of Innovative Research in Science, Engineering and Technology 2(7) (2013) 4.