Detection of Lead and Cadmium Ions by Voltammetry using Antimony Impregnated Activated Carbon

MUHAMMAD OMER FAROOQI[1], AQEEL AHMAD TAIMOOR[1*], SAAD AL-SHAHRANI[1], DUMITRU BALEANU[2,3], SAMI ULLAH RATHER[1]
[1] King Abdulaziz University – Jeddah, Saudi Arabia. P.O. Box: 80200. Zip Code: 21589
[2] Department of Mathematics and Computer Sciences, Faculty of Arts and Sciences, Cankaya University, TR - 06530, Ankara, Turkey
[3] Institute os Space Sciences Magurele, RO-077125, Bucharest, Roamnia

This work deals with antimony-impregnated activated carbon electrode for the detection of heavy metal ions. Activated carbon is employed to enhance the surface area of the working electrode. Square-wave Anodic Stripping Voltammetry is performed to analyze the electrolytic solution. The peak currents for cadmium and lead are 29.2 and 49.4μA respectively, in 100 μg/L of cadmium and lead solution, which are considerably higher when equated with the previous reported values. Results also indicate that antimony-impregnated activated carbon is better when compared with the ratio of antimony amount to minimum detection limit.

Keywords: anodic stripping voltammetry, working electrode, antimony, impregnation

Heavy metals are elements that have specific gravity of at least 5 times as that of water [1]. Mainly the transition metals, some metalloids, lanthanides, and actinides are considered heavy metals. There are in total 35 toxic elements, which are of concern due to occupational or residential exposure. 23 of them are heavy metals [2]. Some of these (like iron) are needed in minute quantities by human body. However an excess can cause fatal diseases such as Parkinson, muscular dystrophy, multiple sclerosis and cancer [3].

Modern day industrialization and manufacturing activities resulted in the contamination of water bodies by the runaway wastes leading to the buildup of heavy metals. The heavy metal ions can exist for decades, even centuries in water. Heavy metal pollutants tend to localize and lay dormant through precipitation of their compounds or by ion exchange into soils and muds. Knowing all these aspects, the World Health Organization (WHO) has established a standard for maximum levels of these heavy metals in drinking water. Mercury, antimony, lead and cadmium have an upper limit of 1.0, 5.0, 10.0 and 3.0 μg/L respectively [4].

Several techniques have been developed to detect the concentration of these heavy metal ions in water up to micro or even nano grams per liter concentration [5]. These techniques include: Voltammetry, Atomic absorption spectrometry, Inductively coupled plasma mass spectroscopy, Capillary electrophoresis, X-ray fluorescence spectrometry, Optical sensors, Aptamers sensors and Quantum-Dot-Labeled DNAzymes. Voltammetry is one of the most widely used electrochemical detection technique. Several variations of this technique are developed including linear sweep voltammetry, staircase voltammetry, squarewave voltammetry, cyclic voltammetry, stripping voltammetry, alternating current voltammetry, rotated electrode voltammetry, normal pulse voltammetry and differential pulse voltammetry. This research uses square-wave anodic stripping voltammetry (SWASV) as the detection technique due to its superiority over other techniques, including little or no sample pre-treatment, low cost instrumentation, quick and reproducible results, compact analytical set and minimum personnel training needed.

Major work in the field of voltammetry has been carried out using in-situ electrode preparation [6-10]. Mercury is generally selected as the working ion due to its excellent detection efficiency [11-14]. However the poisonous nature of mercury has led researchers to search for more environmental friendly elements like bismuth or antimony [6-9, 15-19]. The working ions are traditionally studied on the non-porous glassy carbons as a support material [7,8,12-14, 20-23]. However recently the porous supports have been used to obtain better surface properties and enhanced detection abilities [18]. These materials are developed using several techniques however, commercially available porous activated carbon as support material has not been tested yet. This may be because of its messy handling and orientation dependent electrical conductivity.

This work consists of ex-situ working electrodes preparation as in-situ detection inherently involves working ion contamination in the test solution. This ex-situ preparation is done by impregnation of antimony working ions over activated carbon. The selected analyte ions to be detected are lead and cadmium. Antimony is selected instead of mercury because of the stated reason. This ex-situ preparation of the working electrode is done to achieve superior detection efficiency and to control surface characteristics. A schematic comparison of the two schemes is given in figure 1. In-situ method works by the simultaneous additions of working and analyte ions into the solution followed by deposition and stripping of both at their respective reduction potentials. On the other hand, in ex-situ method, the working ions are already anchored on the electrode surface, leaving the analyte ions to be present in the solution only. In this way, a better deposition and stripping of analyte ions are facilitated.

Experimental part

Antimony Impregnation

All chemicals were of chemical reagent grade purity. Activated carbon from *Norrit* was regenerated at 220°C with a ramp of 25°C/min for 2 h in ECF–12/4A furnace provided by *Lanten* to remove any impurity present on the surface. Antimony trichloride ($SbCl_3$) from *Sigma Aldrich* was taken as the precursor for the subsequent

---

* *email: taimooruet@gmail.com; Tel.: +9665330062417*

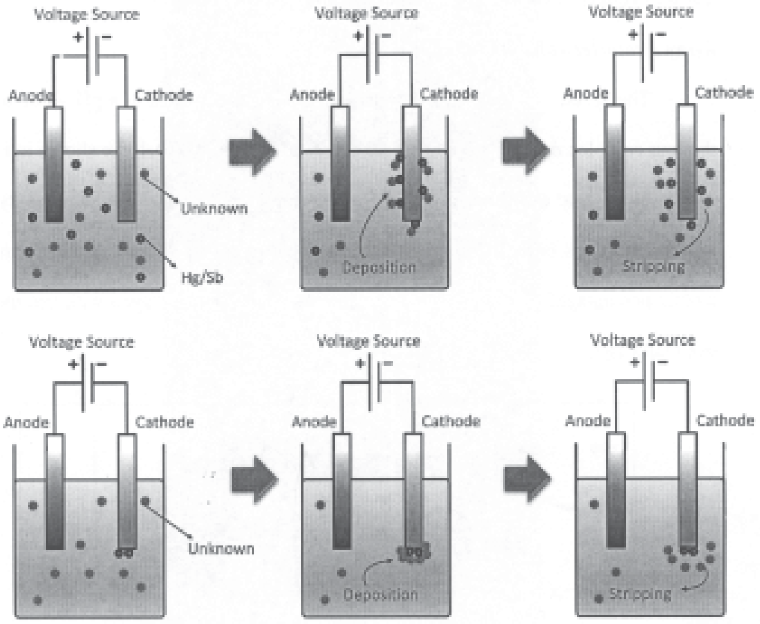

Fig. 1. Figurative demonstration of the difference between in-situ (a) and ex-situ (b) methods

impregnation of antimony metal over activated carbon support. 37% HCl from *Scharlau* was taken as the supporting solution for the impregnation. Vacuum impregnation was carried out at 90°C and -600 mbar pressure for 4.5 h in XA-43 rotary vacuum evaporator provided by *BIBBY*. Four samples were prepared after impregnation with antimony concentrations of 2, 3, 4 and 5% by weight. Drying of samples was done at 120°C with a ramp of 12°C/min for 2 h in JSON-150 oven provided by *JSR* to remove the water contents and other volatile impurities from the prepared samples. Subsequent calcination was performed under nitrogen atmosphere at 300°C with a ramp of 10°C/min for 2 h in CTF–12/C5 muffle furnace provided by *Carbolite* to remove the impregnation impurities from the samples prepared.

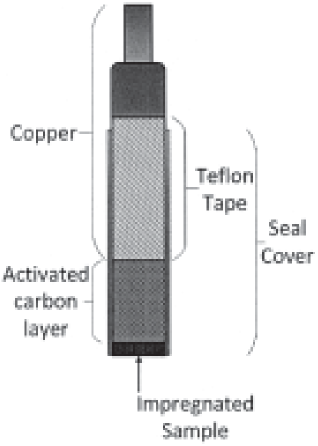

Fig. 2. AIAC working electrode. Copper as the base conductor and carbon layer to prevent any short-circuiting by the solution. AIAC is sticked to the surface with the help of paraffin as binder

Electrode preparation

The catalyst samples prepared were then reduced and tested in electrochemical cells. Paraffin (C_{14}) as a binder was used to hold the catalyst powder over a specially developed copper-plastic piston-working electrode as shown in figure 2. Usually a layer of impregnated carbon paste contained 0.05 g activated carbon (0.0025 g antimony) and 0.08 g paraffin. Carbon was used as a counter electrode and reference electrode was Ag/AgCl. Analyte solution consisted of 100 μg/L Pb^{+2} and Cd^{+2} (precursors: Lead Nitrate and Cadmium Chloride Monohydrate from *Loba Chemie*), unless mentioned otherwise, supported in a 0.01 M HCl solution (*p*H = 2) to remove the effect of migration current.

Voltammetry

The three-electrode system was used to carry out electrochemical tests on PG STAT-101 potentiostat provided by *AUTOLAB* and powered by *NOVA* software. Deposition potential of -0.1 V was given to the solution with a deposition time of 10 min , unless stated otherwise. Stepping potential was set to 4 mV, frequency was set to 30 Hz and amplitude to 50 mV. During deposition, the working electrode acts as a cathode and reduces the metal ions to metal atoms

$$M^{2+} + 2e^{-} \rightarrow M \qquad (1)$$

The counter electrode completes the other half-cell by working as an anode and dissociates water molecules to liberate oxygen

$$2H_2O \rightarrow 4H^{+} + O_2 + 4e^{-} \qquad (2)$$

During stripping step, the working electrode acts as an anode and oxidizes the metal atoms back to metal ions

$$M \rightarrow M^{2+} + 2e^{-} \qquad (3)$$

while the counter electrode becomes cathode and completes the other half-cell by hydrogen ions reduction to hydrogen gas

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (4)$$

Results and discussions

In order to assess the effect of antimony amount on detection efficiency of analyte ions, stripping voltammetry was performed on the four prepared samples having 'Sb' weight percentages of 2, 3, 4 and 5%, with the results shown in figure 3. The results consist of separated and fairly well developed stripping peaks for both cadmium and lead. The characteristic peaks are obtained at -0.76 V for cadmium and -0.53 V for lead. The peak heights increase with the increase in the amount of antimony. Maximum values of 29.2μA and 49.4μA for cadmium and lead respectively are obtained for 5% AIAC sample. This observation is consistent with the previous studies i.e. peak height is proportional to the working ions concentration [6,9]. These peak currents are more than previously reported values [6-8, 16, 17], when compared to the amount of antimony used as working ion. This may be

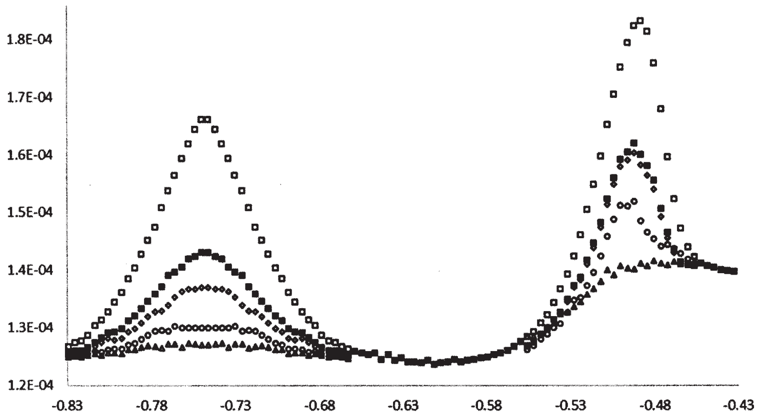

Fig. 3.SWASVs of 100μg/L Cd(II) and Pb(II) at the ex situ prepared AIAC electrodes. Solution: 0.01 M HCl (*p*H 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV. 5%(□), 4%(▪), 3%(◇), 2%(o), AC(▲)

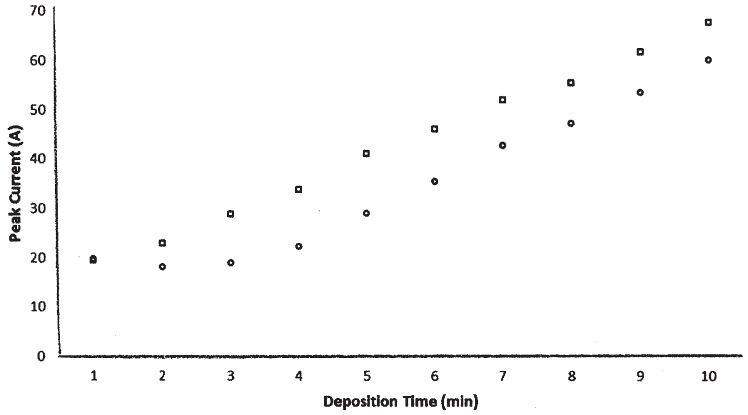

Fig. 4.Deposition time test of ex situ prepared AIAC electrodes with 100μg/L Cd(II) and Pb(II). Solution: 0.01 M HCl (*p*H 2), deposition at -0.1 V with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV. Cd(II) (o), Pb(II) (□)

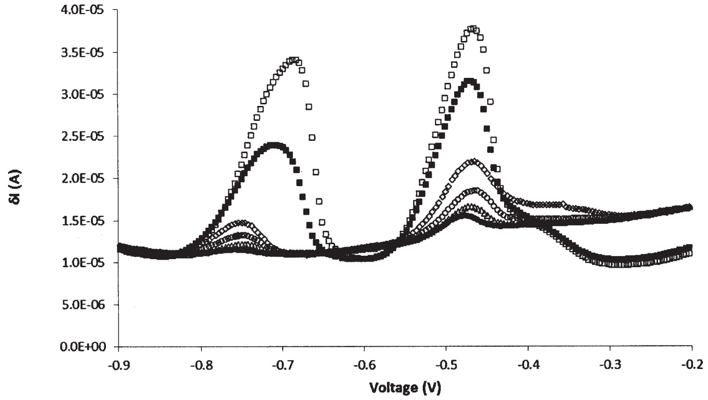

Fig. 5. SWASVs of 50-100μg/L Cd(II) and Pb(II) at the ex situ prepared 5% AIAC electrodes. Solution: 0.01 M HCl (*p*H 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV. 100(□), 90(▪), 80(◇), 70(o), 60(Δ), 50(▲)

because of the higher available surface area offered by the AIAC for the analyte ions deposition and better antimony dispersion obtained via impregnation. Furthermore, no peak voltage shift was observed for either cadmium or lead with the increase in the amount of antimony. This shows that the diffusional and capacitive currents are negligible for the selected voltage ramp, which may become important for narrow pore sized materials like activated carbon. It is important to note that antimony stripping is not observed at the oxidation potential of +0.1 V against Ag/AgCl reference electrode (not shown in the figure) indicating chemical adsorption of the antimony over the electrode surface.

The reproducibility of manufactured electrode was investigated employing 10 different electrodes all having 5% antimony concentrations. All tests were performed in 100μg/L concentration solutions of both analyte metal ions. The results show that AIAC has an excellent reproducibility and the standard deviation for cadmium and lead is no more than $8.37x10^{-6}$ μA and $1.06x10^{-5}$ μA respectively. A 5% AIAC electrode was tested under the conditions as of figure 3, twenty times consecutively, to check the reusability. The results have shown the excellent ability of the electrode to repeat the measurement with almost negligible error. Standard deviations of $6.32x10^{-6}$ μA and $1.06x10^{-5}$ μA for lead and cadmium were observed respectively. This repeatable behavior of AIAC can be attributed to the impregnated antimony that does not tend to dissolve at its oxidation potential during successive tests.

A series of deposition time tests were performed in 100 μg/L analyte solution and the data is presented in figure 4. As the deposition time increases stripping current increases linearly. Figure 5 shows various voltammograms obtained for 5% AIAC for successive addition of cadmium and lead in 10 μg/L steps in the concentration range of 50 – 100 μg/L. The calibration curves for both metal analyte ions are provided in figure 6 in which an exponential trend is observed. This non- linear behaviour can be related to small amount of antimony employed for the detection of analyte ions, which is further investigated and is a subject matter of our next study. In this study the carbon paste layer utilized contains 1.5 mg/L antimony, compared to previous studies usually having 500 mg/L antimony (in-situ) [6, 10] and 10 mg/L antimony (ex-situ) [17, 19]. Even with almost ten times less antimony, a higher signal to noise ratio is obtained. No peak for either cadmium or lead is observed below 50 μg/L concentration. Possible reason for this

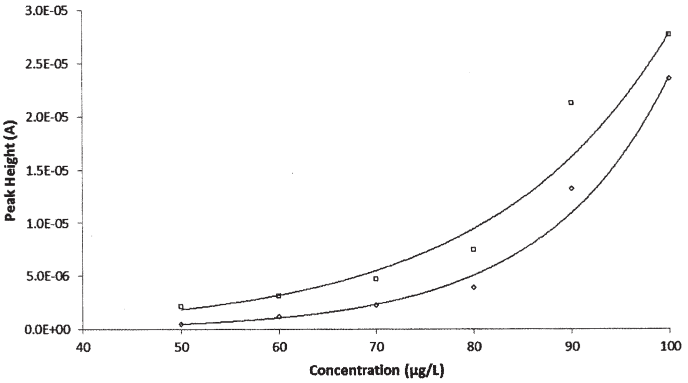

Fig. 6. Peak heights of Cd(II) and Pb(II) in SWASVs of 50-100 µg/L Cd(II) and Pb(II) at the ex situ prepared 5% AIAC electrodes. Solution: 0.01 M HCl (*p*H 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV. Cd(II) peak height(%), Pb(II) peak height(☐)

detection limit may be because of the hydrogen over potential. Although this potential with respect to antimony is negative [24], but it cannot be neglected with such small amounts of antimony on the AIAC.

Conclusions

Activated carbon is selected as the support material due to its high surface area. Antimony as working ion was chosen because of its low toxicity as compared to mercury and superior thermal characteristics with respect to bismuth. The results show that the current peaks obtained are directly proportional to the amount of antimony present on the electrode. The analyte peaks are remarkably higher when compared with the amount of antimony employed in previous studies. However, the detection limit of the electrode is lower because of the overall small surface antimony amount used. The detection repeatability and reproducibility are also superior because of the negligible antimony loss during stripping. The chosen impregnation method shows promising and practical results while introducing more antimony over the surface may enhance detection limits. As antimony stripping in electrolyte is quite low, so manufactured electrode is environmental friendly.

References

1. B. RAMOLA AS. Heavy Metal Concentrations in Pharmaceutical Effluents of Industrial Area of Dehradun (Uttarakhand), India. Int J Environ Sci Res. 2013;2(2):140-145.
2. GLANZE WD. Mosby Medical Encyclopedia, Revised Edition. St. Louis, MO: C.V. Mosby; 1996.
3. HOGAN CM. Heavy metal. Encyclopedia of Earth. National Council for Science and the Environment. Washington, D.C.: E. Monosson & C. Cleveland; 2010.
4. *** WHO. Health criteria and other supporting information. Guidelines for drinking-water quality 2. Geneva; 1996:940-949. doi:2nd ed.
5. WANG, J., Analytical Electrochemistry. NJ: Wiley-VCH; 2006.
6. TESAROVA E, BALDRIANOVA L, HOCEVAR SB, SVANCARA I, VYTRAS K, OGOREVC B. Anodic stripping voltammetric measurement of trace heavy metals at antimony film carbon paste electrode. Electrochim Acta. 2009;54(5):1506-1510. doi:10.1016/j.electacta.2008.09.030.
7. HOCEVAR SB, IVAN S, OGOREVC B, VYTR K. Antimony Film Electrode for Electrochemical Stripping Analysis. 2007;79(22):8639-8643.
8. GUZSVÁNY V, NAKAJIMA H, SOH N, NAKANO K, IMATO T. Antimony-film electrode for the determination of trace metals by sequential-injection analysis/anodic stripping voltammetry. Anal Chim Acta. 2010;658(1):12-7. doi:10.1016/j.aca.2009.10.049.
9. SOPHA H, BALDRIANOVA L, TESAROVA E, et al. Insights into the simultaneous chronopotentiometric stripping measurement of indium(III), thallium(I) and zinc(II) in acidic medium at the in situ prepared antimony film carbon paste electrode. Electrochim Acta. 2010;55(27):7929-7933. doi:10.1016/j.electacta.2009.12.089.
10. ASHRAFI AM, VYT AS K. Stripping voltammetric determination of mercury(II) at antimony-coated carbon paste electrode. Talanta. 2011;85(5):2700-2. doi:10.1016/j.talanta.2011.07.078.
11. ZHOU C, LU Y, LI X, LUO C, ZHANG Z. Adsorptive stripping voltammetric determination of antimony. 1998;46:1531-1536.
12. ADELOJU SB, YOUNG TM. Anodic stripping potentiometric determination of antimony in environmental materials. 1995;302:225-232.
13. V ESPB, BRIHAYE C, GILLAIN G, DUYCKAERTS G, ANALYTIQUE LDC, TILMAN S. DETERMINATION OF TRACES OF METALS BY ANODIC STRIPPING. 1983;148:51-57.
14. WOOLEVER CA, STARKEY DE, DEWALD HD. Differential pulse anodic stripping voltammetry of lead and antimony in gunshot residues. 1999;102:45-50.
15. PERLEY GA, COMPANY N. Antimony Electrode for Industrial Hydrogen-Ion Measurements. (1).
16. SVOBODOVA-TESAROVA E, BALDRIANOVA L, STOCES M, et al. Antimony powder-modified carbon paste electrodes for electrochemical stripping determination of trace heavy metals. Electrochim Acta. 2011;56(19):6673-6677. doi:10.1016/j.electacta.2011.05.048.
17. VASKO JOVANOVSKI, SAMO B. HOCˇEVAR BO. Ex Situ Prepared Antimony Film Electrode for Electrochemical Stripping Measurement of Heavy Metal Ions. Electroanalysis. 2009;21(21):2321 – 2324.
18. URBANOVÁ V, VYT AS K, KUHN A. Macroporous antimony film electrodes for stripping analysis of trace heavy metals. Electrochem commun. 2010;12(1):114-117. doi:10.1016/j.elecom.2009.11.001.
19. KOKKINOS C, ECONOMOU A, RAPTIS I, SPELIOTIS T. Novel disposable microfabricated antimony-film electrodes for adsorptive stripping analysis of trace Ni(II). Electrochem commun. 2009;11(2):250-253. doi:10.1016/j.elecom.2008.11.022.
20. ZHU L, XU L, HUANG B, JIA N, TAN L, YAO S. Simultaneous determination of Cd (II) and Pb (II) using square wave anodic stripping voltammetry at a gold nanoparticle-graphene- cysteine composite modified bismuth film electrode. Electrochim Acta. 2014;115:471-477. doi:10.1016/j.electacta.2013.10.209.
21. LV M, WANG X, LI J, et al. Cyclodextrin-reduced graphene oxide hybrid nanosheets for the simultaneous determination of lead (II) and cadmium (II) using square wave anodic stripping voltammetry. Electrochim Acta. 2013;108:412-420. doi:10.1016/j.electacta.2013.06.099.
22. PETROVIC SC, DEWALD HD. Square-wave anodic stripping voltammetry of Zn (II) as a method for probing instabilities at a glassy carbon mercury ® lm microelectrode. 1997;357:33-39.
23. MIRCESKI V, SEBEZ B, JANCOVSKA M, OGOREVC B, HOCEVAR SB. Mechanisms and kinetics of electrode processes at bismuth and antimony film and bare glassy carbon surfaces under square-wave anodic stripping voltammetry conditions. Electrochim Acta. 2013;105:254-260. doi:10.1016/j.electacta.2013.04.152.
24. AMIR M. ASHRAFI KV. Determination of Trace Bismuth(III) by Stripping Voltammetry at Antimony-Coated Carbon Paste Electrode. Int J Electrochem Sci. 2012;7:68-76.

Manuscript received: 11.02.2014