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Hg(II) immobilized MWCNT graphite electrode for the anodic stripping voltammetric determination of lead and cadmium

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ABSTRACT

The preparation of Hg(II)-modified multi walled carbon nanotube (MWCNT) by reaction of oxidized MWCNT with aqueous $HgCl_2$ was carried out. The Hg(II)-modified multi walled carbon nanotube (Hg(II)/MWCNT) dispersed in Nafion solution was used to coat the polished graphite electrode surface. The Hg(II)/MWCNT modified graphite electrode was held at a cathodic potential (−1.0 V) to reduce the coordinated Hg(II) to Hg forming nanodroplets of Hg. The modified electrode was characterized by FESEM/EDAX which provided useful insights on the morphology of the electrode. The SEM images showed droplets of Hg in the size of around 260 nm uniformly distributed on the MWCNT. Differential pulse anodic stripping voltammetry (DPASV) and electrochemical impedance spectroscopy were used to study the Hg(II) binding with MWCNT. Differential pulse anodic stripping voltammetry of ppb levels of cadmium and lead using the modified electrode yielded well-defined peaks with low background current under a short deposition time. Detection limit of 0.94 and 1.8 ng L^{-1} were obtained following a 3 min deposition for Pb(II) and Cd(II), respectively. Various experimental parameters were characterized and optimized. High reproducibility was observed from the RSD values for 20 repetitive measurements of Pb(II) and Cd(II) (1.7 and 1.9%, respectively). The determination of Pb(II) and Cd(II) in tap water and Pb(II) in human hair samples was carried out. The above method of fabrication of Hg(II)/MWCNT modified graphite electrode clearly suggests a safe route for preparing Hg immobilized electrode for stripping analysis.

1. Introduction

Ever since the invention of polarography, mercury has been established as the electrode material of choice for analytical electrochemistry in the negative potential regime. The dropping mercury electrode (DME) and the hanging mercury drop electrode (HMDE) have been used successfully in countless applications involving reduction of organic and inorganic electroactive compounds [1]. However successful, DME and HMDE come with serious problems such as potential risks of poisoning, contamination and disposal associated with the use of mercury in these techniques. Moreover it is not suitable for on-site analysis or in flow systems. Hence attempts have been made to address the above limitations and disadvantages. Mercury film electrodes (MFE's), prepared by coating a suitable substrate to give a thin 'film' of metallic mercury, have been used to circumvent the problems associated with Hg contamination [2,3]. MFE's can be of fairly small size, provide a larger surface-to-volume ratio, are mechanically more stable than mercury drops and offer great scope for different cell configurations (e.g. rotating electrodes and flow-systems) and for also chemical modification of their surface. Additionally, as the preparation of MFE's requires only minute quantities of mercury, the consumption of metallic mercury is minimized.

The most common substrate used for mercury film modified electrodes is carbon due to its chemical inertness, low residual current, wide operating potential and low cost. Glassy carbon, a vitreous form of isotropic carbon, is the preferred material in most cases [4]. It has been suggested that the coating of the glassy carbon electrode with Hg film can be combined with polymer membranes [5]. The Hg film was formed either before or after the polymer coating. Wang et al. [6] used a cellulose acetate film over a previously Hg film coated glassy carbon electrode. Morrison et al. [7] used Nafion or cellulose acetate-coated mercury film electrodes for the electrochemical speciation analysis of Cu complexes.

Carbon-based nanomaterials especially carbon nanotubes have been shown to be ideal for sensor applications since they are conductive, easily functionalized, and possess very large surface area. Carbon nanotubes (CNTs) represent an increasingly important group of nano materials with unique geometric, mechanical, electronic and chemical properties [8,9]. Such properties of CNTs also make them extremely attractive in electrochemical detection. Recent studies demonstrated that CNTs can impart strong

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electrocatalytic activity and minimize surface fouling on electrochemical devices [10,11]. The surface of the carbon nanotubes can be activated or functionalized. The oxygen-containing activated sites are ideal for the immobilization and stabilization of molecules, enzymes, metal nanoparticles, etc. [12–18].

Electrochemical detections of metal ions have widely been studied using CNT modified electrode. For example, Yuan et al. developed an electrode by casting a dispersed solution of MWCNTs in Nafion on GCE [19]. It was applied for the detection of europium(III) by differential pulse adsorptive stripping voltammetry under a wide linear range from 40 nM to 10 mM. Sun et al. used SWCNTs-Nafion film for the determination of Cd(II) in water [20]. Profumo et al. have prepared chemically modified MWCNTs electrode to detect trace amounts of As(III) and Bi(III) in natural and high-salinity waters [21].

Optical methods of analysis like atomic absorption spectrophotometry (AAS), and conventional analytical techniques such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence (XRF), neutron activation analysis (NAA), etc. are being used for trace element detection. However they are impractical for on-site screening or for quantification as part of a decision tool owing to their size, high labor and analytical costs. Anodic stripping voltammetry (ASV) is widely used for the measurement of metal ions and is one of the most sensitive methods for determination of trace levels of numerous ions [22–24]. Electrodes modified with a mercury film on a glassy carbon electrode has been effectively used for stripping analysis [2]. It is a convenient and highly sensitive technique based on the ability of mercury to form amalgams with other metals during a preconcentration step [25].

In this work Hg(II) was coordinated to an activated MWCNT by complexation [26]. The Hg(II) modified MWCNT, referred as Hg(II)/MWCNT was immobilized onto a polished graphite rod after dispersing in Nafion. By application of a constant potential of −1.0 V, the Hg(II) bound to the oxygen-containing functional groups of MWCNT [27] gets reduced to form nanodroplets of Hg. Thus introduction of Hg using MWCNT presents an alternative way for preparing Hg-film electrodes. MWCNT as well as Nafion stabilize the mercury mechanically on the surface. The simultaneous determination of Cd(II) and Pb(II) in ppb levels was done with the modified electrode using Differential Pulse Anodic Stripping Voltammetry (DPASV). The above ions in tap water and human hair were also estimated using the modified electrode.

2. Experimental

2.1. Reagents

The MWCNTs used in this work were synthesized by catalytic decomposition of acetylene over Ni/Cr hydrotalcite-type anionic clay catalyst and the purity is more than 95% [28]. Analytical-reagent grade chemicals (Aldrich, Merck) were used to prepare stock solutions and buffers. All the chemicals were used without further purification. All the solutions were prepared with deionized water. 10 mL of stock Hg(II)chloride solution (1.0 M) was prepared by dissolving $HgCl_2$ in absolute ethanol and acidifying with 0.1 mL of concentrated acetic acid. A 0.5% solution of Nafion was prepared by diluting with dry ethanol. Spectroscopic grade low density graphite rods (Aldrich, USA Product number: 496537-43.3G) of 0.3 cm circular diameter and 4.0 cm length were used.

2.1.1. Human hair sample preparation

The extraction of Pb from human hair was carried out according to previous report [29]. Hair sample was taken from a volunteer. The solution obtained was brought to experimental pH before carrying out the analysis.

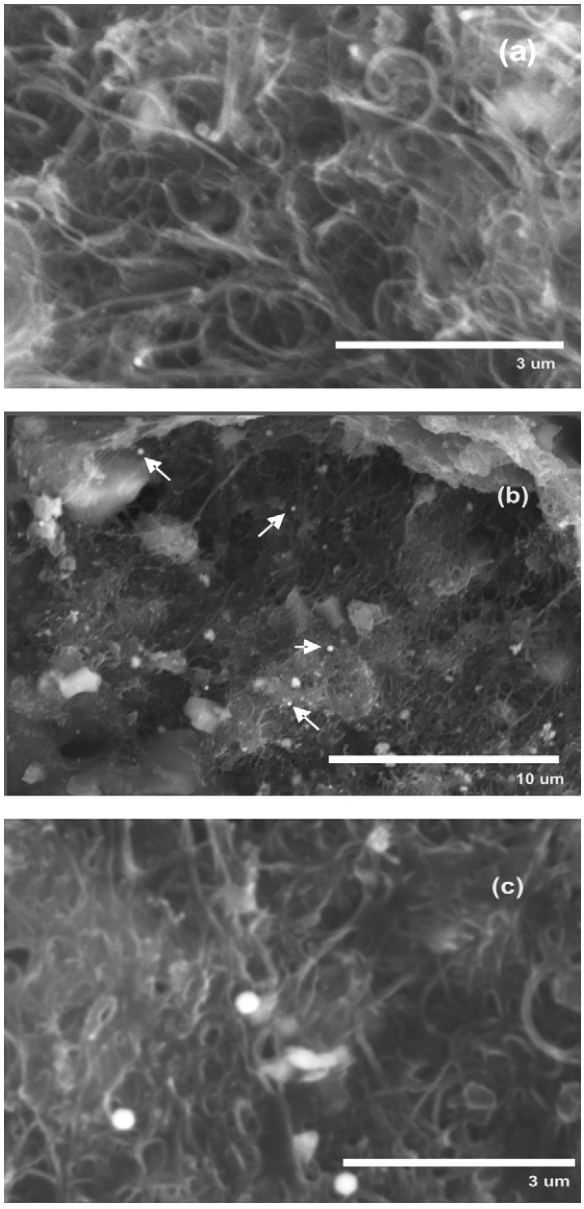


Fig. 1. FESEM image of (a) COOH-MWCNT/Nafion modified graphite electrode, (b) Hg/MWCNT modified graphite electrode after being held at −1.0 V for 300 s to reduce Hg(II) to Hg(0) and (c) Hg/MWCNT modified graphite electrode at higher magnification.

2.2. Apparatus

All the voltammetric determinations were carried out with a CHI 660B electrochemical workstation (CH Instruments, USA). A conventional three-electrode system was used that consisted of the Hg/MWCNT modified graphite electrode as the working electrode (3 mm diameter), a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE). All experiments were conducted under ambient temperature conditions of 24 ± 2 °C.

Field Emission Scanning Electron Microscopy (FESEM) images were obtained by using a Hitachi SU-6600 microscope (Japan) using an accelerating voltage of 15 kV without sputter coating. EDAX analysis was done using a Horiba EMAX X-ray analysis spectrome-

ter. For AAS measurements of Cd(II) and Pb(II), a Perkin Elmer 5100 AAS spectrometer was used.

2.3. Electrode fabrication

2.3.1. Purification/oxidation of CNTs

Although many oxidants such as HNO_3, H_2SO_4, Br_2, and RuO_4 [30,31] have been employed for CNT purification/activation, in the current work, in order to obtain high yields of purified carbon nanotubes as well as high percentages of oxygen containing functional groups on the surface of the nanotubes, raw MWCNTs were purified/oxidized using a $H_2SO_4/KMnO_4$ solution as the oxidant [27].

2.3.2. Synthesis of Hg(II)MWCNT complexes

The preparation of Hg(II)/MWCNT was carried out by procedure already reported [26]. About 2 mg of purified/activated MWCNT was mixed with 3 mL of 1.0 M $HgCl_2$ aqueous solution and stirred for 5 h. Two types of surface-confined Hg(II) complexes are formed and have been identified as $(CNT–COO)_2Hg^{II}$ and $(CNT\text{-}O)_2Hg^{II}$ [26]. The Hg(II)-modified MWCNTs obtained after filtration was thoroughly washed with distilled water and dried at room temperature under vacuum for 14 h.

2.3.3. Preparation of Hg(II)/MWCNT modified graphite electrode

The graphite rods were cut into the required dimension (0.3 cm circular diameter and 4.0 cm length). The lower end of the graphite electrode was polished over a fine grain emery paper followed by polishing on an A4 paper and the final mirror polish was obtained with velvette cloth for modification. About 0.6 mg of Hg(II)/MWCNT was dispersed homogenously in 1 mL of 0.5% Nafion by sonication for 10 min. The desired amount from the mixture was uniformly coated on a smoothly polished graphite electrode and was allowed to dry at room temperature for 2 h.

3. Results and discussion

3.1. Field Emission Scanning Electron Microscope (FESEM)/Energy Dispersive X-ray analysis (EDAX) characterization of the Hg(II)/MWCNT modified electrode

Scanning electron microscopy (SEM) can give useful insights on the changes over the MWCNT surface. The Hg(II)/MWCNT modified graphite electrode was characterized by FESEM and EDS analysis and the same was compared with MWCNT without Hg. Mere activated MWCNT dispersed in Nafion (in a similar ratio) as mentioned in Section 2.3.3 was used for electrode fabrication. Fig. 1(a) shows the FESEM image of the MWCNT/Nafion modified graphite electrode wherein it is observed that the MWCNT are uniformly dispersed. The FESEM images of the Hg(II)/MWCNT modified graphite electrode after reduction (at −1.0 V in 0.1 M perchloric acid for 300 s) at different magnifications are shown in Fig. 1(b and c). The sequence of the events of mercury nanodroplet formation is shown in Scheme 1. The Fig. 1(b and c) shows the formation of nano droplets of Hg of equal size (260 nm) which are fairly distributed in the MWCNT matrix. These Hg droplets pre-concentrate the reduced metal ions (analyte), during the deposition process.

The Hg/MWCNT modified graphite electrode was characterized by EDS to obtain the semi-quantitative information about the Hg nanodroplet in the MWCNT. Fig. 2 shows the energy dispersive X-ray analysis of the surface of Hg/MWCNT modified graphite electrode. It can be observed that the region analyzed (i.e., Fig. 1c) shows a higher content of Hg which can be ascribed to the formation of Hg droplets. The S and F peaks were obtained due to the presence of Nafion.

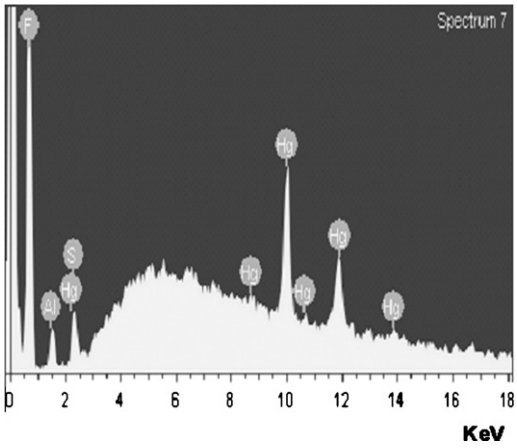


Fig. 2. EDAX spectra of the Hg/MWCNT modified graphite electrode after being held at −1.0 V for 300 s. Electrolyte: 0.1 M Perchloric acid.

3.2. Differential pulse anodic stripping voltammetric (DPASV) characterization of Hg(II)/MWCNT modified graphite electrode.

The Hg(II)/MWCNT modified graphite electrode was characterized by DPASV. The modified electrode was held at a negative potential of −1.0 V in 0.1 M perchloric acid for 300 s for the reduction of Hg(II) bound to the MWCNT. When the modified electrode was scanned from −0.6 to 0.6 V, it displayed a sharp peak at 0.4 V (Fig not shown) due to stripping of Hg present on MWCNT.

$$Hg(\text{nanodroplets}) - 2e^- \rightarrow Hg^{2+}(\text{soln}) \quad (1)$$

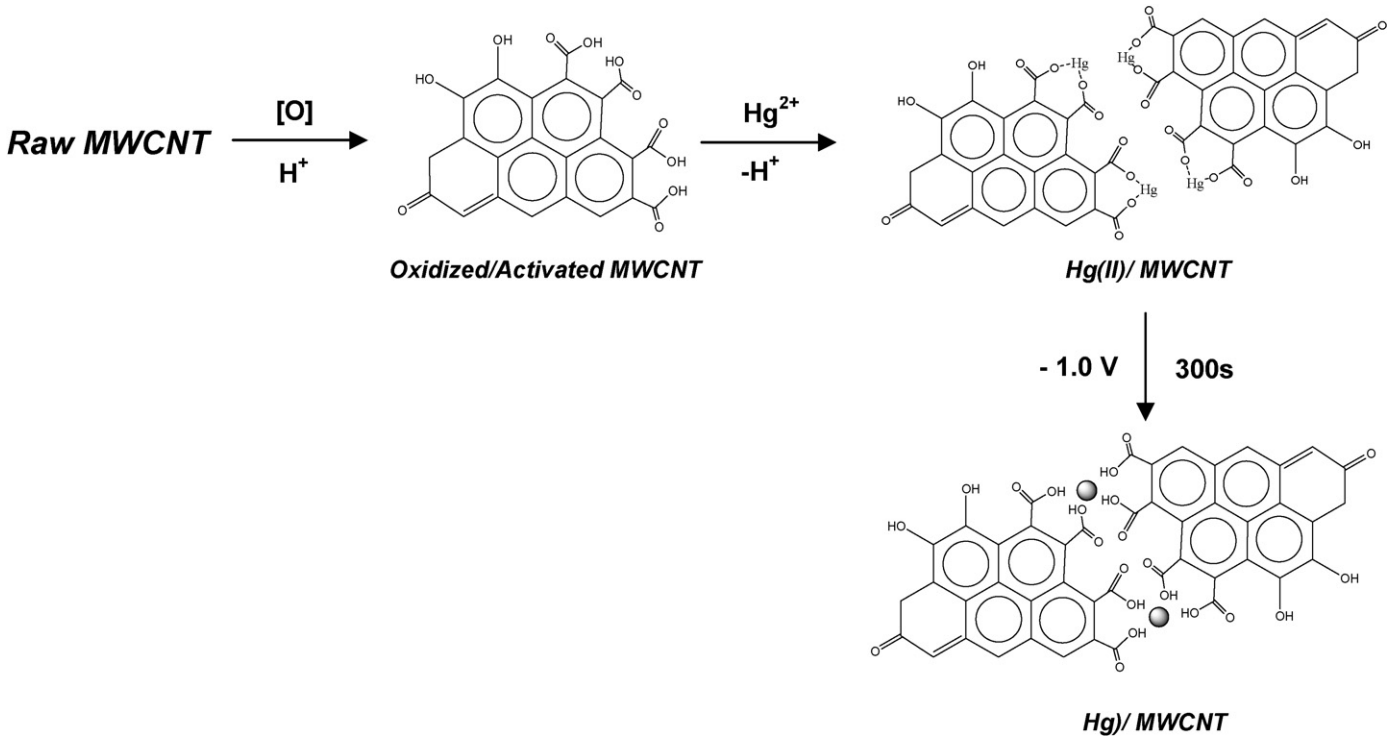
3.3. Electrochemical impedance study of the Hg(II)/MWCNT modified graphite electrode

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for studying the interface properties of surface modified electrodes. EIS is based on the response measurement of the electrochemical cell to simple amplitude potential. The surface changes on the electrode causes changes in the ac response. This change can be modulated according to Randle's equivalent circuit [32]. Thus two frequency regions, high and low can be distinguished to understand the change in the impedance. It relies on the fact that the ac current densities in the solution very near to the working electrode are proportional to the local impedance properties of the electrode.

Fig. 3 shows the EIS spectra of the (a) MWCNT/Nafion modified graphite electrode, (b) Hg(II)/MWCNT modified graphite electrode and (c) Hg(0)/MWCNT modified graphite electrode in 5 mM $K_4[Fe(CN)_6]$ in 0.1 M acetate buffer solution. After fitting suitable equivalent circuit, the electron transfer resistance (R_{ct}) was calculated. An R_{ct} value of 302 Ω, 212 Ω and 189 Ω were obtained for MWCNT/Nafion modified graphite electrode, Hg(II)/MWCNT modified graphite electrode and Hg/MWCNT modified graphite electrode, respectively. The observation implied that the Hg(II) coordination to MWCNT could increase the electron transfer rate on the electrode surface, furthermore when the coordinated Hg(II) was reduced to Hg nanodroplets, the electron transfer rate increased due to the metallic Hg. A substantial reduction in the R_{ct} value (113 Ω) was observed between the MWCNT/Nafion modified graphite electrode and Hg/MWCNT modified graphite electrode which confirms the formation of metallic mercury at the electrode surface.

3.4. Optimization of the electrode modification

The analytical performance of the Hg/MWCNT modified graphite electrode was initially evaluated by DPASV of Cd(II)



Scheme 1. Schematic representation of the Hg(II) binding to MWCNT and formation of nanodroplets by reduction.

and Pb(II) using standard solutions. The electrode modification procedure was optimized using the stripping analysis of Cd(II) and Pb(II) ions. The three main parameters that can be considered in this particular electrode modification are, concentration of Nafion, effect of Hg(II)MWCNT: Nafion ratio, and the volume of Hg(II)MWCNT/Nafion suspension coated on the graphite electrode.

The concentration of Nafion used was a key factor in the electrode modification. The effect of Nafion concentration was studied in the range from 0.25% to 1.0%. The stripping currents of the target metals ions showed an increase upto 0.5% of Nafion and later showed a decrease for higher concentrations of Nafion. An optimized concentration of 0.5% was used for further studies. Studies on the effect of Hg(II)MWCNT: Nafion ratio on the stripping current of Cd(II) and Pb(II) showed that the Hg(II)MWCNT: Nafion ratio proved very critical in the electrode modification. The Hg(II)MWCNT: Nafion ratio was varied keeping the Hg(II)MWCNT weight as constant (0.6 mg) and varying the volume of Nafion from 0.6 to 1.2 mL. It was observed that the stripping currents for the metal ions increased in the beginning and reached a maximum at a Nafion volume of 1.0 mL which later decreased for higher Nafion volume (volume >1.0 mL) as illustrated in Fig. 4A. The decrease in response at higher volume ratio of Nafion is due to the very thick Nafion film formed after coating as observed in previous report [33]. A Nafion volume of 1.0 mL produced the best stripping response for the metal ions.

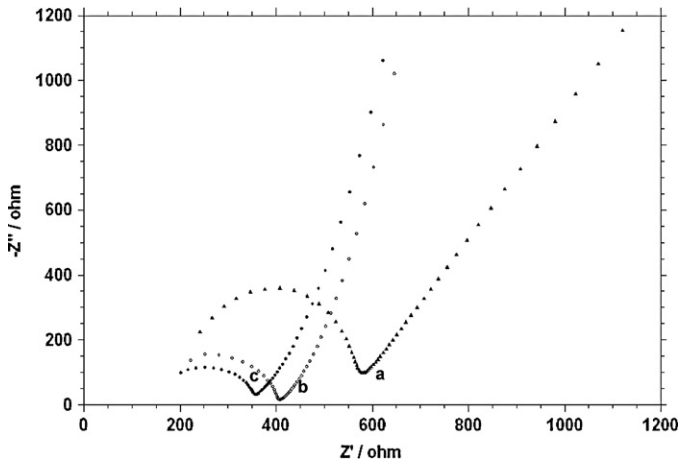


Fig. 3. Nyquist plots of (a) MWCNT/Nafion modified graphite electrode, (b) Hg(II)/MWCNT modified graphite electrode and (c) Hg/MWCNT modified graphite electrode in 5 mM $K_4[Fe(CN)_6]$ in 0.1 M acetate buffer solution.

The effect of volume of Hg(II)MWCNT/Nafion suspension coated on the graphite electrode on the stripping currents of Cd(II) and Pb(II) is illustrated in Fig. 4B. The above said effect was studied by varying the volume of Hg/MWCNT/Nafion suspension from 5 μL to 20 μL. The stripping current for the target metals gradually increased with well-defined and sharp stripping peaks upto 15 μL of suspension but at higher volume of suspension the stripping currents decreased drastically. This phenomenon could be explained by the fact that at higher volume of suspension, Nafion develops cracks due to contractive forces within the film. These cracks decrease the active surface on the electrode and the efficiency of the accumulation process itself is decreased in the process.

3.5. Effect of supporting electrolyte

The effect of different supporting electrolytes of the same concentration (0.1 M) on the DPASV response of Cd(II) and Pb(II) was tested and the results are shown in Fig. 5A. As shown in figure, 0.1 M acetate buffer solution was found to be the most suitable electrolyte for stripping analysis as it gave the best stripping response. The effect of concentration of the acetate buffer (pH 4.5) on the performance of the Hg/MWCNT modified graphite electrode was also studied. As shown in Fig. 5B the stripping currents for Cd(II) and Pb(II) showed a rapid increase with the increase of buffer con-

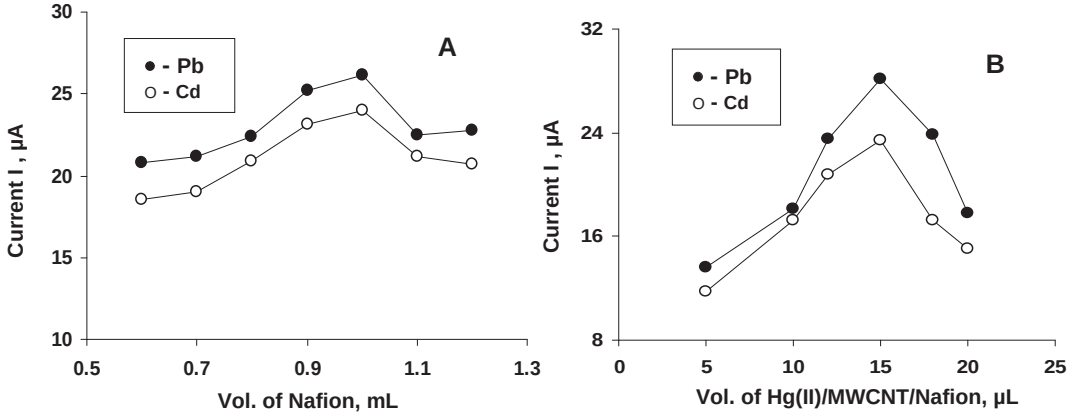


Fig. 4. (A) Plot of DPASV stripping currents of 0.15 µg L^{-1} of Cd(II) and 0.25 µg L^{-1} of Pb(II) as a function of volume of Nafion added to 0.6 mg of Hg(II)MWCNT in 0.1 M acetate buffer solution. (B) Effect of volume of Hg(II)MWCNT/Nafion suspension loading on the DPASV stripping currents of 0.15 µg L^{-1} of Cd(II) and 0.25 µg L^{-1} of Pb(II) in 0.1 M acetate buffer solution. Deposition potential −1.2 V, amplitude: 0.03 V, increment potential: 0.003 V, Quiet time: 15 s, pulse width: 30 mV.

Table 1
The analytical parameters for determination of metal ions.

Ions	Linear range (µg L^{-1})	Linear equation	*R*	LOD (ng L^{-1})[a]	Precision (RSD%)[a]
Cd	0.2–50	$y = 20.929 \times +43.83$	0.9977	1.8	3.1
Pb	0.2–50	$y = 12.263 \times +48.96$	0.9986	0.94	2.8

[a] An average of five replicate measurements.

centration from 0.02 to 0.1 M. The stripping signals of both metal ions decreased slightly at higher concentrations, indicating that the amalgam formation with the Hg nano droplets under the applied conditions were highly dependent on the ionic strength of the electrolyte solution. The same phenomenon was also observed in previous cases involving the role of ionic strength in the accumulation process [34].

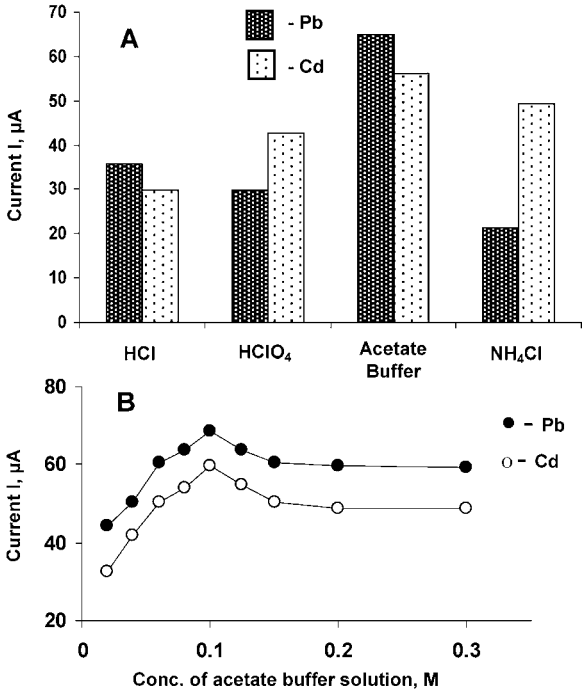


Fig. 5. (A) Effect of electrolyte (0.1 M) on the stripping currents of 0.3 µg L^{-1} Cd (II) and 0.56 µg L^{-1} Pb(II) and (B) Effect of buffer concentration on the stripping currents of 0.3 µg L^{-1} Cd(II) and 0.56 µg L^{-1} Pb(II) at the Hg/MWCNT modified graphite electrode. Conditions as in Fig. 4.

3.6. Optimization of measurement parameters

In order to adopt DPASV method for the determination of sub-ppb concentration of Cd(II) and Pb(II), three main parameters were optimized, which are namely pulse amplitude (ΔE), step potential (E_s), and pulse width ($t_{pw} = t_e$ (equilibrium time) + t_s (current sampling time)). The experiments were carried out with 30 ng L^{-1} of Cd(II) and Pb(II) and the above said parameters were systematically changed. The peak width increased linearly from 32 mV to 80 mV with increase in pulse amplitude from 10 mV to 40 mV. The stripping peak potential for Cd(II) and Pb(II) shifted by 10 mV in the negative direction. Pulse amplitude of 30 mV was chosen as the optimum value considering the peak width. E_s was changed in the range of 1–4 mV which caused an increase in peak current upto 3 mV, but further increase in E_s resulted in a decrease of peak current. Therefore an E_s of 3 mV was chosen for subsequent experiments. The pulse width was changed from 10–50 ms. The stripping peak currents for Cd(II) and Pb(II) decreased with increase in pulse width from 20 ms to 50 ms. Considering the reproducibility, signal to background ratio, a t_{pw} value of 30 ms was chosen for subsequent work.

The effect of deposition potential on the accumulation of Cd(II) and Pb(II) on the Hg/MWCNT modified graphite electrode was studied in the range of −0.6 to −1.4 V. The stripping peak currents were observed at −0.6 to −0.8 V for Cd(II) and Pb(II), respectively. The stripping currents for the Cd(II) and Pb(II) increased considerably with increase in deposition potential of −1.2 V and leveled off in the range of −1.2 to −1.4 V. Hydrogen evolution becomes a significant factor in the medium used [35] when the deposition potential was more negative than −1.3 V and hence the reproducibility of stripping currents of Cd(II) and Pb(II) become poor. Further, the effect of deposition time (t_{dep}) on the stripping peak currents of the metal ions was studied in the range of 30–300 s as shown in Fig. 6. The stripping currents for 0.1 µg L^{-1} Cd(II) and 0.2 µg L^{-1} Pb(II) increased linearly with the increase in deposition time upto 180 s. The stripping signals became almost constant when the deposition time was longer than 180 s ($t_{dep} > 180$ s). Hence for subsequent studies a deposition time of 180 s was chosen. The cad-

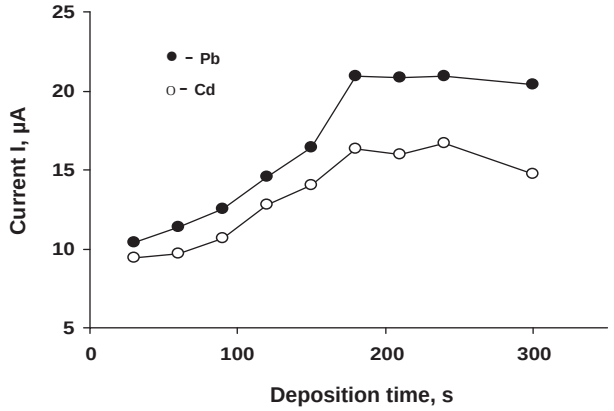


Fig. 6. The effect of deposition time on the stripping peak currents of and of Pb(II) and Cd (II) at the Hg/MWCNT modified graphite electrode, respectively. Conditions as in Fig. 4.

mium (E_{Cd}) and lead (E_{Pb}) peak potential were independent on the deposition potential but were dependent on the deposition time (i.e., for t_{dep} = 30 s, E_{Cd} = 0.855 V, E_{Pb} = 0.620 V, and for t_{dep} = 300 s, E_{Cd} = 0.890 V, E_{Pb} = 0.632 V).

3.7. Comparison of stripping analysis of Cd and Pb at bare graphite, MWCNT modified graphite and Hg/MWCNT modified graphite electrodes

Fig. 7A shows the DPASV for Cd(II) and Pb(II) determination with the bare graphite electrode, MWCNT modified graphite electrode and Hg/MWCNT modified graphite electrode. Both MWCNT modified graphite electrode and Hg/MWCNT modified graphite electrode displayed separate peaks for Cd and Pb following the 180 s of deposition. Hg/MWCNT modified graphite electrode displayed well-defined, sharp peaks showing the best response among the three electrodes. A 9 times enhancement in the peak current was observed with the Hg/MWCNT modified graphite electrode with respect to the bare electrode and 5 times with respect to the MWCNT/Nafion modified graphite electrode. As expected the MWCNT/Nafion modified graphite showed better response when compared to the bare electrode. The MWCNT as already reported, with closed topology and much larger surface area, exhibits strong adsorptive ability and hence improves their surface concentration [36]. The adsorption efficiency of Cd(II) and Pb(II) is much higher over the Hg/MWCNT modified graphite electrode when compared to the bare and MWCNT/Nafion modified graphite electrode. The reason is mainly due to the presence of Hg nanodroplets in the Hg/MWCNT modified graphite electrode. At the working pH (pH 4.5) Nafion, which is acting as the binder, is negatively charged due to the sulfonate groups present. As a result of this negative charge, the polymeric membrane acts as a cation exchanger facilitating the non-faradaic preconcentration of metal ions [37]. Hence, the stripping peak current increases remarkably at the Hg/MWCNT modified graphite electrode due to presence of Hg(0) with which the analyte metal form amalgam and is also assisted by the aforementioned reasons. In general, the Hg immobilized MWCNT modified electrode display relatively better signal to background characteristics, the enhanced sensitivity (ppb level detection) being mainly due to the formation of nano droplets of mercury on the electrode surface.

A low background current was observed for the Hg/MWCNT modified graphite electrode despite the use of nondeaerated solution (Fig. 7A). We found that the Hg/MWCNT modified graphite electrode is less susceptible to oxygen interference. This was indicated not only from the DPASV experiments but also from linear sweep voltammetric studies. Conducting such experiments in non-deaerated solution yielded a flat baseline using the Hg/MWCNT modified graphite electrode.

3.8. Calibration curve

After the optimization of the different parameters, stripping of Cd(II) and Pb(II) additions over two different concentration ranges of 0.01–0.05 $\mu g\,L^{-1}$ and 0.2–5 $\mu g\,L^{-1}$ were investigated. The stripping current was found to be linear with various concentrations of Cd(II) and Pb(II) in the ranges studied. A series of stripping voltammogram at low and higher concentrations are shown in Fig. 7B and C, respectively. The modified electrode was also investigated at even higher concentrations upto 50 $\mu g\,L^{-1}$ of Pb and Cd. The analytical performance parameters (linear limit range, limit of detection (LOD), correlation coefficient of calibration curves) of the developed stripping method were determined and is presented in Table 1. It is clear from the table that this method of simultaneous determination of Cd(II) and Pb(II) has a wide determination range and a very low limit of detection.

3.9. Reproducibility of stripping analysis using the Hg/MWCNT modified graphite electrode

The reproducibility of the stripping analysis using the Hg/MWCNT modified graphite electrode was evaluated by 20 repetitive measurements of 2 $\mu g\,L^{-1}$ of Cd(II) and Pb(II) with a single Hg/MWCNT modified graphite electrode. The R.S.D was found to be 1.9% for Cd(II) and 1.7% for Pb(II). Repetitive measurements with the modified electrode gave a R.S.D value less than 2% for Cd and Pb, which was better and superior to the MWCNT/Nafion modified graphite electrode (containing no coordinated Hg(II)) fabricated in the present study and also reported earlier [38]. The reproducibility among various Hg/MWCNT modified graphite electrode preparations was also estimated by comparing the stripping peaks of 2 $\mu g\,L^{-1}$ of Cd(II) and Pb(II) at all the Hg/MWCNT modified electrodes prepared. The R.S.D were found to be 3.3% and 2.9% for Cd(II) and Pb(II) respectively, which was better than the electrodes containing mere MWCNT which gave a R.S.D greater than 5%. The above observation revealed that the inclusion of Hg(II) in the MWCNT by coordination and successive reduction and amalgam formation with the target metal (Cd and Pb) significantly improved the reproducibility. The reproducibility of determination is a clear indication of the Hg nanodroplets anchored strongly to the MWCNT and thereby leaching of Hg into the experimental solution is greatly minimized.

3.10. Interferences

The selectivity of the method was tested by evaluating the possible interferences in the determination of Cd(II) and Pb(II). The selectivity was studied by spiking the interfering ions in 500 fold excess with 5 $\mu g\,L^{-1}$ of Cd(II) and Pb(II). It was observed that a large number of anions (Cl^-, Fl^-, SO_4^{2-}, and NO_3^-) in this 500 fold excess did not have any influence on the stripping currents of Cd(II) and Pb(II). Cations such as NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+} and Mn^{2+} did not show much interference as they are normally inactive in voltammetry. Co^{2+} and Ni^{2+} were observed not to interfere as these metal ions require a significantly higher deposition potential than applied in the present study. A stripping peak at −1.1 V from Zn^{2+} was observed when the deposition potential was held at −1.3 V and the peak height was larger when reduction was done at more negative potentials. The peak for Zn(II) however did not influence the Cd(II) and Pb(II) signals. The above observation is an indication that the Hg/MWCNT modified graphite electrode was suitable for multielement determination.

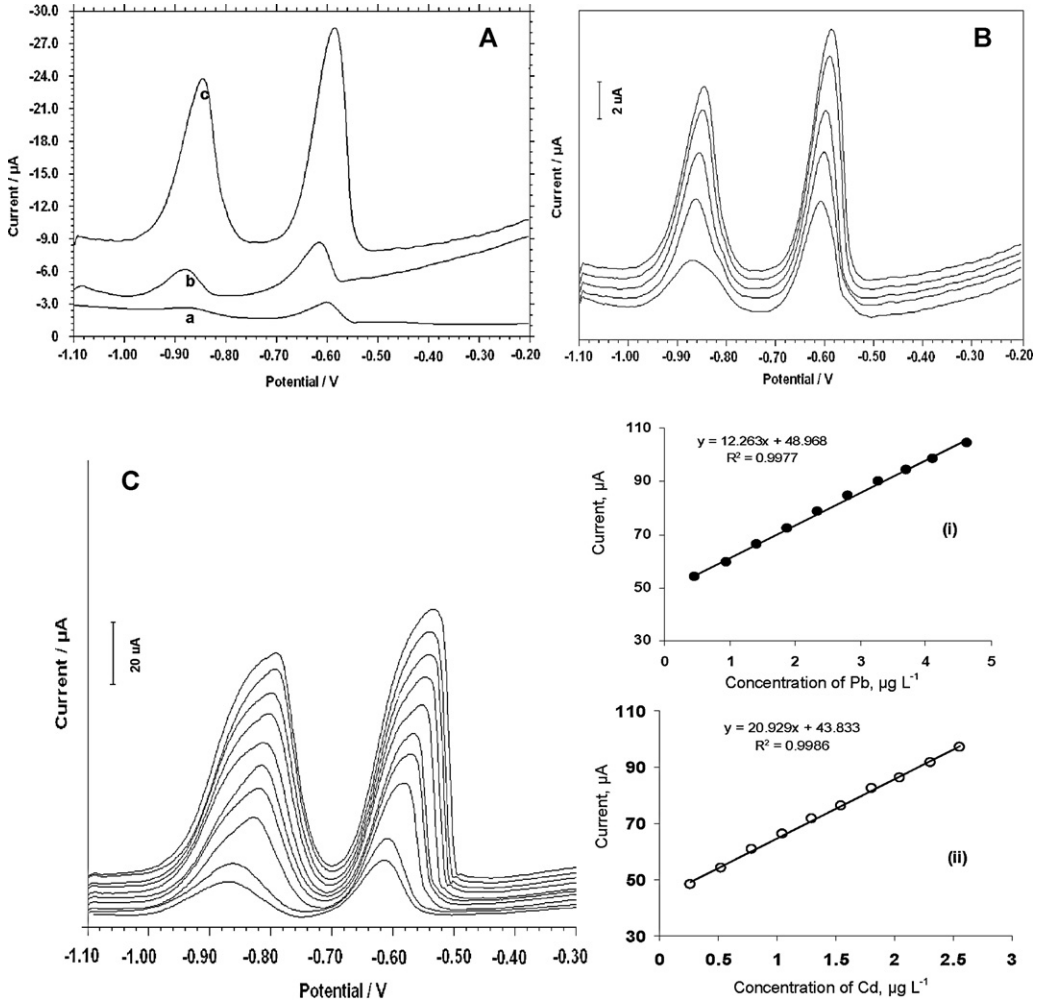


Fig. 7. (A) Stripping current for the solution containing 0.15 µg L^{-1} of Cd(II) and 0.25 µg L^{-1} of Pb(II) at the (a) bare, (b) MWCNT modified graphite electrode and (c) Hg/MWCNT modified graphite electrodes. (B) Stripping peak currents for Cd(II) and Pb(II) in the range of 0.01–0.05 µg L^{-1} at the Hg/MWCNT modified graphite electrode. (C) Stripping peak currents for Cd(II) and Pb(II) in the range of 0.2–5 µg L^{-1} at the Hg/MWCNT modified graphite electrode and insets (i) and (ii) are the corresponding calibration plot for Pb and Cd. Conditions as in Fig. 4.

The effect of different concentrations of Cu(II) on the stripping response of 2 µg L^{-1} of Cd(II) and Pb(II) was evaluated. It was observed that from a concentration ratio of 1:1 and above, the stripping response of the target metal ions was suppressed at the Hg/MWCNT modified graphite electrode and this substantially negates the benefit of using Hg nanodroplets. The suppression of the stripping is due to the competition between the Hg nano droplets and copper for Pb(II). Copper forms intermetallic compound with Pb thereby competing with mercury [39,40]. This interference was however alleviated by a method previously described i.e., by the addition of ferrocyanide [41]. In the present study 1.4×10^{-5} M of ferrocyanide was sufficient to alleviate the interference of copper (upto 500 µg L^{-1}). The addition of ferrocyanide must be done prior to the deposition step because it becomes impossible to remove the copper after it has been deposited.

3.11. Application to human hair and tap water

The Hg/MWCNT modified graphite electrode was applied for the analysis of Cd and Pb in human hair and tap water. A small hump at −0.8 V was observed along with a sharp peak at −0.6 V for tap water which is a fact that Cd(II) coexist with Pb(II) in tap water. In the case of hair samples a sharp peak particularly around −0.6 V was seen and no additional peaks were observed. These experiments demonstrate that it is possible to determine the above metals coexisting at varying concentrations by a judicious choice of experimental parameters. The same ions were also determined by AAS, which was used as a reference method. The results obtained with the determination of the target metal ions in tap water and human hair are summarized in Table 2.

Table 2
The results of the determination of Pb and Cd in tap water and human hair with DPASV and AAS.

Real sample		DPASV (µg L^{-1})[a] (Present method)	AAS (µg L^{-1})
Tap water	Pb	1.7 ± 0.06	1.8 ± 0.05
	Cd	0.14 ± 0.04	0.13 ± 0.02
Human hair	Pb	11.2 ± 0.2	10.8 ± 0.3

[a] An average of five replicate measurements.

4. Conclusion

We have demonstrated that the stripping voltammetric performance of the Hg/MWCNT modified graphite electrode is superior to that of bare graphite and MWCNT/Nafion modified graphite electrodes. The formation of Hg nanodroplets in the MWCNT makes it more suitable for detection of metal ions at very high sensitivity and

with very low detection limits. The use of the Hg/MWCNT modified graphite electrode with such response characteristics should facilitate the decentralized testing of heavy metals and development of metal sensors without the fear of Hg leaching. Analysis of these metal ions using our method is highly advantageous in comparing the cost effectiveness and simplicity of traditional methods.

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