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Detection of Trace Heavy Metal Ions Using Carbon Nanotube-Modified Electrodes

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Abstract
A sensitive voltammetric method for detection of trace heavy metal ions using chemically modified carbon nanotubes (CNTs) electrode surfaces is described. The CNTs were covalently modified with cysteine prior to casting on electrode surfaces. Cysteine is an amino acid with high affinities towards some heavy metals. In this assay, heavy metals ions accumulated on the cysteine-modified CNT electrode surfaces prior to being subjected to differential pulse anodic stripping voltammetry analysis. The resulting peak currents were linearly related to the concentrations of the metal ions. The method was optimized with respect to accumulation time, reduction time and reduction potential. The detection limits were found to be 1 ppb and 15 ppb for Pb^{2+} and Cu^{2+} respectively. The technique was used for the detection of Pb^{2+} and Cu^{2+} in spiked lake water. The average recoveries of Pb^{2+} and Cu^{2+} were 96.2% and 94.5% with relative standard deviations of 8.43% and 7.53% respectively. The potential for simultaneous detection of heavy metal ions by the modified CNTs was also demonstrated.

Keywords: Nanotubes, Heavy metals detection, Stripping voltammetry, Chemically modified electrodes, Cysteine, Trace analysis

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1. Introduction

Heavy metals are major contributors of pollution to the biosphere due to their toxicity and intrinsically persistent nature. Detection and monitoring of these environmental pollutants in soil, water and air is very important in the overall health of humans, and animals. Current methods for heavy metal detection that include spectroscopic methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrometry (ICPAES), and inductively coupled plasma mass spectrometry (ICPMS) are sensitive and selective. However, these methods require sophisticated instrumentation, skilled personnel and are expensive to run and maintain. Therefore, there is need to develop a simple, sensitive, selective, portable sensing platform for heavy metals.

We and other researchers have recently shown that electrochemical techniques such as differential pulse voltammetry and square-wave stripping voltammetry using modified electrodes are alternative and very attractive methods for mercury-free heavy metal detection [1–9]. Unlike spectroscopic methods, voltammetric methods using modified electrodes offer ultrasensitive, portable and ease-to-use systems combined with low-cost voltammetric instrumentation. The use of the CMEs tremendously improves the efficiency of preconcentration and detection of heavy metals. This improvement is much more than the 'classical' anodic stripping voltammetric methods are capable of achieving [10]. Many materials have been utilized in the modification of electrodes including conducting polymers [1, 11–16], zeolites [17], carbon pastes [17–24], metal oxides [25–29] and very recently carbon nanotubes [30–38].

Carbon nanotubes (CNTs) are becoming popular electrode materials due to their unique properties such as increased electrode surface area [39]. fast electron transfer rate [40], significant mechanical strength and good chemical stability [41, 42]. Recent studies have demonstrated that CNTs impart strong electrocatalytic activity and minimize electrode fouling [43–45]. The electrocatalytic effect of CNTs has been attributed to the activity of the edge-plane-like graphite sites at the CNTs ends [46].

In this article, we describe a sensitive method for detection of heavy metals using L-cysteine-functionalized carbon nanotube electrodes (MWNT-CO-Cys). L-Cysteine is a nonessential amino acid with a very high binding constant for some toxic heavy metal ions. It has previously been utilized in the stripping analysis of Cu^{2+} ions [47–50], modified gold electrodes [51] and colorimetric analysis of Cu^{2+} with modified gold nanoparticles [52]. Here, we describe the synthesis, characterization and application of the L-cysteine modified CNTs in the detection of heavy metal ions in a mercury-free system.

2. Experimental

2.1. Materials and Instrumentation

Multiwall carbon nanotubes (MWNTs, 20–30 nm outer diameter) were purchased from Nanocs Inc. (New York, NY). Glassy carbon electrodes of diameter 3.0 mm were obtained from Bioanalytical Systems Inc. (West Lafayette, IN). Solutions standards of Cu^{2+} and Pb^{2+} (in 20% HNO_3) and a Daigger Centrifuge were obtained from Fisher Scientific (Fair Lawn, NJ). Test solutions were made from the standards by dilution using de-ionized water. All electrochemical experiments were performed with a multi-channel VMP3 potential/galvanostat (Ametek Princeton Applied Research, Oak Ridge, TN). Scanning electron microscope images were recorded with JEOL Scanning Electron Microscope. Fourier transform infrared (FTIR) spectroscopy was performed on an FTS 7000 from Thermo Corporation. The FTIR spectrometer was equipped with DTGS KBr detector in the region $400–4000\ cm^{-1}$. An average of twenty scans ($4\ cm^{-1}$ resolution) were obtained and then averaged.

2.2. Carboxylation of MWNTs

The MWNTs were first carboxylated by sonicating 0.7 g of the material in a 150 mL mixture of concentrated H_2SO_4 and HNO_3 (3 : 1, v/v) for 4 hours. 250 mL of deionized water was added and the reaction allowed to cool to room temperature. The suspension was filtered through 0.25 micron pore-size membrane filter, washed with 0.05 M NaOH followed by washing with deionized water to pH 7.0 and dried at 110 °C. The resulting carbon nanotubes are refered to as MWNT-COOH in this document.

2.3. Functionalization of MWNT-COOH

0.5 g of MWNT-COOH were suspended in a solution containing 0.1 M 1-ethyl-3-(3-dimethylaminopropyl) carbo-diimide hydrochloride (EDC) and a 0.1 M of *N*-Hydrox-ysuccinimide (NHS) in 0.1 M acetate buffer (pH 5.5) for 1 hour with constant agitation. The nanotubes were centri-fuged at 6000 rpm and the solution phase was discarded. The nanotubes were washed three times with deionized water. They were then suspended in a solution containing 0.1 M cysteine in acetate buffer for 1 hour with constant stirring. Once again, the nanotubes were centrifuged at 6000 rpm and the solution phase was discarded. The nanotubes were washed with deionized water and centrifuged. The washing process was repeated three times. The water was discarded and nanotubes dried in ambient atmosphere and stored in the refrigerator. The resulting cysteine-modified nanotubes are referred to as MWNT-CO-Cys in this document.

2.4. Electrode Preparation

Glassy carbon electrodes (GCE) were polished sequentially with 1 micro and 0.05 micron size alumina powder, sonicated and rinsed with deionized water before use. A 10 mg/mL suspension of MWNT-CO-Cys in water was sonicated for 10 minutes. 10 μL of the MWNT-CO-Cys suspension was cast on the GCE electrode and left to dry at ambient conditions. This modified GCE electrode is denoted as GCE-MWNT-CO-Cys.

2.5. Electrochemical Experiments

A three-electrode configuration was employed, consisting of GCE-MWNT-CO-Cys as the working electrode, Ag/AgCl containing 3 M KCl was the reference electrode and platinum gauze was the counter electrode, respectively. All the solutions used for electrochemical experiments were deoxygenated by purging with pure nitrogen (99.99%) for 5 minutes prior to analysis. Cyclic voltammograms (CVs) were obtained by scanning from -0.8 V to $+0.1$ V and back at a scan rate of $50\ mV\ s^{-1}$. To accumulate analytes on electrode surface, GCE-MWNT-CO-Cys electrode was immersed in a stirred (300 rpm) acetate buffer solution containing a known concentration of metal ion at a specific amount of time. The electrode was removed after accumu-lation, rinsed with deionized water, dried and transferred to a fresh 0.1 M acetate buffer solution of pH 5.5 for differ-ential pulse anodic stripping voltammetry (DPASV). The differential pulse anodic stripping voltammograms were recorded at $36\ mV\ s^{-1}$ scan rate and 4 mV step height. At least three differential pulse anodic stripping voltammo-grams were recorded for each run.

3. Results and Discussion

Figure 1 shows the SEM image of MWNT-CO-Cys cast on the electrode surface. The nanotubes were several microns in length and the SEM reveals a mat-like electrode surface. The nanoscale nature of the nanotubes reflects the large increase in the apparent surface area of the electrode compared with the bare GCE. Figure 2 shows cyclic voltammograms (CVs) for cysteine-functionalized carbon nanotubes on glassy carbon electrode (GCE-MWNT-CO-Cys) after accumulation in a blank buffer solution and a buffer solution containing Cu^{2+}. The voltammogram of GCE-MWNT-CO-Cys in the blank buffer solution was relatively featureless (Fig. 2A) compared to that recorded after accumulation of Cu^{2+} which exhibited a prominent anodic and a smaller cathodic peak at approximately -0.02 V and -0.15 V versus Ag/AgCl electrode respec-tively (Fig. 2B). The GCE-MWNT-COOH electrode system (without cysteine) exhibited featureless voltammograms (data not shown) after having been in a solution containing Cu^{2+} to accumulate the ions. This implies that binding of cysteine is required for Cu^{2+} to be accumulated so that a
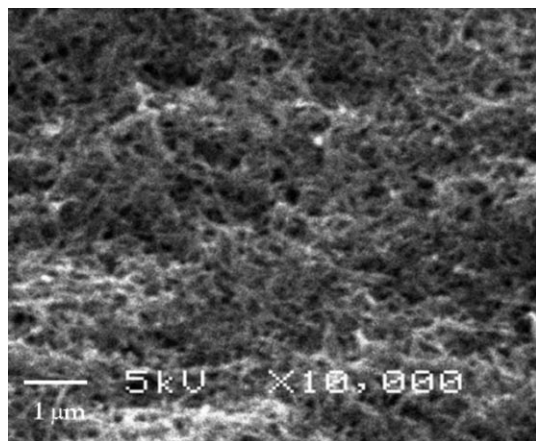
Fig. 1. SEM image of a film of MWNT-CO-Cys cast on electrode surface.

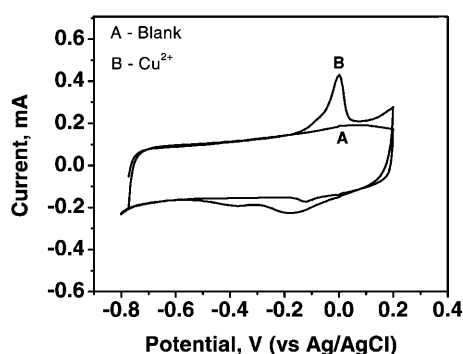Fig. 3. FTIR spectra: MWNT (A), MWNT-COOH (B), MWCNT-CO-Cys (C).

Fig. 2. CV of GCE-MWNT-CO-Cys electrode before (A) and after (B) accumulation in 0.1 M acetate buffer pH 5.5 containing 5 ppm Cu^{2+}. Scan rate 50 mV s^{-1}.

Fig. 4. Differential pulse anodic stripping voltammogram of GCE-MWNT-CO-Cys electrode after accumulation in 0.1 M acetate buffer pH 5.5 containing 20 ppm Cu^{2+} (A) and 0.5 ppm Pb^{2+} (B).

peak can be observed meaning that the metal ion was complexed rather than just being deposited on the nanotubes. The cathodic peak corresponds to reduction of Cu^{2+} that was complexed with cysteine on the GCE-MWNT-CO-Cys during accumulation step. The anodic peak, on the other hand, is due to oxidation of Cu^{0} to Cu^{2+}. This observation further reinforces the fact that cysteine was indeed covalently bound to the carbon nanotubes.

Further evidence of cysteine binding was observed in the FTIR spectra as shown in Figure 3. As expected, the FTIR spectrum of pristine MWNTs (Fig. 3A) showed no obvious peak indicating absence of functional groups. However on oxidation of the MWNTs several peaks were observed. The peak at about 1750 cm^{-1} (Fig. 3B) indicated presence of carbonyl group (C=O stretch) introduced on the MWNTs to yield the oxidized MWNT-COOH. The broad peak at about 3400 cm^{-1} is due to O–H stretch. Figure 3C shows FTIR spectrum after functionalization of MWNT-COOH with cysteine to form MWNT-CO-Cys. Cysteine on the carbon nanotube introduced secondary amide groups as was reflected by the emergence of the characteristic secondary amine peak at about 1650 cm^{-1}. These FTIR spectra provided further evidence that cysteine was covalently attached to the MWNTs.
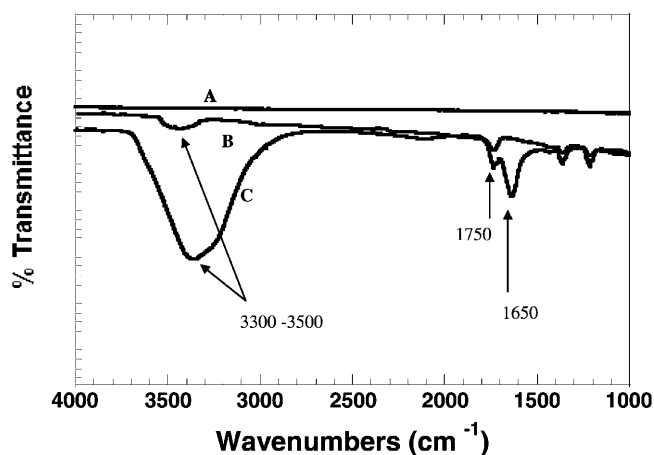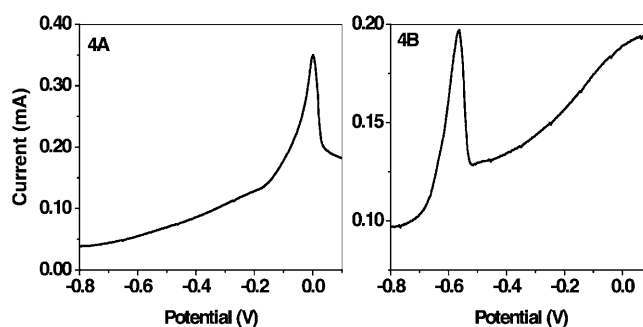
From cyclic voltammetry data, (Fig. 2) the anodic peak was more prominent and sharper than the cathodic peak. We therefore recorded the differential pulse voltammetry experiments by scanning towards less negative and more positive potentials as opposed to scanning in the opposite direction for optimization and analytical applications. Figure 4A represents the differential pulse anodic stripping voltammograms of GCE-MWNT-CO-Cys after accumulation in 20.0 ppm of Cu^{2+} solution. As expected, a peak at about -0.02 V was attributed to oxidation of Cu. Similar differential pulse anodic stripping voltammogram of the GCE-MWNT-CO-Cys were obtained after accumulation in 0.5 ppm of Pb^{2+} solution (Fig. 4B). The peak at about -0.6 V attributed to the oxidation of Pb.

3.1. Principle of Detection

Based on the above observations, the proposed mechanism of accumulation, reduction and anodic stripping analysis is outlined in scheme 1. The first step involves complex formation between the immobilized cysteine and the heavy metal ion M^{2+} (Scheme 1A). The second step is the
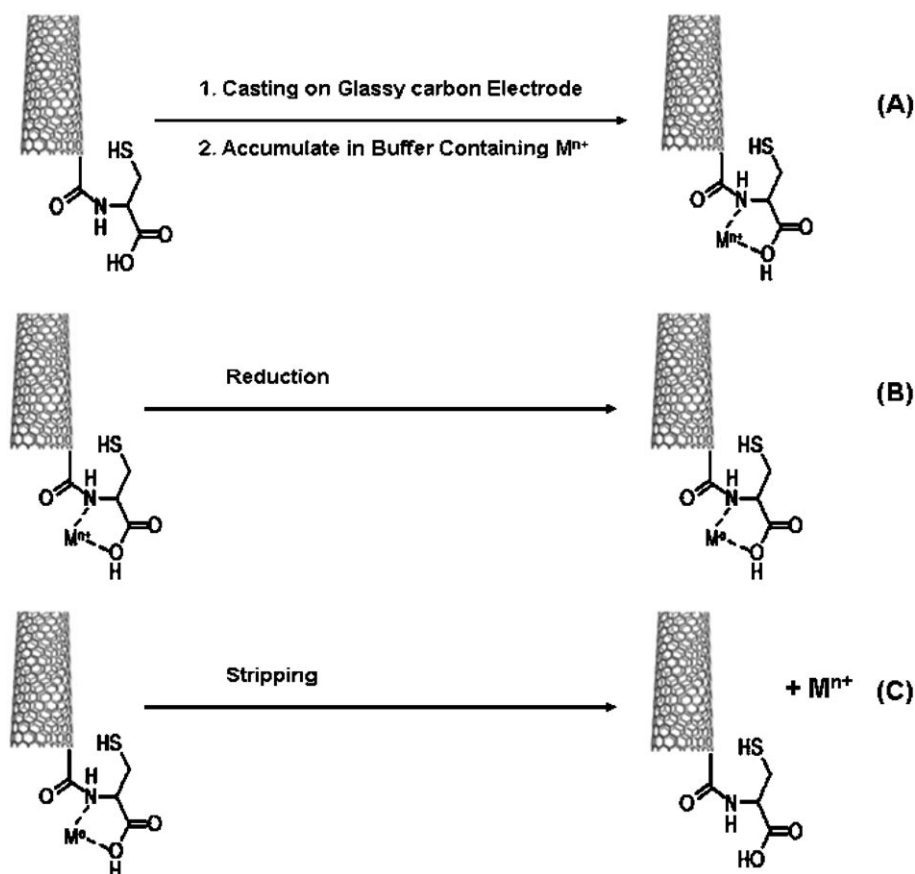
Scheme 1. Proposed accumulation and voltammetric mechanism.

reduction of the accumulated M^{2+} ions to M^0 by application of negative potential (Scheme 1B). The third step is the stripping step where M^0 is electrochemically stripped back into the solution by scanning towards positive potentials (Scheme 1C). The resulting stripping peak was found to be proportional to the amount of M^{2+} in the accumulation solution.

3.2. Optimization

Accumulation time, reduction time and reduction potential are very important parameters for stripping analysis as they have a large effect on the stripping signal. These parameters were optimized using Cu^{2+} as the analyte. In our set up, accumulation time was represented by the length of time allowed for the complexation reaction between the GCE-MWNT-CO-Cys electrode system and the Cu^{2+} prior to stripping analysis. The accumulation time was therefore varied from 0 to 30 minutes followed by stripping analysis. The stripping signal reached a maximum after 10 minutes of accumulation time. No significant increase in the stripping peak was recorded on increasing the accumulation time. This indicates that the complexation reaction between the GCE-MWNT-CO-Cys electrode system and Cu^{2+} reached equilibrium at this time and a steady state situation was

achieved. Therefore an accumulation time of 10 minutes was used in subsequent experiments.

The duration and magnitude of applied reduction potential are also important parameters as they influence the rate and efficiency of conversion of the complexed Cu^{2+} on the electrode to Cu^0 prior to being stripped back into the solution. These parameters were sequentially optimized in a similar manner as described above for accumulation time resulting in an optimized reduction time of 180 seconds and a reduction potential of -1.0 V.

3.3. Calibration, Detection Limit, and Interferences

GCE-MWNT-CO-Cys electrode systems were exposed to standard solutions containing different concentrations of Cu^{2+} and Pb^{2+} in 0.1 M acetate buffer pH 5.5 and using the optimum conditions described above. The resulting differential pulse voltammograms are shown in Figure 5. Well-defined peaks, with peak currents proportional to the concentrations Cu^{2+} and Pb^{2+} metal ions were observed at -0.02 V and -0.6 V respectively. Insets of Figure 5 represent the calibration curves for Cu^{2+} and Pb^{2+} versus the corresponding stripping peak currents. The calibration curves were linear up to 1.5 ppm for Cu^{2+} and up to 750 ppb for Pb^{2+}. The detection limit (based on three times
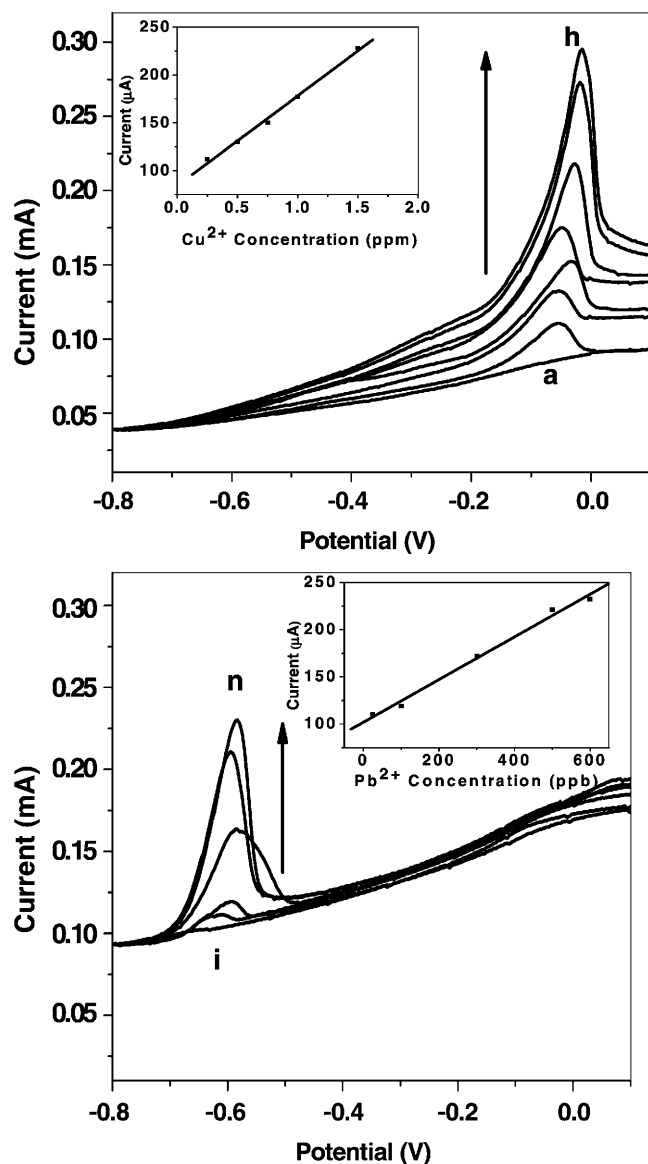
Fig. 5. A) Differential pulse anodic stripping voltammograms of Cu^{2+} accumulated on GCE-MWNT-CO-Cys electrode: a) to h) 0, 0.25, 0.5, 0.75, 1.0, 5, 10, and 20 ppm Cu^{2+}. Accumulation time 30 minutes in 0.1 M acetate buffer pH 5.5. Voltammetric conditions: 0.1 M acetate buffer pH 5.5, reduction time 3 minutes, reduction potential -1.0 V. Inset: Calibration curve for Cu^{2+}. B) Differential pulse anodic stripping voltammograms of Pb^{2+} accumulated on GCE-MWNT-CO-Cys electrode: i) to n) 0, 25, 100, 300, 500, and 600 ppb Pb^{2+}. Accumulation time 30 minutes in 0.1 M acetate buffer pH 5.5. Conditions: Same as in Fig. 4A. Inset: Calibration curve for Pb^{2+}.

the mean of blank measurements) was calculated by making replicate current measurements at -0.02 V and -0.6 V for blank solutions. The detection limit was found to be 15 ppb Cu^{2+} and 1 ppb Pb^{2+}.

From the interference studies performed, it was found that anions including 40 fold Cl^-, 30 fold SO_4^{2-} and four fold CO_3^{2-} did not have any significant effect on the stripping peak current. Equimolar amounts of Cu^{2+} and Pb^{2+} in sub ppm concentration levels did not have a significant effect on
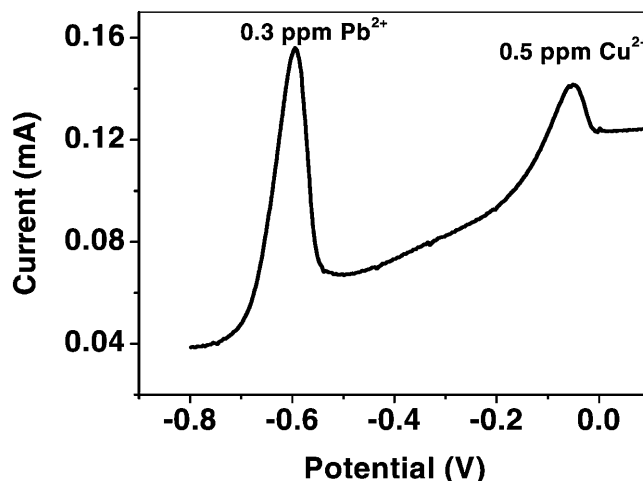

Fig. 6. Typical differential pulse anodic stripping voltammograms of 0.25 ppm Cu^{2+} and 0.3 ppm Pb^{2+} accumulated on GCE-MWNT-CO-Cys electrode. Accumulation time 30 minutes in 0.1 M acetate buffer pH 5.5. Voltammetric conditions: 0.1 M acetate buffer pH 5.5, reduction time 3 minutes, reduction potential -1.0 V.

the stripping current of either metal. However, when the concentration of Cu^{2+} was increased 4 fold, the Pb^{2+} peak current was decreased by about 40%. Such effects have been reported [53] and are related to the formation of Pb-Cu solid solutions [54]. Cd^{2+} had no effect on the Cu^{2+} but its effect on Pb^{2+} peak current was similar to Cu^{2+}. Also Ni^{2+} reduced the Pb^{2+} peak current by as much as 21%. These interferences are not unusual since l-cysteine has significant affinities to some heavy metals.

After demonstrating the feasibility of the technique for the detection of more than one heavy metal ion, we investigated the technique for potential use in simultaneous detection of multiple heavy metal ions. The potential for multi metal ion detection was demonstrated by the differential pulse voltammogram of the GCE-MWNT-CO-Cys electrode system after accumulation in a solution containing 0.3 ppm Pb^{2+} and 0.25 ppm Cu^{2+}. The resulting voltammogram exhibited prominent and well resolved peaks (Fig. 6). This implies that the system has great potential for multianalyte detection as long as the redox potentials of the analytes do not overlap.

3.4. Environmental Application

The performance the GCE-MWNT-CO-Cys electrode system in practical analytical work was evaluated by the determination of Cu^{2+} and Pb^{2+} in lake water from Lake Springfield (Springfield MO, USA). To quantify the amount of Cu^{2+} and Pb^{2+} in the lake water, samples of spiked (sub ppm levels) and unspiked lake water were analyzed using the standard addition method with the optimized conditions realized above. Cu^{2+} and Pb^{2+} ions were undetectable in the unspiked samples. In general the average recoveries of Cu^{2+} and Pb^{2+} ions from 4 independent measurements were

94.5% and 96.2% in the spiked water samples with relative standard deviations of 7.56% and 8.43% respectively.

4. Conclusions

In conclusion, we have developed a new technique which could potentially be used for the determination trace levels of heavy metals in aqueous media. The method uses ʟ-cysteine covalently bound on MWNTs as a chelator to complex heavy metal ions prior to their reduction and stripping analysis. The MWNTs not only maintain an electrically conducting surface but also increase the apparent surface area of the electrode. While the method has demonstrated detection of Cu^{2+} and Pb^{2+}, it can readily be designed for detection of other metals and/or other analytes by the modification of the carbon nanotubes using appropriate chelates. The potential of this electrode system for the simultaneous detection of different analytes was demonstrated. The potential to modify carbon nanotubes with multiple chelating molecules with different selectivities towards various analytes is currently being pursued in our lab and the results will be reported soon. Our results suggest that this system offers a great promise towards the versatile simultaneous detection of a wide variety multiple important analytes.

5. Acknowledgements

6. References

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