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Differential Pulse Anodic Stripping Voltammetry Determination of Lead(II) and Cadmium(II) with Multiwalled Carbon Nanotubes-Thiol Functionalized Chitosan Modified Bismuth Film Electrode

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A sensitive electrochemical method for simultaneous determination of lead and cadmium was developed using multiwalled carbon nanotubes-thiol functionalized chitosan (MWCNTs-CS-SH) modified glassy carbon electrode in 0.1 mol L^{-1} acetate buffer with pH 4. The thiol functionalized chitosan was prepared by covalent tethering with cysteamine using glutaraldehyde, then reduced by sodium borohydrate. The anodic oxidation of Pb(II) and Cd(II) produced two well-defined and separated stripping peaks at about -0.58 V for Pb(II) and -0.82 V for Cd(II), respectively. Linear responses were obtained in the range from 4 to 20 mg L^{-1}, with a limit of detection of 0.4 μg L^{-1} for both metal ions under optimized conditions. Several important operational parameters influencing the electroanalytical stripping response of MWCNTs-CS-SH modified electrode were optimized, such as the concentration of Bi(III) ions, deposition potential, deposition time and pH value of the acetate buffer. The influences of emulsifiers to the stripping analysis were also investigated.

Keywords: Stripping voltammetry, Functionalized chitosan, Bismuth film, Lead, Cadmium.

INTRODUCTION

Trace elements, especially heavy metals, even at low concentrations (< 2 ppb) are considered to be one of the main sources of pollution in the environment, since they have a significant effect on ecological quality[1]. Among the metal contaminants, heavy metal ions such as Pb^{2+} and Cd^{2+} are the two major pollutants which can cause profound biochemical and neurological changes in the body[2,3]. The major sources of lead arise from the burning of leaded gasoline in vehicle and the industrial releases due to lead mining, smelting and refining operations. Other potential sources of lead in the environment include lead-acid batteries, paints, incinerators and waste disposal. On the other hand, the major sources of cadmium are from industrial emission from smelter and metallurgical processing, incineration, nickel-cadmium batteries, cadmium pigmented plastics, ceramics, glasses, paints and enamels[4-6].

The determination of heavy metal ions has been of prime importance. Different techniques and methods, including atomic absorption spectroscopy[7], inductively coupled plasma-atomic emission spectroscopy[8], inductively coupled plasma-mass spectrometry[9], ion chromatography[10] and a variety of electrochemical techniques[11,12] have been used for the analysis of heavy metals in water resources and food materials.

Electrochemical stripping voltammetry has long been recognized as a powerful technique for trace metals owing to its remarkable sensitivity, relatively inexpensive instrumentation, ability for multi-element determination and capable of determining elements accurately at trace and ultra trace levels. Mercury electrodes have been traditionally used for stripping analysis[13] because of its high sensitivity, cyclic operation, avoiding many problems of electrode poisoning in complex matrices. Unfortunately, the toxicity of mercury and its difficulties in handling, storage and disposal severely restrict its use as an electrode material. Recently, the bismuth film electrode was introduced for the electrochemical measurements of heavy metals[14]. Similar to mercury, bismuth is capable of forming fused alloys with heavy metals[15] and exhibits high hydrogen overpotential[16]. In addition to the attractive electrochemical properties, bismuth is more environmentally friendly and less toxic. The bismuth can be constructed by electrodeposition on a suitable supporting substrates including glassy carbon[17,18], screen-printed carbon ink[19].

Carbon nanotubes (CNTs) have been considered as a promising material for metal support because of their excellent electrical properties, high surface-to-volume ratio, significant mechanical strength and good chemical stability[20-22]. Carbon nanotubes can be generally classified as multi-walled carbon nanotubes (MWCNTs) and single walled carbon nanotubes (SWCNTs). Multi-walled carbon nanotubes are central tubules of nanometric diameter surrounded by graphitic layers separated by 3.4 Å and SWCNT is only a tubule with no graphitic layers[23]. The applications of MWCNTs in electronic biosensors as a catalyst support[24] or an electrode material[25] have been reported in the literature. Commonly, MWCNTs aggregate into bundles due to the van der Waals force. When working with MWCNTs, the main challenge is dispersing them homogeneously. Chitosan (CS) has been used as a medium for dispersion of MWCNTs in aqueous solution. For instance, Fatibello-Filho *et al.*[26,27] used crosslinked CS modified carbon nanotubes paste electrodes to determine heavy metals. Tsai *et al.*[28,29] made amperometirc biosensor with MWCNTs-CS nanocomposites.

Chitosan is a converted polysaccharide obtained from deacetylation of natural chitin. It exhibits excellent membrane-forming ability, biocompatibility, non-toxicity, high mechanical strength and hydrophilicity[30]. Chitosan is widely used to capture and reclaim metals or proteins. The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. Functional groups with a known affinity for specific metals can be attached to other substances in order to create an effective adsorbent[31]. The thiol (-SH) group is known to form stable complexes with soft heavy metals of high polarizability such as Hg, Ag, Au and to a lesser extent, Cd and Pb, while failing to coordinate well with the more abundant smaller, lighter metals such as Ca, Na and Mg[32,33]. For example, Xie *et al.*[34] reported that trace Hg was determinated in real samples with the thiol functionalized chitosan-MWCNT nanocomposite film electrode. A MWCNTs-CS nanocomposite film presents a better tensile modulus and strength than a pure chitosan film that has been reported in the literature[35]. Chitosan-solubilized MWCNTs modified electrodes have been applied to biosensor applications such as lactate[36,37], glucose[38-41] and cholesterol [42].

In this paper, our goal was to develop a highly sensitive, rapid and low-cost method for determination of lead(II) and cadmium(II) by differential pulse anodic stripping voltammetry using MWCNTs-thiol functionalized CS modified bismuth film electrodes. In addition, we also optimized conditions of the modified electrodes for trace heavy metals analysis.

EXPERIMENTAL

All the chemicals used in this study were of analytical grade. All solutions were prepared with doubly distilled water. $Bi(NO_3)_3·5H_2O$ was purchased by Chengdu Kelong Chemical Reagent Factory, China. $Pb(NO_3)_2$ and $Cd(NO_3)_2·4H_2O$ were provided by Nanjing Ning Test Chemical Reagents Limited Company, China. Chitosan (CS), glutaraldehyde, cysteamine, $CH_3COONa·3H_2O$, CH_3COOH, Tween-80 and polyethylene glycol (PEG) were purchased by National Pharmaceutical Industry Corporation, China. Carbon nanotubes (MWCNTs) were supplied by Shenzhen Nanotech Port Co. Ltd (NTP), China.

Electrochemistry experiments were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China). All experiments were carried out using a conventional three-electrode system with a modified glassy carbon disk electrode (3 mm diameter, CHI104, CHI Instruments) as the working electrode, a platinum wire as the auxiliary electrode (CHI150) and a saturated calomel electrode (SCE) (CHI115) as the reference electrode. All potential values were given with respect to SCE. Stirring was carried out using a magnetic stirrer (Jintan City Medical Instrument Plant, China).

Preparation of MWCNTs-CS-SH modified electrodes: MWCNTs were purified and acidified prior to use by stirring them in 2 mol L^{-1} aqueous nitric acid for 24 h. Then the suspension was filtered and the solid was carefully washed by doubly distilled water until the pH was near 7.

The thiol functionalized CS (CS-SH) was synthesized according to literatures[34]. In brief, 20 mL 0.50 wt % CS solution was added drop-by-drop into 20 mL 50 % glutaraldehyde under magnetic stirring and then allowed to react for 48 h at room temperature. The unreacted glutaraldehyde was removed by dialyzing the reaction mixture for 24 h against acetate buffer solution (pH 5) and a glutaraldehyde functionalized CS was obtained. Then, the glutaraldehyde functionalized CS was allowed to react with cysteamine for 24 h. Again, the dialysis was used to remove unreacted cysteamine from the reaction mixture. Finally, the obtained Schiff bases were reduced to more stable secondary amines using sodium borohydrate and a final CS-SH solid was obtained after centrifugation. The prepared CS-SH was characterized by FT-IR spectrophotometry (Fig. 1). The two bands in 595 and 1655 cm^{-1} were assigned to the thiol groups of CS-SH[43].

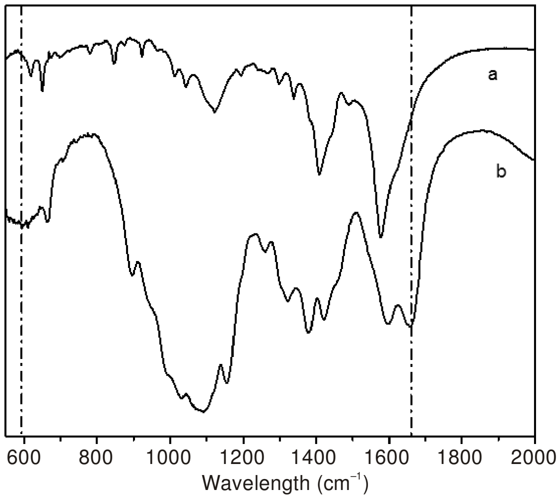

Fig. 1. FT-IR spectra of CS (a) and CS-SH (b)

A 3 mg mL^{-1} CS-SH solution was prepared by dissolving CS-SH in 0.1 mol L^{-1} acetate buffer solution (pH 5). Then, 1 mg MWCNTs was added in 1 mL CS-SH solution with the aid of ultrasonic agitation for 0.5 h to form a homogeneous MWCNTs-CS-SH suspension and the suspension was stored at 4 ºC.

The glassy carbon electrode (GCE) was sequentially polished with water slurry of 1.0, 0.3 and 0.05 μm $Bi(NO_3)_3$ powder, rinsed thoroughly with ethanol and doubly distilled water. A 3 μL drop of the MWCNTs-CS-SH solution was placed on the surface of the polished glassy carbon electrode with a micropipette and solvents were left to evaporate at room temperature.

For comparison, MWCNTs modified glassy carbon electrode was prepared by adding 3 μL drop of 1 mg mL^{-1}

MWCNTs with the same process of that of MWCNTs-CS-SH modified electrode.

Procedure: Detection of trace metals was carried out by means of differential pulse anodic stripping voltammetry measurement without removing oxygen from the solution. The three electrodes were immersed into a 10 mL electrochemical cell, containing 0.1 mol L^{-1} acetate buffer solution (pH 4.0), appropriate bismuth, lead and cadmium. A deposition potential of -1.30 V (*vs*. SCE) for 300 s, if not stated otherwise, was applied to the working electrode under stirring conditions. The stirring was stopped and after 15 s equilibration time, the differential pulse anodic stripping voltammograms were recorded between -1.3 and 0.1 V with amplitude of 50 mV, pulse width of 50 ms and potential step of 4 mV. A 20 s conditioning step at +0.30 V (with solution stirring) was used to remove the target metals and the bismuth film before the next cycle. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

The morphology of MWCNTs (a) and MWCNTs-CS-SH (b) modified glassy carbon electrodes were examined by SEM (Fig. 2). It could be observed from Fig. 2a that MWCNTs were densely packed with uniform diameters, *ca*. 30 nm. A homogenous dispersion of MWCNTs in CS-SH matrix throughout the electrode surface could be seen in Fig. 2b.

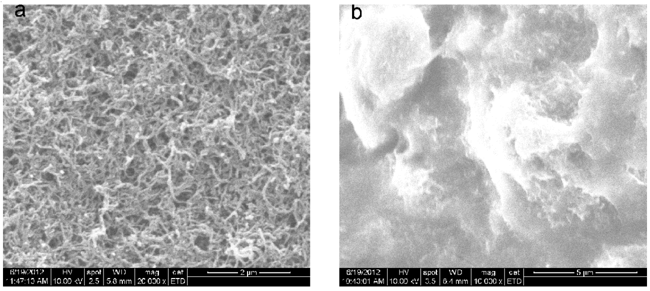

Fig. 2. SEM images of MWCNTs (a) and MWCNTs-CS-SH (b) modified GCE

Stripping voltammograms of Pb(II) and Cd(II) at the bare GCE, MWCNTs-CS modified and MWCNTs-CS-SH modified GCEs were illustrated in Fig. 3. Stripping voltammograms were obtained between -1.0 and -0.45 V in 0.1 mol L^{-1} acetate buffer solution (pH 4) containing 300 μg L^{-1} Bi(III), 20 μg L^{-1} Pb(II) and Cd(II). Small and somewhat distorted stripping peaks of Pb(II) and Cd(II) were observed at the bare GCE. Under comparable conditions, well-resolved and clearly defined peaks were obtained at MWCNTs-CS modified GCE. However, more intense anodic stripping peaks at MWCNTs-CS-SH modified GCE were illustrated in Fig. 3. The peaks at -0.82 and -0.58 V were for Cd(II) and Pb(II), respectively. These highest peaks could be attributed to the improvement of metal adsorption properties. Because the abundant thiol groups in the CS-SH film, it could effectively deposit Pb and Cd from bulk solution to the electrode surface.

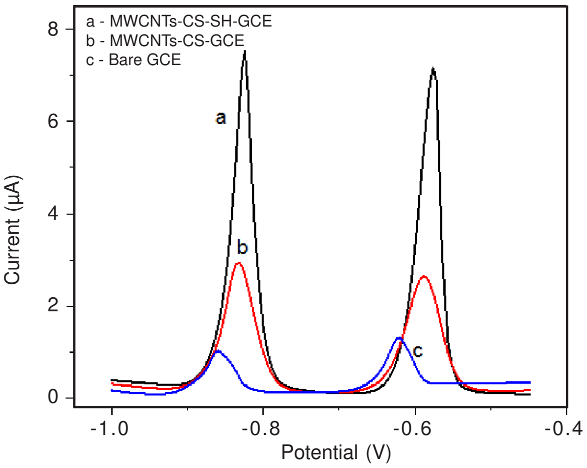

Fig. 3. Differential pulse anodic stripping voltammograms of 20 μg L^{-1} Pb(II) and Cd(II) at MWCNTs-CS-SH modified (a), MWCNTs-CS modified (b) and bare (c) GCEs with 300 μg L^{-1} Bi (III) in 0.1 mol L^{-1} acetate buffer (pH 4)

To obtain a stable homogeneous MWCNTs-CS-SH dispersion solution, proper concentration of chitosan solution was a crucial factor. The viscosity of the chitosan solution increased with increasing the concentration of chitosan. Too high viscosity would induce uneven dispersing of MWCNTs and non-uniform thickness of the film; on the contrary, unduly low viscosity would weaken the immobilization of MWCNTs, thereby debasing the stability of MWNTs-modified electrode. Thus, 3 mg mL^{-1} chitosan solution was used in experiment.

Fig. 4 was the influence of Bi(III) ion concentrations, in the range 20-300 μg L^{-1}, on the peak currents of Pb(II) and Cd(II) in 0.1 mol L^{-1} acetate buffer solution (pH 4) containing 20 μg L^{-1} Pb(II) and Cd(II). Inset 4a showed that the height of the peak currents increased rapidly with increasing concentrations of Bi(III) ion, especially from 100-200 μg L^{-1}. The concentration of the Bi(III) ion could decide the thickness of the Bi deposit, but the concentration region of 100-200 μg L^{-1} could be more favorable for metal ions diffusing out of the Bi deposit film. After 300 μg L^{-1}, peak currents increased slowly and 300 μg L^{-1} was selected as the optimum Bi(III) concentration. The peak positions were slightly affected (Inset 4b) because their anodic peaks were associated with Bi(III) ions, more or less subject to Bi(III) ion concentration influences.

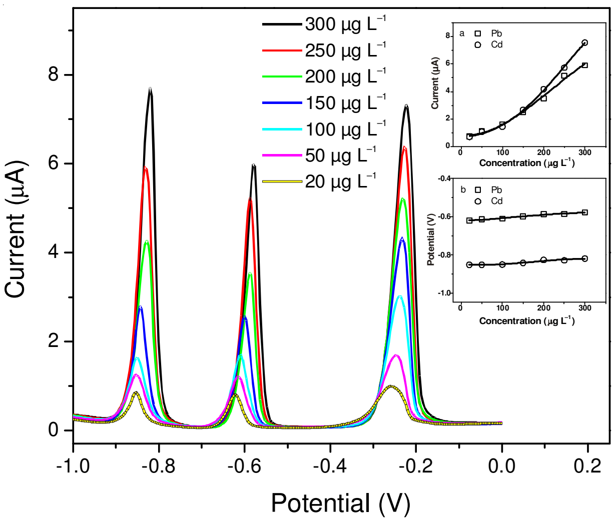

Fig. 4. A series of stripping voltammograms of Pb(II) and Cd(II) at MWCNTs-CS-SH modified GCE with different Bi(III) concentration, 20-300 μg L^{-1}. Inset 4a and 4b are the relationship between Bi(III) concentration with stripping peak currents and peak positions, respectively. Other conditions are the same as in Fig. 3

Deposition potential and deposition time were very important factors for stripping voltammetry method, which influenced the sensitivity and selectivity of the determination. The effect of the deposition potential on the peak currents of two metal ions was studied in Fig. 5a, with the potential range from -1.00 to -1.40 V for 0.1 mol L^{-1} acetate buffer solution (pH 4) containing 300 µg L^{-1} Bi(III), 20 µg L^{-1} Pb(II) and Cd(II). The negative shifts deposition potential could obviously improve the reduction of Pb(II) and Cd(II) on the electron surface and increase the peak currents. For Cd(II), the peak currents showed a consecutive increase pattern with the deposition potential and it grew slowly after -1.30 V. Compared with Cd(II), the peak currents of Pb(II) showed similar increase trend, but they increased slightly fast after -1.30 V. Considering the above mentioned observations and with respect to the higher hydrogen evolution at -1.30 V, -1.30 V was selected as the optimum deposition potential[44].

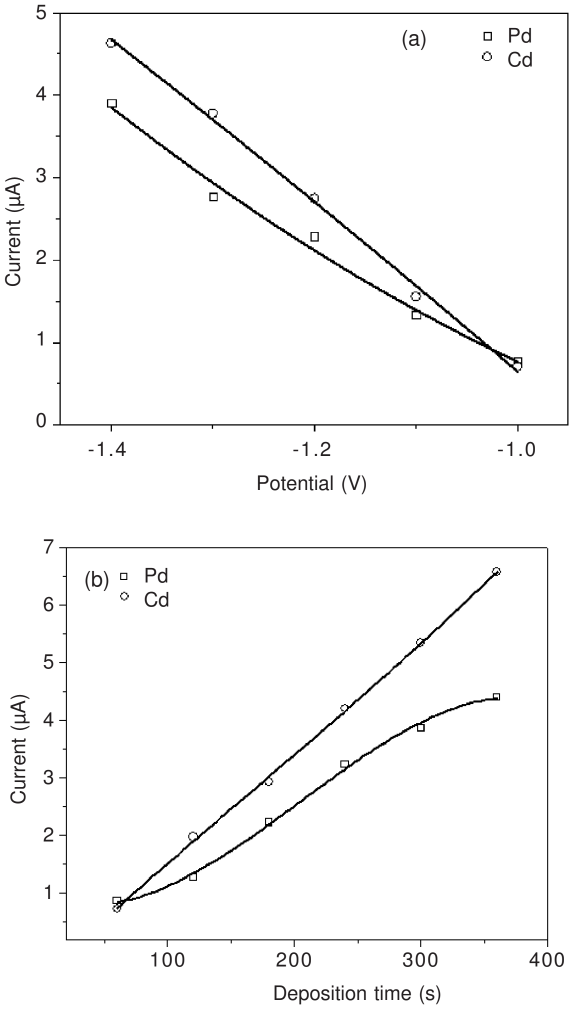

Fig. 5. Effects of deposition potential (a) and deposition time (b) on the stripping peak currents of Pb(II) and Cd(II) at MWCNTs-CS-SH modified GCE. Other conditions are the same as in Fig. 3

The metal deposition time was studied in the range 60-360 s in Fig. 5b, for 0.1 mol L^{-1} acetate buffer solution (pH 4) containing 300 µg L^{-1} Bi(III), 20 µg L^{-1} Pb(II) and Cd(II). It could be clearly seen, that the deposition time influenced the signal ratio between the two metal ions. The peak currents for Cd(II) increased linearly with the deposition time. This is because more and more Cd(II) accumulated on the MWCNTs-CS-SH surface as time growth. While for Pb(II), the peak currents increased slowly and reached a plateau at 300 s. Further increase of deposition time did not obviously cause enhancing the peak currents, which was probably due to the saturation loading of the electrode surface, so the prolonged deposition time did not cause more Pb(II) to be reduced. In this work, 300 s was selected as the deposition time.

The influence of pH on the determination of Pb(II) and Cd(II) was investigated in Fig. 6 for 0.1 mol L^{-1} acetate buffer solution containing 300 µg L^{-1} Bi(III), 20 µg L^{-1} each of Pb(II) and Cd(II), with pH changed from 3 to 5. At first, the peak current increased as the pH increased (from pH 3-4 in Inset 6a). It has been reported that the pKa of chitosan was between 6.39 and 6.51 with the molecule weight changing from 1370 to 60 kDa[45]. In this work, the molecular weight of chitosan was 62 kDa, so its pKa should between 6.39 and 6.51 and closed to 6.51. The protonation/deprotonation effects of the CS amino groups made CS water-soluble at pH sufficiently below its pKa, but insoluble at pH near or above its pKa[46]. The pH of 3 was lower than its pKa, so the protonation of CS amino group and some MWCNTs carboxylic groups made larger electrostatic repulsion with heavy metal ions. As pH increased, the electrostatic repulsion became smaller, then the peak current increased and reached a maximum value at pH 4. Continuous increase of pH led to a decrease of the peak current, which was because the increased competition between the heavy metal ions and the sodium ions of the buffer solution for other binding sites[47]. Therefore, pH 4 of acetate buffer solution was found to be the most suitable medium for stripping analysis. Negative shifts in the peak potentials occurred for both Pb(II) and Cd(II) when increasing the pH of the solution (Inset 6b), indicating that protons, hydrolysis reaction from the OH and SH groups, participated in the reduction process of these heavy metals.

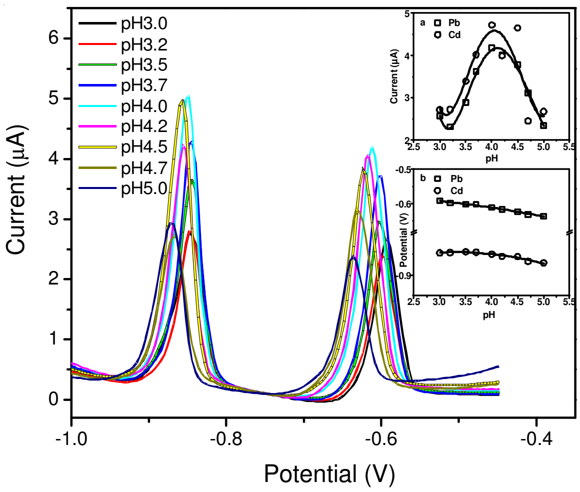

Fig. 6. Effect of pH of acetate buffer on the stripping voltammograms of Pb(II) and Cd(II) at MWCNTs-CS-SH modified GCE. Inset 6a and 6b are the relationship between pH with stripping peak currents and peak potentials, respectively. Other conditions are the same as in Fig. 3

Fig. 7 was a series of stripping voltammograms for Pb(II) and Cd(II) at concentration range 4-20 µg L^{-1} in 0.1 mol L^{-1}

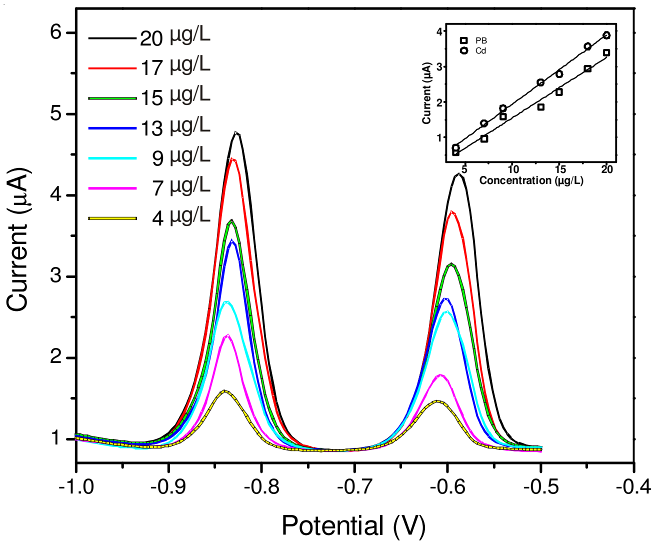

Fig. 7. A series of stripping voltammograms for Pb(II) and Cd(II) with concentration range 4-20 µg L^{-1} at MWCNTs-CS-SH modified GCE. Inset is the calibration curve between stripping peak current and concentration. Other conditions are the same as in Fig. 3

acetate buffer solution (pH 4) with Bi(III) concentration of 300 µg L^{-1}, deposition potential of -1.30 V, deposition time of 300 s. Inset showed the calibration plot. It was clear that the anodic stripping peak currents increased substantially linearly with the increase of metal ions concentration. The correlation coefficients were 0.990 and 0.998 for Pb(II) and Cd(II), respectively. The limits of determination were 0.40 µg L^{-1} for both Pb(II) and Cd(II) under the same condition.

We also studied the effect of emulsifiers on the stripping analysis. Fig. 8 was the influence of two emulsifier, 0.1 mol L^{-1} for both PEG and Tween-80, on the stripping voltammograms for 0.1 mol L^{-1} acetate buffer solution (pH 4) containing 300 µg L^{-1} Bi(III), 20 µg L^{-1} Pb(II) and Cd(II). Emulsifers were added to the acetate buffer solution simultaneously with Bi(III), Pb(II) and Cd(II) ions. From Fig. 8, we could see that both PEG and Tween did not affect the peak potentials, However, they showed different influences on the peak currents. Compared with no emulsifier, the peak current increased with the presence of PEG and decreased with Tween. The PEG contained many hydroxyl groups and its presence made the MWCNTs-CS-SH modified GCE with more hydroxyl groups, which might contribute to the more adsorption of heavy metal ions. As for Tween, the larger end groups lipophilic polyether somewhat inhibited the adsorption of heavy metal ions.

Conclusion

In this work, a novel MWCNTs-CS-SH modified bismuth film electrodes were proposed for determination of trace Pb(II) and Cd(II) by differential pulse anodic stripping voltammetry. The MWCNTs-CS-SH modified bismuth film electrodes exhibited good performance due to the stronger adsorbability between abundant thiol groups in the CS-SH and heavy metals as well as good conductivity of the MWCNTs-CS-SH nanocomposite film. The Bi(III) concentration, deposition potential, deposition time, pH of acetate buffer solution were optimized to obtain the highest sensitivity. The influence of emulsifiers to the stripping analysis were also investigated.

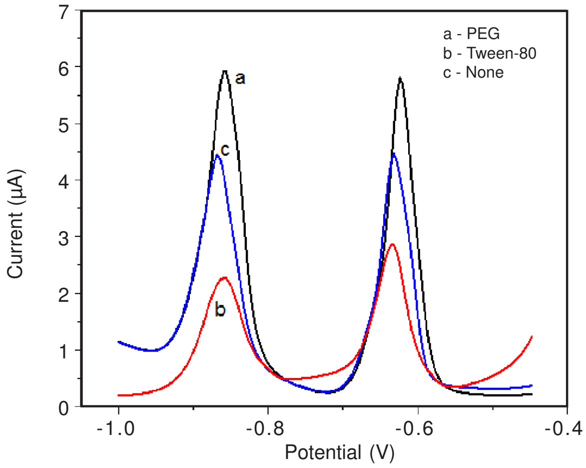

Fig. 8. Effect of the presence of PEG (a) and Tween-80 (b) as well as the absence of emulsifier (c) on the stripping voltammograms of Pb(II) and Cd(II) at MWCNTs-CS-SH modified GCE. Other conditions are the same as in Fig. 3

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