



Simultaneous determination of ultratrace lead and cadmium by square wave stripping voltammetry with in situ depositing bismuth at Nafion-medical stone doped disposable electrode

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ABSTRACT

An ultrasensitive electrochemical method for simultaneous determination of lead and cadmium was first developed using the novel bismuth–Nafion–medical stone doped disposable electrode (an improved wax-impregnated graphite electrode). Through the synergistic sensitization effect of the resulting composite material, the disposable electrode showed remarkable electrochemical responses to lead and cadmium. The oxidation of the two metals produced two well-defined and separated square wave peaks at about -0.62 V for Pb^{2+} and -0.85 V for Cd^{2+} , respectively. The effects of the amount of medical stone, concentration of Nafion, thickness of bismuth, pH of buffer solution, deposition potential, accumulation time, voltammetric measurement and possible interferences were investigated in detail. Under the optimal conditions, the fabricated electrode exhibited linear ranges from 2.0 to $12.0 \mu\text{g L}^{-1}$ with detection limit of $0.07 \mu\text{g L}^{-1}$ for lead and 2.0 – $12.0 \mu\text{g L}^{-1}$ with detection limit of $0.47 \mu\text{g L}^{-1}$ for cadmium. The assay results of heavy metals in wastewater with the proposed method were in acceptable agreement with the atomic absorption spectroscopy method.

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1. Introduction

Lead or cadmium is one of the most serious environmental contaminants [1], which are highly toxic to nervous, immune, reproductive and gastrointestinal systems of both humans and animals [2,3]. So the development of highly sensitive method for determining trace amounts of lead and cadmium has received considerable attention. Over the past decades, many techniques have been employed for the determination of heavy metals. The typical methods for the simultaneous detection of metal ions are inductively coupled plasma-mass spectrometry [4], X-ray fluorescence spectrometry [5] and atomic absorption spectrometry (AAS) [6]. However, these methods need expensive and complex instruments. Due to its low cost, high sensitivity, easy operation and the ability of analyzing element speciation, anodic stripping voltammetry (ASV) has become one of the most favorable electrochemical techniques for the determination of heavy metal ions [7]. In ASV, the traditional working electrode for simultaneous voltammetric determination is general hanging drop mercury electrode [8,9]. However, the toxicity of the Hg is undesirable for disposable in situ sensing applications [10]. Thus it is very necessary to develop

a sensitive and non-toxic electrode for the determination of heavy metals.

Bismuth-film electrodes (BiFEs) have been proved to offer comparable performance to mercury electrode in ASV [11–19]. BiFEs, owning all the advantages of mercury electrodes, are environmentally friendly due to its negligible toxicity. Compared to the performance of mercury electrodes, BiFEs are less sensitive to dissolved oxygen and have a wide potential window for electrochemical analysis. However, various surfactants in real samples can be adsorbed on the surface of BiFEs, which will result in serious interference and bad analytical performance [20]. Electrode modified with a permselective Nafion membrane can decrease this interference and improve the mechanical stability of bismuth film [21]. The cation-exchange property of Nafion allows the preconcentration of cationic target analytes and the exclusion of anionic interferences. Therefore, Nafion has been used as coating polymer especially for trace metal speciation studies [22–29].

Medical stone is a kind of compound minerals with innocuous characteristic, which contains many metal elements such as Ca, Mg, Si, Al, Fe, K, Na, lanthanon, radioelement and so on. The material is widely used in medical care, food, antiseptics and decontamination fields. It can absorb or dissolve some substances such as metal ions and adjust pH of the solution. The porous medical stone with 10 nm aperture (see Fig. 1) has huge specific surface area and can be used as an excellent absorbent, which can accumulate more analytes

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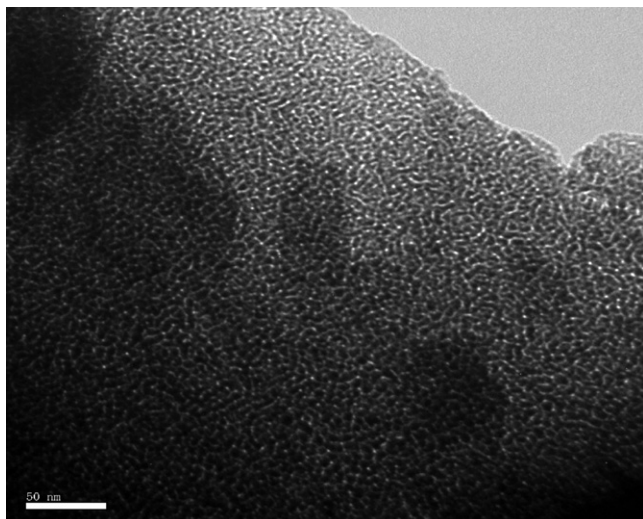


Fig. 1. TEM image of nano-aperture medical stone.

onto the electrode surface and improve the analysis sensitivity. As far as we know, the medical stone has been seldom used as a sensitized electrode material at present.

Disposable electrode was often modified with different materials for determining many kinds of analytes [30–37]. Here, a novel in situ bismuth–Nafion–medical stone doped disposable electrode was proposed. The fabricated electrode with high selectivity and sensitivity is stable, convenient and inexpensive, which can be successfully used for ASV detecting Pb^{2+} and Cd^{2+} in the real waste water sample.

2. Experimental

2.1. Reagents and solutions

Medical stone was provided by cooperator in Japan. Crystalline flake graphite and paraffin oil were from Shanghai Reagent Corporation (China). Stock solution of 100 mg L^{-1} Bi^{3+} , Pb^{2+} and Cd^{2+} was prepared by dissolving $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and CdCl_2 , respectively. Unless otherwise stated, 0.10 mol L^{-1} sodium acetate buffer solution (pH 4.5) served as the supporting electrolyte. All reagents were of analytical grade and used without any further purification. Each electrochemical experiment was carried out at room temperature. All solutions were prepared with distilled water.

2.2. Apparatus

CHI760D electrochemical workstation (Shanghai CH Instruments, China) was used for all the electrochemical measurements. A conventional three-electrode system was used throughout the experiments, including a bismuth–Nafion–medical stone doped disposable electrode (BINMSDE) used as working electrode, a platinum wire counter electrode and a saturated calomel electrode used as the reference. All potentials mentioned in this work refer to the reference electrode. A magnetic stirrer (Model 90) was used to stir the testing solution during the preconditioning and preconcentration steps. The pH measurements were carried out with a PHS-25 pH-meter (Shanghai Leici Instrument Plant, China) at room temperature. Structural observation of medical stone was performed in Philips Tecnai 12 transmission electron microscope (Netherlands). The model surveyor apparatus used in this study was a Zeeman electrothermal AAS (PerkinElmer, Spectra AAnalyst 800) with the hollow cathode lamps ($\lambda = 283.3 \text{ nm}$, bandwidth 0.5 nm for Pb and $\lambda = 228.8 \text{ nm}$, bandwidth 0.5 nm for Cd). The spectrom-

eter's graphite tubes were designed with an integrated platform. Preconcentration and determination of Pb^{2+} and Cd^{2+} by GF AAS via chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidene propylamine ion exchanger.

2.3. Fabrication of electrodes

BINMSDE was prepared according to the following procedure. First, a disposable electrode composed of prepreg substrate and copper foil was fabricated by automatic vacuum laminating machine. Prior to pressing, prepreg substrate (Fig. 2A-b), copper foil (Fig. 2A-c) and heat-resistant plastic film as an auxiliary material (Fig. 2A-a) were lapped together into a panel (Fig. 2A). They were put into a pressing instrument after many panels were accomplished (Fig. 2B). When the pressing process finished, the heat-resistant plastic film was removed and the panel was cut into many pieces. Each piece was drilled with a 1.0 mm hole in diameter at one end and a 5.0 mm hole at the other end (Fig. 2C). Second, the doped disposable electrode was prepared by mixing the crystalline flake graphite, medical stone and paraffin liquid with an appropriate mass ratio of 140/1/60. Followed, they were uniformly ground in a mortar by pestle and then a proper portion of the resulting paste was packed firmly into the hole of 5.0 mm in diameter and smoothed by spatula, and the other hole was connected with conducting wire (Fig. 2D). After the step of stuffing, the medical stone doped disposable electrode (MSDE) was coated with Nafion with different concentration, resulting in a Nafion modified MSDE (NMSDE). The fabrication process of undoped disposable electrode (DE) was the same as that of MSDE only without medical stone. Third, The BINMSDE was formed by in situ depositing bismuth film on the NMSDE in analyte solution containing Bi^{3+} at -1.2 V for a defined period of time under stirred conditions followed by a 5 s rest period, which can be seen in Fig. 2E.

2.4. Analytical procedure

Stripping voltammetric measurements were performed in 0.10 mol L^{-1} pH 4.5 sodium acetate buffer solution, if not stated otherwise. The metal ions in the buffer solution were preconcentrated at -1.2 V with stirring. After a 5 s equilibration period, the voltammograms were recorded by applying a positive-going SWV potential scan from -1.4 to -0.4 V (50 mV potential amplitude, 50 Hz frequency, 8 mV step potential and 5 min deposition time). A 20 s conditioning step at $+0.4 \text{ V}$ (with solution stirring) was used to remove the target metals and the bismuth film before the next cycle. The wastewater sample was supplied from a sewage treatment plant in Yangzhou and filtered through a $0.22 \text{ }\mu\text{m}$ membrane (Millipore). The sample was diluted with 0.1 mol L^{-1} pH 4.5 acetate buffer solution before determination.

3. Results and discussion

3.1. Voltammetric characterization of different electrode

Fig. 3 shows the square wave anode stripping voltammograms (SWASVs) of $10.0 \text{ }\mu\text{g L}^{-1}$ Pb^{2+} and $100.0 \text{ }\mu\text{g L}^{-1}$ Cd^{2+} at DE, MSDE, NMSDE and BINMSDE. The response of the DE (curve 1) is poor with two small peaks. However, the signal of the MSDE (curve 2) is remarkably enhanced than that at the DE, which can be interpreted as that the medical stone can effectually increase the rates of metal ions preconcentration from aqueous solution to the surface of the electrode by ion exchange and adsorption. As can be seen from curve 3, the peak currents of lead and cadmium at the NMSDE are more intense than that at the MSDE. This can be attributed to the Nafion film for efficient accumulation of Pb^{2+} and Cd^{2+} close to the electrode surface. Curve 4 represents that the peak currents of

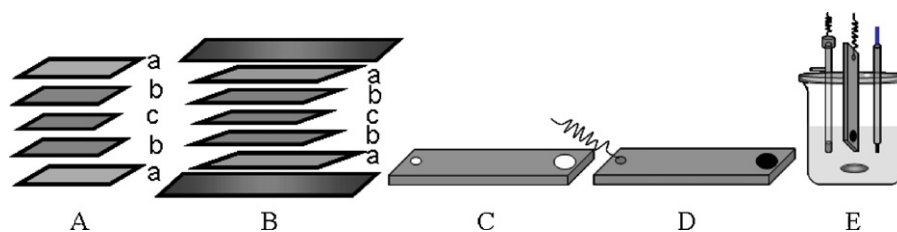


Fig. 2. Detailed fabrication process of bismuth–Nafion–medical stone doped disposable electrode and three-electrode system. The a, b and c in A means heat-resistant plastic film, prepreg substrate and copper foil, respectively.

Pb^{2+} and Cd^{2+} at the BINMSDE are higher than that at the NMSDE, which clearly confirms that the bismuth film is essential to the efficient metal ions deposition. On the contrary, the oxidized species at the NMSDE were able to diffuse away from the electrode before significant replating occurs [38].

3.2. Optimization of the modified electrode

In order to perform the simultaneous determination of the two metal ions in real samples, the key parameters which especially influence the electroanalysis have to be optimized. The parameters including amount of medical stone, concentration of Nafion, thickness of bismuth, pH of buffer solution, deposition potential, accumulation time and voltammetric measurement were investigated, respectively.

3.2.1. Amount of medical stone

The effect of the amount of medical stone within the MSDE was evaluated (Fig. 4A). Medical stone as modifier can greatly improve the sensitivity of determination, which is due to the nano-aperture structure and ion exchange characteristic of the medical stone. Therefore, more Pb^{2+} and Cd^{2+} were accumulated on the MSDE surface. The peaks intensity increased with the amount of modifier increasing, because the concentration of medical stone on the surface of the doped electrode increased correspondingly. At 5% of medical stone, relative to the mass of compound (crystalline flake graphite, medical stone and paraffin liquid), the largest peak current was obtained. However, the continuous increase of the amount of modifier caused a decrease of peak current, because excessive medical stone may result in the decrease of conductivity of the doped electrode. So the best ratio of the modifier in compound composition was 5% (w/w).

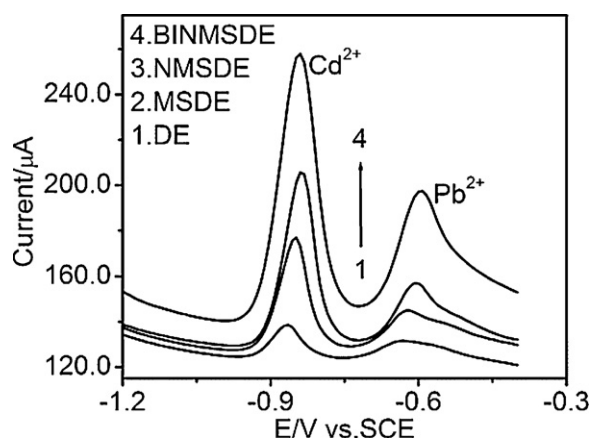


Fig. 3. SWASVs of $10.0 \mu\text{g L}^{-1}$ Pb^{2+} and $100.0 \mu\text{g L}^{-1}$ Cd^{2+} in 0.1 mol L^{-1} pH 4.5 sodium acetate buffer solution at the different electrodes. Curves (1) DE, (2) MSDE, (3) NMSDE and (4) BINMSDE. Deposition potential: -1.2 V ; accumulation time: 60 s.

3.2.2. Concentration of Nafion

The chemically modified electrodes prepared by drop coating of $3.0 \mu\text{L}$ of coating solution containing different wt% Nafion (0.2–0.8%) were examined under identical experimental conditions. Fig. 4B shows the effect of the thickness of the Nafion film on the SWASV responses of the electrode towards Pb^{2+} and Cd^{2+} . It can be seen that at the beginning the peak current of the metal ions increased and reached a maximum at 0.5% Nafion concentration and a large decline in sensitivity has been observed at the further increase of the Nafion thickness. This is in accord with earlier report [22]. This phenomenon can be explained by the fact that thick Nafion film displayed large cracks due to contractive force within the film. Through these openings in the polymer structure the oxidized species can diffuse away from the electrode surface before significant replating occurs so that the redox cycling mechanism is impeded [25].

3.2.3. Thickness of bismuth

The thickness of the bismuth film could be controlled by varying the Bi^{3+} concentration in the sample, which had a profound effect on the electrochemical responses of the modified electrodes. High concentration of Bi^{3+} did not affect the peak position of Pb^{2+} and Cd^{2+} but influenced the stripping currents of Pb^{2+} and Cd^{2+} . The stripping currents of Pb^{2+} and Cd^{2+} rapidly increased with the concentration of Bi^{3+} increasing from 50 to $200 \mu\text{g L}^{-1}$ and then decreased at the concentration of Bi^{3+} more than $200 \mu\text{g L}^{-1}$ (Fig. 4C). This may be attributed to the formation of bismuth multilayers on the electrode surface at high concentration of Bi^{3+} , which is not favorable for metal ions diffusing out of the bismuth film during the stripping step [39].

3.2.4. pH of buffer solution

The effect of pH of buffer solution on the electrochemical responses of Pb^{2+} and Cd^{2+} was also studied. Fig. 4D shows that the optimal pH range for the determination of the two metal ions is between pH 3.6 and 5.3. Under pH 4.5 the smaller response of the BINMSDE can be interpreted with the competition between the analytes and the hydrogen ions for the ion-exchange sites on the surface of BINMSDE. The pH dependence of the voltammetric responses also suggest that the electrode may be effectively renewed in acid solution. Increasing the pH above 4.5 the reason for the decline of the stripping responses may also be due to the competition between the analytes and the sodium ions of the buffer solution for the binding sites besides the hydrolysis [40]. Therefore, pH 4.5 of acetate buffer solution was found to be the most suitable “medium” for stripping analysis.

3.2.5. Deposition potential

The influence of the deposition potentials on metal stripping signals were tested. As shown in Fig. 4E, when the accumulation time was first set at 60 s and the deposition potential changed from -0.8 to -1.4 V for $100 \mu\text{g L}^{-1}$ of Cd^{2+} and $10 \mu\text{g L}^{-1}$ Pb^{2+} , the negative shifts of deposition potential can obviously improve the reduction of Pb^{2+} and Cd^{2+} on the surface of BINMSDE and increase the peak

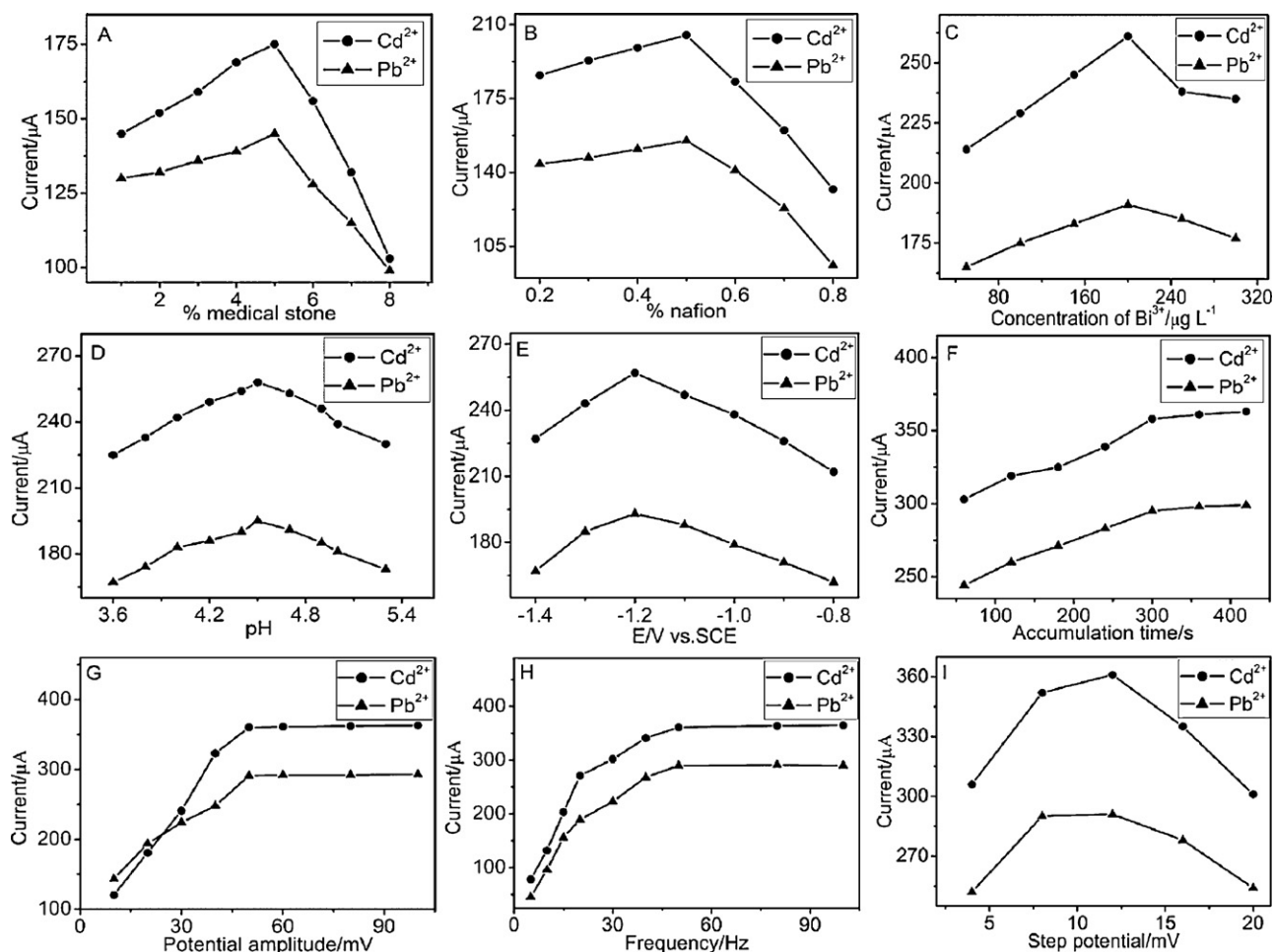


Fig. 4. Effects of (A) amount of medical stone, (B) concentration of Nafion, (C) thickness of bismuth, (D) pH of buffer solution, (E) deposition potential, (F) accumulation time (G) potential amplitude, (H) frequency and (I) step potential on the SWASV peak heights for 100 μg L⁻¹ of Cd²⁺ and 10 μg L⁻¹ of Pb²⁺ in 0.1 mol L⁻¹ sodium acetate buffer solution at modified electrode.

current. When the deposition potentials applied become more negative potential than -1.2 V, the reproducibility of stripping currents of Pb and Cd become poor, because hydrogen evolution is beginning to be significant in acetate buffer at such negative potential [41]. The hydrogen bubbles might damage the metal alloys deposited on the electrode surface and lead to decrease in current signals at very negative potentials. Therefore, -1.2 V was adopted for the following experiments due to the sensitivity and reproducibility.

3.2.6. Accumulation time

The preconcentration time for metal was also studied from 60 s to 420 s in 0.1 mol L⁻¹ pH 4.5 acetate buffer solution containing 100 μg L⁻¹ of Cd²⁺ and 10 μg L⁻¹ Pb²⁺ (Fig. 4F). The stripping currents of Cd and Pb increased respectively along with the accumulation time prolonged. As accumulation time longer than 300 s, the curves of peak current versus time began to level off. This can be attributed to the thickness of the composite film would be increased as the accumulation time prolonged, which would affect the electron transfer rate of metal stripping [42]. Therefore, the stripping currents increased slowly. Therefore, 300 s was adopted as optimal accumulation time for the following experiments.

3.2.7. Voltammetric parameters

In order to obtain well-defined SWASV response signals, the voltammetric measurement parameters (potential amplitude, frequency and step potential) have also been optimized (Fig. 4G–I). The heights of Pb²⁺ and Cd²⁺ increased almost linearly with the increas-

ing pulse amplitude (Fig. 4G) but the resolution and the shape of the metal peaks also deteriorated above 50 mV. In the beginning the increase of the SW frequency resulted in a relatively fast increase in the peak heights of Pb²⁺ and Cd²⁺ owing to the increase in the effective scan rate up to 50 Hz. (The SW frequency together with the step potential defines an effective scan rate.) However, above 50 Hz the peak currents started to level off and the peaks to distort (Fig. 4H). The increase of the step potential did not significantly enhance the peak heights of Pb²⁺ and Cd²⁺ despite of the dramatic increase in the effective scan rate (Fig. 4I). At first the peak currents raised with the step potential increasing then reached a maximum and started to decrease. Therefore, the well-shaped SWASV current peaks for quantitative measurements at low metal ion concentrations were obtained at 50 mV potential amplitude, 50 Hz frequency and 8 mV step potential.

3.3. Calibration curve

Calibration curves for the simultaneous determination of Pb²⁺ and Cd²⁺ at BINMSDE were achieved by SWASV under optimal conditions. The SWASVs of the different concentrations of Pb²⁺ and Cd²⁺ were illustrated in Fig. 5. The resulting calibration plots are linear over the range from 2.0 to 12.0 μg L⁻¹ for both Pb²⁺ and Cd²⁺. The calibration curves and correlation coefficients are $y = 0.12 + 3.26x$, $r = 0.9980$ and $y = 6.22 + 6.99x$, $r = 0.9981$ for Cd²⁺ and Pb²⁺, respectively. The detection limits of 0.47 μg L⁻¹ for Cd²⁺ and 0.07 μg L⁻¹ for Pb²⁺ are obtained at a signal-to-noise ratio of

Table 1
Comparison of present work and other modified electrode for the determination of Pb^{2+} and Cd^{2+} .

| Electrode | Modifier | Method | LOD ^a of Cd ($\mu\text{mol L}^{-1}$) | LOD ^a of Pb ($\mu\text{mol L}^{-1}$) | Ref. |
|-------------------|--|--------------------|---|---|-----------|
| CPE ^b | $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed-oxide | DPASV ^c | – | ≈ 0.0011 | [43] |
| CPE ^b | Diacetyldioxime | DPASV ^c | 0.04 | 0.01 | [44] |
| CPE ^b | Antimony film | SWASV ^d | ≈ 0.0071 | ≈ 0.00097 | [45] |
| Pt | Kaolin | SWASV ^d | 0.0054 | – | [46] |
| Pt | Kaolin | SWASV ^d | – | 0.0036 | [47] |
| CILE ^e | Hydroxyapatite | SWASV ^d | 0.0005 | 0.0002 | [7] |
| BINMSDE | Bismuth–Nafion–medical stone | SWASV ^d | 0.0042 | 0.00034 | This work |

^a Limit of detection.

^b Carbon paste electrode.

^c Differential pulse anodic stripping voltammetry.

^d Square-wave anodic stripping voltammetry.

^e Carbon ionic liquid electrode.

Table 2
Measurement results of Pb^{2+} and Cd^{2+} in real wastewater sample ($n=3$)^a.

| Analyte | AAS (mg L^{-1}) | This method (mg L^{-1}) | Added (mg L^{-1}) | Found (mg L^{-1}) | R.S.D. (%) | Recovery (%) |
|------------------|----------------------------|------------------------------------|------------------------------|------------------------------|------------|--------------|
| Pb^{2+} | 0.2435 | 0.2512 | 0.1 | 0.3489 | 3.1 | 97.7 |
| | 0.0117 | 0.0113 | 0.01 | 0.0211 | 2.8 | 98.0 |
| | 0.0039 | 0.0041 | 0.0015 | 0.0058 | 3.6 | 113.3 |
| Cd^{2+} | 0.4431 | 0.4365 | 0.1 | 0.5346 | 2.3 | 98.1 |
| | 0.0089 | 0.0092 | 0.01 | 0.0203 | 3.2 | 111.0 |
| | 0.0045 | 0.0043 | 0.0015 | 0.0059 | 3.9 | 106.7 |

^a n is the repetitive measurements number.

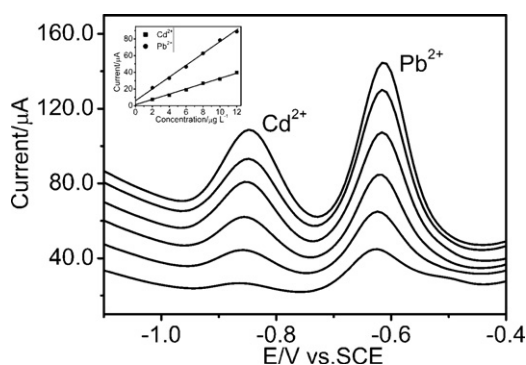


Fig. 5. SWASVs and respective calibration curves of Pb^{2+} and Cd^{2+} in 0.1 mol L^{-1} sodium acetate buffer solution (pH 4.5) at BINMSDE. Voltammograms are for 2, 4, 6, 8, 10, and $12 \mu\text{g L}^{-1}$ from bottom to top. $E_{\text{deposition}} = -1.2 \text{ V}$, $t_{\text{deposition}} = 300 \text{ s}$, step potential = 8 mV , potential amplitude = 50 mV , frequency = 50 Hz .

3 which are lower than that reported [43–47], which is shown in Table 1. Though, the detection limits of Cd^{2+} and Pb^{2+} is worse than that reported [7], the proposed method shows excellent selectivity for Cd^{2+} and Pb^{2+} in 50-fold mass ratio of CTAB, Triton X-100 and 100-fold mass ratio of SDS due to the effect of Nafion film, in addition, the fabricated electrode is more stable, convenient and inexpensive.

3.4. Stability and reproducibility

The reproducibility of one hundred twenty modified electrodes of same batch was studied under optimized conditions. One-sixth of them were randomly chosen for reproducibility assay and each modified electrode was performed three times in the standard solution containing $8.0 \mu\text{g L}^{-1}$ Pb^{2+} and Cd^{2+} . The result indicated that the change of peak heights were less than 2.7%. However, the reproducibility of the renewed electrode surfaces was difficult to control by the reported [7]. The stripping voltammograms of the same modified electrode were also recorded every other day over a month, and the maximum deviations obtained were 3.3% and 3.6%, respectively. The results indicate that the BINMSDE has good repro-

ducibility and long-time stability, which is better than that reported [7].

3.5. Interference of foreign species

The interference of some substances on the stripping voltammetric measurements was examined in 0.1 mol L^{-1} acetate buffer solution containing $10.0 \mu\text{g L}^{-1}$ Pb^{2+} and Cd^{2+} . Each substance was considered as interfering agent when the electrochemical signal exhibited a deviation more than $\pm 5\%$. A 500-fold mass ratio of SCN^- , Cl^- , F^- , SO_4^{2-} , NO_3^- , NH_4^+ , Li^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Al^{3+} , 300-fold mass ratio of Mn^{2+} , 200-fold mass ratio of Zn^{2+} , Co^{2+} , Ni^{2+} , 100-fold mass ratio of SDS, 50-fold mass ratio of CTAB and Triton X-100 had no influence on the signals of Pb^{2+} and Cd^{2+} . However, Cu^{2+} and Ag^+ with more positive reduction potential competed with Bi^{3+} , Pb^{2+} and Cd^{2+} for electrodeposition on the surface of electrode, which had a significant influence on the stripping response. In addition, Hg^{2+} could increase the stripping peak current of Pb^{2+} and Cd^{2+} due to the formation of amalgam on the electrode surface at -1.2 V .

3.6. Analysis of real sample

In order to illustrate its application in real samples analysis, the BINMSDE was employed to detect Pb^{2+} and Cd^{2+} in wastewater. The pretreated real wastewater samples were diluted with 0.1 mol L^{-1} acetate buffer solution when the analyte concentration was beyond the linear range. As can be seen from Table 2, the result of the electrochemical experiment accorded very well with those obtained by AAS, which confirmed the accuracy and reliability of the approach. It has a great potential for the practical determination of Pb^{2+} and Cd^{2+} in wastewater.

4. Conclusion

In this work, a novel BINMSDE is proposed for determination of trace Pb^{2+} and Cd^{2+} . Due to the synergistic effect of the medical stone, Nafion and bismuth film, the BINMSDE exhibits ultra-sensitivity and excellent selectivity. Compared to the expen-

sive atomic spectroscopy (AAS, ICP-MS) and the traditional mercury film electrodes, the proposed BINMSDE-based SWASV method is environment-friendly, stable, convenient and inexpensive. The assay results of heavy metals in wastewater with the proposed method were consistent with the AAS method. The fabricated BINMSDE can be used as a promising alternative for determination of heavy metals at trace levels in real samples.

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References

- [1] D.D. Runnells, T.A. Shepherd, E.E. Angino, Metals in water. Determining natural background concentrations in mineralized areas, *Environ. Sci. Technol.* 26 (1992) 2316–2323.
- [2] T. Kemper, S. Sommer, Estimate of heavy metal contamination in soils after a mining accident using reflectance spectroscopy, *Environ. Sci. Technol.* 36 (2002) 2742–2747.
- [3] A. Jang, Y. Seo, P.L. Bishop, The removal of heavy metals in urban runoff by sorption on mulch, *Environ. Pollut.* 133 (2005) 117–127.
- [4] A. Milne, W. Landing, M. Bizimis, P. Morton, Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS), *Anal. Chim. Acta* 665 (2010) 200–207.
- [5] O.W. Lau, S.Y. Ho, Simultaneous determination of traces of iron, cobalt, nickel, copper, mercury and lead in water by energy-dispersive X-ray fluorescence spectrometry after preconcentration as their piperazino-1,4-bis(dithiocarbamate) complexes, *Anal. Chim. Acta* 280 (1993) 269–277.
- [6] J.M. Jurado, M.J. Martín, F. Pablos, A. Moreda-Piñeiro, P. Bermejo-Barrera, Direct determination of copper, lead and cadmium in aniseed spirits by electrothermal atomic absorption spectrometry, *Food Chem.* 101 (2007) 1296–1304.
- [7] Y.H. Li, X.Y. Liu, X.D. Zeng, Y. Liu, X.T. Liu, W.Z. Wei, S.L. Luo, Simultaneous determination of ultra-trace lead and cadmium at a hydroxyapatite-modified carbon ionic liquid electrode by square-wave stripping voltammetry, *Sens. Actuators B* 139 (2009) 604–610.
- [8] E. Shams, A. Babaei, M. Soltaninezhad, Simultaneous determination of copper, zinc and lead by adsorptive stripping voltammetry in the presence of Morin, *Anal. Chim. Acta* 501 (2004) 119–124.
- [9] A.A. Ensaifi, T. Khayamian, S.S. Khaloo, Application of adsorptive cathodic differential pulse stripping method for simultaneous determination of copper and molybdenum using pyrogallol red, *Anal. Chim. Acta* 505 (2004) 201–207.
- [10] R.O. Kadara, I.E. Tothill, Resolving the copper interference effect on the stripping chronopotentiometric response of lead(II) obtained at bismuth film screen-printed electrode, *Talanta* 66 (2005) 1089–1093.
- [11] J. Wang, J.M. Lu, Ü.A. Kirgöz, S.B. Hocoavar, B. Ogorevc, Insights into the anodic stripping voltammetric behavior of bismuth film electrodes, *Anal. Chim. Acta* 434 (2001) 29–34.
- [12] K. Vytrās, I. Švancara, R. Metelka, A novelty in potentiometric stripping analysis: total replacement of mercury by bismuth, *Electroanalysis* 14 (2002) 1359–1364.
- [13] D. Demetriades, A. Economou, A. Voulgaropoulos, A study of pencil-lead bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry, *Anal. Chim. Acta* 519 (2004) 167–172.
- [14] L. Baldrianova, I. Švancara, M. Vlcek, A. Economou, S. Sotiropoulos, Effect of Bi(III) concentration on the stripping voltammetric response of in situ bismuth-coated carbon paste and gold electrodes, *Electrochim. Acta* 52 (2006) 481–490.
- [15] L. Baldrianova, I. Švancara, S. Sotiropoulos, Anodic stripping voltammetry at a new type of disposable bismuth-plated carbon paste mini-electrodes, *Anal. Chim. Acta* 599 (2007) 249–255.
- [16] H. Xu, L.P. Zeng, D.K. Huang, Y.Z. Xian, L.T. Jin, A nafion-coated bismuth film electrode for the determination of heavy metals in vegetable using differential pulse anodic stripping voltammetry: an alternative to mercury-based electrodes, *Food Chem.* 109 (2008) 834–839.
- [17] L. Jiang, Y.N. Wang, J.W. Ding, T.T. Lou, W. Qin, An ionophore-nafion modified bismuth electrode for the analysis of cadmium(II), *Electrochim. Commun.* 12 (2010) 202–205.
- [18] E.O. Jorge, M.M. Rocha, I.T.E. Fonseca, M.M.M. Neto, Studies on the stripping voltammetric determination and speciation of chromium at a rotating-disc bismuth film electrode, *Talanta* 81 (2010) 556–564.
- [19] X.Y. Xie, H.Q. Luo, N.B. Li, Determination of azo compounds by differential pulse voltammetry at a bismuth/poly(p-aminobenzene sulfonic acid) film electrode and application for detection in food stuffs, *J. Electroanal. Chem.* 639 (2010) 175–180.
- [20] A. Economou, P.R. Fielden, Mercury film electrodes: developments, trends and potentialities for electroanalysis, *Analyst* 128 (2003) 205–213.
- [21] J. Wang, R.P. Deo, S. Thonggamdee, B. Ogorevc, Effect of surface-active compounds on the stripping voltammetric response of bismuth film electrodes, *Electroanalysis* 13 (2001) 1153–1156.
- [22] G. Kefala, A. Economou, A. Voulgaropoulos, A study of Nafion-coated bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry, *Analyst* 129 (2004) 1082–1090.
- [23] S. Legeai, O. Vittori, A Cu/Nafion/Bi electrode for on-site monitoring of trace heavy metals in natural waters using anodic stripping voltammetry: an alternative to mercury-based electrodes, *Anal. Chim. Acta* 560 (2006) 184–190.
- [24] C. Gouveia-Caridade, R. Pauliukaite, C.M.A. Brett, Influence of Nafion coatings and surfactant on the stripping voltammetry of heavy metals at bismuth-film modified carbon film electrodes, *Electroanalysis* 18 (2006) 854–861.
- [25] B. Hoyer, T.M. Florence, G.E. Batley, Application of polymer-coated glassy carbon electrodes in anodic stripping voltammetry, *Anal. Chem.* 59 (1987) 1608–1614.
- [26] B. Hoyer, T.M. Florence, Application of polymer-coated glassy carbon electrodes to the direct determination of trace metals in body fluids by anodic stripping voltammetry, *Anal. Chem.* 59 (1987) 2839–2842.
- [27] J.B. Jia, L.Y. Cao, Z.H. Wang, Nafion/poly(sodium 4-styrenesulfonate) mixed coating modified bismuth film electrode for the determination of trace metals by anodic stripping voltammetry, *Electroanalysis* 19 (2007) 1845–1849.
- [28] W.W. Zhu, N.B. Li, H.Q. Luo, Anodic stripping voltammetry determination of Pb(II) and Cd(II) at a bismuth/poly(aniline) film electrode, *Anal. Lett.* 39 (2006) 2273–2284.
- [29] I. Adraoui, M.E. Rhazi, A. Amine, Fibrinogen-coated bismuth film electrodes for voltammetric analysis of lead and cadmium using the batch injection analysis, *Anal. Lett.* 40 (2007) 349–368.
- [30] N.S. Lawrence, L. Jiang, T.G.J. Jones, R.G. Compton, Voltammetric characterization of a N,N'-diphenyl-p-phenylenediamine-loaded screen-printed electrode: a disposable sensor for hydrogen sulfide, *Anal. Chem.* 75 (2003) 2054–2059.
- [31] D.M. Jenkins, B. Chami, M. Kreuzer, G. Presting, A.M. Alvarez, B.Y. Liaw, Hybridization probe for femtomolar quantification of selected nucleic acid sequences on a disposable electrode, *Anal. Chem.* 78 (2006) 2314–2318.
- [32] G.D. Liu, Y.Y. Lin, H. Wu, Y.H. Lin, Voltammetric detection of Cr(VI) with disposable screen-printed electrode modified with gold nanoparticles, *Environ. Sci. Technol.* 41 (2007) 8129–8134.
- [33] L. Civit, H.M. Nassef, A. Fragoso, C.K. O'Sullivan, Amperometric determination of ascorbic acid in real samples using a disposable screen-printed electrode modified with electrografted o-aminophenol film, *J. Agric. Food Chem.* 56 (2008) 10452–10455.
- [34] Q.T. Zhang, L. Jagannathan, V. Subramanian, Label-free low-cost disposable DNA hybridization detection systems using organic TFTs, *Biosens. Bioelectron.* 25 (2010) 972–977.
- [35] C. Kokkinos, A. Economou, M. Koupparis, Determination of trace cobalt(II) by adsorptive stripping voltammetry on disposable microfabricated electrochemical cells with integrated planar metal-film electrodes, *Talanta* 77 (2009) 1137–1142.
- [36] A. Crew, D.C. Cowell, J.P. Hart, Development of an anodic stripping voltammetric assay, using a disposable mercury-free screen-printed carbon electrode, for the determination of zinc in human sweat, *Talanta* 75 (2008) 1221–1226.
- [37] S.R. Lee, Y.T. Lee, K. Sawada, H. Takao, M. Ishida, Development of a disposable glucose biosensor using electroless-plated Au/Ni/copper low electrical resistance electrodes, *Biosens. Bioelectron.* 24 (2008) 410–414.
- [38] G. Kefala, A. Economou, Polymer-coated bismuth film electrodes for the determination of trace metals by sequential-injection analysis/anodic stripping voltammetry, *Anal. Chim. Acta* 576 (2006) 283–289.
- [39] L.Y. Cao, J.B. Jia, Z.H. Wang, Sensitive determination of Cd and Pb by differential pulse stripping voltammetry with in situ bismuth-modified zeolite doped carbon paste electrodes, *Electrochim. Acta* 53 (2008) 2177–2182.
- [40] F. Torma, M. Kádár, K. Tóth, E. Tatár, Nafion®/2,2-bipyridyl-modified bismuth film electrode for anodic stripping voltammetry, *Anal. Chim. Acta* 619 (2008) 173–182.
- [41] A. Królicka, A. Bobrowski, A. Kowal, Effects of electroplating variables on the voltammetric properties of bismuth deposits plated potentiostatically, *Electroanalysis* 18 (2006) 1649–1657.
- [42] J. Wang, Ü.A. Kirgöz, J.M. Lu, Stripping voltammetry with the electrode material acting as a 'built-in' internal standard, *Electrochim. Commun.* 3 (2001) 703–706.
- [43] M. Ghiaci, B. Rezaei, R.J. Kalbasi, High selective SiO₂-Al₂O₃ mixed-oxide modified carbon paste electrode for anodic stripping voltammetric determination of Pb(II), *Talanta* 73 (2007) 37–45.
- [44] C.G. Hu, K.B. Wu, X. Dai, S.S. Hu, Simultaneous determination of lead(II) and cadmium(II) at a diacetyldioxime modified carbon paste electrode by differential pulse stripping voltammetry, *Talanta* 60 (2003) 17–24.
- [45] E. Tesarova, L. Baldrianova, S.B. Hocoavar, I. Švancara, K. Vytrās, B. Ogorevc, Anodic stripping voltammetric measurement of trace heavy metals at antimony film carbon paste electrode, *Electrochim. Acta* 54 (2009) 1506–1510.
- [46] M.A. El Mhammedi, M. Achak, M. Hbid, M. Bakasse, T. Hbid, A. Chtaini, Electrochemical determination of cadmium(II) at platinum electrode modified with kaolin by square wave voltammetry, *J. Hazard. Mater.* 170 (2009) 590–594.
- [47] M.A. El Mhammedi, M. Achak, M. Bakasse, A. Chtaini, Electroanalytical method for determination of lead(II) in orange and apple using kaolin modified platinum electrode, *Chemosphere* 76 (2009) 1130–1134.