

Evaluation of Trace Heavy Metal Levels in Soil Samples Using an Ionic Liquid Modified Carbon Paste Electrode

Jianfeng Ping,[†] Jian Wu,^{*,†} Yibin Ying,[†] Maohua Wang,[‡] Gang Liu,[‡] and Miao Zhang[‡]

[†]College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310029, P. R. China

[‡]Key Lab on Modern Precision Agriculture System Integration Research, Ministry of Education, Department of Electronic Engineering, China Agricultural University, Beijing 100083, P. R. China

ABSTRACT: An ionic liquid *n*-octylpyridinium hexafluorophosphate (OPFP) modified carbon paste electrode was developed. This ionic liquid modified carbon electrode showed better electrochemical activities compared with the traditional carbon paste electrode which employed the paraffin oil as the binder. With the electrochemically deposited bismuth film, the developed electrode exhibited well-defined and separate stripping voltammetric peaks for cadmium and lead. The linear range of the bismuth film electrode was from 1.0 $\mu\text{g L}^{-1}$ to 100.0 $\mu\text{g L}^{-1}$ for both metal ions with a deposition time of 120 s and a deposition potential of -1.2 V in pH 4.5 acetate buffer solution. The detection limit was 0.10 $\mu\text{g L}^{-1}$ for cadmium and 0.12 $\mu\text{g L}^{-1}$ for lead with a deposition time of 180 s. The electrode was also applied to determine cadmium and lead in soil sample extracts. Results suggested that the proposed electrode was sensitive, reliable and effective for the determination of trace heavy metals.

KEYWORDS: ionic liquid, bismuth film, anodic stripping voltammetry, soil

INTRODUCTION

In recent years, an increasing demand for the assessment of environmental damage induced by heavy metal pollution has emerged.¹ This pollution, contaminating agricultural lands and other resources, has given rise to various problems in land use, groundwater and ecosystems.² Moreover, the heavy metals can cause many disorders in animals and tend to accumulate in the food chains.^{3,4} They can be immediately poisonous or result in long-term health problems when they reach high levels in the human body. Therefore, the determination of toxic heavy metals in the environment is of great importance. Spectroscopic methods such as atomic absorption spectrometry and X-ray fluorescence spectrometry are frequently used to determine heavy metals due to their high sensitivity and accuracy, but still face some drawbacks such as their being expensive and time-consuming and only measuring one element at a time.⁵ Electrochemical methods, especially electrochemical stripping analysis (ESA), have been widely recognized as a powerful tools for simultaneous determination of several metal ions, due to the combination of an effective preconcentration step with advanced electrochemical measurements of the accumulated analytes.^{6–8} Furthermore, analytical instruments for ESA are relatively portable, compact and inexpensive compared with its spectroscopic counterparts, providing considerable feasibility for on-site measurements, e.g., biomedical, environmental and industrial monitoring.⁹

In most cases, mercury electrodes are preferred for stripping analysis due to their high reproducibility and sensitivity.^{10,11} However, the toxicity of mercury makes it undesirable for sensing applications. A great variety of electrode materials have been proposed as alternatives such as gold, platinum, silver, bismuth, alloys, etc.^{12–15} Among these, bismuth is an environmentally friendly material with very low toxicity and possesses a comparable performance to mercury in stripping analysis.¹⁵ Bismuth

films have been investigated on numerous substrates, particularly on carbon paste electrodes (CPEs). Bismuth film deposited CPEs exhibit some advantages over other substrates in stripping analysis of bismuth film electrodes including low cost, simple preparation and renewable surface.^{7,16} However, the inherent disadvantages of CPEs such as low mechanical stability and reproducibility limit their practical applications.¹⁷ Therefore, new electrode materials for stripping analysis are still highly desired to meet the growing demands for on-site environmental monitoring of trace heavy metal ions.

Recently, room temperature ionic liquids (RTILs) have attracted great attention in the field of chemistry due to their excellent properties such as high chemical and thermal stability, negligible vapor pressure and good conductivity.^{18,19} The capability of RTILs combining with carbon materials to form conductive composites makes them very attractive for the preparation of various electrodes.^{20,21} IL-carbon composites such as IL-graphite, IL-carbon nanotubes, IL-mesoporous carbon, IL-carbon nanofibers and IL-graphene have been developed for detection and analysis.^{21–25} These ionic liquid modified carbon electrodes show some advantages over traditional CPEs, such as high conductivity and sensitivity, fast electron transfer and good antifouling ability for electroanalysis.

In this paper, an ionic liquid *n*-octylpyridinium hexafluorophosphate (OPFP) modified carbon paste electrode (IL-CPE) was developed and further modified with bismuth film to simultaneously determine lead (Pb) and cadmium (Cd) ions by using square wave anodic stripping voltammetry (SWASV). With the good conductivity of ionic liquid and high sensitivity of bismuth

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film, this sensing electrode exhibited good stripping performance for the analysis of Pb(II) and Cd(II). Furthermore, the developed electrode was applied to determine Pb(II) and Cd(II) in real soil samples.

EXPERIMENTAL PROCEDURES

Reagents. All chemicals were of analytical grade and used without any further purification. Ionic liquid *n*-octylpyridinium hexafluorophosphate (OPFP, 99%) was purchased from Shanghai Chengjie Co., Ltd. (Shanghai, China). Graphite powder (size <30 μm , spectral pure) and paraffin oil were obtained from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China). Standard solutions of Bi(III), Cd(II) and Pb(II) (1000 mg L^{-1}) were prepared and diluted as required. An acetate buffer solution (0.1 mol L^{-1} , pH 4.5) was used as the supporting electrolyte. Millipore-Q ($18.2 \text{ M}\Omega \text{ cm}$) water was used for all experiments.

Apparatus. Voltammetric measurements were carried out on a CHI 440 electrochemical workstation (CH Instruments USA). The electrochemical cell was assembled with a conventional three-electrode system: a saturated Ag/AgCl reference electrode, a Pt wire auxiliary electrode, and the prepared carbon paste working electrodes. A multimeter was used for ohmic resistance measurements. All the experiments were performed at room temperature.

Electrode Preparation. The preparation of ionic liquid modified carbon paste electrode (IL-CPE) was similar to our previous report.²⁰ First, 0.6 g of graphite powder and 0.4 g of OPFP was hand-mixed in a mortar using a pestle for 30 min. Then a portion of the resulting paste was packed firmly into the electrode cavity (1.8 mm diameter) of a glass sleeve. The electrode was then heated in an oven to a temperature higher than the melting point of OPFP (mp 65°C) for 2 min. Electrode contact was established via a copper wire. For comparison, the traditional carbon paste electrode (CPE) was prepared by a 70/30 (w/w) graphite to paraffin oil. The new surface of these working electrodes was obtained by smoothing the electrodes with a weighing paper.

Soil Sample Extract Preparation. The soil samples were collected from some regions with cultivated lands (China), which are near industrial areas. The treatment (extraction process) of samples was performed according to the reports.^{26,27} First, 1 g of soil sample was heated in an oven at 80°C for one hour. Then, the soil sample was placed in an extraction tube with 40 mL of 0.1 mol L^{-1} acetic acid. The mixed sample was sonicated for 1 h. Then the mixture was centrifuged for phase separation and the aqueous phase was filtered with filters of $0.22 \mu\text{m}$ pore size. After these processes, the free metal ions in the soil samples were extracted. Prior to the test, the pH of the obtained extract solutions was adjusted to 4.5 by using 0.1 mol L^{-1} NaOH solution.

Procedures. The square wave anodic stripping voltammetry (SWASV) experiments comprised an electrochemical preconcentration step usually at -1.2 V for 120 s, an equilibration period of 10 s, and a square wave stripping scan from -1.2 V to $+0.2 \text{ V}$. The parameters for the square wave measurement are as follows: square wave amplitude, 25 mV; potential step, 5 mV; frequency, 20 Hz. Before each measurement, a precondition/"clean" step at potential of $+0.2 \text{ V}$ was applied for 30 s. A magnetic stirrer was used to stir the test solutions during the preconcentration and precondition steps.

RESULTS AND DISCUSSION

Basic Characteristics of IL-CPE. Figure 1 shows typical cyclic voltammograms for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at the IL-CPE and CPE. It is clear that the electron transfer rate was sluggish, with a peak-to-peak separation of 210 mV at the CPE. On the contrary, the IL-CPE exhibited a well-shaped cyclic response for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple with a peak-to-peak separation of 70 mV, suggesting the dramatic increase in the electron transfer rate due to the high

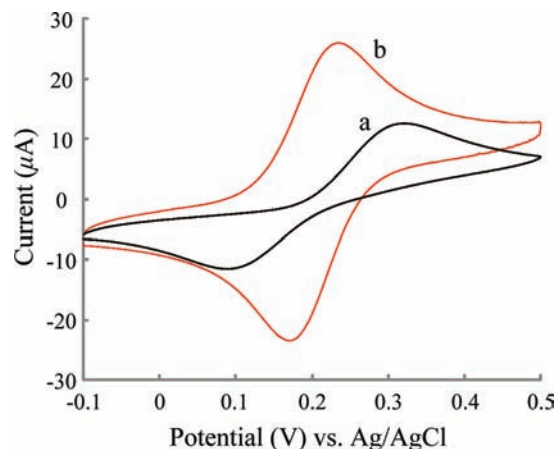


Figure 1. Cyclic voltammograms for $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$, (a) CPE and (b) IL-CPE. Scan rate: 100 mV s^{-1} .

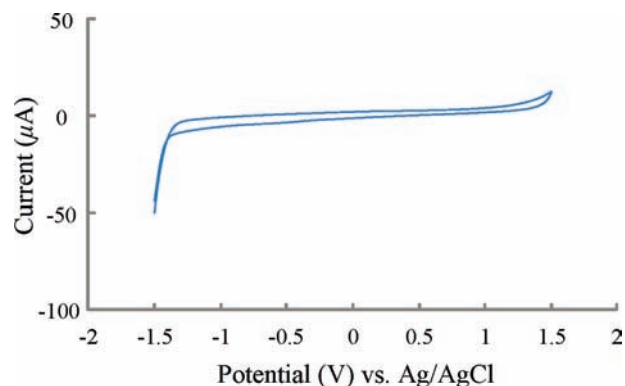


Figure 2. Cyclic voltammogram of the IL-CPE in acetate buffer solution (0.1 mol L^{-1} , pH 4.5). Scan rate: 100 mV s^{-1} .

conductivity of OPFP. It is reported that the ionic liquid present in the carbon electrode not only acted as binder to fill in the blanks of the carbon paste but also formed a layer of ionic liquid on the electrode surface.^{17,20} Therefore, the OPFP in carbon electrode could facilitate the electron transfer rate between the electron surface and electroactive species.

Before studying the stripping performance of IL-CPE, the hydrogen evolution process at the electrode surface was investigated due to its profound effect on the stripping analysis.⁸ Figure 2 shows the cyclic voltammogram of IL-CPE in acetate buffer solution (0.1 mol L^{-1} , pH 4.5). As shown, the background current of IL-CPE was very low with a wide electrochemical window which was extended to $\sim 2.5 \text{ V}$. The cathodic limit of IL-CPE in the buffer solution was about -1.3 V , which was sufficient for the stripping analysis of Cd and Pb.

Stripping Response of IL-CPE. Figure 3 shows the square wave anodic stripping voltammograms of Cd(II) and Pb(II) at the bare CILE, bismuth film modified CPE (BiF/CPE) and bismuth film modified IL-CPE (BiF/IL-CPE). As can be seen in Figure 3b, the response at the bare CILE was very poor with two small peaks. In contrast, after the addition of $1000 \mu\text{g L}^{-1}$ Bi(III) to the sample, and simultaneously depositing it along with the target metal ions on to the IL-CPE, the obtained electrode exhibited high sensitivity toward Cd(II) and Pb(II) detection with well-defined, sharp and separate stripping peaks (Figure 3c).

This phenomenon could be attributed to the fact that bismuth can form an “alloy” with Cd and Pb which makes Cd(II) and Pb(II) reduced more easily.¹⁵ The stripping response of heavy metal ions at the BiF/IL-CPE was also superior to that of BiF/CPE (Figure 3a). The improved performance could be ascribed to the enhanced conductivity of the IL-CPE which employs the conductive ionic liquid as the binder, while the poor conductivity was found on the surface of CPE which uses nonconductive paraffin oil as the binder.

Effect of Experimental Parameters. The stripping analysis of metal ions at the BiF/IL-CPE was investigated in several supporting electrolytes such as phosphate buffer, HCl, acetate buffer and

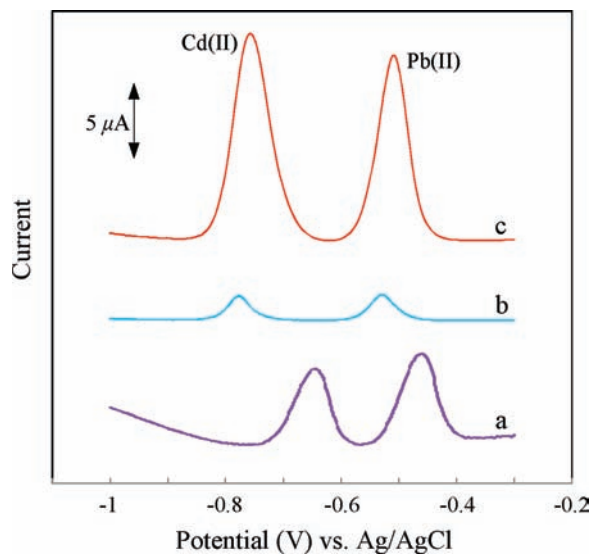


Figure 3. SWASVs of $50 \mu\text{g L}^{-1}$ Cd(II) and Pb(II) in 0.1 mol L^{-1} acetate buffer solution at the different electrodes. Curves (a) BiF/CPE, (b) IL-CPE and (c) BiF/IL-CPE. Deposition time: 120 s. Deposition potential: -1.2 V . Concentration of Bi(III): $1000 \mu\text{g L}^{-1}$.

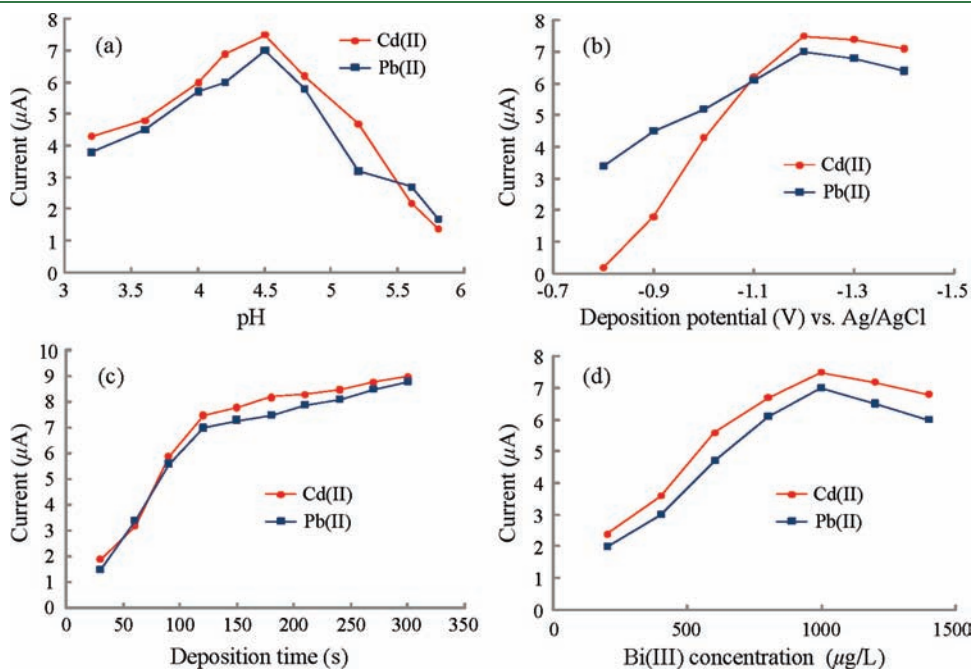


Figure 4. Effects of (a) pH of supporting electrolyte, (b) deposition potential, (c) deposition time and (d) Bi(III) concentration on the stripping voltammetric responses of $25 \mu\text{g L}^{-1}$ Cd(II) and Pb(II) at the in situ plated BiF/IL-CPE. Other conditions were as in Figure 3.

HClO_4 . Among these mentioned electrolytes, the BiF/IL-CPE showed the best stripping performance in acetate buffer. And the effect of pH value of the acetate buffer on the stripping currents of Cd(II) and Pb(II) is shown in Figure 4a. The peak currents increased along with the increase of pH (from 3.2 to 4.5). When the pH of acetate buffer solution was higher than 4.5, a fast decrease of the stripping peaks was observed, which might be attributed to the hydrolysis of bismuth ion that resulted in the decrease of the reduction rate of metal ions.⁸ These results indicated that the bismuth metal alloy formation greatly depends on the pH of the solution. Therefore, all further experiments were carried out at the acetate buffer with a pH value of 4.5.

Figure 4b illustrates the influence of deposition potential varied in the range of -1.4 and -0.8 V on the stripping response of Cd(II) and Pb(II). As shown, when the deposition potential shifted from -0.9 V to -1.2 V , the stripping peak currents increased remarkably. However, as the deposition potential became more negative than -1.2 V , the peak currents reduced due to the hydrogen evolutions that could reduce the surface activities of the electrode. Furthermore, other chemicals might be reduced at these potentials and interfere the determination of Cd(II) and Pb(II). Consequently, -1.2 V was used as the optimal deposition potential for the subsequent experiments.

Figure 4c shows the effect of deposition time on the stripping peak currents. For both metal ions, the results plotted in Figure 4c exhibited a similar pattern. As the deposition time increased from 30 to 120 s, the stripping peak currents of Cd(II) and Pb(II) increased linearly. However, the linear trend was not obvious with the further prolonging of the deposition time; only a slight increase of the stripping responses was found due to the saturation loading of the electrode surface. On the basis of this study, a deposition time of 120 s was selected as the optimal result.

The thickness of the bismuth film depends on the Bi(III) ion concentration in the bulk solutions. The effect of the Bi(III) concentration on the stripping peak currents is displayed in Figure 4d with the range from 200 to $1400 \mu\text{g L}^{-1}$. Both the

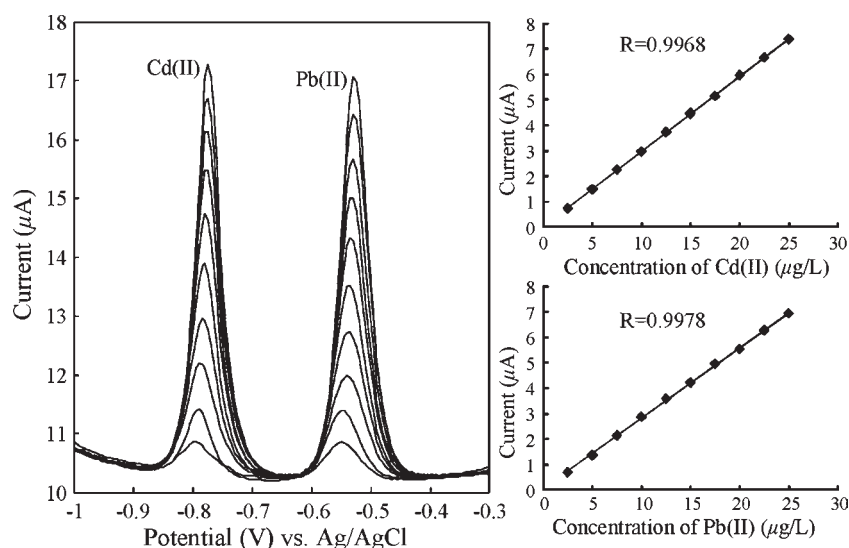


Figure 5. SWASVs for the successive additions of Cd(II) and Pb(II) in $2.5 \mu\text{g L}^{-1}$ steps at the BiF/IL-CPE (left part of figure). The right part of the figure shows the calibration curves for the determination of Cd(II) and Pb(II). Other conditions were as in Figure 3.

Table 1. Normalized Current, $I_p/I_{p_{\text{max}}}$, Expressed as a Percentage, for $50 \mu\text{g L}^{-1}$ Cd(II) and Pb(II) at Different Concentrations of Surfactants (mg L^{-1}) for the BiF/CPE and BiF/IL-CPE

| metal ion | electrode | $I_p/I_{p_{\text{max}}} (\%)$ | | | | | | | | |
|-----------|------------|-------------------------------------|----|----|----------------------------|----|----|-----------------------------|----|----|
| | | Triton X-100 (mg L^{-1}) | | | SDS (mg L^{-1}) | | | CTAB (mg L^{-1}) | | |
| | | 5 | 10 | 15 | 5 | 10 | 15 | 5 | 10 | 15 |
| Cd(II) | BiF/CPE | 76 | 63 | 52 | 85 | 78 | 67 | 75 | 63 | 50 |
| | BiF/IL-CPE | 78 | 69 | 62 | 89 | 84 | 78 | 77 | 64 | 52 |
| Pb(II) | BiF/CPE | 79 | 67 | 52 | 83 | 78 | 65 | 78 | 67 | 53 |
| | BiF/IL-CPE | 82 | 71 | 63 | 88 | 84 | 78 | 79 | 67 | 54 |

responses of Cd(II) and Pb(II) increased when the Bi(III) concentrations increased from 200 to $1000 \mu\text{g L}^{-1}$. However, in the case of Bi(III) concentrations higher than $1000 \mu\text{g L}^{-1}$, the stripping responses of metal ions decreased gradually, and the peaks became wider, probably due to the fact that thicker bismuth film might hinder the mass transfer of metal ions during the stripping step. Therefore, a Bi(III) concentration of $1000 \mu\text{g L}^{-1}$ was chosen to get satisfactory sensitivity for the determination of metal ions.

Analytical Performance. Calibration curves for the simultaneous determination of Cd(II) and Pb(II) at the BiF/IL-CPE were investigated by SWASV under the optimal conditions. Figure 5 illustrates the stripping response of the BiF/IL-CPE without any interference while simultaneously increasing the concentrations of both metal ions from 2.5 to $25 \mu\text{g L}^{-1}$ in $2.5 \mu\text{g L}^{-1}$ per increment. The resulting calibration plots were favorably linear with the above range with the linear correlation coefficients of 0.9968 and 0.9978 for Cd(II) and Pb(II), respectively. The linear range of the bismuth film coated electrode was from $1.0 \mu\text{g L}^{-1}$ to $100.0 \mu\text{g L}^{-1}$ for both metal ions. The BiF/IL-CPE also showed satisfactory detection limits (S/N is 3) of $0.10 \mu\text{g L}^{-1}$ for Cd(II) and $0.12 \mu\text{g L}^{-1}$ for Pb(II) in combination with a 180 s deposition time, while repetitive measurements of $25 \mu\text{g L}^{-1}$ Cd(II) and Pb(II) exhibited good reproducibility with the relative standard deviations of 2.4% and 1.7% for Cd(II) and Pb(II), respectively ($n = 10$). Lower detection limits for both metal ions could be expected by prolonging the deposition time.

Interference Study. It is reported that the bismuth film electrodes are prone to being fouled by surface-active compounds and cause deactivation of the electrode surface.^{15,16} Here, the effects of three different types of surfactants, including cetyltrimethylammonium (CTAB), sodium dodecylsulfate (SDS) and Triton X-100, on the responses of the metal ions at the BiF/IL-CPE were investigated and compared with other electrodes. Table 1 summarizes the data on the normalized current, $I_p/I_{p_{\text{max}}}$ measured for $50 \mu\text{g L}^{-1}$ Cd(II) and Pb(II) in acetate buffer solution with different concentrations of surfactants. Obviously, the cationic surfactant CTAB exhibited the most obvious decrease in the stripping currents owing to electrostatic repulsion with lead and cadmium, while anionic surfactant SDS produced the least significantly decrease in stripping currents. The Triton X-100 induced moderate influence on the current signals. Compared with the BiF/CPE, it is clear that the BiF/IL-CPE was much more tolerant to the presence of the surface-active compounds for the detection of metal ions. Such a minimization of the surfactant's fouling effect was in agreement with the good antifouling ability of IL constructed carbon electrode. This characteristic could be ascribed to the presence of a layer of OPFP film on the graphite, which acts as a protective layer promoting the resistance to fouling.

Soil Sample Extract Analysis. The feasibility of the proposed electrode for the use in the determination of metal ions in soil sample extracts was investigated. The determination of Cd(II)

Table 2. Comparison of BiF/IL-CPE and AAS for the Determination of Cd(II) and Pb(II) in Real Soil Sample Extracts

| sample no. | BiF/IL-CPE | | AAS ^a | |
|------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | Cd(II) ($\mu\text{g L}^{-1}$) | Pb(II) ($\mu\text{g L}^{-1}$) | Cd(II) ($\mu\text{g L}^{-1}$) | Pb(II) ($\mu\text{g L}^{-1}$) |
| 1 | 1.82 ± 0.048 ^b | 2.46 ± 0.052 | 1.74 ± 0.042 | 2.54 ± 0.039 |
| 2 | 12.83 ± 0.077 | 15.43 ± 0.089 | 12.72 ± 0.053 | 15.61 ± 0.051 |
| 3 | 1.11 ± 0.035 | 13.24 ± 0.078 | 1.15 ± 0.043 | 13.07 ± 0.056 |
| 4 | 28.95 ± 0.098 | 0.54 ± 0.032 | 29.38 ± 0.058 | 0.56 ± 0.032 |

^a Atomic absorption spectrometry. ^b Value is the mean of six measurements ± standard deviation.

and Pb(II) at the BiF/IL-CPE was performed by the addition of their standard solutions into the extract solutions. Results obtained by this method were compared with those by atomic absorption spectrometry (AAS). As can be seen in Table 2, the difference of the measured data of Cd(II) and Pb(II) concentrations obtained by the BiF/IL-CPE and AAS was less than 5%, indicating the good accuracy and reliability of the proposed method. Therefore, the proposed BiF/IL-CPE could provide an effective method for the simultaneous determination of Cd(II) and Pb(II) at low $\mu\text{g L}^{-1}$ levels in real samples.

In summary, an ionic liquid OPFP modified carbon paste electrode was fabricated and further modified with bismuth film for the simultaneous determination of Cd(II) and Pb(II). With the high conductivity and good antifouling ability of IL-CPE and the unique features of the bismuth film, the developed electrode exhibited very attractive stripping performance. The effect of experimental parameters and the influence of several surfactants on the stripping behavior were studied. The linear range was from 1.0 $\mu\text{g L}^{-1}$ to 100.0 $\mu\text{g L}^{-1}$ for both the metal ions and the detection limits were 0.10 $\mu\text{g L}^{-1}$ and 0.12 $\mu\text{g L}^{-1}$ for Cd(II) and Pb(II), respectively. Furthermore, the developed electrode was successfully applied to the determination of the heavy metal ions in soil sample extracts. This work proposed a nontoxic, high sensitive, reproducible and stable electrode, which holds great promise for its wide application in trace determination of metal ions in the environmental and biological analysis.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wujian69@zju.edu.cn.

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