

Research Article

Simultaneous Determination of Copper, Lead, and Cadmium at Hexagonal Mesoporous Silica Immobilized Quercetin Modified Carbon Paste Electrode

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A new method was developed for simultaneous determination of copper, lead, and cadmium, based on their voltammetric response at a carbon paste electrode modified with hexagonal mesoporous silica (HMS) immobilized quercetin (HMS-Qu/CPE). Compared with quercetin modified carbon paste electrode (Qu/CPE) and quercetin ionic liquid modified carbon paste electrode (Qu-IL/CPE), the HMS-Qu/CPE exhibited improved selectivity and high sensitivity toward the detection of copper, lead, and cadmium. The properties of the HMS-Qu/CPE in 0.1 M HCOONa-HCl buffer solution (pH4.7) were investigated by adsorptive stripping voltammetry (ASV) and electrochemical impedance spectroscopy (EIS). The electrochemical behavior of copper, lead, and cadmium at the modified electrodes and factors affecting the preconcentration procedures were also investigated. Detection limits of 5.0, 0.8, 1.0 nM for copper, lead, and cadmium were obtained, respectively. The method is simple, fast, sensitive, and selective, and is successfully applied to soil sample.

1. Introduction

Heavy metal contamination in the environment is a major concern worldwide because of the toxicity of these metals and their potential threat to human health. Currently, quantification of heavy metals relies upon collection of liquid discrete samples for subsequent laboratory analysis using techniques such as ICP-MS, AAS, GC, HPLC, FT-IR, and GS/MS [1]. Electrochemical detection has several advantages over these methods in their simplicity, fast response, and suitability for the preparation of inexpensive and portable instrumentations [2]. Adsorptive stripping voltammetry (ASV) is not only an extremely sensitive electrochemical technique for measuring trace metals but also can carry out simultaneous detection of several metals in various matrices [3, 4]. Chemically modified electrodes (CMEs), with surfaces designed for reacting and binding of target analyte, hold great promise for chemical sensing [5–7]. There are different directions by which CMEs can benefit for analytical application of environmental samples. These include acceleration of electron transfer reactions, preferential accumulation, or

selective membrane permeation [8]. Such steps can impart higher selectivity, sensitivity, and stability on electrochemical devices.

As a member of the flavonoid family, quercetin (Qu) can form stable complexes with various metal cations. Many researches have focused on the application of Qu modified carbon paste electrode (CPE) [9, 10]. However, there are no reports about simultaneous determination of copper, lead, and cadmium by using Qu modified electrode. Ionic liquids (IL) are liquid electrolytes composed entirely of ions. In recent years, IL have emerged as a research frontier due to their unique chemical and physical properties [11–13]. IL, as the modifier, can offer improvements in the stability and reproducibility of electrode, and has attracted much attention in electrochemical field [14–16]. To our knowledge, there is no report about IL modified electrode to determine heavy metal ions.

Ordered mesoporous materials are highly unusual in their textural characteristics: uniform pore sizes, high surface areas, and long-range order of the packing of pores [17–20]. Hexagonal mesoporous silica (HMS), possessing hexagonal

array of pores, is one of the most important mesoporous SiO₂ materials as adsorbents, gas storage materials, separation membranes, catalyst supports, and so on [21]. Yantasee [22–27] and coworkers have reported on simultaneous determination of copper, lead, and cadmium using a carbon paste electrode modified with mesoporous silica. In published documents, polymeric monolayers assembling on the surfaces of ordered mesoporous materials were the focus due to the superior stability and durability of electrode. However, selection of functional chelating agents (ligands) as the modifier may be restricted. Because of the micropore size of HMS limits the entry of large chelating agent leads to reduce the chelation of chelating agent toward metal ions. Otherwise, time-consuming synthesis procedures and preparation of the electrode are also difficult.

In this study, we developed a more simple and sensitive electrochemical method for simultaneous determination of copper, lead and cadmium utilizing the excellent properties of HMS and Qu. In this work, a new quercetin modified carbon paste electrode (Qu/CPE), quercetin ionic liquid modified carbon paste electrode (Qu-IL/CPE), and an HMS immobilized quercetin carbon paste electrode (HMS-Qu/CPE) were fabricated, respectively. The electrochemical responses of copper, lead and cadmium at CMEs were investigated in detail. The results show that HMS-Qu/CPE as a working electrode exhibits higher sensitivity and selectivity toward the detection of copper, lead and cadmium than Qu/CPE, and Qu-IL/CPE. A novel electrochemical method is developed for simultaneous determination of copper, lead, and cadmium, and applied to the analysis of soil samples with satisfying results.

2. Experimental

2.1. Reagents and Chemicals. Qu (purity >98.9%) was obtained from Shanghai Reagent Co. (Shanghai, China), and graphite powder (spectral pure) was obtained from Sinopharm Group Chemical Reagent Co. (Shanghai, China). Tetrafluoroborate 1-butyl-3-methylimidazolium ([Bmim]BF₄) was obtained from Shanghai Ling Feng Reagent Co. (Shanghai, China) and used without further purification. HMS was synthesized as described previously [28]. A stock standard solution of Cu(II) (0.01 M) was prepared by dissolving 0.1589 g of copper powder (Shanghai Reagent Company, China) in 4.0 M nitric acid 20 mL, then the resulting solution was moved into the 250 mL volumetric flask, added twice-distilled water to the mark and stirred. A stock standard solution of Pb(II) (0.01 M) was prepared by dissolving 0.5179 g lead powder (Tianjin Reagent Company, China) in 4.0 M nitric acid 20 mL, then the resulting solution was moved into the 250 mL volumetric flask, added twice-distilled water to the mark and stirred. A stock standard solution of Cd(II) (0.01 M) was prepared by dissolving 0.2810 g of cadmium powder (SHRC, China) in 3.0 M hydrochloric acid 20 mL, then the resulting solution was moved into the 250 mL volumetric flask, added twice-distilled water to the mark and stirred. An oxygen free nitrogen (OFN) gas (99.9995%, Jinan Gas

Company, China) was used to purge the solution and to remove dissolved oxygen. All reagents were analytical grade materials. Twice-distilled water was used throughout the experiments.

2.2. Apparatus. Cyclic voltammetries (CV) and differential pulse voltammetries (DPV) were performed on electrochemical Analyzer (Chenhua Instrumental Co., China) CHI 842B controlled by a personal computer. Electrochemical impedance spectroscopy (EIS) was carried out by electrochemical Analyzer (ZAHNER Co., Germany) IM6ex and the frequency range was from 60 kHz to 0.1 Hz with an amplitude of 5 mV. A three-electrode system was employed, including a modified carbon paste electrode as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl (3 M KCl) electrode as the reference electrode.

2.3. Electrode Preparation. The conventional CPE was prepared by mixing graphite powder and paraffin oil in a ratio of 5:2 (w/w) in a mortar. The resulting paste was packed firmly into the cavity (5 mm diameter) of a glass tube. A copper wire fixed to a graphite rod and inserted into the glass tube served to establish electrical contact with the analyzer. Qu-IL/CPE was prepared by dissolving 0.0240 g Qu in 50 mL ethanol and uniformly mixing with graphite powder. The ethanol was allowed to evaporate in a moment. 0.05 g paraffin oil and 0.6 mL [Bmim] BF₄ were added, and mixed until obtaining a uniformly wetted paste. A portion of the resulting paste was packed firmly into the cavity (5 mm diameter) of a glass tube. The electrical contact was established via a copper wire. Qu/CPE was prepared in the same fashion, but no [Bmim] BF₄ was added. HMS-Qu/CPE was fabricated by dissolving 0.0240 g Qu in 50 mL ethanol and mixed the solution with 0.1 g HMS. The ethanol was allowed to evaporate. The paraffin oil was mixed with graphite powder until a uniformly wetted paste was obtained. A portion of the resulting paste was packed firmly into the cavity (5 mm diameter) of a glass tube and the electrical contact was established by a copper wire. The surface of the electrodes was smoothed on a weighing paper and rinsed carefully with twice-distilled water prior to the each measurement.

2.4. Sample Solution Preparation. Soil samples were collected from Jinan Environmental Monitoring Central Station. The samples were dried, ground, and sifted by the 60 mesh nylon sieve. 0.5 g of powder was accurately weighed into the decomposing cell. 5.0 mL nitric acid, 5.0 mL hydrochloric acid, and 5.0 mL peroxide were added. The sample solution into decomposing cell is decomposed by microwave [29]. The resulting solution was moved into the 50 mL volumetric flask, and water was added to the mark and stirred. Placed 1 mL of sample solution was placed into 10 mL volumetric flask, and 0.1 M HCOONa-HCl buffer solution was added to the mark and stirred.

2.5. Voltammetric Analysis Procedure. Unless otherwise stated, 0.1 M HCOONa-HCl solution (pH4.7) was used as

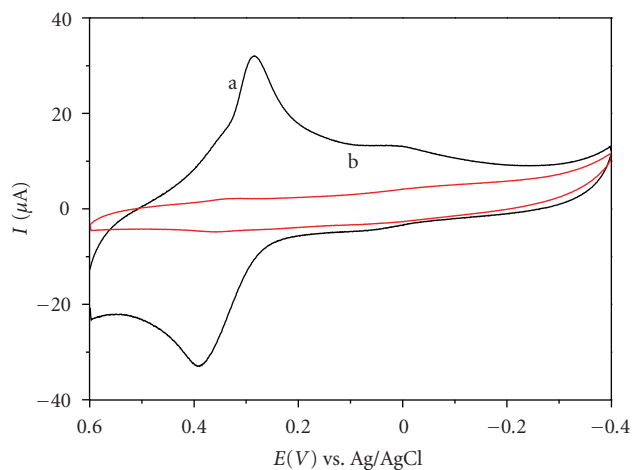


FIGURE 1: The cyclic voltammograms of Qu/CPE (a) and CPE (b) in 0.1 M HCOONa-HCl buffer (pH4.7), scan rate $0.1 \text{ V} \cdot \text{s}^{-1}$.

a supporting electrolyte for the determination. The multicomponent Cu(II)/Pb(II)/Cd(II) solution was deaerated with pure nitrogen for 10 min. The measurements were carried out after a preconcentration step, in which the solution was stirred during preconcentration time of 120 s at preconcentration potential of 0.6 V. After a rest period of 30 s, the response curve was recorded by scanning the potential in the negative direction with differential pulse voltammetry (DPV) technique.

3. Results and Discussion

3.1. Electrochemical Characterization of Qu/CPE. The electrochemical behaviors of Qu/CPE and CPE were investigated in pH4.7 HCOONa-HCl buffer solution. Figure 1 shows the cyclic voltammograms of Qu/CPE (Figure 1, curve a) and CPE (Figure 1, curve b). A pair of well-defined redox peaks of Qu was observed at Qu/CPE, the anodic peak potential E_{pa} at 0.394 V, cathode peak potential E_{pc} at 0.284 V, and peak-to-peak separation (ΔE_p) of 0.11 V. The result indicates that Qu can undergo redox reaction at modified electrode. The redox peaks of Qu were also observed at Qu-IL/CPE and HMS-Qu/CPE.

3.2. The Electrochemical Behavior of Copper, Lead, and Cadmium at Different Modified Electrodes. Figure 2 shows the electrochemical responses of $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution at Qu/CPE, Qu-IL/CPE, and HMS-Qu/CPE. At the Qu/CPE (Figure 2, curve a) and Qu-IL/CPE (Figure 2, curve b), two reduction peaks are observed for copper and lead at -0.11 V and -0.48 V , respectively, and no obvious reduction peak of cadmium is observed. At the Qu-IL/CPE, the reduction peak currents of copper and lead are largely increased, indicating that the chemical and physical properties of IL improve the sensitivity of electrode. At the HMS-Qu/CPE (Figure 2, curve c), the reduction

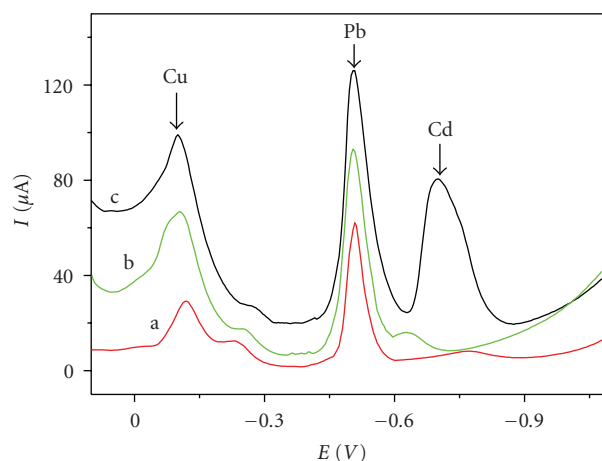


FIGURE 2: The differential pulse voltammograms of $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution at Qu/CPE (a), Qu-IL/CPE (b) and HMS-Qu/CPE (c). Condition: 0.1 M HCOONa-HCl (pH4.7), preconcentration potential 0.6 V, preconcentration time 120 s, potential scan range 0.6 V to -1.0 V .

peak of cadmium appears at potential of -0.69 V and peak currents of $60.9 \mu\text{A}$. The peak currents of copper and lead are also obviously increased from $31.8 \mu\text{A}$ to $33.6 \mu\text{A}$ and from $82.8 \mu\text{A}$ to $102.3 \mu\text{A}$ compared with that of Qu-IL/CPE. This tremendous increase in the current density for copper, lead, and cadmium with the HMS-Qu/CPE is apparently due to the cooperative effect of HMS and Qu. Meanwhile the reduction currents of Qu at different modified electrodes are remarkably lower in multicomponent Cu(II)/Pb(II)/Cd(II) solution than those in the blank solution. The reduction current change (ΔI_p) of Qu at different modified electrodes was in a sequence of:

$$\begin{aligned} & \text{Qu/CPE} (\Delta I_p = 97.4 \mu\text{A}) \\ & < \text{Qu-IL/CPE} (\Delta I_p = 117.4 \mu\text{A}) \\ & < \text{HMS-Qu/CPE} (\Delta I_p = 153.8 \mu\text{A}). \end{aligned} \quad (1)$$

According to above comparison, the concentration of free Qu at HMS-Qu/CPE is the lowest, suggesting that HMS-Qu/CPE can produce more complexes than other modified electrodes.

The chelation of Qu with metal ions in acidic solution has been studied in the previous literatures [9, 10]. When Qu was immobilized on the surface of HMS, effective reaction sites of Qu with metal ions on HMS are remarkably increased due to the high surface area and strong adsorption ability of HMS. Therefore, HMS-Qu/CPE exhibits better capability of adsorptive preconcentration, higher sensitivity and selectivity than Qu/CPE and Qu-IL/CPE. The result indicates that HMS-Qu/CPE is very satisfactory for the development of the simultaneous determination of copper, lead, and cadmium.

EIS experiments were carried out using different modified electrodes at the frequency range from 60 kHz to 0.1 Hz at the perturbation amplitude of 5 mV. Figure 3 shows that the semicircle in high frequency region was not obvious and the straight lines in low-frequency region were obvious in

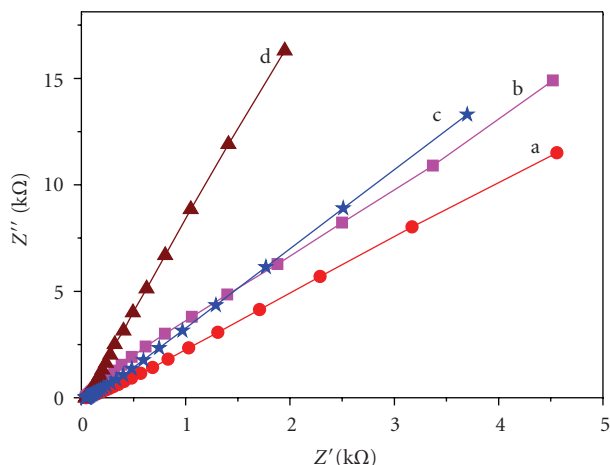


FIGURE 3: Nyquist plots for bare CPE (a), Qu/CPE (b), Qu-IL/CPE (c) and HMS-Qu/CPE (d) in $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution and 0.1 M HCOONa-HCl buffer (pH4.7) attached by the corresponding fitted plots (lines). Condition: perturbation amplitude 5 mV , the frequencies swept from 60 kHz to 0.1 Hz , initial potential 0.45 V .

different modified electrodes. The result indicates that the electron transfer rate is fast and the process of electrode reaction is controlled mainly by adsorption and diffusion. The variety of linear slopes at different modified electrodes may be attributed to the different capacitance characteristic of electric double-layer at modified electrodes [30], which indicated that the surfaces of different electrodes had different specific adsorptions. The specific adsorption of HMS-Qu/CPE was the intensest, Qu/CPE and Qu-IL/CPE showed no obvious difference. These results suggested that HMS-Qu/CPE can effectively improve selectivity and sensitivity and achieved simultaneous determination of copper, lead, and cadmium by the strong chelation and adsorption of HMS-Qu/CPE with metal ions.

3.3. Effect of Some Parameters on Voltammetric Analysis.

Voltammetric behavior of the metal ions at HMS-Qu/CPE was evaluated in terms of the influence of stripping parameters such as effect of pH, preconcentration time, and preconcentration potential. The effect of pH was studied by using different types of supporting electrolytes for their suitability in the simultaneous detection of these metals. The HCOONa-HCl buffer solution was found to be more suitable for its better sensitivity. The effect of pH on peak currents was studied in HCOONa-HCl buffer solution. As shown in Figure 4, the peak currents of copper, lead, and cadmium is maximum at pH4.7. Preconcentration time has a significant influence on simultaneous determination. The effect of preconcentration time on the magnitude of the stripping peak current was examined in the range of $20\text{--}150 \text{ s}$, and shown in Figure 5. Taking into account the sensitivity and resolutions of adjacent peaks, preconcentration time is optimized to 120 s in the experiments. Preconcentration potential was also varied starting from 0.3 V to 0.8 V . The

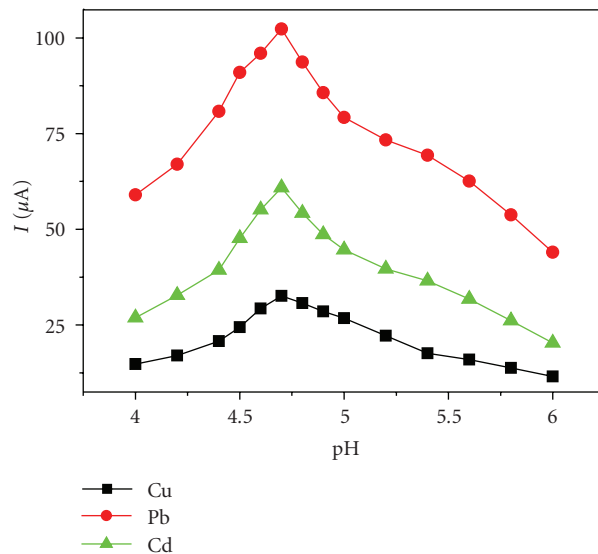


FIGURE 4: Effect of pH ($4.0\text{--}6.0$) on peak current at HMS-Qu/CPE in $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution and 0.1 M HCOONa-HCl buffers. Condition: preconcentration potential 0.6 V , preconcentration time 120 s , potential scan range 0.6 V to -1.0 V .

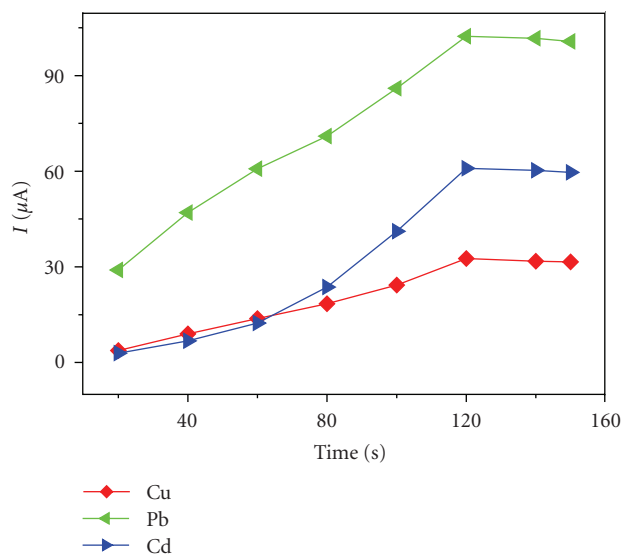


FIGURE 5: Effect of preconcentration time ($20\text{--}150 \text{ s}$) on peak current at HMS-Qu/CPE in $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution and 0.1 M HCOONa-HCl buffer (pH4.7). Condition: preconcentration potential 0.6 V , potential scan range 0.6 V to -1.0 V .

result showed that lower preconcentration potential might increase the possibility of interference between ions in this study, therefore, the preconcentration potential was applied at 0.6 V . At optimized experimental condition, three peaks are observed for copper, lead, and cadmium at -0.11 V , -0.48 V and -0.69 V , respectively.

TABLE 1: The liner range, linear regression equation, and detection limit of copper, lead, and cadmium at HMS-Qu/CPE.

Analyte	Linear range (μM)	Regression equation	Correlation coefficient ($n = 6$)	Detection limit (nM)
Cu(II)	0.02–6.0	$I_p(\mu\text{A}) = 29.81 + 0.68c (\mu\text{M})$	0.9956	5.0
Pb(II)	0.01–8.0	$I_p(\mu\text{A}) = 96.61 + 1.37c (\mu\text{M})$	0.9974	0.8
Cd(II)	0.004–2.0	$I_p(\mu\text{A}) = 58.06 + 0.85c (\mu\text{M})$	0.9928	1.0

TABLE 2: The results for determination of copper, lead, and cadmium in soil sample.

Analyte	Sample	Found ($n = 6, \mu\text{g/g}$)	Average value ($\mu\text{g/g}$)	FAAS ($\mu\text{g/g}$)	RSD (%)
Cu(II)	Soil 1 [#]	9.76, 10.03, 10.47, 9.88, 10.33, 9.69	10.026	10.064	3.15
	Soil 2 [#]	24.57, 25.41, 25.67, 24.49, 24.63, 25.36	25.024	24.888	2.14
Pb(II)	Soil 1 [#]	12.21, 12.67, 12.89, 12.32, 13.01, 12.28	12.563	12.518	2.71
	Soil 2 [#]	34.29, 34.45, 34.21, 34.17, 34.33, 34.36	34.391	34.299	2.25
Cd(II)	Soil 1 [#]	1.22, 1.19, 1.14, 1.36, 1.20, 1.38	1.247	1.27	7.73
	Soil 2 [#]	1.27, 1.26, 1.46, 1.41, 1.36, 1.29	1.342	1.316	6.12

In pH4.7 HCOONa-HCl buffer solution, the relationship between the peak current and concentration was studied by AdSV. Linear range and detection limits of copper, lead, and cadmium were shown in Table 1.

The interference experiment of some cations and anions was also investigated. Under the optimum conditions, relative error of determination was chosen in the order of 5% or smaller in $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution. The results showed that 1000-fold Al(III), K (I), sulfate, phosphate and nitrate, 200-fold Mg(II), Sc(III), Co(II) and Ni(II), 50-fold Mo(VI), V(V) and In(III), 25-fold Ag(I) and Cr(VI), did not interfere with the determination.

Under the optimum conditions, the stability and reproducibility of HMS-Qu/CPE were studied in $1.0 \mu\text{M}$ (each) multicomponent Cu(II)/Pb(II)/Cd(II) solution. After continuous determination 20 times, average stripping peak currents of copper, lead, and cadmium were $31.8 \mu\text{A}$, $104.8 \mu\text{A}$ and $59.5 \mu\text{A}$, respectively. The relative standard deviations (RSD) were 3.9%, 3.2% and 7.8%, respectively. In addition, after 30 days of storage in dry conditions, no significant change in current response was observed, suggesting that the modified electrode has an excellent reproducibility and stability.

3.4. Application to Real Samples. In order to ascertain the potential application, this newly developed method was employed to determine copper, lead, and cadmium in soil sample. The concentration of copper, lead, and cadmium was determined by the standard addition method, and the results were listed in Table 2. In order to testify the accuracy of this method, the concentration of copper, lead, and cadmium was also detected by FAAS [31]. The results obtained by two methods are in good agreement, indicating that this method is reliable and accurate.

4. Conclusion

A series of new quercetin modified carbon paste electrodes were fabricated. The electrochemical responses of copper, lead, and cadmium at HMS-Qu/CPE were improved in comparison with Qu/CPE and Qu-IL/CPE. The HMS-Qu/CPE exhibited dramatically high sensitivity and selectivity due to high surface area, numerous active sites, and strong adsorption ability of HMS. After optimizing the parameters such as pH value, preconcentration time, and preconcentration potential, a novel electrochemical method is simple, fast, sensitive, and selective, and can simultaneously determine three metals with high accuracy and stability. Moreover, the HMS-Qu/CPE was successfully used as a sensor for simultaneous determination of copper, lead, and cadmium in soil sample.

Acknowledgments

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