

Research Article

Simultaneous Determination of Zn(II), Cd(II), Pb(II), and Cu(II) Using Differential Pulse Anodic Stripping Voltammetry at a Bismuth Film-Modified Electrode

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The simultaneous electrochemical determination of Zn(II), Cd(II), Pb(II), and Cu(II) in the aqueous solution has been developed on the basis of the bismuth film glassy carbon electrode (GCE) using differential pulse anodic stripping voltammetry (DP-ASV). The bismuth film electrode (BiFE) was prepared by adding 500 ppb bismuth(III) directly to the sample solution and simultaneously depositing bismuth and the metal analytes on GCE. The optimal operational parameters, namely, accumulation potential (-1.6 V), accumulation time (110 s), pulsed amplitude (0.07 V), and scan rate (0.021 V·s⁻¹), were found using a Box-Behnken design. Under the optimum conditions, a linear relationship exists between the current and the concentration of Zn(II), Cd(II), Pb(II), and Cu(II) in the range between 5.0 ppb and 110.0 ppb with the detection limits of 1.07 for Zn(II), 0.93 ppb for Cd(II), 0.65 ppb for Pb(II), and 0.94 ppb for Cu(II) calculated on the basis of a signal-to-noise ratio equal to 3 (S/N = 3). The interference experiments show that Co(II), Ni(II), and Fe(III) have a little influence on the DP-ASV signals of Zn(II), Cd(II), Pb(II), and Cu(II). In addition, a high reproducibility was indicated from small relative standard deviations (1.03%, 1.74%, 1.32%, and 4.74%) for 25 repeated measurements of 15 ppb copper, lead, cadmium, and zinc solutions. BiFE was successfully applied to determine Zn(II), Cd(II), Pb(II), and Cu(II) in river samples, and the results are in a good agreement with those determined with graphite furnace atomic absorption spectrometry (GF-AAS).

1. Introduction

Heavy metal pollution (Hg(II), Pb(II), Cd(II), and Ni(II)) has become one of the most critical environmental problems today. Unlike organic pollutants, heavy metals are non-biodegradable. They are found in industrial wastewater, and their discharge to the environment is alarming owing to their acute toxicity to aquatic and terrestrial life, including humans [1]. Of these, excessive intake of copper (over 1.0 mg·L⁻¹ in drinking water) accumulates in the livers of humans and animals, which causes hemochromatosis and

gastrointestinal catarrh diseases [1]. Lead is a highly toxic and cumulative poison and accumulates mainly in the bones, brain, kidneys, and muscles. Lead poisoning in humans causes severe damage to the kidneys, nervous and reproductive systems, liver, and brain [2, 3]. Cadmium (Cd) is one of the most toxic pollutants in aquatic systems. It cannot be removed easily from water systems by self-purification and could pose a serious threat to the environment and human health [4]. The longtime accumulation (30 years) of Cd through the food chain can lead to serious osteoporosis-like bone diseases [5]. Zinc, an important element for living

organisms, when exceeding the specific limits, accumulates in nature as it cannot be biodegraded. Zinc is associated with short-term “metal-fume fever,” nausea, diarrhea, depression, lethargy, and neurological signs, such as seizures and ataxia [6, 7]. Therefore, the determination of heavy metals in the human environment is very necessary and important. There are several methods to determine heavy metals in water. The most widely used methods for heavy metal determination include atomic absorption spectrometry (AAS) [8], flame atomic absorption spectrometry (FAAS) [9], inductively-coupled plasma mass spectrometry (ICP-MS) [10], graphite furnace atomic absorption spectrometry (GF-AAS), and X-ray fluorescence [11], and they are employed currently for trace analysis of heavy metals. Among these methods, anodic stripping voltammetry approaches are an emerging and attractive method because the main advantages of this technique can be ordered as high selectivity, sensitivity, *in situ* operation, and low cost.

In 2000, a new type of electrode, the bismuth film-modified electrode (denoted as BiFE), was found as an alternative to mercury film electrodes (MFEs) [12], which are highly toxic. The significant advantage of BiFEs is that they are environmentally friendly since the toxicity of bismuth and its salts is negligible. However, the advantageous analytical properties of BiFEs in the voltammetric analysis, roughly comparable to those of MFEs, are assigned to the property of bismuth to form “fused alloys” with heavy metals, which is analogous to the amalgams that mercury form [13]. Wang et al. [12] reported that bismuth-coated carbon electrodes display an attractive stripping voltammetric performance that is similar to that of common mercury film electrodes and could be utilized to simultaneously determine Cu(II), Cd(II), and Pb(II) in aqueous solutions. Wu et al. [14] reported the simultaneous determination of Pb, Cd, and Zn using DP-ASV at a bismuth/poly(*p*-aminobenzene sulfonic acid) film electrode. Lead and cadmium in rice samples are determined by means of ASV using a bismuth film/crown ether/Nafion-modified screen-printed carbon electrode [15]. Li et al. [16] reported the simultaneous detection of ultratrace lead and cadmium by square wave stripping voltammetry with *in situ* depositing bismuth at the Nafion-medical stone-doped disposable electrode, and the assay results of heavy metals in wastewater with the proposed method were in a good agreement with the atomic absorption spectroscopy method. To the best of our knowledge, a few articles have attempted to study the simultaneous determination of Zn(II), Cd(II), Pb(II), and Cu(II) by BiFE.

This article demonstrates the attractive stripping voltammetric behavior of BiFE. BiFE was prepared by simultaneously accumulating bismuth and the target heavy metals (Cu, Pb, Cd, and Zn). The Box–Behnken design was conducted to optimise the operational parameters. BiFE displays well-defined, sharp, and highly reproducible stripping peaks for low (ppb) concentrations of copper, lead, cadmium, and zinc over a low background current. The simultaneous determination of copper, lead, cadmium, and zinc in real samples was also addressed.

2. Experimental

2.1. Materials. All solutions were prepared using double-distilled water. The zinc, cadmium, lead, copper, and bismuth standard stock solutions (1000 ppm Zn, Cd, Pb, and Cu or 5 (Bi) wt.% nitric acid) were obtained from Aldrich and diluted as required. An acetate buffer solution (0.10 M, pH 4.5) served as the supporting electrolyte.

2.2. Apparatus. Stripping voltammetry was performed with a CPA-HH5 Computerized Polarography Analyzer (Vietnam). A glassy carbon electrode (GCE) (3 mm diameter, BAS) served as a working electrode, with Ag/AgCl (3 M KCl) and platinum wire acting as the reference and counter electrodes, respectively. Graphite furnace atomic absorption spectroscopy (GF-AAS) was performed in ZEE nit 700P (Analytik Jena, Germany) as a reference method.

2.3. Procedure. The glassy carbon electrode was polished using 1.0 μm Al_2O_3 slurry, rinsed with ethanol/water and dried. The analytes (Zn, Cd, Pb, and Cu) were accumulated on the surface of GCE at a potential of -1.4 V (E_{acc}) for 120 s of accumulation (t_{acc}). During this step, the electrode was rotated at a constant rate of 1000 rpm. After that, the electrode rotation was ceased; then, cyclic voltammograms (CVs) were recorded from -1.5 V to $+0.1\text{ V}$ (forward potential scan) and then from $+0.1\text{ V}$ to -1.5 V (reverse potential scan) at a scan rate of $0.2\text{ V}\cdot\text{s}^{-1}$.

Stripping voltammetric measurements were conducted with an *in situ* accumulation of the bismuth film and target metals (Zn, Cd, Pb, and Cu). The three electrodes were immersed in a 10 mL electrochemical cell containing 0.1 M acetate buffer (pH 4.5) and an appropriate amount of bismuth. The accumulation potential at -1.4 V was applied to the carbon working electrode under stirring. After the accumulation step (120 s), stirring was stopped, and after 10 s, the voltammogram was recorded by applying a positive-going differential pulse voltammetric potential scan (with an amplitude of 50 mV and a potential step of 6 mV). The scan was terminated at 0.1 V. All experiments were carried out at room temperature.

2.4. Operational Parameters of Box–Behnken Central Design (BBD). The operational parameters were optimised by using BBD. The effect of accumulation potential (x_1), accumulation time (x_2), pulse amplitude (x_3), and scan rate (x_4) on the peak current of BiEF was studied. The number of experiments (N) required for the performance of this design is defined as $N = 2k \cdot (k - 1) + C_0$, where k is the number of factors ($k = 4$) and C_0 is the number of replicates at the center point [17]. Thus, a total of 27 experiments were carried out for optimising these four variables. Each independent variable is considered at three levels: low, medium, and high, coded as -1 , 0 , and $+1$, respectively (Table 1). The center points were used to determine the error. On the basis of the experimental data, a second-order polynomial model is

TABLE 1: Factors in BBD and their levels.*

Level	Accumulation potential (x_1 , V)	Accumulation time (x_2 , s)	Pulse amplitude (x_3 , V)	Scan rate (x_4 , V·s ⁻¹)
High level (+1)	-1.0	20	0.01	0.01
Central level (0)	-1.5	100	0.05	0.02
Low level (-1)	-2.0	180	0.09	0.03

* 15 ppb concentration of Zn, Cd, Pb, and Cu in 500 ppb Bi and 0.1 M acetate buffer (pH 5).

obtained. The relationship between the response and the variables could be presented as follows:

$$\begin{aligned}
 y = & b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 + b_4 \cdot x_4 + b_{11} \cdot x_{12} \\
 & + b_{22} \cdot x_{22} + b_{33} \cdot x_{32} + b_{44} \cdot x_{42} + b_{12} \cdot x_1 \cdot x_2 \\
 & + b_{13} \cdot x_1 \cdot x_3 + b_{14} \cdot x_1 \cdot x_4 + b_{23} \cdot x_2 \cdot x_3 + b_{24} \cdot x_2 \cdot x_4 \\
 & + b_{34} \cdot x_3 \cdot x_4,
 \end{aligned}
 \tag{1}$$

where y is the predicted response value (anodic peak current, I_{pa}); x_1 , x_2 , x_3 , and x_4 are the independent variables; b_0 is the intercept term (the mean value of response at the center points); b_1 , b_2 , b_3 , and b_4 are the linear coefficients; b_{12} , b_{13} , and b_{14} and b_{23} , b_{24} , and b_{34} are the cross-product coefficients; and b_{11} , b_{22} , b_{33} , and b_{44} are the quadratic-term coefficients. The design and analysis of the experiment were carried out using Minitab version 16. The definition of the factors and their level values are shown in Table 1.

2.5. Sample Preparation. One milliliter of the sample solution was adjusted to pH 5 with NaOH or HCl and diluted to 5 mL with a 0.1 M acetate buffer (pH 5), and then it was placed in the cell without deaeration. Stripping voltammetric measurements were performed with an *in situ* accumulation of bismuth and the target metals (Zn, Cd, Pb, and Cu), and the accumulation was carried out for 110 s at -1.6 V, while the solution was stirred. After the solution was kept standstill for 10 s, DP-ASV was recorded. The metal analytes in the river water were determined by means of GF-AAS for the sake of comparison.

3. Results and Discussion

3.1. Effect of Bismuth Concentration. The influence of the bismuth ion concentration on the anodic current peak (I_{pa}) of the metals was studied in the range 0–1000 ppb for a solution containing 15 ppm Zn(II), Cd(II), Pb(II), and Cu(II) in a 0.1 M acetate buffer (pH 4.5) at bare GCE. Very small and distorted stripping peaks of the metal analytes are observed at bare GCE, and the signal of Zn is not obtained (Figure 1(a)). When bismuth (500 ppb) was added to the sample, distinct and undistorted stripping peaks for the analytes are achieved, indicating that bismuth is responsible for the attractive electrochemistry behavior. It is supposed that the amount of the Bi(III) ion decides the thickness of the Bi film, whereas the film thickness does not influence the peak position of any metals. Figure 1(b) presents the effect of Bi concentration on the anodic peak current. The anodic peak of cadmium increases significantly with the bismuth concentration from 0 to 400 ppb and then levels off. A

similar trend is observed for Pb below 600 ppb, and the anodic peak of lead fluctuates slightly after this concentration. The copper and zinc peaks increase significantly with the bismuth concentration up to 500 ppb, and the rise becomes slight afterwards. The results suggest that the appropriate combination of sensitivity, peak sharpness, and background current (especially close to the Zn peak) was performed for Bi(III) concentration of 500 ppb.

3.2. Effect of pH. The effect of pH on the stripping peak current of Zn(II), Cd(II), Pb(II), and Cu(II) at BiFE was studied (Figure 2(a)). The optimal pH ranges are 5.0–6.0 for Zn(II) and Cd(II) and 4.0–6.0 for Pb(II) and Cu(II) (Figure 2(b)). If the acidity is higher or lower than the optimum ranges, the responses of Zn(II) and Cd(II) decrease. For Pb(II) and Cu(II) peak currents, I_{pa} decreases slightly in pH from 4.0 to 6.0 and declines significantly with the further increasing pH. The best compromise of I_{pa} could be obtained at pH 5.0–6.0. In the present study, we choose pH of 5.0 for the next experiments.

Figure 2(c) provides the linear plots of pH dependence of peak potential (E_p). The linear equations are expressed as follows:

$$\begin{aligned}
 E_{p,Zn} &= (-0.87 \pm 0.05) + (-0.059 \pm 0.007) \cdot \text{pH}, \\
 &R^2 = 0.941, p < 0.001, \\
 E_{p,Cd} &= (-0.62 \pm 0.02) + (-0.052 \pm 0.003) \cdot \text{pH}, \\
 &R^2 = 0.984, p < 0.001, \\
 E_{p,Pb} &= (-0.31 \pm 0.02) + (-0.060 \pm 0.003) \cdot \text{pH}, \\
 &R^2 = 0.990, p < 0.001, \\
 E_{p,Cu} &= (0.20 \pm 0.03) + (-0.054 \pm 0.004) \cdot \text{pH}, \\
 &R^2 = 0.977, p < 0.001.
 \end{aligned}
 \tag{2}$$

The linear relationship of E_p vs. pH exhibits a high statistical significance with high determination coefficients (0.941–0.990, $p < 0.05$). The slopes of the lines are very close to the theoretical value of 0.059 for the Nerstian equation, indicating that the redox reaction involves the equal number of protons and electrons.

3.3. Effect of CV Scan Rate. The relationship between the peak current and the scan rate could provide important information about the electrochemical mechanism. Therefore, the effect of scan rate on the peak potential (E_p) and peak current (I_p) was investigated using CV, as shown in Figure 3(a). If the electrooxidation reaction is reversible, E_p is independent on v , and vice versa. As can be seen from

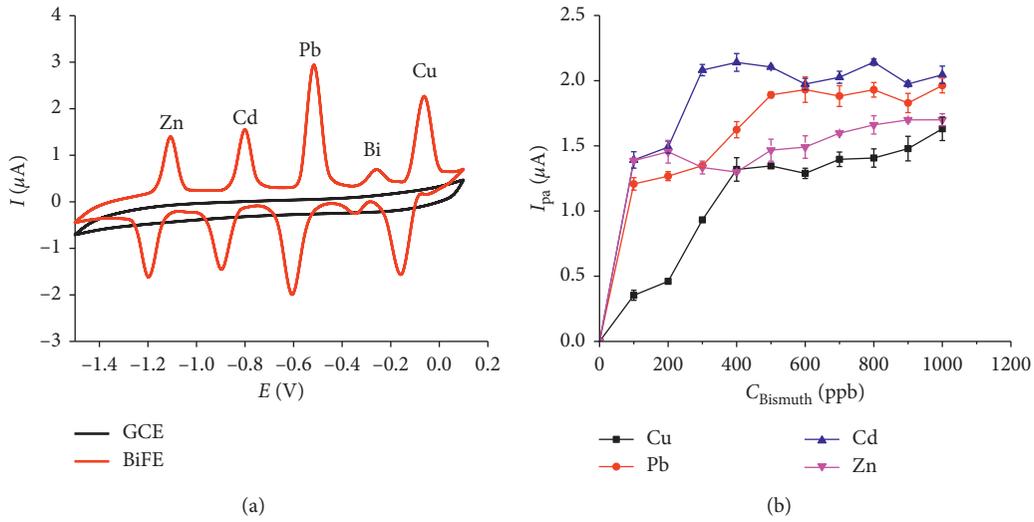


FIGURE 1: (a) Differential pulse stripping voltammograms of 15 ppm Zn(II), Cd(II), Pb(II), and Cu(II) at GCE without and with 500 ppb Bi(II) in 0.1 M acetate buffer (pH 4.5); (b) the influence of the bismuth ion concentration on anodic current peaks (I_{pa}) (accumulation for 120 s at -1.4 V).

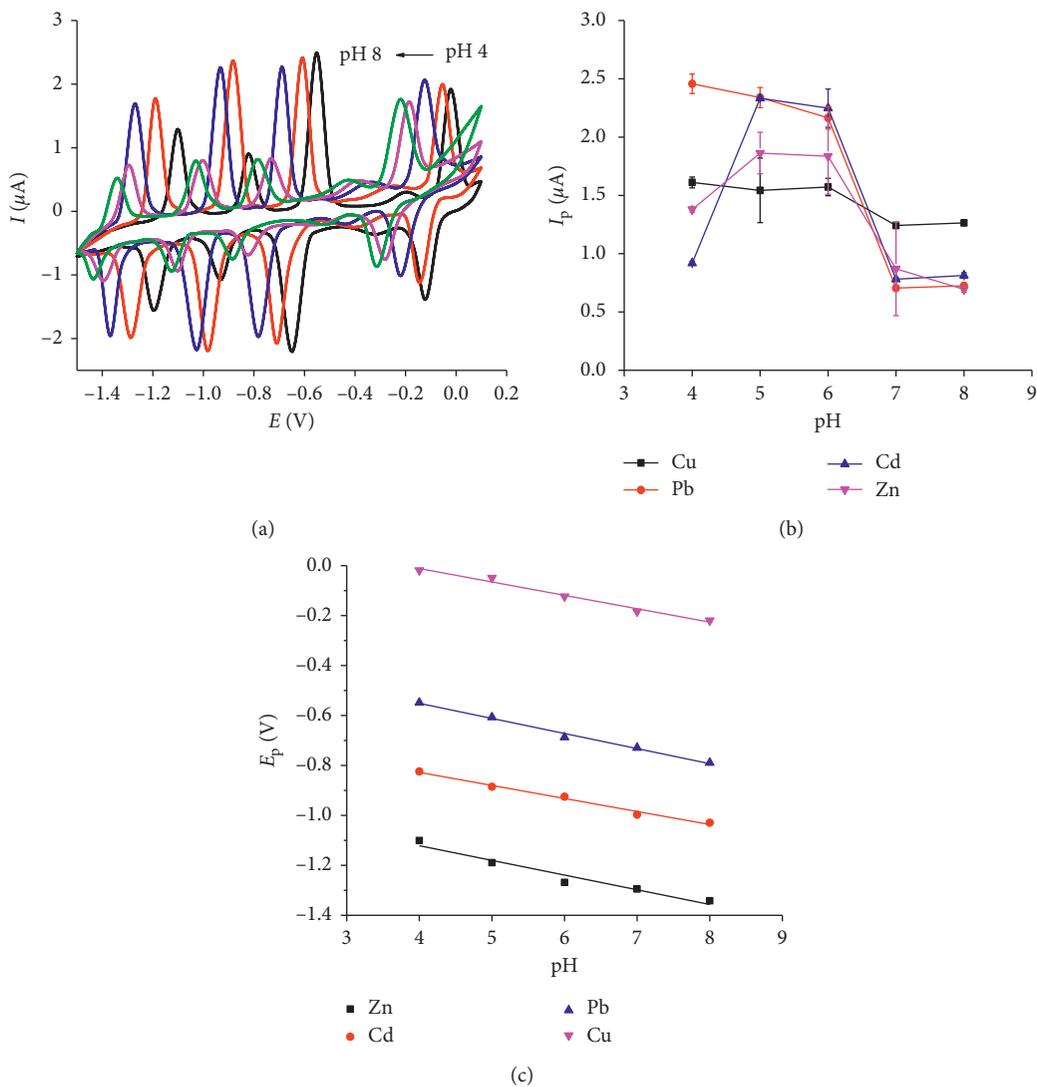


FIGURE 2: (a) CV curves of Zn, Cd, Pb, and Cu at different pH values (15 ppm Zn(II), Cd(II), and Pb(II), 500 ppb Bi(II) in 0.1 M acetate buffer, and accumulation for 120 s at -1.4 V); (b) pH dependence of I_p ; (c) pH dependence of E_p .

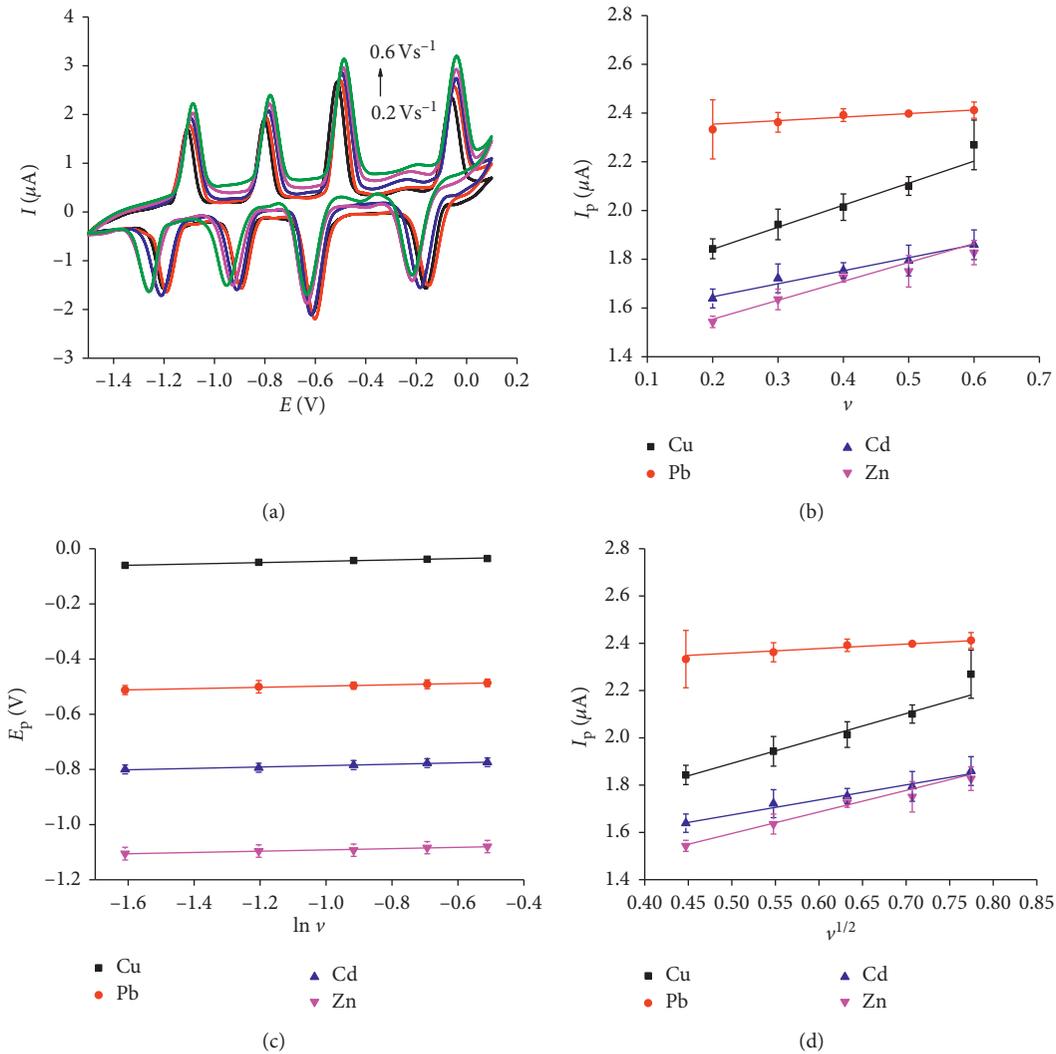


FIGURE 3: (a) CVs of analytes (Zn, Cd, Pb, and Cu) with increasing scan rate (ν); (b) plot of I_{pa} vs. scan rate (ν); (c) plot of E_p vs. $\ln \nu$; (d) plot of I_{pa} vs. $\nu^{1/2}$ (conditions: 15 ppm Zn(II), Cd(II), Pb(II), and Cu(II) in 0.1 M acetate buffer (pH 5), 500 ppb Bi, and accumulation for 120 s at -1.4 V).

Figure 3(a), the anodic peak potential (E_p) shifts to a higher potential with the increase in the scan rate, and then it is suggested that the electron transfer in analyte electro-oxidation is irreversible. The anodic peak current (I_{pa}) increases with the increase in the scan rate from 0.2 to $0.6 \text{ V}\cdot\text{s}^{-1}$, as shown in Figure 3(b), suggesting that the electron transfer reaction involves a surface-confined process.

The relationship between the peak potential (E_p) and the natural logarithm of the scan rates is described by Laviron's equation [18]:

$$E_p = E^0 + \frac{RT}{\alpha n F} \ln \frac{\alpha n F k_s}{RT} + \frac{RT}{\alpha n F} \ln \nu, \quad (3)$$

where α is the charge transfer coefficient, k_s is the heterogeneous electron transfer rate constant of the surface-

confined redox couple, n is the number of electrons transferred, ν is the scan rate ($\text{V}\cdot\text{s}^{-1}$), and E^0 is the formal redox potential, $T = 298 \text{ K}$, $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $F = 96480 \text{ C}\cdot\text{mol}^{-1}$.

The plots of E_{pa} of the analytes versus $\ln \nu$ are shown in Figure 3(c). The linear regression equations are as follows:

$$E_{pa,Zn} = (-1.069 \pm 0.002) + (0.023 \pm 0.002) \cdot \ln \nu, \quad (4)$$

$$R^2 = 0.986,$$

$$E_{pa,Cd} = (-0.761 \pm 0.002) + (0.025 \pm 0.002) \cdot \ln \nu, \quad (5)$$

$$R^2 = 0.988,$$

$$E_{pa,Pb} = (-0.475 \pm 0.001) + (0.023 \pm 0.001) \cdot \ln \nu, \quad (6)$$

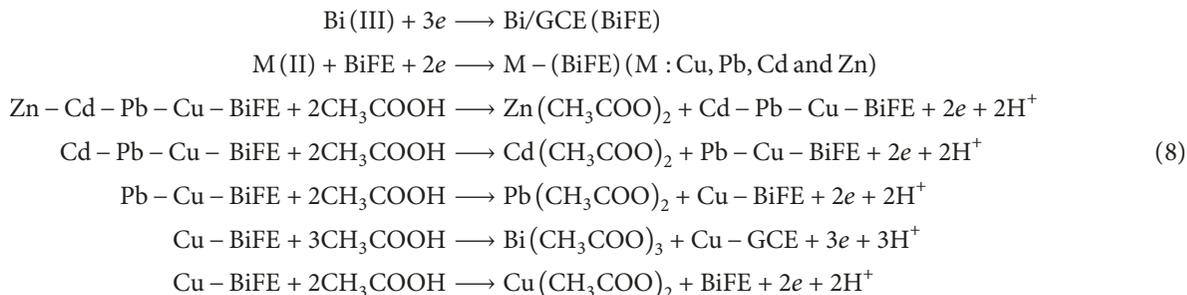
$$R^2 = 0.995,$$

$$E_{pa,Cu} = (-0.0210 \pm 0.0001) + (0.024 \pm 0.001) \cdot \ln v, \quad (7)$$

$$R^2 = 0.997.$$

The value of $\alpha \cdot n$ in equation (3) for Zn, Cd, Pb, and Cu can be derived from the slope of regression equations (4)–(7), and they are 1.11, 1.02, 1.11, and 1.05, respectively.

The value of α is assumed to be equal to 0.5 for an irreversible system [19]. Therefore, the number of electrons transferred (n) in the electrooxidation of Zn, Cd, Pb, and Cu is 2.23, 2.05, 2.23, and 2.10, respectively. Consequently, with $n = 2$, the oxidation mechanism for Zn, Cd, Pb, and Cu could involve two electrons and two protons at pH 5. The reactions at the electrode are as follows:



In order to decide whether the electrooxidation reaction is controlled by adsorption or diffusion, the plots of peak current (I_p) against $v^{1/2}$ are drawn (Figure 3(d)). If the linear plot of I_p vs. $v^{1/2}$ crosses the origin, the process is controlled by diffusion [20]. In the range 0.2 to 0.6 $\text{V} \cdot \text{s}^{-1}$, the linear regression equations of I_{pa} for Zn, Cd, Pb, and Cu oxidation versus $v^{1/2}$ are as follows:

$$I_{pa,Cu} = (1.37 \pm 0.07) + (1.10 \pm 0.10) \cdot v^{(1/2)}, \quad (9)$$

$$R^2 = 0.958,$$

$$I_{pa,Pb} = (2.26 \pm 0.02) + (0.19 \pm 0.04) \cdot v^{(1/2)}, \quad (10)$$

$$R^2 = 0.867,$$

$$I_{pa,Cd} = (1.35 \pm 0.03) + (0.63 \pm 0.04) \cdot v^{(1/2)}, \quad (11)$$

$$R^2 = 0.980,$$

$$I_{pa,Zn} = (1.14 \pm 0.04) + (0.91 \pm 0.06) \cdot v^{(1/2)}, \quad (12)$$

$$R^2 = 0.981.$$

Although the plots of I_p versus $v^{1/2}$ are linear with high determination coefficients (0.958–0.981, $p \geq 0.001$), the intercepts do not cross the origin because the 95% confidence intervals for the intercepts do not contain zero (see the intercepts of equations (9)–(12)). This means that the electrode process of analyte electrooxidation is not controlled by diffusion.

3.4. Optimising the Operational Parameters Using BBD. A total of 27 experiments consisting of 24 standard cube points and 3 center points in the cube were carried out. The design of experiments and response values (I_p : anodic stripping current) of Cu, Pb, Cd, and Zn corresponding to each run is listed in Table 2.

The analysis of the data using Minitab 16 gives the following regression equations for I_p :

$$\begin{aligned} I_{p,Zn} = & 1.53 - 0.14 \cdot x_1 + 0.07 \cdot x_2 + 0.14 \cdot x_3 \\ & + 0.06 \cdot x_4 - 0.30 \cdot x_1^2 - 0.24 \cdot x_2^2 - 0.15 \cdot x_3^2 - 0.22 \cdot x_4^2 \\ & + 0.03 \cdot x_1 \cdot x_2 + 0.01 \cdot x_1 \cdot x_3 + 0.02 \cdot x_1 \cdot x_4 \\ & - 0.01 \cdot x_2 \cdot x_3 - 0.02 \cdot x_2 \cdot x_4 + 0.02 \cdot x_3 \cdot x_4, \end{aligned}$$

$$R^2 = 0.999,$$

$$\begin{aligned} I_{p,Cd} = & 2.02 - 0.16 \cdot x_1 + 0.08 \cdot x_2 + 0.17 \cdot x_3 + 0.09 \\ & \cdot x_4 - 0.33 \cdot x_1^2 - 0.24 \cdot x_2^2 - 0.16 \cdot x_3^2 - 0.26 \cdot x_4^2 - 0.03 \\ & \cdot x_1 \cdot x_2 - 0.02 \cdot x_1 \cdot x_3 - 0.00 \cdot x_1 \cdot x_4 - 0.01 \\ & \cdot x_2 \cdot x_3 - 0.03 \cdot x_2 \cdot x_4 + 0.05 \cdot x_3 \cdot x_4, \end{aligned}$$

$$R^2 = 0.998,$$

$$\begin{aligned} I_{p,Pb} = & 3.34 - 0.25 \cdot x_1 + 0.15 \cdot x_2 + 0.25 \cdot x_3 + 0.11 \\ & \cdot x_4 - 0.51 \cdot x_1^2 - 0.42 \cdot x_2^2 - 0.24 \cdot x_3^2 - 0.40 \cdot x_4^2 + 0.01 \\ & \cdot x_1 \cdot x_2 + 0.02 \cdot x_1 \cdot x_3 + 0.01 \cdot x_1 \cdot x_4 \\ & + 0.02 \cdot x_2 \cdot x_3 + 0.02 \cdot x_2 \cdot x_4 - 0.01 \cdot x_3 \cdot x_4, \end{aligned}$$

$$R^2 = 0.999,$$

$$\begin{aligned} I_{p,Cu} = & 3.33 - 0.27 \cdot x_1 + 0.13 \cdot x_2 + 0.26 \cdot x_3 + 0.13 \\ & \cdot x_4 - 0.53 \cdot x_1^2 - 0.41 \cdot x_2^2 - 0.26 \cdot x_3^2 - 0.40 \cdot x_4^2 \\ & + 0.01 \cdot x_1 \cdot x_2 - 0.02 \cdot x_1 \cdot x_3 - 0.00 \cdot x_1 \cdot x_4 \\ & + 0.01 \cdot x_2 \cdot x_3 + 0.01 \cdot x_2 \cdot x_4 - 0.00 \cdot x_3 \cdot x_4, \end{aligned}$$

$$R^2 = 0.998.$$

(13)

The values of the coefficient of determination are 0.999, 0.998, 0.999, and 0.998 for Zn, Cd, Pb, and Cu, respectively, indicating an excellent agreement between experimental and predicted values. The positive and negative signs in each equation imply the synergistic and antagonistic effect of the variables. Although the magnitude of the coefficients in the equations varies, their sign is the same, indicating that the

TABLE 2: Design matrix and responses for full factorial design.

Run	Coded variable levels				Anodic peak current, I_{pa} (μA)			
	x_1	x_2	x_3	x_4	Cu	Pb	Cd	Zn
1	0	-1	0	-1	2.291	2.294	1.332	0.918
2	+1	0	-1	0	2.053	2.079	1.233	0.789
3	-1	-1	0	0	2.543	2.531	1.510	1.104
4	0	-1	-1	0	2.297	2.305	1.336	0.909
5	+1	0	+1	0	2.513	2.596	1.531	1.101
6	0	0	-1	-1	2.254	2.317	1.401	0.980
7	-1	0	-1	0	2.524	2.612	1.483	1.076
8	0	0	-1	+1	2.532	2.562	1.488	1.059
9	+1	0	0	-1	1.991	2.066	1.181	0.788
10	0	+1	-1	0	2.554	2.560	1.577	1.090
11	+1	-1	0	0	1.988	1.999	1.241	0.770
12	+1	+1	0	0	2.250	2.307	1.326	0.959
13	0	0	0	0	3.302	3.359	2.022	1.532
14	-1	+1	0	0	2.773	2.806	1.719	1.185
15	-1	0	0	+1	2.831	2.804	1.699	1.189
16	0	-1	0	+1	2.509	2.451	1.533	1.073
17	0	+1	0	-1	2.516	2.556	1.567	1.105
18	+1	0	0	+1	2.259	2.312	1.377	0.966
19	0	+1	+1	0	3.077	3.101	1.863	1.357
20	0	-1	+1	0	2.766	2.781	1.748	1.226
21	0	0	+1	-1	2.811	2.862	1.624	1.230
22	0	0	0	0	3.358	3.332	2.022	1.537
23	-1	0	0	-1	2.554	2.587	1.485	1.099
24	0	0	+1	+1	3.082	3.057	1.893	1.407
25	0	+1	0	+1	2.783	2.775	1.667	1.179
26	-1	0	+1	0	3.046	3.064	1.871	1.356
27	0	0	0	0	3.342	3.338	2.032	1.530

impact of each variable on the intensity of the peak current has the same tendency. The tests for the significance of the regression model for the response of analytes were adjusted, and the ANOVA tests are presented in Table 3. The non-significant lack-of-fit (0.654 for Cu, 0.541 for Pb, 0.086 for Cd, and 0.132 for Zn) confirms the validity of these quadratic models in the present study. From the statistical point of view, the coefficient with the p value > 0.05 is insignificant. This means that their contribution to the peak currents is negligible, and these effects should be discarded from the model. Thus, the predictive models become as follows:

$$\begin{aligned}
I_{p,Zn} &= 1.53 - 0.14 \cdot x_1 + 0.07 \cdot x_2 + 0.14 \cdot x_3 \\
&\quad + 0.06 \cdot x_4 - 0.30 \cdot x_1^2 - 0.24 \cdot x_2^2 - 0.15 \cdot x_3^2 - 0.22 \cdot x_4^2 \\
&\quad + 0.03 \cdot x_1 \cdot x_2 + 0.02 \cdot x_1 \cdot x_4 - 0.01 \cdot x_2 \cdot x_3 - 0.02 \\
&\quad \cdot x_2 \cdot x_4 + 0.02 \cdot x_3 \cdot x_4, \quad R^2 = 0.999, \\
I_{p,Cd} &= 2.02 - 0.16 \cdot x_1 + 0.08 \cdot x_2 + 0.17 \cdot x_3 \\
&\quad + 0.09 \cdot x_4 - 0.33 \cdot x_1^2 - 0.24 \cdot x_2^2 - 0.16 \cdot x_3^2 - 0.26 \cdot x_4^2 \\
&\quad - 0.03 \cdot x_1 \cdot x_2 - 0.02 \cdot x_1 \cdot x_3 - 0.01 \cdot x_2 \cdot x_3 - 0.03 \\
&\quad \cdot x_2 \cdot x_4 + 0.05 \cdot x_3 \cdot x_4, \quad R^2 = 0.998, \\
I_{p,Pb} &= 3.34 - 0.25 \cdot x_1 + 0.15 \cdot x_2 + 0.25 \cdot x_3 \\
&\quad + 0.11 \cdot x_4 - 0.51 \cdot x_1^2 - 0.42 \cdot x_2^2 - 0.24 \cdot x_3^2 - 0.40 \cdot x_4^2, \\
&\quad R^2 = 0.999, \\
I_{p,Cu} &= 3.33 - 0.27 \cdot x_1 + 0.13 \cdot x_2 + 0.26 \cdot x_3 + 0.13 \\
&\quad \cdot x_4 - 0.53 \cdot x_1^2 - 0.41 \cdot x_2^2 - 0.26 \cdot x_3^2 - 0.40 \cdot x_4^2, \\
&\quad R^2 = 0.998.
\end{aligned} \tag{14}$$

For the sake of simplicity, the I_p signal of Zn was used to optimise the experimental conditions because it is the lowest of those of the four metals at the same concentration. The profile for predicted values in Minitab 16 was performed for the optimisation process. The optimisation design matrix (Figure 4) represents the maximal $I_{p,Zn}$ ($1.59 \mu\text{A}$) at the optimal conditions: accumulation potential -1.6 V , accumulation time 110 s , pulse amplitude 0.07 V , and scan rate $0.021 \text{ V}\cdot\text{s}^{-1}$. To evaluate the repeatability of the model, the experiment under optimal conditions was repeated three times, and the obtained $I_{p,Zn}$ is 1.55 , 1.57 , and $1.60 \mu\text{A}$. The one-sample t -test proves that there is no statistical difference among these values ($t(2) = 1.147$, $p = 0.37 > 0.05$). These optimal operational parameters were utilized for further experiments.

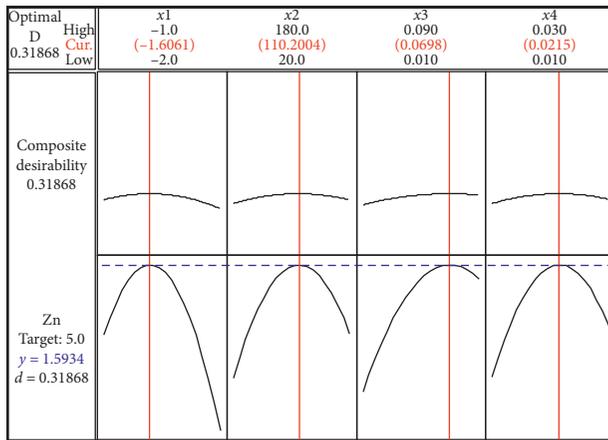
3.5. Interference Study. The interference study was performed by adding various foreign substances to a standard solution containing 15 ppb of Zn(II), Cd(II), Pb(II), and Cu(II) and 500 ppb Bi(III) in the 0.1 M acetate buffer ($\text{pH } 5$) at the accumulation potential of -1.6 V and accumulation time of 110 s . The ratios of interference to Zn(II), Cd(II), Pb(II), and Cu(II) for the $\pm 5.0\%$ signal change are 15 for Co(II), 15 for Ni(II), and 45 for Fe(III) (Tables S1–S3).

3.6. Precision and Limit of Detection (LOD). An appropriate precision is another attractive feature of bismuth electrodes. A series of 25 repetitive measurements of a solution containing 15 ppb zinc, cadmium, lead, and copper results in highly reproducible stripping peaks with a relative standard deviation of 1.74% , 1.29% , 1.07% , and 0.76% , respectively, less than $1/2 \text{ RDS}_H$ (Table S4). Such a good precision is attributed to the reproducible film renewal accrued from the *in situ* bismuth film. Compared with the “stabilization” period required for *in situ* plating of mercury-film electrodes [21], BiFE displays a highly stable response starting with the first run.

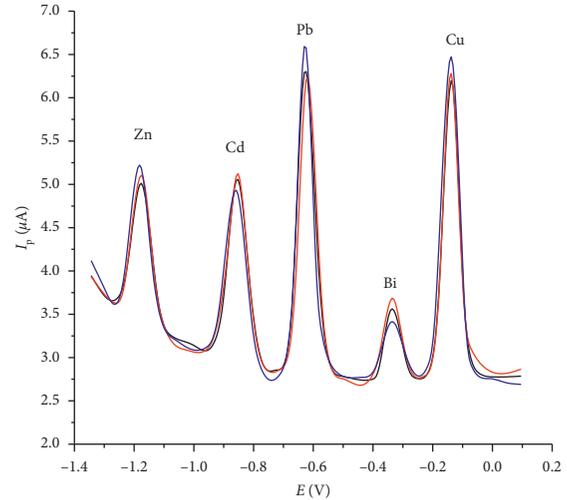
To verify the practicality of BiFE for the simultaneous determination of Zn(II), Cd(II), Pb(II), and Cu(II), the stripping process of these four metal ions in the mixture was also investigated (Figure 5). In each measurement, the concentration of one species changes while keeping that of the others constant. It can be seen from Figure 5(a) that the peak current of Cu(II) is positively proportional to its concentration from 5 to 110 ppb when keeping the concentration of Zn(II), Cd(II), and Pb(II) constant; meanwhile, the response of Zn(II), Cd(II), and Pb(II) is practically unaltered with the increasing Cu(II) content (a slight increase in the peak heights of lead and cadmium with increasing zinc concentration is merely due to the additive signal contribution of the slightly overlapping copper peak). A similar situation is observed with Zn(II), Cd(II), and Pb(II) (Figures 5(b)–5(d)). No interference can be detected for the determination of Zn(II), Cd(II), Pb(II), or Cu(II) by the coexistence of the other three species. Therefore, it can be concluded that, in the quaternary mixtures containing Zn(II), Cd(II), Pb(II), and Cu(II), the stripping peaks of the four analytes are clearly separated from each other.

TABLE 3: Analysis of variance (ANOVA) for BBD.

Terms	Coefficient $I_{pa,Cu}$	p value	Coefficient $I_{pa,Pb}$	p value	Coefficient $I_{pa,Cd}$	p value	Coefficient $I_{pa,Zn}$	p value
Constant	3.33	≤ 0.001	3.34	≤ 0.001	2.03	≤ 0.001	1.53	≤ 0.001
x_1	-0.27	≤ 0.001	-0.25	≤ 0.001	-0.16	≤ 0.001	-0.14	≤ 0.001
x_2	0.13	≤ 0.001	0.15	≤ 0.001	0.08	≤ 0.001	0.07	≤ 0.001
x_3	0.26	≤ 0.001	0.25	≤ 0.001	0.17	≤ 0.001	0.15	≤ 0.001
x_4	0.13	≤ 0.001	0.11	≤ 0.001	0.09	≤ 0.001	0.06	≤ 0.001
x_1^2	-0.53	≤ 0.001	-0.51	≤ 0.001	-0.33	≤ 0.001	-0.30	≤ 0.001
x_2^2	-0.41	≤ 0.001	-0.42	≤ 0.001	-0.24	≤ 0.001	-0.24	≤ 0.001
x_3^2	-0.26	≤ 0.001	-0.24	≤ 0.001	-0.16	≤ 0.001	-0.15	≤ 0.001
x_4^2	-0.40	≤ 0.001	-0.40	≤ 0.001	-0.26	≤ 0.001	-0.22	≤ 0.001
$x_1 \cdot x_2$	0.01	0.556	0.556	0.313	-0.03	0.005	0.03	≤ 0.001
$x_1 \cdot x_3$	-0.02	0.270	0.270	0.056	-0.02	0.032	0.01	0.129
$x_1 \cdot x_4$	0.00	0.857	0.857	0.347	0.00	0.634	0.02	0.001
$x_2 \cdot x_3$	0.01	0.335	0.335	0.055	-0.03	0.005	-0.01	0.026
$x_2 \cdot x_4$	0.01	0.381	0.381	0.063	-0.03	0.017	-0.02	0.002
$x_3 \cdot x_4$	0.00	0.900	0.900	0.131	0.05	≤ 0.001	0.02	≤ 0.001
Lack-of-fit		0.654		0.541		0.086		0.132
Regression		≤ 0.001		≤ 0.001		≤ 0.001		≤ 0.001



(a)



(b)

FIGURE 4: (a) Profiles for predicted values; (b) reliability function for peak current of Zn.

The linear calibration graphs for Zn(II), Cd(II), Pb(II), and Cu(II) are as follows:

$$\begin{aligned}
 I_{p,Zn} &= (0.58 \pm 0.03) + (0.091 \pm 0.001) \cdot C_{Zn}, & R^2 &= 0.998, \\
 I_{p,Cd} &= (-0.57 \pm 0.05) + (0.251 \pm 0.001) \cdot C_{Cd}, & R^2 &= 0.999, \\
 I_{p,Pb} &= (0.12 \pm 0.03) + (0.278 \pm 0.001) \cdot C_{Pb}, & R^2 &= 0.999, \\
 I_{p,Cu} &= (-0.6 \pm 0.6) + (0.439 \pm 0.009) \cdot C_{Cu}, & R^2 &= 0.996.
 \end{aligned} \tag{15}$$

The detection limits are 1.07, 0.93, 0.65, and 0.94 ppb for Zn, Cd, Pb, and Cu, respectively ($3\sigma/b$).

The simultaneous determination of Zn, Cd, Pb, and Cu was also performed using the DP-ASV method. The electrochemical signals of Zn, Cd, Pb, and Cu were recorded simultaneously when increasing the concentration of the analytes in the 0.1 acetate buffer solution with pH = 5.

Figure 6 shows the DP-ASV curves obtained for the solutions containing an equal concentration of Zn, Cd, Pb, and Cu in the range from 5 to 110 ppb. The linear regression equations between I_{pa} and corresponding concentration are as follows:

$$\begin{aligned}
 I_{p,Zn} &= (0.6 \pm 0.1) + (0.093 \pm 0.001) \cdot C_{Zn}, & R^2 &= 0.999, \\
 I_{p,Cd} &= (0.01 \pm 0.29) + (0.260 \pm 0.009) \cdot C_{Cd}, & R^2 &= 0.989, \\
 I_{p,Pb} &= (3.2 \pm 0.2) + (0.232 \pm 0.005) \cdot C_{Pb}, & R^2 &= 0.996, \\
 I_{p,Cu} &= (-1.3 \pm 0.2) + (0.456 \pm 0.005) \cdot C_{Cu}, & R^2 &= 0.999.
 \end{aligned} \tag{16}$$

In the range of 5 to 110 ppb, the values of LOD are 2.95, 1.84, 1.29, and 1.11 ppb for Zn, Cd, Pb, and Cu, respectively. It is worth noting that the values of LOD of Cu, Pb, Cd, and Zn in the simultaneous and individual determination are

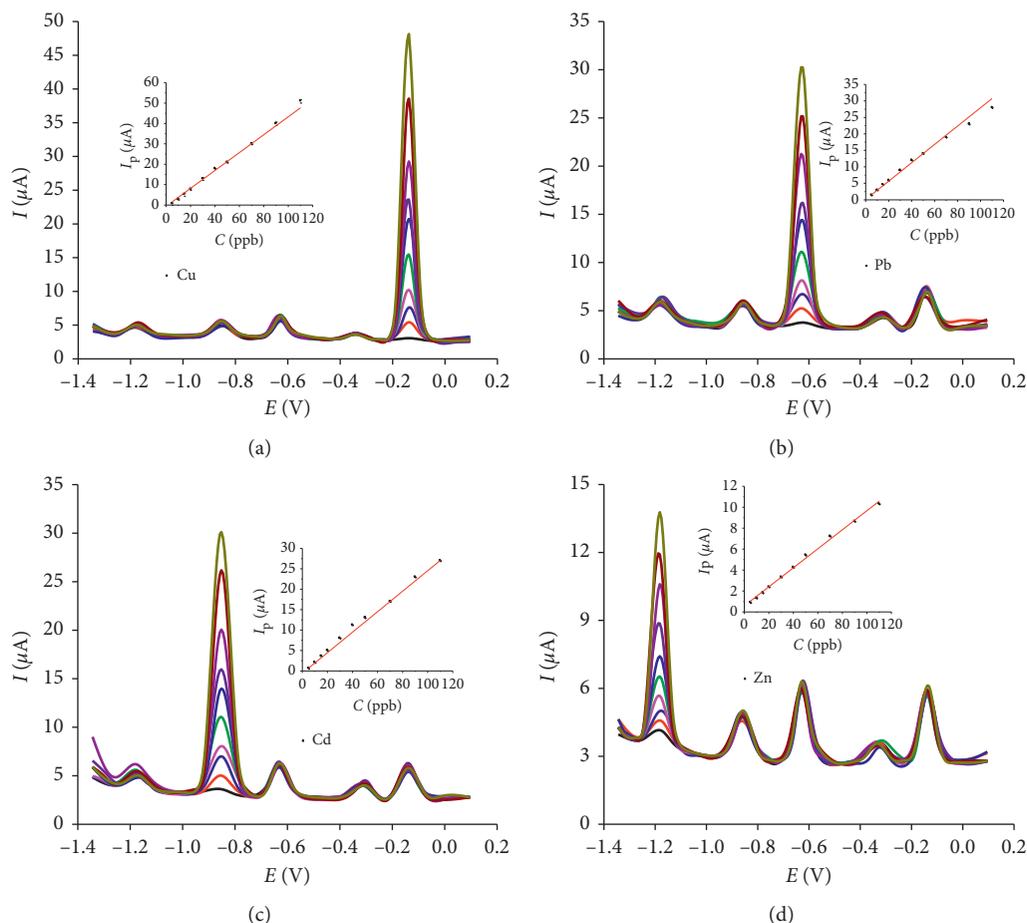


FIGURE 5: (a) DP-ASVs of Zn(II), Cd(II), Pb(II), and Cu(II) oxidation with different concentrations in acetate buffer (pH 5) at BiFE. (a) Zn(II), Cd(II), and Pb(II) fixed at 15 ppb; Cu(II) (from 5.0 to 110.0 ppb): 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, 50.0, 70.0, 90.0, and 110.0 ppb; inset: the calibration curves of Cu(II); (b) Zn(II), Cd(II), and Cu(II) fixed at 15 ppb; inset: the calibration curves of Pb(II) (from 5.0 to 110.0 ppb); (c) Zn(II), Pb(II), and Cu(II) fixed at 15 ppb; inset: the calibration curve of Cd(II) (from 5.0 to 110.0 ppb); (d) Cd(II), Pb(II), and Cu(II) fixed at 15 ppb; inset: the calibration curve of Zn(II) (from 5.0 to 110.0 ppb). Acetate buffer: pH 5; Bi(III): 500 ppb; accumulation potential -1.6 V; accumulation time 110 s; accumulation potential -1.6 V; accumulation time 110 s; pulsed amplitude 0.07 V; scan rate 0.021 V·s $^{-1}$.

very close to each other. This suggests that the simultaneous voltammetric determination of Cu, Pb, Cd, and Zn is possible at BiFE in the mixed samples without any cross interference. This linearity is also relevant for the determination of Zn, Cd, Pb, and Cu in water.

A comparison of the developed method with other voltammetric methods for Zn, Cd, Pb, and Cu determination is listed in Table 4. It could be noticed that LOD of Zn, Cd, Pb, and Cu from this method is lower or comparable with that obtained on the basis of modified electrodes in the literature. Overall, BiFE proves to be an effective electrode for the simultaneous determination of Zn, Cd, Pb, and Cu.

3.7. Practical Application. Water samples taken randomly from five rivers in Quang Binh province, Vietnam, namely, Cau Rao, Kien Giang, Nhat Le, and Son and Gianh river were used to determine the concentration of copper, lead, cadmium, and zinc using the proposed method (DP-ASV) and GF-AAS for the sake of comparison. Table 5 lists the content of Zn, Cd, Pb, and Cu in the samples determined by

using these two methods. The paired t -test was used to compare the data. With the significant level $\alpha = 0.05$, the data show that the amounts of Zn, Cd, Pb, and Cu determined with the proposed method are not statistically different from those determined with GF-AAS (Cu: $t(4) = 0.291$; $p = 0.785$; Pb: $t(4) = 0.347$; $p = 0.746$; Cd: $t(4) = 0.975$; $p = 0.385$; Zn: $t(4) = 1.545$; $p = 0.197$). The recovery measurements were also performed to evaluate the accuracy of the method. The data provide good average recoveries, ranging from 92% to 105% for Cu, 91% to 102% for Pb, 96% to 108% for Cd, and 92% to 106% for Zn, suggesting that the developed method does not suffer from any significant effects of matrix interference.

4. Conclusion

In this article, the differential pulse anodic stripping voltammetry was used to determine Zn, Cd, Pb, and Cu in the rivers at a bismuth film-modified electrode. Simultaneous determination of Zn, Cd, Pb, and Cu using DP-ASV on BiFE displayed low detection limit, excellent long-time stability,

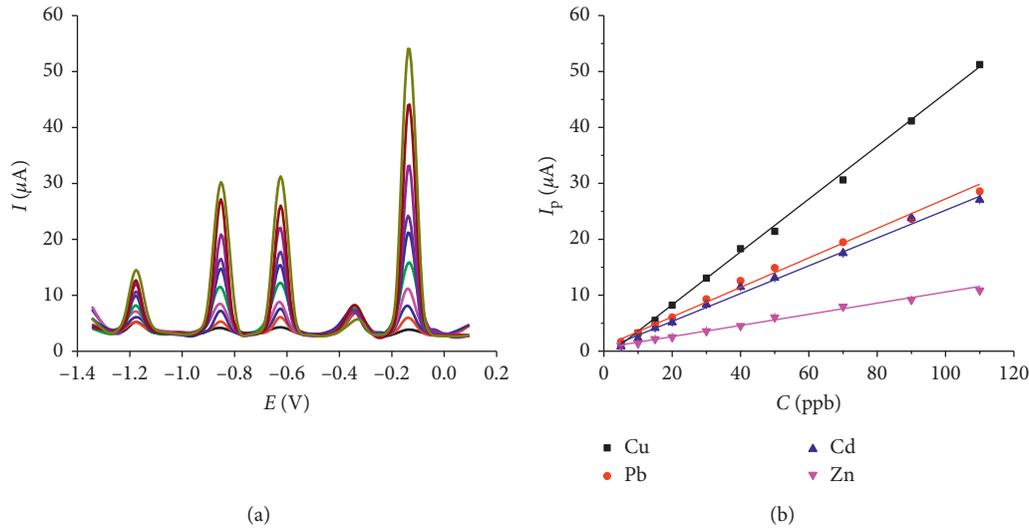


FIGURE 6: (a) DP-ASVs curves obtained for the oxidation of Zn(II), Cd(II), Pb(II), and Cu(II) at equal concentrations in the 0.1 acetate buffer solution (pH = 5): 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, 50.0, 70.0, 90.0, and 110.0 ppb; (b) linear plots of $I_{pa,Cu}$, $I_{pa,Pb}$, $I_{pa,Cd}$ and $I_{pa,Zn}$ with their concentration (acetate buffer: pH 5; Bi(III): 500 ppb; accumulation potential -1.6 V; accumulation time 110 s; accumulation potential -1.6 V; accumulation time 110 s; pulsed amplitude 0.07 V; scan rate 0.021 V·s $^{-1}$).

TABLE 4: Comparison of some figures of merit related to different electrodes for the determination of analytes.

Electrode	Method	LOD (ppb)				Reference
		Cu(II)	Pb(II)	Cd(II)	Zn(II)	
G/PANI/SPE	SqWASV	N/A	0.1	0.1	1.0	[22]
GCE	DP-ASV	39	16.6	9.6	14.7	[23]
Hg-Bi/SWNTs/GCE	SqWASV	N/A	1.3	0.98	2	[24]
	LSV	1.50	4.04	2.91	1.68	
Glassy carbon mercury film	DPV	1.11	1.54	2.21	1.29	[25]
	SWV	0.55	1.70	1.09	0.52	
BiFE	SqWASV	N/A	1.64	0.82	0.08	[26]
BiFE	SqWASV	N/A	0.41	0.49	—	[27]
BiFE	DP-ASV	0.94	0.65	0.93	1.07	The present work

— and N/A: not applicable.

TABLE 5: Concentration of Cu, Pb, Cd, and Zn determined using DP-ASV and GF-AAS for the water samples taken from the rivers.

River	DP-ASV (ppb)				GF-AAS (ppb)			
	Cu	Pb	Cd	Zn	Cu	Pb	Cd	Zn
Cau Rao river	9.1 ± 2.5	13.3 ± 1.4	2.9 ± 0.7	12.5 ± 0.5	8.7 ± 1.5	14.5 ± 3.6	3.2 ± 0.5	13.7 ± 2.8
Kien Giang river	7.2 ± 3.9	17.2 ± 7.3	3.1 ± 0.9	7.8 ± 2.8	6.5 ± 2.1	18.8 ± 4.2	2.5 ± 0.6	7.3 ± 1.8
Nhat Le river	8.6 ± 3.1	22.5 ± 3.6	3.1 ± 0.4	6.2 ± 2.6	9.4 ± 1.2	21.8 ± 3.1	3.5 ± 0.7	6.9 ± 1.5
Gianh river	5.5 ± 1.8	11.2 ± 4.4	3.1 ± 1.6	7.9 ± 1.7	5.8 ± 0.9	10.2 ± 2.7	2.6 ± 0.5	8.7 ± 1.6
Son river	4.6 ± 2.1	7.3 ± 2.1	2.9 ± 0.9	5.5 ± 1.4	4.2 ± 0.3	7.1 ± 1.2	2.1 ± 0.6	5.6 ± 1.4

Number of experiments $n = 3$.

and high reproducibility. The limits of detection were found to be 1.07, 0.93, 0.65, and 0.94 ppb for Zn, Cd, Pb, and Cu, respectively. The proposed method was successfully employed for the determination of Zn, Cd, Pb, and Cu in river water in an agreement with GF-AAS analysis.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

Table S1: effect of Co(II) on the stripping peak current. Table S2: effect of Ni(II) on the stripping peak current. Table S3: effect of Fe(II) on the stripping peak current. Table S4:

repeatability of Ip according to the analyte concentration. (Supplementary Materials)

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