Anodic stripping voltammetric detection of Zn(II), Cd(II) and Pb(II) of coal gangue at bismuth film glassy carbon electrodes

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Abstract. For coal gangue it is very important to detect the heavy metals of the products in view of environment risk control, because the heavy metals in coal gangue can cause multiple significant toxic effects. Most of the techniques now available are more suitable for laboratory conditions only and usually cost much testing time. In this work, we develop a new rapid detecting method of Zn(II), Cd(II) and Pb(II) in coal gangue based on anodic stripping voltammetry. Through a large number of experiments, operational parameters have been optimized. This work provides a quick and convenient detection method for heavy metals in coal gangue.

1. Introduction

A large amount of coal gangue will be produced during coal mining and washing, which is an inevitable and complex solid waste discharged during coal production. In 2013, China produced about 750 million tons of coal gangue. Existing coal gangue in large quantities causes much serious environmental problem and has great impact on the eco-environment of the mining area and its surroundings. [1]. A variety of metals, such as copper, lead, zinc, chromium, cadmium, arsenic and mercury, will wind into the air after the powder is formed in the solid surface by weathering which can enter the water through the rain and snow leaching, or flow directly into the vicinity of rivers or seep into the ground. Heavy metals have significant biological toxicity and can not be degraded by microorganism, which have various forms of mutual conversion and dispersion, being enriched and then enter the body through the food chain, causing chronic poisoning.

The utilization of coal gangue to make products with high value attracts much attention of scientists and the engineers. Usually, coal gangue can be made into various building materials and products [2], most of which contain various heavy metals such as Pb, Cd, Cr, Hg and Cu. When present in excess or under the wrong conditions, heavy metals can result in multiple toxic effects [3-4]. Therefore it is very important to detect the heavy metals of the products in view of environment risk control.

People have developed many detection methods for determination of heavy metals, [5-7] including inductively coupled plasma mass spectrometry (ICPMS) [8], graphite furnace atomic absorption

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spectrometry,[9] and high-performance liquid chromatography with ICPMS.[10] However, the most reliable techniques are more suitable for laboratory conditions only and usually cost much testing time. Consequently they cannot be used for routine in-field monitoring of a large number of samples. Therefore, it is needed to develop a new rapid determining method to solve these problems. Voltammetric stripping techniques provide accurate measurements of low concentrations of metal ions at the ppb levels with rapid analysis times and low-cost instrumentation.

In this study we present the electrochemical detection of Zn(II), Cd(II) and Pb(II) of coal gangue at bismuth film glassy carbon electrodes. Through a large number of experiments, operational parameters have been optimized. This work provides a quick and convenient detection method for heavy metals in coal gangue.

2. Experimental

2.1. Reagents and Preparation of Solution to Be Measured

All of the reagents were obtained from AkzoNobel Co., China and Alfa Aesar, China and were of analytical grade and hence used without further purification. Coal gangue samples were collected from one coal mine of Shanxi Province, China.

Before the anodic stripping voltammetric detection of heavy metals, it is necessary to dissolve the heavy metal elements into the water solution. Coal gangue is a kind of hard solid substance, and it is difficult to dissolve. The common methods to dissolve are wet digestion, dry ashing and microwave digestion, while wet digestion and microwave digestion are the most common methods.

Preparation of all the solutions was conducted by using de-ionized water. Most of the samples can be digested by wet method to achieve satisfactory digestion effect. The experimental conditions are as follows: the amount of coal gangue samples is 0.3~0.4 g, and the acids used for digestion are 5 mL HNO_3, 1 mL HF, 1 mL $HClO_4$ and 1 mL H_3PO_4.

3. Determination of Measuring Parameters

The main influence factors for electrochemical method for the determination of heavy metal content are as follows: electrode material, scanning mode, electrolyte type and pH, the accumulation potential and the accumulation time and other factors. It is needed to select different experimental parameters according to the measured elements.

3.1. Scanning Mode

Different current formula of the dissolution peak obtained by different scanning modes, and also is the current magnitude. In addition, the sensitivity of different scanning modes is also different because the ability to eliminate background currents is different. In order to select the optimal scanning mode, we compared the advantages and disadvantages of the following scanning modes, including differential pulse voltammetry (DPV), square wave voltammetry (SWV), conventional pulse voltammetry (NPV) and linear scanning voltammetry (LSV). The parameter setting for the above four modes are shown in Table 1.

Table 1. The parameter setting for the four modes: DPV, SWV, NPV and LSV

	Parameter Setting
DPV	potential increment: 5mV; amplitude: 25mV; pulse width: 0.05s; detecting width:0.04s; pulse period: 0.5s
SWV	frequency: 15Hz; potential increment: 50mV; amplitude: 25mV
NPV	potential increment: 5mV; pulse width: 0.05s; detecting width:0.04s; pulse period: 0.2s
LSV	scanning speed : 0.1V/s; sample interval: 1mV

The dissolution curves of potential vs current for 50 μg /L Pb^{2+}, Cd^{2+} and Zn^{2+} obtained with bismuth film glassy carbon electrodes by using four scanning methods are shown in Figure 1.

From Figure 1 we can conclude that good stripping peak signals were got by the four scanning modes for all the three elements with evident separation. But compared to the other two modes, the stripping peaks for NPV and LSV are weak, and their baselines showed an upward trend. Further comparison between SWV and DPV shows that the baseline of SWV is more stable. Therefore, we uses square wave scanning (SWV) in this study.

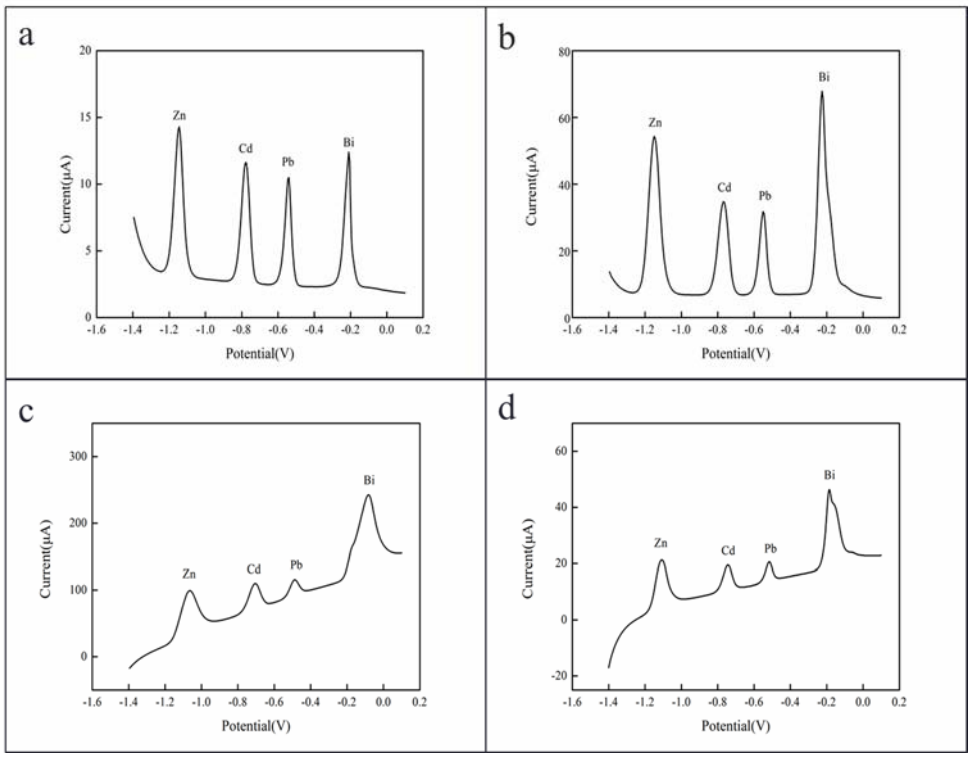


Figure 1. The dissolution curves of potential vs current obtained by using four scanning methods. (a, DPV; b, SWV; c, NPV; d, LSV)

3.2. Effect of Bi^{3+} Concentration

We studied the relationship between stripping peak signals and concentration of Bi^{3+} (Figure 2) at 0, 50, 100, 150, 200, 250, 300, 400 μg/L when the concentration of Pb^{2+}, Cd^{2+} and Zn^{2+} were maintained at 50 μg /L. Figure 2 shows that when the concentration of Bi^{3+} was low, the stripping peaks of Zn^{2+}, Cd^{2+}, Pb^{2+} were significantly increased with the increase of concentration of Bi^{3+}, after Bi^{3+} concentration reached 200 μg/L, the stripping peaks showed a downward trend, because when the concentration of Bi^{3+} is too large, the electrode is tightly wrapped by Bi^{3+}, which affects the adsorption of the electrode to other elements. Therefore the concentration of Bi^{3+} is chosen as 200 g/L in our study.

3.3. Effect of pH of Base Solution

We detected the current of stripping peaks of Pb^{2+}, Cd^{2+} and Zn^{2+}, respectively, when pH of base solution changed from 1.0 to 7.0. The results were demonstrated in Figure 3. As can be seen from Figure 3, the variation trend of the peak current of the three elements increases first and then decreases with the increase of the pH of base solution. Among them, the peak current reached the maximum for Zn^{2+} and Pb^{2+} when the pH of base solution was 5.0, and for Cd^{2+} it was 6.0. Considering that Cd^{2+} is much sensitive at pH 5.0, the optimum pH for base solution we chosen is 5.0.

3.4. Effect of accumulation Time

We detected the current of stripping peaks of Pb^{2+}, Cd^{2+} and Zn^{2+}, respectively, with different accumulation time from 60s to 780s when the concentration of these three elements were 50μg/L. The results were shown in Figure 4. The experimental results show that the peak current of Pb^{2+}, Cd^{2+} and Zn^{2+}increases obviously with the increase of accumulation time, when the accumulation time goes greater than 660s, the variation trend of peak current is slow. Considering the experimental efficiency, 660s was chosen as the optimal accumulation time.

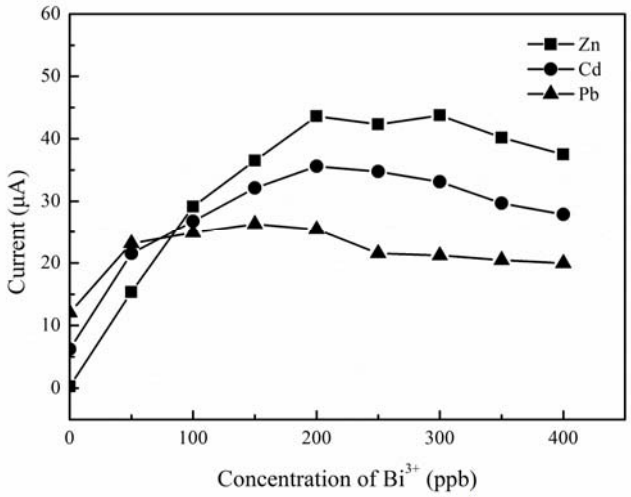


Figure 2. The stripping peak signals of Pb^{2+}, Cd^{2+} and Zn^{2+} at different concentration of Bi^{3+}.

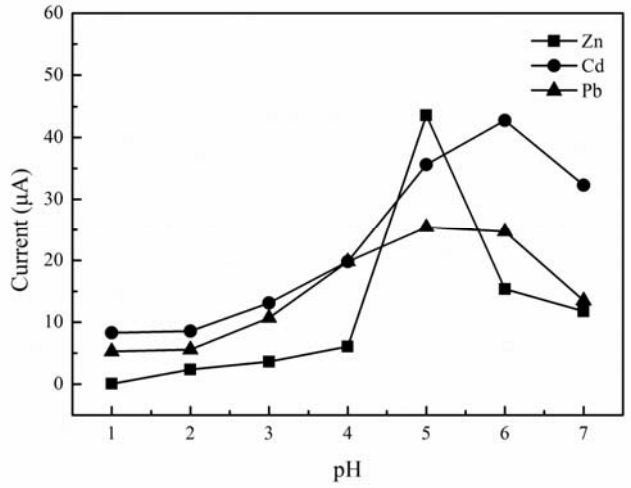


Figure 3. The stripping peak current of Pb^{2+}, Cd^{2+} and Zn^{2+} at different pH.

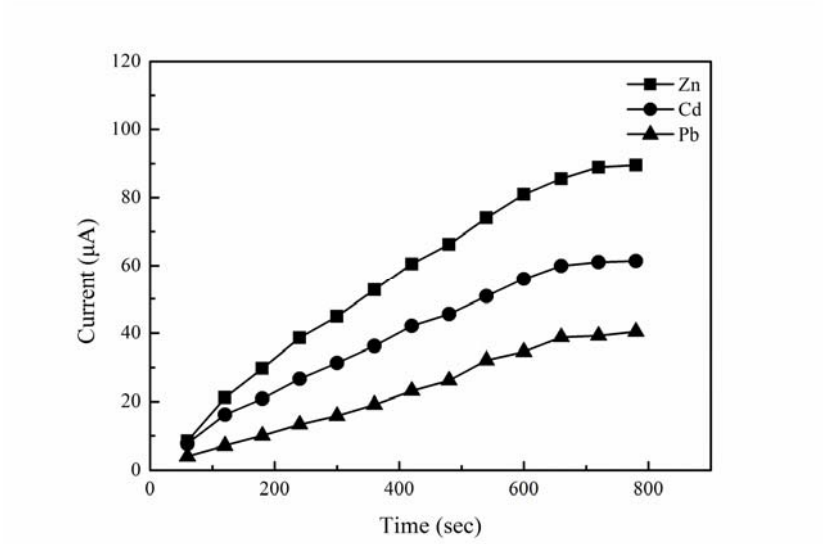


Figure 4. The stripping peak current of Pb^{2+}, Cd^{2+} and Zn^{2+} with different accumulation time.

3.5. Effect of pH of Accumulation Potential

Same as above we detected the current of stripping peaks of Pb^{2+}, Cd^{2+} and Zn^{2+}, respectively, with different accumulation potential from -0.6V to -1.8V when the concentration of these three elements were 50μg/L. As shown in Figure 5, when the accumulation potential changed from -0.6 to -1.6V the stripping peak current increased gradually. When the accumulation potential is lower than -0.7V, the lead dissolution signal occurred, and when the accumulation potential is lower than -0.9V, stripping signal tends to be stable. For cadmium, when the accumulation potential is lower than -0.9V, the signal appeared, and after the accumulation potential is lower than -1.0V the stripping signal tends to be stable. For zinc, when the accumulation potential reached to -1.3V, the stripping signal appeared and the signal reaches a maximum value at -1.4V. After lower than -1.4V, the signal sharply declined. Considering the maximum dissolution peak of the three elements, the optimal accumulation potential we chosen is -1.4V.

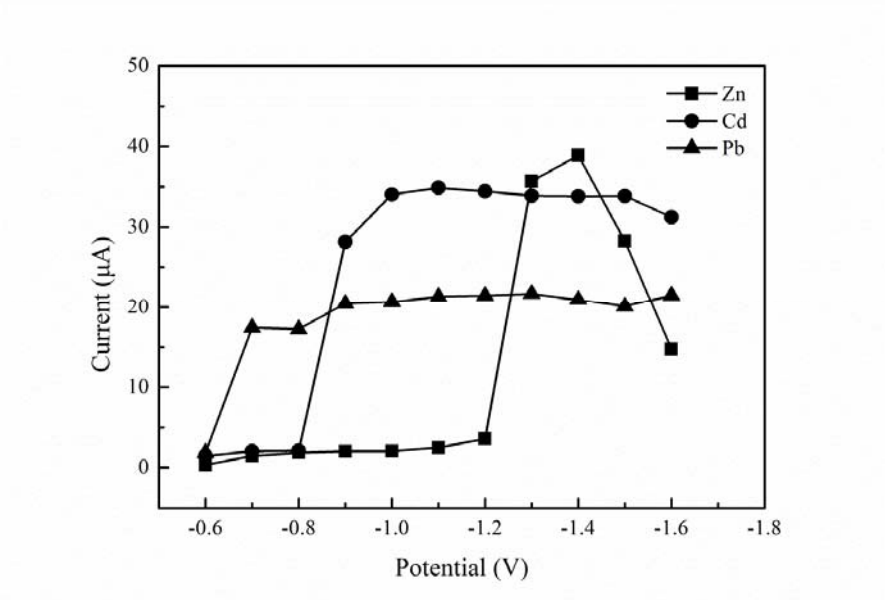


Figure 5. The stripping peak current of Pb^{2+}, Cd^{2+} and Zn^{2+} with different accumulation potential.

4. Conclusion

From the experimental results mentioned above, the optimized operational parameters have been obtained as Table 2.

Table 2. The optimized operational parameters for anodic stripping voltammetric detection of Zn(II), Cd(II) and Pb(II) of Coal Gangue

Parameter	Value	Parameter	Value
Working Electrode	Glassy Carbon Electrodes	Reference Electrode	Saturated Calomel Electrode
Auxiliary Electrode	Platinum Wire Electrode	Electrolyte	0.1mol/L HAc-NaAc pH 5.0
scanning mode	square wave voltammetry (SWV)	Bi^{3+} Concentration	200 μg/L
Accumulation Potential	-1.4 V	Accumulation Time	660 s
Stationary Time	30 s	Scanning Potential	-1.4~0.2 V
Potential Increment	4 mV	Amplitude	50 mV
Frequency	15 Hz	Sensitivity	10^{-4}A/V

5. Acknowledgement

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