TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Sử dụng điện cực platin nano hình hoa biến tính trên bề mặt điện cực glassy cacbon để xác định Chì bằng phương pháp Von - Ampe hòa tan anot

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TÓM TẮT

Chì (II) được xác định bằng phương pháp Von – Ampe hòa tan anot sử dụng điện cực platin nano hình hoa biến tính trên bề mặt điện cực glassy cacbon (PtNFs/GCE). Các điều kiện thí nghiệm tối ưu là dung dịch đệm axetat 0,1 mol.L^{-1} (pH = 4,5), thế điện phân làm giàu -1,1 V, thời gian điện phân làm giàu 120 s, biên độ xung 60 mV và tốc độ quét 0,23 V.s^{-1}. Khoảng nồng độ tuyến tính là 1-100 µg.L^{-1} với R = 0,9981. Giới hạn phát hiện và giới hạn định lượng của phương pháp phân tích được xác định lần lượt là 0,398 µg.L^{-1} và 1,272 µg.L^{-1}. Ảnh hưởng của một số ion kim loại như Zn, Cd, Cu đã được nghiên cứu. Điện cực đã được áp dụng để xác định chì (II) trong một số mẫu nước sông, nước hồ với kết quả hoàn toàn phù hợp về mặt thống kê với phương pháp quang phổ hấp phụ nguyên tử lò graphite (GFAAS).

Từ khóa: *Phương pháp điện hóa, chì, platinum nanoflowers, biến tính điện cực, glassy cacbon.*

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Using platinum nanoflowers modified glassy carbon electrode for determination of Lead by anodic stripping voltammetric method

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ABSTRACT

Lead (II) was determined by anodic stripping voltammetric method using platinum nanoflowers modified glassy carbon electrode (PtNFs/GCE). Optimal experimental conditions were found acetate buffer solution 0.1 mol.L^{-1} (pH = 4.5), an preconcentration potential of -1.1 V, preconcentration time of 120 s, pulse amplitude of 60 mV and scan rate of 0.23 V.s^{-1}. The peak current response increased linearly with the metal concentration in a range of 1-100 µg.L^{-1} with R = 0.9981. The limit of detection and limit of quantity were 0.398 µg.L^{-1} and 1.272 µg.L^{-1}, respectively. The interference effects of some metal ions such as Zn, Cd, and Cu were studied. The PtNFs/GCE was applied to analysis of lead (II) in some river water, and lake water samples with results in satisfactory statistical agreement with graphite furnace atomic absorption spectroscopy (GFAAS).

Keywords: *Lead, electrochemical method, platinum nanoflowers, modified electrode, glassy carbon electrode.*

1. INTRODUCTION

Pollution caused by heavy metals poses a serious menace to human health and ecological systems.[1] Among heavy metals, lead is especially pointed out for its toxicity and negative effects on human beings and living organisms, including carcinogenic and mutagenic effects.[2,3]

Accordingly, it is highly desirable to develop highly sensitive methods for the determination of trace amounts of lead. A wide range of analytical methods are normally exploited for the quantification of lead that includes atomic absorption spectrometry,[4] inductively coupled plasma mass spectrometry,[5] atomic fluorescence spectrometry.[6] However, they still have some drawbacks such as the expensive and sophisticated equipment, complex operation, impossibility for on-site measurement, highly qualified operator demand. Recently, electrochemical methods[7,8] are promising techniques for the determination of lead ions due to their low cost, high sensitivity, easy operation, and ability to analyze element speciation.

In recent years, modified electrodes have attracted much interest. Modified electrodes can be prepared by deposition of various compounds such as conducting polymers, metal complexes, transition metals and metal oxides on various electrodes.[9,10] Metal nanoparticles have drawn renewed attention in recent years due to their wide range of applications in nanosensor, biosensors and many other fields.[11] They have special properties such as large surface area, catalyst, mechanical and electronics. Previous studies indicated that Pt nanoparticles could

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increase the surface area and conducive to electron transfer with strong catalytic properties, and have attracted more and more interests as electrode modified materials.[12,13]

In this work, the electrochemical behavior of lead has been investigated with sensitive, fast and simple different pulse anodic stripping voltammetry (DPASV) method. This preliminary work is an initial step toward the fabricating one type of electrochemical sensors used for sensitive determination of Pb (II) at trace concentration.

2. MATERIALS AND METHODS

2.1. Reagents and apparatus

Reagents: Hexachloroplatinic (IV) acid hexahydrate ($H_2PtCl_6.6H_2O$) was used for the PtNFs modified GCE. It was purchased from Merck (KGaA, 64271 Darmstadt Germany). The electrolyte solution is made up of 1 mM H_2PtCl_6 and 0.1 M H_2SO_4 solution and a $[Fe(CN)_6]^{3-}$ redox system in 0.2 M phosphate buffer solution pH = 7 was used for the study of electrochemical properties. CH_3COOH, $CH_3COONa.2H_2O$, NaOH, K_2HPO_4, KH_2PO_4, H_3PO_4, H_3BO_3, KCl, HCl were purchased from Merck (KGaA, 64271 Darmstadt Germany). Lead stock solution (1000 ppm) purchased from Merck (KGaA, 64271 Darmstadt Germany) was used for dilution. All of the solutions were prepared by using distilled water.

2.2. Preparation of modified electrode

The electrodeposition of platinum nanoparticles on the bare glassy carbon electrode (GCE) was carried out in H_2SO_4 0.1 M solution containing 1.0 mM H_2PtCl_6 at a constant potential of -0.2 V and deposition time of 150 s. Following that, the Pt/GCE was gently cleaned with distilled water before use.

2.3. Electrochemical measurements

Electrochemical measurements were performed using an Autolab Electrochemical (CPA-HH5). Electrochemical measurements were performed by a custom-made multi-functional potentiostat/galvanostat manufactured at Vietnam Academy of Science and Technology, Hanoi, Vietnam. The formation of PtNFs/GCE and their properties were investigated by cyclic voltammetric method (CV). Measurements performed in 5 mM $[Fe(CN)_6]^{3-}$ from -0.3 V to 0.8 V at a scan rate of 0.1 $V.s^{-1}$ was used to predict electrochemical features of electrodes and compare their electrochemically active surface areas. Detection of Pb(II) was performed by different pulse voltammetry (DPV) in an acetate buffer solution, pH of 4.5; the accumulation of Pb was carried out at a constant potential of -1.1 V for 120s; the potential was scanned from -1.2 V to +0.2 V with pulse amplitude 0.060 V; pulse time 0.050 s; step potential 0.007 V; step time 0.03s; sweep rate 0.23 $V.s^{-1}$. All experiments described in this section were performed at room temperature (25 ± 1 ^{0}C).

3. RESULTS AND DISCUSSION

3.1. Optimization of experimental parameters

3.1.1. Effect of electrochemical technologies

Electrochemical technologies such as differential pulse voltammetry (DPV), square wave voltammetry (SWV), and normal pulse voltammetry (NPV) are studied. These electrochemical techniques are comparatively used in the detection of Pb(II) on the PtNFs/GCE as shown in Figure 1. The result shows that the electrochemical signal of DPV is larger than that of SWV, and NPV. Therefore, the DPV technique is used in the following electrochemical experiments.

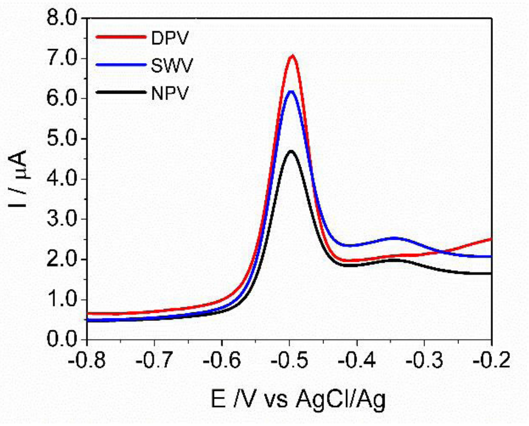

Figure 1. Different electrochemical techniques for the detection of Pb(II) in 0.1 $mol.L^{-1}$ acetate buffer (pH 4.5) solution containing 10 $\mu g.L^{-1}$ Pb(II).

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3.1.2. Effect of electrolytic solution

The effect of the various electrolytic solution including acetate buffer solution (ABS), Britton - Robinson buffer solution (BRBS), phosphate buffer solution (PBS), KCl/HCl on the stripping peak currents of Pb(II) is studied (Figure 2). The concentration of Pb(II) was 10 µg.L^{-1}. The best electrolytic solution is received in acetate buffer solution. Thus, 0.1 mol.L^{-1} acetate buffer solution is chosen as the electrolytic solution in the subsequent experiments.

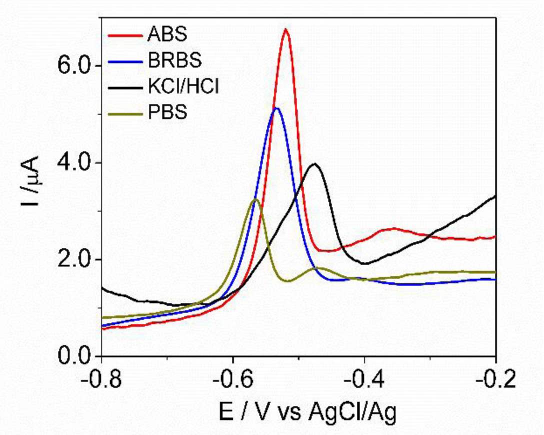

Figure 2. Effect of electrolytic solution on the peak current of 10 µg.L^{-1} Pb(II).

3.1.3. Effect of solution pH

The effect of pH on the stripping peak current was studied in 0.1 M acetate buffer solution, with pH values ranging from 2.0 to 6.0 (Figure 3). With increasing pH, the stripping peak increased initially and then decreased at higher pH. Possibly because in the low pH, metal exists as a weak link (labile form), so it can be reduced and accumulated easily on the electrode surface. In the high pH, metal can be in the form of strong bonds (bound form), so it is difficult to be eliminated. As a result, less efficient enrichment happens, leading to the lower stripping peak current. Particularly**,** the peak current reaches a maximum value at pH 4.5. The continuous increase in pH values results in a decrease in peak current. In order to obtain good sensitivity, we chose pH 4.5 as the optimal pH value for subsequent experiments.

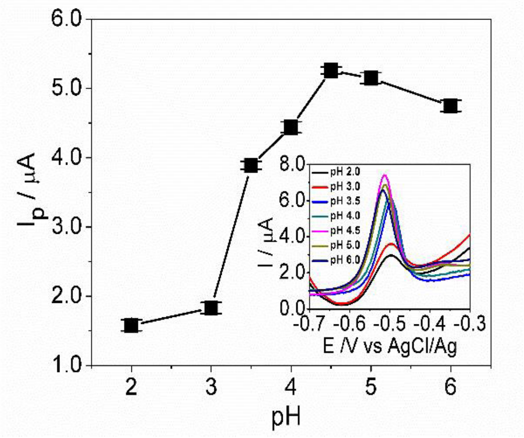

Figure 3. Effects of pH value on the peak current of 10 µg.L^{-1} Pb(II) in an acetate buffer solution.

3.1.4. Effect of Pb preconcentration time and potential on its signal

The preconcentration time and potential (accumulation time/ potential) are the time/ potential to accumulate the analyte onto the electrode surface. The influences of accumulation time and potential on Pb stripping signal were studied in the ranges from 60 s to 300 s and from -0.8 V to – 1.4 V, respectively that have been shown in our previous publication.[14] According to the results, an accumulation time of 120s was chosen as the optimal value since it provided high peak current. In addition, under this optimized condition, the time of analysis performance could be economized and the wide range of calibration curve could be acquired. Besides, -1.1 V was chosen as the preconcentration potential for the subsequent experiments because of the highest Pb signal and the lowest relative standard deviation obtained at this value.

3.1.5. Optimization of DPV parameters

The pulse voltammetric response depends considerably on instrumental conditions. To obtain a much more sensitive peak current, the optimum instrumental conditions, for example, amplitude and step potential, were studied for 10 µg.L^{-1} Pb(II) solution. The effect of pulse amplitude and step potential were studied. The result is the best peak definition was recorded

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when using 60 mV pulse amplitude, and 7 mV step potential.

3.2. Calibration data and detection limit

The linear range and detection limit were evaluated under the optimized conditions. The analytical calibration curve was obtained by varying the concentration of Pb(II) in the accumulating medium, in the range from 1 μg.L^{-1} to 100 μg.L^{-1}. Figure 4 shows the DPASV responses for the determination of Pb(II) at the PtNFs/GCE in 0.1 M acetate buffer solution (pH 4.5). The different pulse peak current showed a linear range of Pb(II) concentration: 1 μg.L^{-1} - 100 μg.L^{-1} with correlation coefficients of 0.9981. The corresponding calibration plot is $y = 0.371x + 1.603$ (x: concentration (μg/L), y: current (μA)). The limit of determination (LOD) calculated using the definition $3S_B/b$ (where S_B is the standard deviation of 10 measurements of the blank and b is the slope of the calibration line), was calculated to be 0.398 μg.L^{-1}. The comparison results of the proposed sensor with some reported sensors for the determination of Pb(II) are given in Table 1. It can be seen that the PtNFs/GCE offered a wider linear range than the one in many previous reports.[15,16] The limit of detection (LOD) of this our electrode is higher than that of some sensors reported in Table.[15,16] It can be attributed to the longer Pb deposition period (300 s) and more negative accumulation potential (-1.4 V),[17] while, in reference,[15] the authors used different analysis method–adsorptive stripping voltammetry method that spend much more time on Pb adsorption onto electrode surface (40 min) for preconcentration. Thus, the analysis procedure in this study waste less time. Furthermore, the LOD is much lower than recent publication with LOD of 1.12 μg·L^{-1}.[18] In addition, this electrode is prepared more simply than the ones in[16]. Meanwhile, the LOD obtained by using this electrode is far below the acceptable limit by World Health Organisation.

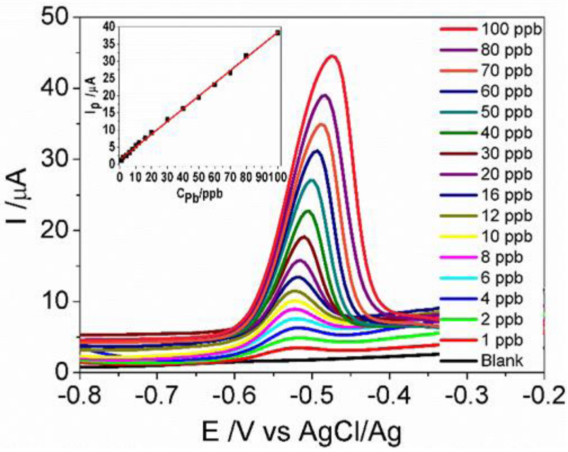

Figure 4. DPASVs of Pb(II) samples ranging in concentration from 1 to 100 μg.L^{-1} and relationship between Pb(II) concentrations with corresponding peak current (inset).

Table 1. A comparison of the different methods reported for the detection of Pb(II).

Electrode	Modifier	Method	LOD (μg.L^{-1})	Linear range (μg.L^{-1})	Ref
GCE	ETO	AdSV	0.035	0.104-2.07	[15]
GCE	PANI/MMT	DPASV	0.207	0.828-20.7	[16]
GCE	EG/Bi	DPASV	0.11	1-100	[17]
GCE	$ZnFe_2O_4$	DPASV	1.12	10-130	[18]
GCE	PtNFs	DPASV	0.398	1 – 100	This work

GCE: glassy carbon electrode; EG/Bi: electrochemically deposited graphene/bismuth; AdSV: adsorptive stripping voltammetry; ETO: etodolac; PANI/MMT: polyaniline/montmorillonite; $ZnFe_2O_4$: Nano sized zinc ferrite; SWASV: square wave anodic stripping voltammetry.

3.3. Repeatability of PtNFs/GCE

A series of repetitive DPASV response measurements for 10 µg.L^{-1} Pb(II) in 0.1 M acetate buffer solution was performed to further evaluate the stability of the PtNFs/GCE. As shown in Figure 5, the relative standard deviation (RSD) values were calculated to investigate repeatability of the PtNFs/GCE is 1.51%. Therefore, the PtNFs/GCE has an excellent stability for repetitive DPASV measurements.

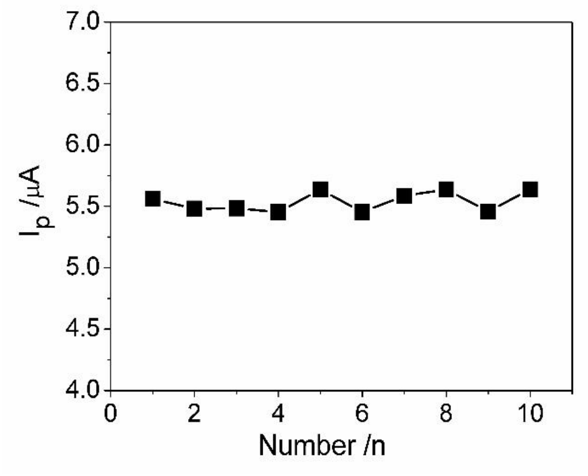

Figure 5. The stability of 10 repetitive measurements of 10 µg.L^{-1} Pb(II) on the PtNFs/GCE in solution.

3.4. Interference study

Analytical selectivity is one of the important parameters that affect the accuracy of the analysis. In order to evaluate the selectivity of the proposed method for the determination of lead, the influence of some metal ions such as zinc, cadmium, and copper on the stripping voltammetric measurements were examined in 0.1 M acetate buffer containing lead (20 µg.L^{-1}) under the optimized working conditions (Figure 6). The results showed that the effect of zinc, cadmium ions on the Pb signal is insignificant in the large concentration. When 1500 µg.L^{-1} of cadmium ions, 1600 µg.L^{-1} of zinc were added, stripping response of lead decreased by 15.56%, 14.45%, respectively. Cu (II) affected lead stripping response at the concentration ratio (ppb/ppb) of Cu^{II}/Pb^{II} > 10. Furthermore, there is a small peak observed at about -0.4 V when the concentrations of Cu(II) increased to 200 µg.L^{-1}. This peak may be attributed to the formation of a Pb-Cu alloy.[19] However, the addition of ferrocyanide ions can overcome the effect of Cu (II) because it forms a stable complex with Cu(II), as suggested previously.[19]

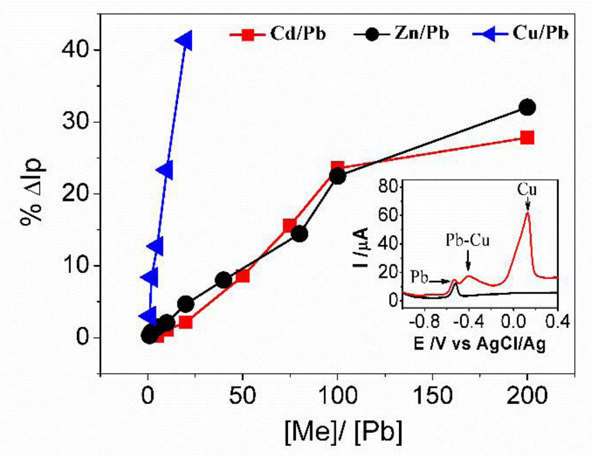

Figure 6. Influence of zinc, cadmium, and copper on the anodic stripping peak current of 20 µg.L^{-1} Pb(II) on PtNFs/GCE under the optimized working conditions.

3.5. Analysis of real samples

The PtNFs/GCE was employed for the determination of Pb(II) in the local environment by using standard addition method. All water samples were added to 0.1 mol.L^{-1} acetate buffer (pH = 4.5) and determined under the optimal conditions. The experimental values were shown in Table 2. The comparative results as shown in Table 2 suggest that the concentrations of lead ions were in good agreement with the results found in the graphite furnace atomic absorption spectrometry (GFAAS) measurement. Therefore, the PtNFs/GC electrode is potentially useful for the analysis of trace heavy metals in real samples.

Table 2. Analytical results for the determination of lead (n=3) in real water samples.

Sample	Pb(II) (µg.L^{-1})			
	Sample location	DPASV[a]	GFAAS[b]	Error (%)
Phu Hoa Lake's water	13°46'18.6"N 109°11'23.9"E	12.04±0.34	12.83±ND	6.16
Ha Thanh River's water	13°47'21.9"N 109°13'15.9"E	11.62±0.26	12.30±ND	5.52
Thi Nai Lake's water	13°47'00.7"N 109°13'53.2"E	9.38±0.20	10.30±ND	8.93
Nui Mot Lake's water	13°47'34.5"N 108°58'50.8"E	9.44±0.41	8.70±ND	8.50
Tra O Lake's water	14°18'15.4"N 109°07'28.4"E	7.41±0.18	7.80±ND	5.01

DPASV: different pulse anodic stripping voltammetry; GFAAS: graphite furnace atomic absorption spectrometry
[a]Mean of three repetitive measurements at a 95% confidence level; [b]n=1, ISO/IEC17025:2005
ND: Not determined

4. CONCLUSIONS

This work is useful for producing the electrochemical sensor for determination of Pb(II) at trace concentration. A simple, sensitive, and inexpensive method for determination of lead is proposed. The PtNFs/GCE demonstrated better detection sensitivity and higher DPASV signals than the bare GCE, with the limit of detection of about 0.398 µg.L^{-1}. Further studies will be focused on detection of other metals (cadmium, zinc, cobalt, mercury, etc.) by combining with different electrochemical technique.

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