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AC-P-077	**Environmental Friendly Electrochemical Sensor Based on of Bi/poly(L-cys)/GCE for zinc detection**

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Electrochemical sensors based on bismuth modified poly (L-cysteine)/glassy carbon electrode (Bi-poly(L-cys)/GCE) as an environmentally-friendly electrode to detect zinc by anodic stripping voltammetry. Bi film was prepared by an in situ plating of bismuth onto the poly(L-cys)/GCE. The operational parameters such as L-cysteine concentration, bismuth concentration, preconcentration potential, and preconcentration time were optimized. Under the optimum conditions, the sensitivity of the Bi-poly(L-cys)/GCE higher than the bare GCE, Bi/GCE, and poly(L-cys)/GCE was 8.5, 6.3, and 3.6 times respectively. The linear range was 0.005-0.100 mg L^{-1} (r = 0.999) with a detection limit of 0.002 mg L^{-1} and a quantitation limit of 0.008 mg L^{-1}. This method could possibly be applied to determine zinc in real samples such as food, soil, and wastewater.

Keywords: Anodic stripping voltammetry; Zinc; L-cysteine; Bi-poly(L-cys)/GCE; Environmentally-friendly

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Environmental friendly electrochemical sensor based on of Bi/poly(L-cys)/GCE for zinc detection

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An environmentally-friendly electrochemical sensors based on bismuth modified poly (L-cysteine) / glassy carbon electrode (Bi/poly(L-cys)/GCE) has been developed to detect zinc ion by anodic stripping voltammetry. The Bi film was prepared by an in situ plating of bismuth onto the poly(L-cys)/GCE. The operation parameters such as L-cysteine concentration, bismuth concentration, preconcentration potential, and preconcentration time were optimized. Under the optimum conditions, the sensitivity of the modified electrodes (Bi/poly(L-cys)/GCE, Bi/GCE, and poly(L-cys)/GCE) compared with the bare GCE was 8.5, 6.3 and 3.6 times respectively. The linear range was 0.005-0.100 mg L^{-1} (r = 0.999) with a detection limit of 2.0 µg L^{-1} and a quantitation limit of 8.0 µg L^{-1}. This method showed a potential be applied for zinc ion determination in real samples such as food, soil, and wastewater

1. Introduction

Zinc (Zn) is an essential nutrient for the growth, it is an important trace element needed by plants in small amounts, but yet crucial to plant development. In plants, Zn is a key constituent of many enzymes and proteins. In the case of soil that has too much phosphorous (P) or phosphate (PO_4^{3-}), will lead to zinc deficiency in soils due to the formation of insoluble zinc phosphate ($Zn_3(PO_4)_2$) resulting in plants absorb less zinc.[1] However, zinc deficiency frequently found in almost all plants and it is a common problem in agricultural land around the world.

The normally methods were used to determine zinc as atomic absorption spectrophotometry (AAS) and inductively coupled mass spectrometry (ICP-MS). There provided high accuracy, precision and sensitivity, however they require expensive instrumentation, have high operating costs with long analysis time.[2] The anodic stripping voltammetry (ASV) technique was interesting, because it can provide a high sensitivity, low detection limit, reduced consumption of chemical and sample, and short analysis time.[3,4] For determination of metal ions by ASV in the past mainly used mercury electrodes.[5] However, mercury is highly toxic and can be harmful to researchers, users, and the environment, therefore analytical methods that are used glassy carbon electrode (GCE) more environmentally friendly and safe for the operator are being developed based on the concept of green chemistry.[6] Various materials with electrical properties are improve the GCE such as graphene.[7] Graphite.[8] and multiwalled carbon nanotube (MWCNTs).[9] Then polymer film modified electrodes using the electropolymerization technique have been considered to be an attractive due to its good stability, homogeneity and good adhesion to the electrode surface, insolubility, increased surface area, and more active sites.[10,11] This work to used GCE as an environmental friendly electrode, it was fabricated by electropolymerization. Bismuth film (BiF) was prepared by an in situ plating of bismuth onto the poly(L-cys)/GCE for determination

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of zinc by ASV. The effect of several operational parameters were studied consisted of L-cysteine concentration, bismuth concentration, preconcentration potential, and preconcentration time, linear range, limit of detection (LOD) and limit of quantitation (LOQ), repeatability.

2. Materials and Methods

2.1 Materials

L-cysteine, bismuth(III) nitrate pentahydrate, zinc acetate dihydrate, and sodium acetate trihydrate were from Ajax finechem (Australia). Acetic acid, hydrochloric acid and nitric acid were from Biolabo (France). All other chemical were of analytical grade. Buffers were prepared with deionized water. Before use, buffer was filtered through a Millipore filter.

2.2 Apparatus

The electrochemical techniques were carried out in a conventional three-electrode cell controlled by 910 PSTAT mini potentiostat (Metrohm Autolab B. V., The Netherlands). Glassy carbon electrode (GCE; diameter 3.0 mm) was used as the working electrode. A silver/silver-chloride electrode (Ag/AgCl) and a platinum wire were used as a Reference electrode and counter electrode, respectively. The pH measurements were performed at a S220 pH meter (Mettler-toledo, Switzerland).

2.3 Fabrication of poly(L-cys)/GCE

The working electrode was first polished with 1.5, 0.5, and 0.05 µm alumina powder and washed with deionized water. The cleaned electrode was immersed in 0.05 mM L-cys in 0.1 M HCl for 10 cycles of potential sweep between -1.2 and +1.8 V at a scan rate 0.1 V s^{-1}. The poly(L-cys)/GCE was then gently washed with water and dried at room temperature.

2.4 ASV measurement

The three-electrode system consisted of a working electrode as modified with poly(L-cys), Reference electrode and counter electrode, were immersed in 0.10 M acetate buffer solution pH 4.5. Amount of Zn(II) and 1.0 mM Bi(III) were simultaneously deposited on the surface of the poly(L-cys)/GCE at -1.40 V for 120 s under stirring. Then the accumulation period, the stirring was stopped and after a 5 equilibrium time, the voltammogram was recorded using a square-wave potential scan between -1.40 and -0.80 V.

3. Results & Discussion

3.1 Optimization of electrode modification

The effect of L-cysteine concentration was studied between 0.010 and 0.075 mM in 0.1 M HCl (Figure 1. (a)) potential scan from -1.2 to +1.8 V, 10 cycles at scan rate 0.1 Vs^{-1} by cyclic voltammetry (CV). When tested with Zn(II) the sensitivity increase with concentration from 0.010 to 0.050 mM, and then decreased. This may be because poly(L-cys) film at GCE surface is too thick, it will have blocked the electron transfer.[12] The concentration of L-cys at 0.050 mM was chosen to study the next parameters.

The numbers of cycles for electro-polymerization of poly(L-cys) at the GCE surface were investigated, between 5 and 25 cycles (Figure 1b). After that tested with Zn(II) the sensitivity increase with number of cycles from 5 to 15, and then decreased. This may be because poly(L-cys) film at GCE surface is too thick, this caused inhibition of electron transfer on the surface.[13] Therefore, electropolymerization of poly(L-cys) at 15 cycles was used for further studied

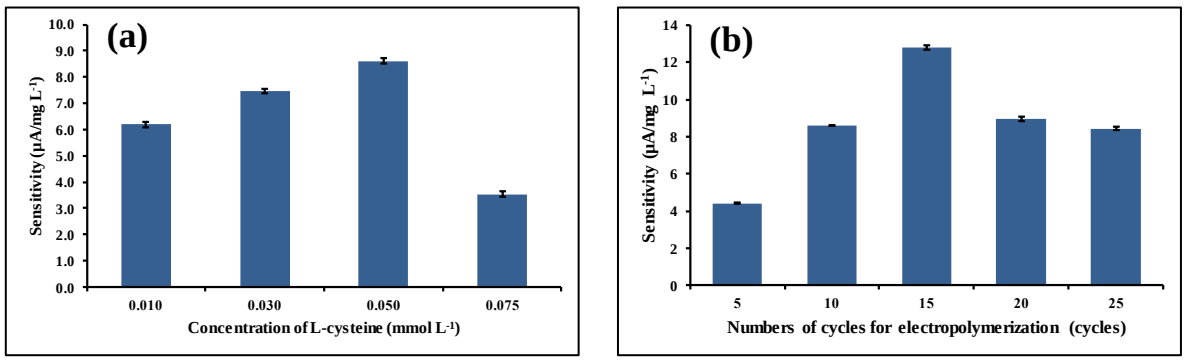

Figure 1. The effect of L-cysteine concentration (a) on the sensitivity of the fabrication electrode and Effect of the numbers of cycles for the electropolymerization (b) of the poly(L-cys) at the GCE surface. The sensitivity is slope of the calibration curve at the concentration of Zn(II) between 0.05 and 0.50 mg L^{-1}. (ASV operation conditions: 60 s preconcentration time, -1.40 V preconcentration potential with stirring, square-wave potential scan between -1.40 and -0.50 V).

3.2 Optimization of the operational conditions for zinc detection

The concentrations of bismuth were studied, between 0.10 and 2.0 mM at the potential -1.4 V for 60 s in acetate buffer pH 4.5. When the concentration increase the sensitivity increased up to 1.0 mM, the increasing of Bi(III) concentration increased the Bi film on the poly(L-cys)/GCE, and resulted in the increasing of Bi-Zn alloying on the electrode surface, thus, increased the anodic peak current. However, the sensitivity decreased when the Bi(III) concentration was higher than 1.0 mM, it probably because Bi(III) film is too thick, it will hold back the Zn and affect the anodic peak current of Zn during the stripping step.[14]

The effect of preconcentration potential was studied, from -1.20 to -1.60 V, 60 s in acetate buffer pH 5.0 (Figure 2a). The sensitivity increased as the preconcentration potential increased, between -1.20 and -1.40 V, and then the sensitivity decrease when preconcentration potentials higher than -1.40 V, it may be because had hydrogen evolution on the electrode surface and inhibited Zn(II) acumination step to affect the sensitivity reduce[15]. Therefore, at -1.20 V was chosen for preconcentration potential.

The effect of preconcentration time was studied in the range of 30 to 240 s, potential -1.40 V, acetate buffer pH 5.0 (Figure 2 b). The sensitivity was increased from 30 to 120 s, and then decreased at the preconcentration time higher than 120 s, this may be because poly(L-cys) film at GCE surface is too thick, this caused inhibition of electron transfer on the surface.[13] Therefore, the preconcentration time at 120 s was chosen.

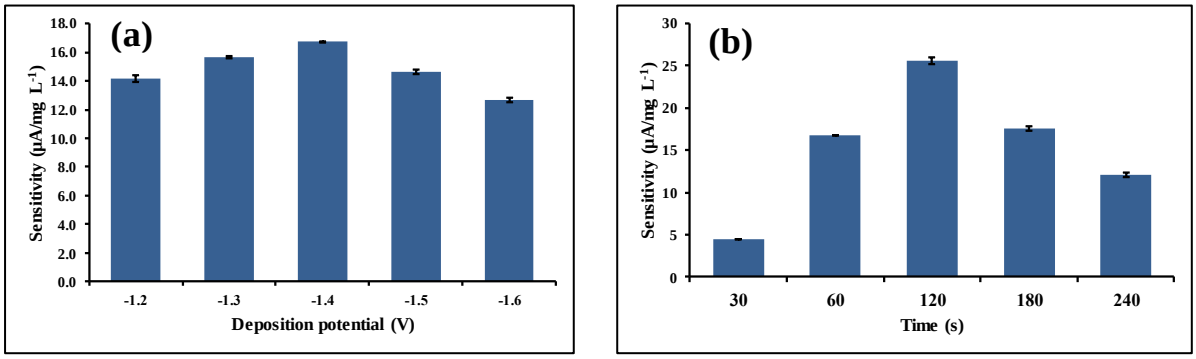

Figure 2. The effect of preconcentration potential (a) and The effect of preconcentration time (b) on the sensitivity of Zn(II) on the Bi/poly(L-cys). The sensitivity is slope of the calibration curve at the concentration of Zn(II) between 0.05 and 0.50 mg L^{-1}. (ASV operation conditions: 60 s preconcentration time, -1.40 V preconcentration potential with stirring, square-wave potential scan between -1.40 and -0.50 V).

3.3 Calibration curve, detection limit and quantitation limit

Under the optimum conditions, the linear range was 0.005 to 0.100 mg L^{-1} (r = 0.999) (Figure 3). The detection limit (LOD) and the quantitation limit (LOQ) were calculated as 2.0 μg L^{-1} and 8.0 μg L^{-1}, respectively, by using the equation LOD = $3S_a/b$ and LOQ $10S_a/b$, S_a is the standard deviation of the intercept and b is the slope of the calibration curve[16]. Then the sensitivity of the modified electrodes (Bi/poly(L-cys)/GCE, Bi/GCE, and poly(L-cys)/GCE) compared with the bare GCE was 8.5, 6.3, and 3.6 times respectively.

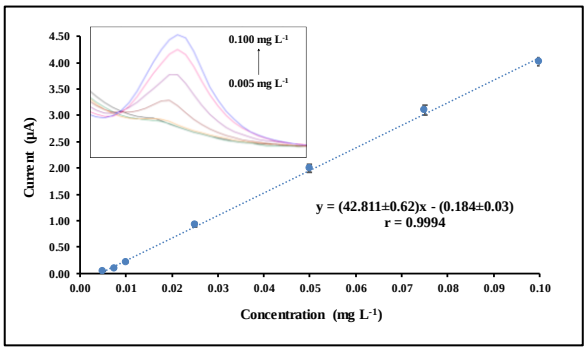

Figure 3. The calibration curve between the anodic peak current and the concentration of Zn(II) in the range from 0.005 to 0.100 mg L^{-1}. The inset shows the anodic stripping voltammograms of Zn(II).

4. Conclusions

This work, glassy carbon electrode has been modified with poly(L-cys) and was used to detected zinc by anodic stripping voltammetry through an *in situ* plating onto the poly(L-cys)/GCE. The detection provided high sensitivity and low detection limit. The Bi/poly(L-cys)/GCE is environmentally friendly and showed a potential be applied for zinc ion determination in real samples such as food, soil, and wastewater.

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