

Voltammetric Determination of Copper(II) at Chemically Modified Carbon Paste Electrodes Containing Alga

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Abstract : The design of appropriate chemically modified electrodes should allow development of new voltammetric measurement schemes with enhanced selectivity and sensitivity. Microorganism like algae has high ability to trap toxic and heavy metal ions and different affinities for metal ions. A copper(II) ion-selective carbon paste electrode was constructed by incorporating alga *Anabaena* into a conventional carbon paste mixture, and then the film of 10% Nafion was coated to avoid the swelling of the electrode surface. Copper ion could be deposited at the 25% alga-modified electrode for 15 min without the applied potential while stirring the solution by only immersing the electrode in a buffer (pH 4.0) containing copper(II). Temperature was controlled at 35 °C. After preconcentration was carried out the electrode was transferred to a 0.1 M potassium chloride solution, and was reduced at -0.6 volt at 25 °C. The differential pulse anodic stripping voltammetry was employed. A well-defined oxidation peak could be obtained at -0.1 volt (vs. SCE). In five deposition / measurement / regeneration cycles, the responses were reproducible and relative standard deviations were 3.3 % for 8.0×10^{-4} M copper(II). Calibration curve for copper was linear over the range from 2.0×10^{-4} M to 1.0×10^{-3} M. The detection limit was 7.5×10^{-5} M. Studies of the effect of diverse ions showed that the coexisting metal ions had little or no effect for the determination of copper. But anions such as cyanide, oxalate and EDTA seriously interfered.

Keywords : voltammetric determination, copper, carbon paste electrode, alga *Anabaena*, Nafion, differential pulse anodic stripping voltammetry

1. Introduction

Microorganisms such as algae[1], bacteria [2,3], yeast [4] and moss[5] have been identified as accumulation of toxic and heavy metal ions. Especially, high binding or biosorption of metal ions to algae has been exploited recently for effective removal and recovery of metal contaminants from water and in the selective recovery of valuable metals[6-9]. The easiest way to remove divalent metal ions from aqueous water is to treat the algal material with diluted mineral acid, this being the method most commonly used by industry. The high metal content of algae due to bioaccumulation and/or adsorption effects on cell walls is well known[10]. The concentration of adsorbed or unadsorbed metal ions was determined spectrometrically and electrochemically[11].

The important issue of chemically modified electrodes is to improve the selectivity and sensitivity, which is determined by the choice of an appropriate modifier in the method using chemically modified carbon paste electrodes. That carbon paste electrodes have a wide range of choice for a modifier is one of its merits. Algae were used as an electrochemical sensor for metal ions because of the ability of algae to rapidly trap metal ions from aqueous solutions and the different affinities of metal ions for algae surfaces[12, 13]. Therefore algae could be used as a modifier[14].

In this study, a green filamentous alga *Anabaena* was chosen as a modifier because it is easy to grow and it has the ability to withstand processing into biosorbent material. An alga-modified carbon paste electrode was used as a sensor for the determination of copper(II) in aqueous solution. Other algae are also highly selective and have high sorption for copper[15,16]. Nafion film was coated to avoid swelling of the surface of an alga-modified electrode. Composition ratio of alga, amounts of Nafion, the difference of Nafion-mixed and Nafion-coated electrodes, pH, preconcentration time, temperature were investigated to obtain optimum condition. The calibration curve and the effect of diverse ions were also investigated by differential pulse anodic stripping voltammetry.

2. Experimental

2.1 Apparatus and Reagents. Chemically modified carbon paste electrodes were prepared as follows; purified graphite powder(Nacalai Tesque) and dried alga(*Anabaena* was cultured in Allen and Arnon medium and centrifuged using Beckman J2-21M/E) was ultrasonically mixed in ethanol to be homogeneous. After evaporation of ethanol, the mixture was well hand-mixed with Nujol oil (Sigma) and was ground in a agate mortar and pestle. A portion of the modified carbon paste was packed into the polyethylene syringe (5-mm I.D.) and copper wire was used to connect the inner carbon paste. And then, the surface was coated with Nafion (Aldrich) film by the drop coating. Scanning electron micrographs of the surface of Nafion-coated electrode was obtained using Hitachi S-4100 scanning electron microscope. The Nafion-coated carbon paste electrode containing alga was used as a working electrode. The preconcentration cell contained sample in 50 mL beaker and measurement cell contained 0.1 M potassium chloride. Reference electrode SCE and auxiliary electrode Pt wire were placed in a measurement cell. Differential pulse and cyclic voltammograms were obtained using EG&G PAR M.174A Polarographic analyzer, M.175 Universal programmer and RE0091 X-Y recorder.

2.2 Analytical procedure. The polished carbon modified electrode containing alga was immersed in 50 mL of a buffer solution (pH 4.0) containing copper(II) without the applied potential while stirring the solution. Temperature was controlled at 35 °C. The copper(II) standard solution was prepared with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Fluka) to be 1.0×10^{-2} M and was properly diluted before use. After preconcentration was carried out the electrode was rinsed with deionized water and then a buffer. Deionized water obtained by a Milli-Q system was used. The copper(II)-deposited electrode was transferred to a new medium (0.1 M KCl), and was prerduced at -0.60 volt at 25 °C for 1 min. Dissolved oxygen in the electrolyte solution was removed by purging with nitrogen. Anodic stripping voltammograms were obtained in the range of -0.60 to +0.10 volt. Differential pulse voltammetric method was performed for all experiments.

3. Results and Discussion

The cyclic voltammograms(a) and the differential pulse voltammograms(b) are presented in Fig. 1. The dashed line and the solid line in Fig. 1 are the cyclic voltammograms obtained using 25% alga modified carbon paste electrode for the blank and the solution which contains 2.0×10^{-3} to 8.0×10^{-3} M and 3.0×10^{-3} M copper(II), respectively. Only the oxidation peak in cyclic voltammograms (a in Fig. 1) was obtained at -0.1 volt and in differential pulse voltammograms (b in Fig. 1) was at -0.1 volt. On the basis of the increase of the peak current at a fixed potential with the increase of deposition time and concentration of copper(II), we confirmed that the peaks observed were the oxidation peak of copper(II). Therefore, the optimum experimental conditions were investigated by differential pulse voltammetry at the oxidation peak of the copper(II)-deposited electrode containing alga.

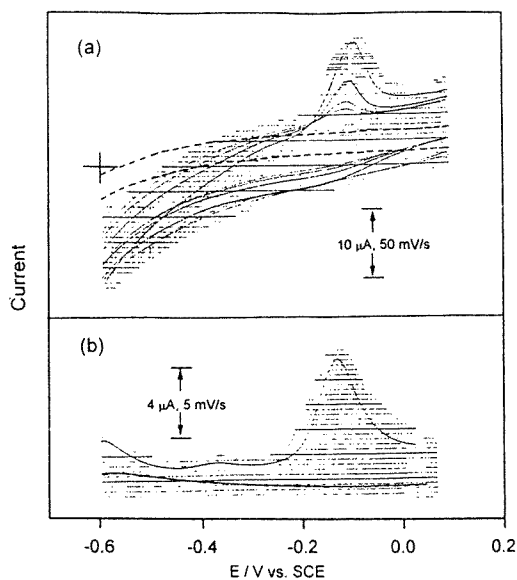


Fig. 1. Cyclic voltammograms(a) and differential pulse voltammograms(b) with 25% alga modified carbon paste electrode in 0.1 M KCl solution: (a) was obtained for 2.0×10^{-3} to 8.0×10^{-3} M and (b) for 3.0×10^{-3} M Cu(II) solution; preconcentration time, 10 min at 35 °C; reduction time, 1 min at -0.6 V; The voltammograms for the blank solution is presented as dashed line.

When an alga modified carbon paste electrode was immersed in an aqueous solution the surface of the

electrode was swelled[17]. Scanning electron micrographs of the surface in Fig. 2 showed the microholes (a and b in Fig. 2) as the case of determination of gold [18]. Nafion film was coated on the surface to reduce these microholes (c in Fig. 2). As the result, the effect of swelling was reduced and the surface of the electrode was more stable. Nafion was mixed with carbon and alga or coated on the surface of an alga modified electrode to obtain the appropriate ratio of alga content. As the coating of Nafion was more stable than the mixing of Nafion the surface of carbon paste electrodes was coated with 10% Nafion.

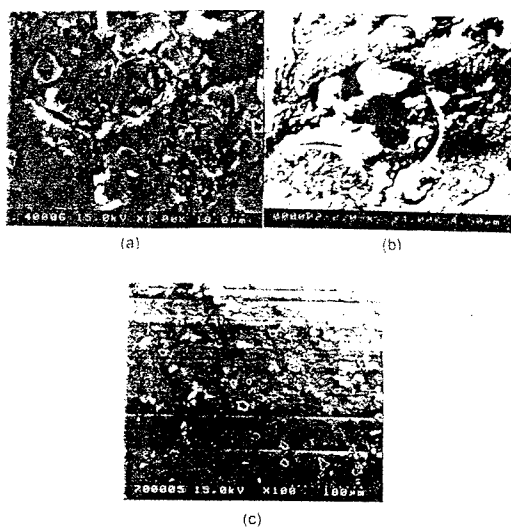


Fig. 2. Scanning electron micrographs of the surface of a carbon paste electrode before:(a,b) and after:(c) coating of Nafion film. (a): 1000x; (b), 4000x; (c), 100x.

The optimum experimental conditions to obtain calibration curve for the determination of copper(II) were found as follows: alga content, 25%; preconcentration pH, 4.0; temperature at preconcentration, 35 °C; preconcentration time, 10 min; prereluction time, 1 min.

The calibration curve for under the optimum experimental conditions was in Fig. 3. The linear range was 2.0×10^{-4} to 1.0×10^{-3} M and the correlation coefficient was 0.996 and the detection limit was found 7.5×10^{-5} M. In five deposition / measurement / regeneration cycles, the responses were reproducible and relative standard deviations were 3.3 % for 8.0×10^{-4} M copper(II).

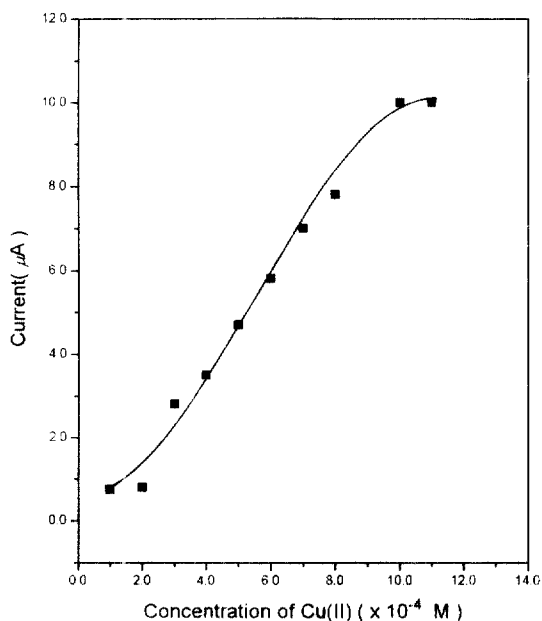


Fig. 3. Calibration curve for the determination of Cu(II) obtained by differential pulse method using a 25% alga modified carbon paste electrode: preconcentration time, 15 min at 35 °C, pH 4.0; reduction time, 1 min; scan rate, 5 mV/s; pulse amplitude, 25 mV.

To test the applicability of the proposed method to the determination of copper(II) in a real sample the effects of diverse ions were investigated. To the aqueous solutions of 3.0×10^{-3} M copper(II), nine diverse ions of 3.0×10^{-3} and 3.0×10^{-2} M were added separately and the peak current for each spiked solution was measured. The results are presented in Table I.

The coexisting metal ion had little or no effect for the determination of copper. But anions such as cyanide, oxalate and EDTA seriously interfered. The proposed method is selective to the determination of copper(II).

Conclusions

Only the oxidation peak for copper(II) obtained at the alga modified carbon paste electrode was at -0.1 volt vs SCE. The coating of Nafion was more stable than the mixing of Nafion.

The optimum experimental conditions to obtain calibration curve for the determination of copper(II) were

found as follows: alga content, 25%; preconcentration pH, 4.0; temperature at preconcentration, 35 °C; preconcentration time, 10 min; prereluction time, 1 min.

The linear range was 2.0×10^{-4} to 1.0×10^{-3} M, the correlation coefficient was 0.996 and the detection limit was found 7.5×10^{-5} M. The responses were producible and relative standard deviations were 3.3%. The coexisting metal ion had little or no effect for the determination of copper.

Table I. Effect of diverse ions on the oxidation peak current of 3.0×10^{-3} M copper(II) using a 25% alga modified carbon paste electrode coated with Nafion^a

Diverse ions	3.0×10^{-3} M		3.0×10^{-2} M	
	i(μ A)	Recovery(%)	i(μ A)	Recovery(%)
Zn ²⁺	14.8	98.7	13.2	88.0
Co ²⁺	15.2	101.3	15.2	101.3
Ni ²⁺	14.8	98.7	14.4	96.0
Cd ²⁺	15.0	100.0	14.8	98.6
Mg ²⁺	16.0	106.7	15.0	100.0
EDTA	15.5	70.0	15.2	60.7
Oxalate ²⁻	9.0	60.0	7.2	48.0
CN	7.6	50.6	6.0	40.0

^aConcentration of Cu(II) is 3.0×10^{-3} M. The peak current for Cu(II) solution containing no interferent ions is 15.0 μ A. Other conditions are the same.

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