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Glassy carbon modified with triazol derivative for analysis of cadmium (II)

Kadmiyum (II) analizi için triazol türevi modifiye edilmiş camsı karbon

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Abstract

Cadmium is recently threatening not only the life of man but also nature and living environment. In addition, cadmium usage is generally decreasing because it is toxic. 3-Methyl-4-(4-hydroxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one (MDT) in 0.1 M supporting electrolyte was attached to glassy carbon electrode (GCE) by the phenol oxidation. The modified surface was investigated by several methods. The stability of the prepared surface was presented. The GCE with MDT was utilized for Cd(II) ions analysis in water samples. The concentration range and the detection limit were 1.0×10^{-9}-1.0×10^{-8} M and 2.0×10^{-10} M, respectively.

Keywords: MDT, Oxidation, Cd (II) ion analysis

Öz

Kadmiyum son yıllarda sadece insan yaşamını değil doğa ve yaşam alanını da tehdit etmektedir. Ayrıca, toksik olmasından dolayı kadmiyum kullanımı genellikle azalmaktadır. Camsı karbon elektrot (GCE), 3-Methyl-4-(4-hydroxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one (MDT)' nin fenol oksidasyonu ile 0.1 M destek elektrolit içinde modifiye olmuştur. Modifiye edilmiş yüzey, birkaç teknik kullanılarak ile karakterize edilmiştir. Hazırlanan yüzeyin kararlılığı gösterilmiştir. MDT ile modifye edilmiş GCE, su örneklerinde Cd(II) iyon analizi için kullanılmıştır. Derişim aralığı ve deteksiyon limiti sırasıyla 1.0×10-9 - 1.0×10-8 M ve 2.0×10-10 M, olarak bulunmuştur.

Anahtar kelimeler: *MDT, Oksidasyon, Kadmiyum (II) iyon analizi*

1 Introduction

The modified surfaces are significant topic in sensor development. A chemically modified electrode is an electrical conductor that has its modified surface for different electrochemical functions. CMEs are modified using advanced approaches to electrode systems by adding a thin film or layer of certain chemicals to change properties of the conductor according to its targeted function. These surfaces are used for crucial targets such as metal detection, sensor development and drug analysis [1]-[3]. The one of the most important methods is phenol oxidation to create modified electrodes such as carbon [4],[5]. The modified electrodes are investigated by electrochemistry and x-ray photoelectron spectroscopy (XPS) [6],[7]. Important papers about Cd(II) ion analysis were evaluated using spectrophotometric methods and flame-atomic absorption spectrometry [8],[9]. Nonetheless, the tecniques have difficult methods to eliminate the excipients. The electrochemical methods can eliminate these difficulties. Because of their speed and sensitivity, the sensitive electrochemical signals can be obtained [10]-[12]. In this report, we formed GCE modified with MDT (MDT/GCE). MDT was utilized as the modifier because it was grafted onto the carbon area by phenol oxidation. The TET/GCE was characterized by SEM and AFM. In addition that, the MDT/GCE was used for of Cd(II) ions analysis.

2 Experimental section

2.1 Reagents

All used chemicals in this study are reagent grade quality. The water samples were taken from Pamukkale University. The MDT/GCE was utilized for working electrode. The 0.1 M acetic acid/sodium acetate was used as supporting electrolyte. The amount of Cd(II) was obtained by regression curves.

2.2 Instrumentation

The whole experiments, the used electrochemical systems and the characterization methods were performed according to our previous report [13]. The modification of GCE was done in 1.0 mM MDT in 0.1M TBATFB between +0.0 V and +3.0 V.

2.3 General procedure for the synthesis of MDT

The molecule of MDT was synthesized and the used instruments are same like our previous paper [14].

3 Results and discussion

3.1 GCE modification

The modifier was onto the glassy carbon electrode by covalent bonds (Figure 1). Firstly, the mechanism forms the oxidation of phenol with one-electron. After that, a carbon-oxygen bond on bare GCE occurs.

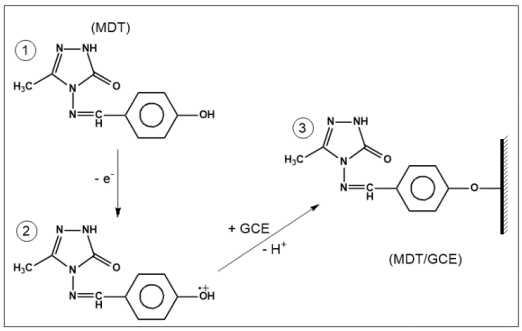

Figure 1: The MDT linkage to GCE.

The MDT was treated to GCE between +0.0 and +3.0 V. The irreversible peak of MDT was on the GCE. This situation verifies the modification owing to attachment of MDT molecules (Figure 2).

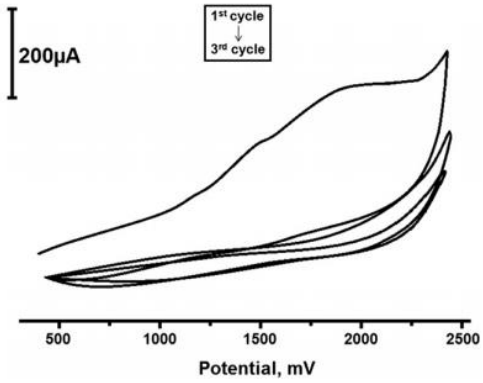

Figure 2: The voltammogram of MDT on bare surface vs. Ag/Ag+ (0.01 M) in 0.1 M supporting electrolyte.

Scanning electron microscope (SEM) images were obtained to indicate the morphologies of the bare GCE and modified electrode. Figure 3A indicates clean surface. After the formation of modifier, a few layers were seen in Figure 3B.

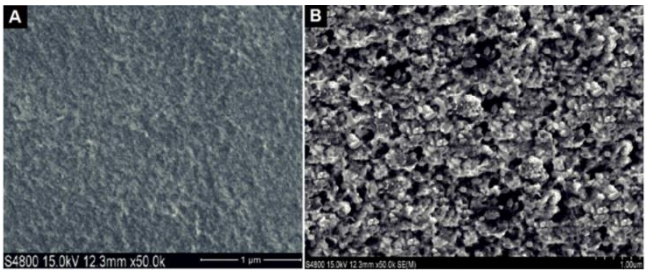

Figure 3: SEM images of (A) bare GCE, (B) MDT/GCE.

The development of MDT/GCE was presented by XPS. The C1s, N1s and O1s bands verified the formation of MDT/GCE (Figure 4). The situation indicated the formation of MDT/GCE.

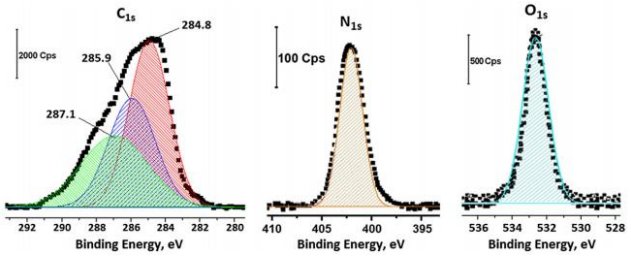

Figure 4: XPS spectrum of MDT/GCE surface.

3.2 Optimization of analytical conditions

When we obtain the most optimal pH, we tried different pH in acetate buffer of pH 5.0 (Figure not shown). So, the most suitable is 5.0 of pH. After that, the MDT/GCE was treated with different periods (5, 10, 15, 20, 25 min). It reached to maximum value at 10 min (Figure not shown).

3.3 Fabrication reproducibility

The fabrication reproducibility was also estimated with six different electrodes that were fabricated independently by the same procedure. The RSD is 0.81% for peak current measuring in 10.0 nM Cd(II) ion which demonstrates the reliability of the fabrication procedure.

3.4 Analytical application

The voltammograms of Cd(II) ion on MDT/GCE are performed (Figure not shown). The peak values of Cd(II) ion are linear with 1.0-10.0 nM. The calibration equation of Cd(II) is y (µA) = 0.1236x (nM) -0.0337. Limit of quantification (LOQ) and Limit of detection (LOD) were estimated by the equations:

$$LOQ = 10\ S / m,\ LOD = 3.3\ S / m \quad (1)$$

Where S is the standard deviation of the intercept and m is the slope of the regression line. The LOQ for Cd(II) was 1.0×10-9 M and the LOD for Cd(II) was 2.0×10-10 M. The MDT/GCE was applied to water samples. Cd(II) concentration was 4.17×10-9 M. Cd(II) concentration was 4.31×10-9 M by atomic absorption spectrometry for the comparison. The results by two methods are in well agreement. In addition, the stability of one MDT/GCE was indicated. After 30 days, the signal values are 96.22% of the first signal for 1.0×10^{-9} M Cd(II).

4 Conclusion

A novel electrode is prepared by phenol oxidation. The modification formations were characterized by SEM and XPS. LOQ and LOD for Cd(II) were 1.0×10^{-9} and 2.0×10^{-10} M. After 30 days, the peak values are almost same for 1.0×10^{-9} M Cd(II) for stability. The developed electrode suggests good sensitivity in the analysis of target.

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