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Electrocatalytic oxidation of sulphide using a pencil graphite electrode modified with hematoxylin

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ABSTRACT

The present study describes a new approach for the investigation of electrocatalytic oxidation of sulphide using a pencil graphite electrode modified with hematoxylin (PGE/HMT). Adsorption procedure was used for the preparation of the modified electrodes. It was observed that PGE/HMT showed a significant electrocatalytic activity toward sulphide oxidation. Cyclic voltammetric studies showed that the peak potential of sulphide shifted from +480 mV at bare PGE to +220 mV at PGE/HMT. The electrocatalytic currents obtained from amperometric measurements at +200 mV versus Ag/AgCl/KCl_{sat} and at pH 8.0 BR buffer solution containing 0.1 M KCl were linearly related to the concentration of sulphide. The calibration graph consisted of a linear segment of 1–200 μM with a detection limit of 0.4 μM (based on $3s_b$). The proposed method was successfully applied to the determination of sulphide in waste waters and was compared with the spectrophotometric method.

1. Introduction

Sulphide contamination is the most important problem facing all water sources and well-known toxic effect and dangerous for many organisms as hydrogen sulphide. Sulphide can release into aquatic environments through the anaerobic degradation of sulphur containing proteins, amino acids, or other types of organic components. Sulphide salts are frequently used in industrial waste streams to minimize the transport of several toxic metals such as mercury and lead into environment through precipitation reactions. In aqueous medium, sulphide can be found in different forms such as dissolved H_2S, bisulphide ion (HS^-, $pK_{a1} = 6.88$) and sulphide ion (S^{2-}, $pK_{a2} = 14.15$) depending on water pH [1]. The level of total sulphide is very important as well as H_2S. The total level of sulphide in waste discharges has been limited because of its toxicity, oxygen depletion, and production of H_2S. Sulphide acts as a lethal cellular poison through the deactivation of aerobic respiration and causes asphyxiation [2]. Therefore, the determination of sulphide species or total sulphide in wastewaters and surface waters has gained a big importance for analytical and environmental chemists [2–23].

Several methods are available to measure sulphide and its species in aqueous medium. A comprehensive review on the analytical methods related with the detection of sulphide was reported by Lawrence et al. [2]. Titrimetric [3,4], spectroscopic [5–7], chromatographic [8–10] and electrochemical [4,11–23] methods have been successfully used for sulphide determination. Among these methods, the electrochemical techniques have some advantages such as easy application, low cost, providing direct, sensitive and fast detection of lower concentrations of H_2S. However, the direct electrochemical oxidation of sulphide is highly irreversible with a great overpotential at the bare electrodes. In addition, the oxidized products of sulphide can be adsorbed on the electrode surface, which may result in the fouling and passivation of the electrode surface leading to poor sensitivity, poor selectivity and unstable analytical signals. In order to overcome these problems, the modification of electrode surface with redox mediators has been extensively used. Approaches based on redox mediators such as ferricyanide [11,12], ferrocene carboxylate [13], ferrocenesulphonate [14], N,N′-diphenyl-p-phenylenediamine [15], cobalt pentacyanonitrosylferrate [16], vanadium pentoxide [17], Cinder/tetracyano nikelate [18], hexadecylpyridinium-bis(chloranilato)-antimonyl(V) [19], 2,6-dichlorophenolindophenol [20] and 2-(4-fluorophenyl)indole-modified xerogel [21] were employed as amperometric sensors for the determination of dissolved sulphide in the aqueous medium. Although some of the redox mediators were used in aqueous medium, the chemically modified electrodes (CMEs) prepared from the redox mediators were extensively preferred due to their very sensitive, fast and stable response to sulphide.

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When compared with other carbon based electrodes, PGEs have same advantages such as high electrochemical reactivity, commercial availability, good mechanical rigidity, disposable, low cost, low technology and easy of modification [24–26]. In addition, it was reported that pencil lead electrodes offer a renewal surface which is simpler and faster than polishing procedures, common with solid electrodes, and results in good reproducibility for the individual surfaces [24]. Thus, recently many scientists have focused on the use of these electrodes in various electroanalytical applications due to the useful properties of PGEs [24–30].

Hematoxylin (7,11b-dihydroindeno[2,1-*c*]chromene-3,4,6a,9,10(6*H*)-pentol, HMT), which is one of the flavonoid compounds, is a derivative of catechol, and also widely used as a biological stain in biomedical research laboratories and diagnostic procedures [31–34]. HMT has the high number of hydroxyl substituent groups and conjugated π orbitals by which HMT is able to donate electrons or hydrogen atoms. Some researchers have been recently guided on the electrochemical properties of HMT modified electrodes and its application as a biosensor to detect NADH, ascorbic acid, adrenaline and uric acid [33–35]. These results show that HMT is a good redox mediator for electrocatalysis of biologically important compounds. However, our literature search demonstrated that no report on the preparation of modified PGE with HMT for the electrocatalytic oxidation of sulphide has been published so far. In this study we describe the electrocatalytic determination of sulphide using a new, simple and disposable electrode (PGE) modified with a good redox mediator (HMT) which have successfully been used for the electrocatalytic oxidation of some important biological compounds.

2. Experimental

2.1. Chemicals

Sodium sulphide ($Na_2S{\cdot}9H_2O$), Hematoxylin (HMT) and all other chemicals were of analytical reagent grade (purchased from Merck). All solutions throughout this work were prepared using deionized water from a Milli-Q (Millipore, Bedford, USA) device.

The stock solution of Na_2S (0.1 M) was prepared by dissolving $Na_2S{\cdot}9H_2O$ crystals in degassed 0.1 M NaOH solution and kept at +4 °C in a refrigerator for maximum one week. Na_2S solution was periodically standardized with the iodometric method.

The stock solution of HMT (1.0 mM) was freshly prepared with methanol. Britton Robinson (BR) buffer solutions with various pH values were prepared by proper mixing of stock standard solutions of H_3PO_4, H_3BO_3, and NaOH.

2.2. Apparatus

Cyclic voltammetric and amperometric experiments were performed in a traditional three electrode system. A platinum wire as the counter electrode, an Ag/AgCl/KCl_{sat} as the reference electrode and a PGE as the working electrode were used. Pencil leads with a diameter of 0.5 mm and a total length of 60 mm (Tombo, Japan) and a mechanical pencil Model T 0.5 (Rotring, Germany), which was used as the holder for the pencil lead, were purchased from a local bookstore. Electrical contact to the lead was obtained by wrapping a metallic wire to the metallic part of the holder. For each measurement, a total of 10 mm of lead was immersed into the solutions.

All electrochemical experiments were carried out using a Compactstat Electrochemical Interface (Ivium Technologies, Eindhoven, The Netherlands). The pH values of the solutions were measured using a HI 221 Hanna pH-meter with a combined glass electrode (Hanna HI 1332).

2.3. Preparation of the modified electrodes

The modification of PGE was achieved by an adsorption procedure. The pencil lead was immersed into the stock HMT solution (1.0 mM in methanol) for 60 s. The obtained modified electrodes (PGE/HMT) were used for the investigation of the electrocatalytic oxidation of sulphide after rinsing with ultrapure water.

2.4. Electrochemical procedure

The electrochemical behaviour of the PGE/HMT was investigated by recording the cyclic voltammogram in 0.1 M BR buffer solution (pH 8.0) containing 0.1 M KCl at a scan rate of 50 mV/s. In order to investigate the effect of the scan rate on the peak potentials and peak currents, the cyclic voltammograms of the PGE/HMT were recorded at different scan rates, in the potential range between −0.25 and +0.60 V. In addition, the effect of pH between 2.0 and 10.0 on the peak potentials of the modified electrodes was also investigated at a scan rate of 50 mV/s.

The electrocatalytic oxidation of sulphide at the PGE/HMT was investigated through the addition of a freshly prepared sulphide solution to the supporting electrolyte solution. The cyclic voltammograms were recorded in the potential range of −0.25 to +0.6 V, in 0.1 M BR buffer solution (pH 8.0) containing 0.1 M KCl at a scan rate of 50 mV/s. The amperometric detection of sulphide depending on its electrocatalytic oxidation was also studied using the PGE/HMT. After the background current reached to a steady state value at +200 mV, which was found as optimum value, aliquots of a stock solution of sulphide were added to the supporting electrolyte.

The used supporting electrolytes were deaerated by allowing highly pure argon to pass through for 5 min before all electrochemical experiments. Samples were collected from Kepez municipal wastewater treatment plant and Biga organized tannery region in Canakkale, Turkey, December 2011. All samples were filtered to remove particulate matter. Then, the sulphide level in waste water samples was determined with proposed method. The proposed method was compared with a spectrohotometric method, which is based on the formation of methylene blue by the reaction between sulphide and N,N′-dimethyl-p-phenylene-diamine (Caro's reaction) [5].

3. Results and discussions

3.1. Preparation of modified electrode and its electrochemical behaviour

The cyclic voltammograms of the PGE/HMT showed that the peak currents of the modified electrodes decreased when the cycle numbers were increased due to desorption of HMT to the supporting electrolyte and they were stable after the 10th scan. The cyclic voltammograms of the PGE/HMT in a 0.1 M BR buffer solution (pH 8.0) containing 0.1 M KCl at various scan rates are shown in Fig. 1A. HMT displayed an anodic peak at about +220 mV which is attributed to the oxidation of cetechol group in structure of HMT to quinone groups and corresponding cathodic peak at about +170 mV. The formal potential ($E^{0'}$ = 195 mV versus Ag/AgCl/$KCl_{(sat)}$) and peak separation potential (ΔE_p = 50 mV) show that well-defined and reproducible anodic and cathodic peaks related to HMT redox system with quasi-reversible behaviour including two protons and two electrons (Scheme 1). The peak currents increased with a small shift of anodic and cathodic peaks potentials when the scan rate increased. It was found that the anodic (I_{pa}) and cathodic (I_{pc}) peak currents of the modified electrode are linearly proportional to the scan rate (ν) between 10 and 200 mV/s (Fig. 1B). These results prove that the electrochemical process at the PGE/HMT is surface-controlled [36].