Electrochimica Acta 227 (2017) 345–356

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A novel Pb-poly aminophenol glassy carbon electrode for determination of tetracycline by adsorptive differential pulse cathodic stripping voltammetry

Zeinab Rajab Dizavandi, Alireza Aliakbar*, Mehdi Sheykhan

Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box 4193833697 Rasht, Iran

ARTICLE INFO

Article history:
Received 6 November 2016
Received in revised form 19 December 2016
Accepted 26 December 2016
Available online 28 December 2016

Keywords:
Tetracycline
Modified electrode
Polymeric electrode
Adsorptive stripping voltammetry

ABSTRACT

A novel type of Pb-polyaminophenol filmed glassy carbon electrode for adsorptive cathodic stripping analysis of trace amounts of tetracycline was developed. The Pb-polymer electrode was fabricated in situ by simultaneous electrodeposition of Pb and cathodic electropolymerization of 4-nitrophenol in a sodium acetate medium at −1.5 volt. The prepared Pb-polymeric film was characterized by CV, FT-IR (ATR), H-NMR, SEM, EDS and a suitable mechanism for the electrode-reaction was proposed. The outputs of some experiments showed that tetracycline can be adsorbed on the surface of this Pb-polymer filmed electrode in an open circuit condition. Therefore it was used in adsorptive cathodic stripping analysis of tetracycline. The response of the electrode was enhanced in the presence of cetyltrimethylammonium bromide. Some parameters affecting the performance of the electrode were studied and optimized. The response of the electrode was linear in the range of $5 \times 10^{-8} - 1 \times 10^{-5}$ mol L^{-1} of tetracycline with a correlation coefficient of 0.9981. The relative standard deviation for 5×10^{-7} mol L^{-1} of tetracycline was 1.8% (n = 5). The L.O.D and L.O.Q were 4×10^{-9} and 1.3×10^{-8} mol L^{-1} of tetracycline, respectively. The introduced electrode was used for determination of tetracycline residues in some samples and the obtained results were in good agreement with the results of HPLC.

1. Introduction

Allen J. Bard defined the chemically modified electrode (CME) as a purposeful modification of the conductive substrate in order to produce an electrode suited to a particulate function and whose properties are different from those of the unmodified substrate [1]. Larry Falkner looks at CMEs as a kind of art. He wrote “this lovely assembly is not a technological object, but it is an artistic one for a scientific clientele. And it shows beautifully the level of control of both structure and function that can be imposed on an electrode” [2]. To achieve these goals, electrochemical techniques based on the nature of the modifying process [3] have been introduced for fabrication of CMEs. Strong and irreversible adsorption [4–6], covalent attachment of a monolayer of different species to the electrode surface [7,8] and coating by polymer films are some options [9–11]. Polymer coating on the electrode surface is a fascinating branch of CME fabrication. Several different types of polymers have been used to modify the electrode surface [12]. Electroactive polymers [13,14], ionic exchange polymers [15,16], size exclusion polymers [17,18], coordinative polymers [19] and conductive polymers [20–23] have been employed extensively for this purpose. One of the main problems in utilizing a polymer for fabrication of CMEs is weak adherence and poor coverage of electrode surface. This weakness can be overcome by simultaneous co-electrodeposition of metal and polymer. This technique helps in the formation of a uniform film on the electrode surface and creates a scaffold for mechanical support of the filmed electrode [24–26]. Utilization of CMEs for measurement of trace species, particularly when combined with preconcentration techniques of stripping voltammetry, is a unique feature of electrochemical methods in analytical chemistry [12].

Surface phenomena are a basic subject in electrochemistry [27]. Although the nature of the electrode surface and the region of the solution in its immediate vicinity play an important role in surface phenomena, there are a sufficient variety of anonymous effects which can be related to surface phenomena [27]. The electrode composition, chiral electrodes, orientation of substrate at the electrode surface, electron transmission by adsorbed aromatic compounds and etc. are the subjects which affect the surface

* Corresponding author.
E-mail addresses: aliakbar@guilan.ac.ir, mehdi_ashournia@yahoo.com (A. Aliakbar).

http://dx.doi.org/10.1016/j.electacta.2016.12.167
0013-4686/

phenomena. Orientation of the substrate at the electrode surface is the most important in surface phenomena. In this respect, surface active agents play an important role. These compounds improve not only sensitivity, but also selectivity of electrochemical methods as they help in increasing the solubility of organic compounds and provide specific orientation to the analyte molecule at the electrode interface [28–31]. This surface phenomenon is due to the unique molecular structure of the surfactant, and there are many published papers dealing with utilization of these kinds of reagents to improve the surface properties of electrodes in electrochemistry.

Among new kinds of environmental contaminants, tetracyclines (TCs) are referred to as modern pollutants, since they have been found in soil and aquatic media [32] and also as residuals in various foods [33]. These compounds are routinely used for human therapy and in the livestock industry [34,35] due to their antibacterial activity against Gram positive and Gram negative microorganisms [36]. Because of their relatively low cost, they are also used as a food additive to enhance the growth rate of farm animals [37]. Therefore TCs are released in to the environment by water discharges, excretion and urine of animal farms as unmodified parent compounds [38,39]. Therefore, sensitive analytical methods are needed for monitoring residual amounts of TC in foods and their release into the environment. Numerous analytical methods have been reported for the determination of tetracycline in various samples, including high performance liquid chromatography (HPLC) [40], capillary electrophoresis (CE) [41], microbiological assay [42], spectrophotometric methods [43] and electrochemical methods [44–47].

In this work a new Pb-polymer filmed glassy carbon electrode for the adsorptive differential pulse cathodic stripping voltammetric (Ads-DPCSV) determination of micro amounts of TC was developed. The polymeric film was characterized by CV, FT-IR (ATR), H-NMR, SEM and EDS. A suitable mechanism for electrode polymerization was offered. The most important point of the prepared electrode is its stability during analysis and repetitive reusability without any considerable change in its performance. Electrode sensitivity was enhanced in the presence of cetyltrimethyamunim bromide.

2. Experimental

2.1. Materials and reagents

All the used chemicals were of analytical grade. 4-nitrophenol, cetyltrimethyamunim bromide (CTAB > 97%), sodium acetate trihydrate, phosphoric acid, sodium hydroxide and methanol were purchased from Merck (Darmstadt, Germany). Tetracycline (TC > 98%) was obtained from Sigma Aldrich (USA). All solutions were prepared using double distilled water with a specific conductance of 2 μS cm^{-1}. Tetracycline standard stock solution was prepared by dissolving TC in methanol (5 mg mL^{-1}). This solution was kept in the dark at 5 °C. The lower concentrations of TC were made daily by stepwise dilution of stock solution in water. All buffer solutions

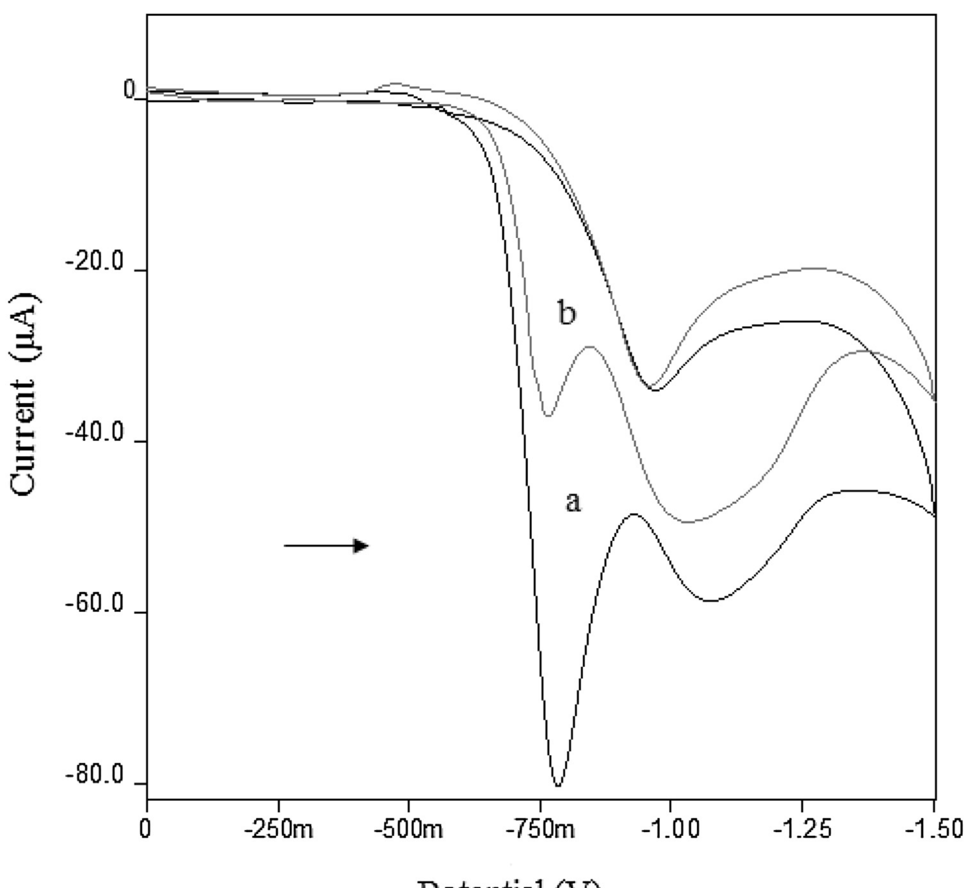

Fig. 1. Cyclic voltamogram of 4-nitrophenol (0.5 mmol L^{-1}) in presence of pb^{2+}(0.15 mmol L^{-1}) in sodium acetate medium (0.05 mol L^{-1}). first cycle (a) second cycle (b), scan rate = 100 mV s$^{-1.}$