Available online at www.sciencedirect.com

ScienceDirect

Sensors and Actuators B 123 (2007) 902–908

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

Development of a voltammetric sensor for chromium(VI) determination in wastewater sample

Márcio F. Bergamini, Daniela P. dos Santos, Maria Valnice Boldrin Zanoni [*]

Departamento de Química Analítica, Instituto de Química-UNESP, C.P. 355, 14801-970 Araraquara, SP, Brazil

Received 8 August 2006; received in revised form 23 October 2006; accepted 26 October 2006
Available online 11 December 2006

Abstract

Screen-printed carbon electrode (SPCE) modified with poly-L-histidine film can be successfully applied for chromium(VI) determination based on its pre-concentration. Optimum adherence and stability of the poly-L-histidine film was obtained by direct addition of PH solution 1% (w/v) on the electrode surface, followed by heating at 80 °C during 5 min. Linear response range, sensitivity and limit of detection were 0.1–150 μmol L^{-1}, 1.13 μA μmol L^{-1} and 0.046 μmol L^{-1}. The repeatability of the proposed sensor, evaluated in terms of relative standard deviation, was measured as 3.2% for 10 experiments in 40 μmol L^{-1} using the same electrode and 4.0% using screen-printed electrode as disposable sensor, respectively. The voltammetric sensor was applied to determination of Cr(VI) and indirect determination of Cr(III) in wastewater samples previously treated by a leather dyeing industry and the average recovery for these samples was around 97%.

Keywords: Chromium(VI); Stripping analysis; Screen-printed modified electrode; Poly-L-histidine

1. Introduction

The development of simple electrochemical sensors based on the use of chemical modified electrodes has been showing larger progress in the electroanalytical chemistry in the last years [1–6]. Screen-printing techniques applied for the fabrication of electrodes have been used to construct versatile devices with great success. The main advantage is associated with their modest cost, potential portability, simplicity of operation, reliability, and the small instrumental arrangement. In addition, the roughness surface of screen-printed carbon electrodes (SPCEs) have also shown to be an excellent approach to modify its surface with specific reagents providing more sensitive methods [7].

Chemically modified electrodes with poly-L-histidine (Fig. 1) have been described in the literature with many applications [8–11]. Histidine has an imidazole group ($pK_a = 6$) that can be adsorbed on the surface of metal silver by covalent bond and employed to facilitate both the reduction and oxidation of myoglobin and cytochrome *c* [8] and also to catalyze the reduction of NAD^+[9]. The modification of glassy carbon and platinum with films of poly-L-histidine have been investigated by electrochemical oxidation of the aminoacid and the yielding electrode have presented potential applicability in electrocatalytic oxidation of ascorbic acid [10] and alternative biocatalyst for L-ascorbate sensor [11].

The extensive use of chromium in the metallurgic, leather tanning, electroplating, lumber, electricity generating, and other industries have promoted enormous ecological impact in numerous sites that are being contaminated by chromium [12–15]. Among them, attention concerning the possible hazards arising from the use of chromium(VI) is evident, especially in leather industry, where chromium is currently used. Although both Cr(III) and Cr(VI) are the most abundant oxidation states, their significant difference in toxicological action leads to the high control of Cr(IV) that is around 1000 times more toxic than the trivalent one [13]. In agreement with Brazilian Legislation (CONAMA) the maximum value permitted to chromium in industrial effluent is 0.5 mg L^{-1} [16]. Therefore, methods for differentiation and quantification of these species are very important in water analysis.

Several analytical methods for Cr(VI) are described, such as atomic spectroscopy [17–19], spectrophotometry [20,21], fluorimetry [22], and chemiluminescence [23]. Electroanalytical methods have also being investigated, which play

---

[*] Corresponding author. Tel.: +55 16 33016619; fax: +55 16 33227932.
E-mail address: boldrinv@iq.unesp.br (M.V.B. Zanoni).

0925-4005/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2006.10.062

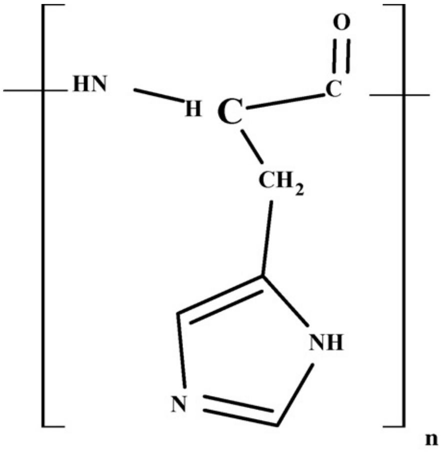

Fig. 1. Poly-L-histidine molecular structure.

a very important role in Cr(VI) redox speciation [24–29]. Cr(VI) has been pre-concentrated and determined on mercury [24] and chemically modified solid electrodes by 4-(mercaptoethil)pyridinium [25], adenine complex [27], quaternary ammonium salts [29] and determined by direct reduction on gold, glassy carbon and boron-doped diamond electrodes [28]. In spite of the most of these methods to present good sensitivity and repeatability its robustness in surface waters is limited. On the other hand, the use of disposable screen-printed electrode modified by poly-L-histidine could be an excellent alternative for rapid determination of chromium(VI).

Therefore, the aim of the present work was to develop a disposable sensor for chromium(VI) using a screen-printed electrode modified by poly-L-histidine (PH) films. The device was applied to direct determination of chromium(VI) and indirect evaluation of chromium(III) in treated wastewater collected from a Brazilian leather industry, where presumably the metal could be pre-concentrated by strong interaction with the imidazole group of the PH film.

2. Experimental

2.1. Apparatus

Voltammetric measurements were carried out with an μAUTOLAB Type III (EcoChemie) controlled by software GPES 4.9 for data acquisition and experimental control. The measurements were performed in a conventional electrochemical cell of 10.0 mL, where the screen-printed carbon electrode was coupled. All pH measurements were made using a Metrohm E500 pH meter with a Metrohm EA 121 glass electrode, which had been calibrated previously.

2.2. Reagents and solutions

All the solutions were prepared with purified water in a Millipore Milli-Q system (Millipoore). All the chemicals were of analytical grade and used without further purification. The supporting electrolyte used for most of experiments was a 0.10 mol L^{-1} acetate buffer solution. Phosphate buffer and KCl/HCl solution were also used for neutral pH (pH 7.0, 7.5) and acidic conditions (pH 3.0, 3.5 and 2.0), respectively. Stock solutions containing 5.0×10^{-3} mol L^{-1} of $Cr_2O_7^{2-}$ were prepared daily by dissolving an appropriate amount of dichromate potassium (Aldrich) in 10 mL of the supporting electrolyte.

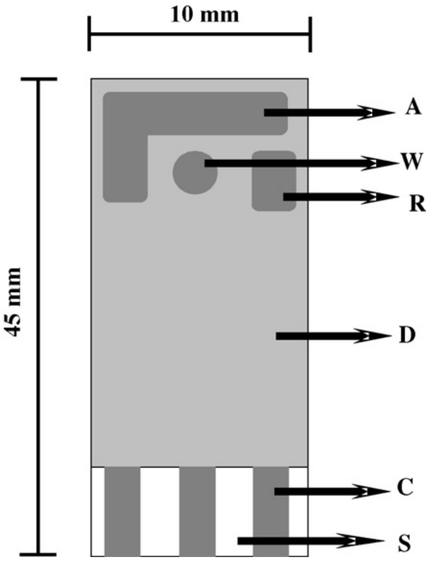

Fig. 2. Screen-printed carbon electrode used in the voltammetric measurements. Ceramic substrate (S), dielectric protection layer (D), electric contact (C), working (W), reference (R) and auxiliary (A) electrodes.

2.3. Screen-printed modified electrode preparation

The bare screen-printed electrode (Oxley Developments, UK; Fig. 2) is based on an alumina ceramic base 45 mm long, 10 mm wide and 0.8 mm of thick, where a working, reference and the auxiliary electrodes are exposed onto the surface. All the electrodes are made by carbon conducting ink. A contacting field works in the end, which is connected with the active part of each electrode by internal carbon conducting parts, covered by a dielectric protection layer. The sensor was connected with a cable to the potentiostat. Some experiments were carried out using the screen-printed carbon electrode with the carbon ink pseudo reference substituted by an external reference electrode of Ag/AgCl (3 mol L^{-1} KCl) as assigned in the text.

The screen-printed carbon electrode modified with poly-L-histidine (PH) was prepared by using three different procedures:

Procedure 1 (SPCE/PH): An aliquot of 10 μL of an aqueous poly-L-histidine solution (1%, m/v) was placed on the screen-printed carbon electrode surface and then submitted to heating during 5 min at 80 °C, where the transformation of the PH structure conformation could improve its adherence onto the electrode surface [30].

Procedure 2 (SPCE/Glu-PH): The PH and glutaraldehyde were prepared using mixture of PH (1%, w/v) and glutaraldehyde (0.05%, w/v) solutions [31]. Aliquot of the 1 μL of glutaraldehyde solution was placed on the screen-printed electrode surface where it was added subsequently aliquot of 9 μL of PH