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Photoelectrochemical determination of inorganic mercury in aqueous solutions

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ABSTRACT

An analytical method using an optical probe in a photoelectrochemical cell for the sensitive and selective determination of aqueous Hg^{2+} is presented. A previously synthesized Hg^{2+} selective chemosensor, proven to be Hg^{2+} sensitive up to $2\,\mu g\,L^{-1}$, has been immobilized onto indium tin oxide (ITO) electrodes in a composite form with polyaniline. The coated ITO electrode was placed in a photoelectrochemical cell under closed circuit conditions in which the optical recognition of the chemosensor was converted to a measurable signal. A composite of the fluorescent chemosensor, Rhodamine 6G derivative (RS), and polyaniline (PANI) was immobilized on ITO glass plates and subjected to photovoltage measurements in the absence and presence of Hg^{2+}. The optical responses of the coated electrode were used to determine the sensitivity and selectivity of the immobilized sensor to Hg^{2+} in the presence of background ions. The optical response of the PANI-dye coated electrode increased linearly with increasing Hg^{2+} concentration in the range 10–150 $\mu g\,L^{-1}$, with a detection limit of $6\,\mu g\,L^{-1}$.

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1. Introduction

Mercury (Hg) is a widespread and highly toxic pollutant. Although industrial usage of Hg has been reduced and is now limited by legislation, contamination still occurs through natural and anthropogenic sources [1]. Hg pollution related diseases are symptomised by serious sensory, motor and cognitive disorders [2]. It is due to these considerable health risks that the Word Health Organisation (WHO) has set the guideline value for inorganic mercury in drinking water at $6\,\mu g\,L^{-1}$ [3]. Therefore analytical methods for the sensitive and selective determination of aqueous Hg^{2+} are crucial for environmental monitoring of all water resources. The most commonly used methods for inorganic Hg (Hg^{2+}) determination are cold vapour atomic absorption spectrometry (CVAAS) [4], cold vapour atomic fluorescence spectrometry (CVAFS) [5], inductively coupled plasma atomic emission spectrometry (ICP-AES) [6], X-ray fluorescence spectrometry [7], anodic stripping voltammetry [8] and inductively coupled plasma mass spectrometry (ICP-MS) [9]. These methods have been proven to be sensitive and accurate, but require tedious sample pre-treatment, sophisticated performance and expensive equipment, thereby making them unsuitable for on-site screening or on-line analyses.

Fluorescence is a powerful optical analytical technique, and when combined with an Hg^{2+} selective molecule, leads to fluorescent-based probes that are capable of detecting extremely low Hg^{2+} concentrations [10,11]. Many fluorescent chemosensors, based on small molecules for Hg^{2+} determination, have been reported previously [12–17]. For photoelectrochemical detection the optical probe will convert the binding process with a selected pollutant into a photovoltage response. When selecting a suitable chemosensor, the following parameters were considered; the sensitivity, class of fluorescence, pH sensitivity, reversibility and selectivity for Hg^{2+} in the presence of background ions. A fluorescent enhancement upon ligating was also preferred, as it was far more sensitive than a fluorescent quenching response [18,19] and reduced the amount of false positive measurements. The Hg^{2+} selective sensor selected for the photoelectrochemical detector is a Rhodamine 6G-based derivative (RS) synthesized by Wu et al. [22]. The RS sensor is highly selective (50-fold) towards Hg^{2+} in the presence of background cations and is capable of detecting Hg^{2+} concentrations as low as $2\,\mu g\,L^{-1}$. RS is a suitable bis-chelating Schiff-based receptor for Hg^{2+} in which the nitrogen affinity of Hg^{2+} is combined with the amide deprotonation ability of Hg^{2+}. The association constant, K_a, for the 2:1 binding process with Hg^{2+} is $2.4 \times 10^9\,M^{-2}$. The RS dye is reported to be pH insensitive in the pH range 5–10 [22]. The ring opened RS dye has a very distinct pink colour and can serve as a visual indicator for the presence of Hg^{2+} and has a high quantum yield of 0.42. In the photoelectrochemical cell used for Hg^{2+} detection, the immobilized fluorescent probe

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facilitates the detection element, which is converted to the electron transfer and a measurable signal.

The method of photoelectrochemical detection of Hg^{2+} was based on photoelectrochemical cells (PECs) which extract electrical energy from light. The principle of the PEC energy conversion is the photo generation of charge carriers (electrons and electropositive holes) which upon absorption of a photon leads to separation of the charge carriers to conductive contacts that will transmit the electricity (photovoltaic effect). Under illumination, Rhodamine 6G (R.6G) electrons are excited to the triplet state from where R.6G radicals are generated [20–22]. Depending on the electron donating or accepting nature of the solvent/environment of the R.6G radicals, electron transfer would occur. When activated, the spiro ring of Hg^{2+} selective Rhodamine 6G hydrozone derivative sensor (RS) was opened to establish a delocalized xanthene moiety which was identical to that of R.6G [23]. It was therefore proposed that in the presence of Hg^{2+}, photon generation of the activated RS–Hg^{2+} would occur and in the presence of a charge separator, an electron current could be achieved.

The conductive properties of polyaniline (PANI) are well known [24,25]. In the proposed photoelectrochemical detection, PANI would facilitate the charge separation to produce the electron current. The photoelectrochemical detection of Hg^{2+} was achieved by the conversion of a photon excitation in the photo-sensitive complex, into an electron transport measured by a voltmeter. The ITO coated electrodes can be designed in a portable photoelectrochemical cell and be used for instant pre-screening of Hg^{2+} in water resources.

2. Experimental

2.1. Materials and reagents

Indium tin oxide (ITO) glass plates had a surface resistivity between 8 and 12 $\Omega\,sq^{-1}$ and were purchased from Aldrich, South Africa. All chemicals and organic solvents used were of Analytical Reagent grade from Sigma Aldrich, South Africa. All aqueous solutions were prepared with ultra pure water obtained using a Milli-Q RG purification system.

2.2. Instrumentation

Surface imaging of the coated electrodes was performed with a Leo 1430VP Scanning Electron Microscope and surface thickness was determined with a Veeco DEKTAK 6 M Surface Profiler. The RS dye was characterised with C^{13} and H^1 NMR, fluorescent emission and UV–vis absorbance. C^{13} and H^1 NMR spectra of RS were determined in DMSO-d_6 with a 400 MHz Oxford instrument. The spectrometric data of RS and RS–Hg^{2+} was determined with a Cintra Double beam UV–vis spectrometer and a Perkin Elmer L550B in 1:1 aqueous dimethylformamide (DMF) solutions.

Electrochemical measurements were performed on an Epsilon BAS potentiostat, with EpsilonEC 2000-XP software. A three-electrode cell was used with the dye coated ITO plate as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The voltammograms were measured in 0.05 M phosphate buffer (pH 7.5) containing 1 mM RS with and without 100 $\mu g\,L^{-1}$ $HgCl_2$, at 100 $mV\,s^{-1}$ scan rate. The flat band potential for the ITO/PANI–RS electrode was determined for applied potentials between 600 and −600 mV in 0.1 mM $K_3Fe(CN)_6$ and 0.05 M KNO_3 under photo illumination. The same three-electrode setup was used for the photoelectrochemical evaluation of the various coated electrodes. For the photoelectrochemical setup the electrolyte was 0.05 M KNO_3 and varying concentrations of $HgCl_2$. An Elmo Omnigraphic 253 slide projector was used as a light source. The Tungsten Halogen lamp emitted 0.86 $mW\,cm^{-2}$ at the point of absorption by the electrode. The collimated beam was isolated in a steel casing to eliminate background light effects. The light was pulsed at 2 s intervals and the photovoltage signals were recorded by means of a DAX data acquisition system.

2.3. Procedure for electrode preparation

Rhodamine 6G hydrozone was synthesized following a published procedure [26] in which the pH of the sensor was modified to increase the yield of the reaction. The Rhodamine 6G hydrozone derivative sensor (RS) was synthesized following the method of Wu et al. [23]. The RS product was purified with a 20 cm preparative column over a silica gel (Merck) 230–400 mesh, 60 Å pore size, and an n-hexane: ethylacetate 1:1 mixture was used as the eluent. The product was collected in the first fraction which was a white product after evaporation. The product structure was confirmed with H^1 and C^{13} NMR [23]. ITO glass plates were cut into approximately 8 mm × 12 mm segments and were sonicated for 10 min in water, ethanol and acetone. PANI was prepared according to standard chemical oxidation polymerization methods [27]. 40 μL of a composite solution of 5 mg PANI and 5 mg RS in 5 mL dimethyl sulfoxide (DMSO) was drop-coated onto the ITO surface and dried at room temperature for 2–5 days.

3. Results and discussion

3.1. Surface morphology

The DMSO/RS drop-coatings dried on the electrode surfaces to form cube-like crystals. The images of the crystals on the electrode surface are shown in Fig. 1. The crystal-composite did not dissolve in water and was bound to the electrode surface. The crystals were cube-like and their size was determined by the solvent evaporation period. After 5 days of drying at 25 °C, the cube lengths were approximately 15 μm. The formation of crystals was favourable as it increased the surface roughness and therefore active surface area on which the RS–Hg^{2+} interaction can take place as well as increased contact with the PANI charge separator. A metallic deposition was observed on the crystal surfaces after analysis of Hg^{2+} samples. The deposition was irreversible and was most likely Hg^0 due to the presence of excess of Hg^{2+} in the evaluated samples. The thickness of the composite layer would determine the distance the electron needed to be transported from the excited molecule to the back contact. The surface image profile in Fig. 2 shows a very rough particulate layer on the ITO surface. Due to the rough non-uniform distribution of the crystal composite, the surface photoactivity would therefore always be taken as an average over a 6 mm × 10 mm electrode surface area. The average film thickness is 1.62 μm with a single 40 μL composite coating.

3.2. Spectrophotometric properties

For the RS–Hg^{2+} complex, the absorbance and emission peak were observed at 536 nm and 558 nm respectively (compared to 538 nm and 560 nm by Wu et al. [23]) confirming the optical properties of the RS–Hg^{2+} complex. For the Hg^{2+} photoelectrochemical detector to successfully convert photo-activity to an electron transport, the conversion needed to be energetically favourable. The RS–Hg^{2+} absorption at 536 nm converted to a 2.35 eV energy band gap with the Planck equation. For PANI it was assumed that the emeraldine form would be the photo-conductive part of the PANI layer as the leucoemeraldine and pernigraniline forms behave more like insulators [28]. The flat band potential for the emeraldine polyaniline was reported to be 0.63 V (*vs* SCE), as calculated with

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