Electrochemical Detection and Removal of Mercury (II) at DNA Modified Carbon Paste Electrode

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**Abstract**

Herein, we report a simple and inexpensive way for the fabrication of a microelectrode, DNA modified carbon paste electrode (DNA-CPE). DNA is deposited onto carbon paste electrode surface by self-assembled monolayers. The electrochemical behaviour of DNA-CPE’s was studied by cyclic voltammetry (SWV) tests. The recorded CV’s showed two redox peaks simultaneously at E oxidation=0.3 V and E reduction=-0.2 V. The recorded SWV curves at DNA-CPE have shown great efficiency in detecting mercury (II) at different concentrations.

**Keywords:** DNA; Modified electrodes; Mercury; SWV; Cyclic voltammetry

**Introduction**

Mercury is the only metal that can be found in the liquid state at room temperature; it enters the environment through not only coal burning but also through mining or industrial wastes. Mercury has the power to form amalgams with several metals, such as silver, it has been widely used in dentistry; but the new legislation prohibited its use because of its toxic effects [1,2]. The most commonly used methods are atomic absorption [3], inductively coupled plasma mass spectrometry [4] and cold vapor atomic fluorescence spectrometry [5].

The electrochemical methods have proved highly effective in detecting mercury, with many advantages, such as, simplicity of implementation and inexpensive. The use of mixed assembled mono layers of DNA has received an increasing attention for the determination of metal ions [6]. In this study, we have prepared a carbon paste electrode on which we have deposited by self-assembly a DNA film. This prepared electrode was used, in conjunction with electrochemical methods, as CV’s and SWV, for the removal and the detection of mercury (II). The DNA-CPE is successively exploited the favorable mechanical and electrochemical properties of carbon paste electrode, and the high flexibility of DNA structure to chelate mercury.

**Experimental**

**Reagents and chemicals**

All the chemicals used in this work, are of high quality. The carbon graphite was purchased from Aldrich, and was used in its state without modification. HgCl$_2$ was obtained from Merck chemicals. Deionised water was used to prepare all solution. The DNA used in this work is taken from quail blood, according to the protocol below:

- 5 l of blood taken from the axillary vein is poured into an Eppendorf containing 500 μl of danazol,
- The solution is stirred for 5 min by vortexing and centrifuged at 6000 rpm/5 min,
- The supernatant is removed and then 400 μl of isopropanol is added to the residue remaining in the Eppendorf,
- The mixture was vortexed and centrifuged at 6000 rpm/5 min,
- The supernatant was removed and 500 μl of pure water was added to suspend the DNA.

**Apparatus**

The electrochemical studies were performed with a potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by a general purpose electrochemical systems data processing software (voltlab master 4 software). The three electrode system consisted of a modified paste electrode as the working electrode, a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

**Electrode preparation**

The DNA-modified carbon paste electrode was prepared by thoroughly hand-mixing of high purity graphite powder (CP), then a portion of the resulting paste was grounded and squeezed into a homemade PTFE cylindrical tube (geometric area 0.1256 cm$^2$) electrode. Inside the tube, the mass was in contact with a bar of carbon, which was in turn connected to an electric wire to complete the measurement circuit. DNA-CPE’s were prepared by immobilizing the DNA system by soaking the preformed carbon paste electrode in a solution containing the DNA solution.

**Results and Discussion**

A carbon paste electrode modified with DNA was carefully washed with distilled water, heated at room temperature and transferred to electrochemical cell containing 0.1 M NaCl electrolyte. Mercury was accumulated at DNE-CPE for 15 min [6]. CV scanning was performed from -2 to 2 V at a scan rate of 100 mV/s.

Figure 1 show the voltammograms recorded, respectively at CPE and DNA-CPE, in 0.1 M NaCl. Two reduction peaks were observed at DNA-CPE towards the negative sweep direction, the first one around
-0.12 V and the second approximately 0.1 V versus SCE; these peaks can correspond to internal reductions of the macro-DNA molecule.

The peak P2 corresponds to the phenomenon of oxidation of Hg and of salting out of Hg2+, by following the mechanism below:

\[ \text{[Hg}^{2+} \text{...DNA-CPE]}_{\text{ads}} + 2e^- \rightarrow \text{[Hg}^{0} \text{...DNA-CPE]}_{\text{ads}} \]

Mercury (II) was pre-concentrated from the solution into the DNA-modified CPE at open circuit potential, then the CV’s was used to reduce Hg2+ (Figure 3-P1), According to the following reaction:

\[ \text{[Hg}^{2+} \text{...DNA-CPE]}_{\text{ads}} + 2e^- \rightarrow \text{[Hg}^{0} \text{...DNA-CPE]}_{\text{ads}} \]
The effect of the scanning rate has been studied, and we find that the anodic and cathode peak current increase linearly for scanning rate value variant between 40 and 140 mV/s (Figures 6 and 7), suggesting that the electrons transfers for mercury at the DNA-CPE is adsorption controlled reaction [7].

The morphology of the prepared electrode surfaces, CPE (a), DNA-CPE (b) and DNA-CPE after accumulating in mercury solution (c), was studied by optical microscopy, (Figure 8). We can see that the DNA film forms a thin layer that covers all carbon surfaces. Mercury adsorbed into DNA film forms a porous structure [8].