

Determination of different metals in wastewater using new microsensors based on diamond doped with boron (BDD)

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ABSTRACT

The electrodes used in our analyzes are electrodes based on microcrystalline boron-doped diamond (BDD), micromachined by femtosecond laser. The electrochemical performance of the new BDD microelectrodes were first evaluated by the method of differential pulse anodic stripping voltammetric (DPASV) for the simultaneous determination at nanomolar level of four heavy metal ions in water: Cd (II), Ni (II), Pb (II), Hg (II) and then by square wave voltammetric method (SWV) for the determination of uranium. With these approaches are obtained low detection limits 0.4, 6.8, 5.5, and 2.3 nM, respectively for Cd (II), Ni (II) Pb (II) and Hg (II) and 0.5 mg L⁻¹ for uranium, less than that of the other sensors described in the literature.

Keywords: Boron doped diamond (BDD), wastewater, uranium, anodic stripping voltammetric impulse (DPASV), square wave voltammetric (SWV), heavy metal ions.

1 INTRODUCTION

The determination of heavy metals by electrochemical presents a significant growth in recent years [1]. Simultaneous detection and identification of these metals in waste waters are still difficult due to their complexation [2]. Nowadays, pollution with heavy metals such as lead and cadmium, and even uranium is one of the most serious environmental and health problems. Monitoring levels of lead ions in drinking water is essential for human health

and safety, [3]. There are many health problems associated with exposure to high levels of lead ions or cadmium [4], due to their tendency to accumulate in the body, [5]. To this end, several methods have been developed to characterize water discharges, such as chromatography and spectrometry (liquid chromatography (HPLC) coupled with mass spectrometry (HPLC-MS), Atomic absorption spectrometry (AAS) or inductively coupled plasma spectrometry (ICP-MS) and X-ray fluorescence. These techniques are very selective and reliable, but they require expensive instruments and sample pretreatment, in addition, they must be handled by experts. To overcome these problems, sophisticated materials and miniaturized and cheaper it was invented [2]. In addition, BDD electrodes are widely used in electroanalytical and environmental applications because of their analytical properties, low noise and a wide window of current-potential resistance in aggressive environments [6].

These new micro-electrochemical cells, micro-machined by femtosecond laser were used for the detection of heavy metals namely cadmium (Cd), lead (Pb), Nickel (Ni) and mercury (Hg) [5] and Uranium (U). In this work, the analytical characteristics of the electrochemical microcell micromachined by femtosecond laser will be related to determination of cadmium, mercury, nickel, lead and uranium using voltammetric techniques DPASV and SWV.

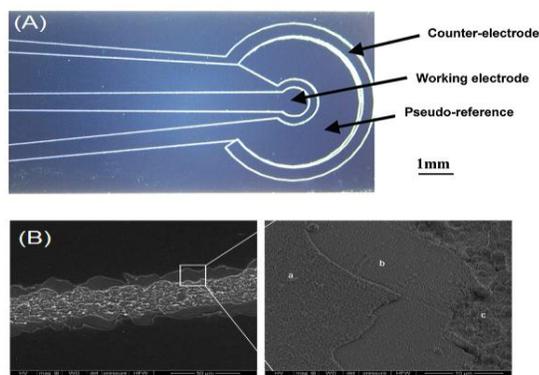
2 EXPERIMENTS AND RESULTS

2.1 Reagents

Cadmium standard solution prepared in 2% nitric acid, 1000 mg/L, standard solution of mercury for environmental analysis, prepared in 9.4% nitric acid at 995 mg/L, standard solution of nickel prepared in 0.9% nitric acid, 1000 mg/L, and lead standard solution prepared in 0.9% nitric acid, at 9954 mg/L, uranium atomic absorption standard solution in 1.2% nitric acid, at 1004 mg/L were provided by SIGMA ADRICH. 6-O-palmitoyl-L-ascorbic (PAA) was purchased from Fluka. Solutions of 0.1M boric acid (H_3BO_3) were prepared by dissolving 3.0915 g of boric acid (Chimie-plus Laboratoires) in 1.0L DDW and pH adjustment to desired values was made with 0.1M HCl. (H_2SO_4) concentrated at 95 to 97%, hydrogen peroxide H_2O_2 , concentrated at 30% used for the cleaning of the micro cell, potassium citrate used as buffer, were supplied by Sigma-Aldrich (Saint-Quentin Fallavier, France). Nitric acid (HNO_3) 68%, hydrochloric acid (HCl) 37% were supplied from VWR International (Fontenay-sous-Bois, France).

2.2 Micro-fabrication of BDD Micro Cell

The work focused on the realization of electrochemical microcells composed of a film of 300 nm thick boron-doped microcrystalline diamond to 1000-1300 ppm (BDD deposited on a silicon layer, isolated by two layers of oxide silicon and silicon nitride ($Si/SiO_2/Si_3N_4$) of 0.5 microns thick. Microcells were cut from the wafer BDD by the Company IMPULSION SAS, using a femtosecond laser (5 kHz, 2.5 W, 800 nm, 150 fs), a scanning head, and a set of XYZ movable plates. Design of the structure of BDD microcell, which includes a working electrode, a counter electrode, and a pseudo-reference is represented in scheme 1 A. Femto Laser Micromachined Groove and the different layers deposits are shown in scheme 1 B.

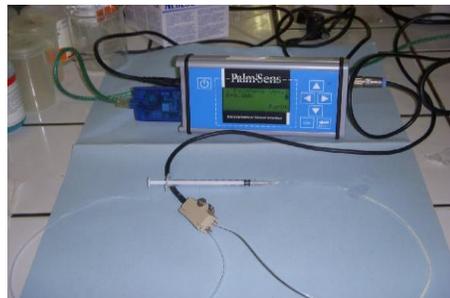


Scheme1: (A). Three electrode micro-cell cut up from the BDD wafer by laser-machining, (B). Femto Laser Micromachined Groove; Right (a) BDD, (b) Silicon Nitride Layers, and (c) Silicon Substrate, On the Groove Edge.

2.3 Electrochemical Measurements

2.3.1 Apparatus

The electrochemical methods were conducted using a potentiostat PalmSens controlled by a computer. The electrochemical cell had a volume of 5 microL. In the other end of the cell, two very thin tubes connected to it (one for injecting the sample and the other for evacuation). The introduction of solutions in the cell were through a syringe with a very fine needle (see Schema2).



Scheme 2: Experimental setup used for our measurements

2.3.2 Measuring Conditions

Before the experiments, BDD micro-cells were cleaned in a mixture of H_2SO_4 (95-97%) / HNO_3 (68%) [V: V = 3:1] at 200-215 °C for 1.5 h, followed by heating at 80°C for 15 min in a mixture of H_2O_2 (30%) / ammonia (25%) [V: V = 1:1], and finally washed with distilled water and ethanol and finally dried with nitrogen. Every day BDD micro-cells should be cleaned and activated with 10 ml Piranha, a mixture of H_2SO_4 (95-97%) / H_2O_2 (30%) [V: V = 7:3] for 5 min. They were then rinsed with distilled water, dried with nitrogen and activated by cyclic voltammetry in 0.1 M HNO_3 . Finally, the DPASV was used primarily for the determination of heavy metals Ni, Pb, Cd, Hg; the method for Uranium square waves has been exploited.

The measurement conditions were optimized for the four metals, first, by varying pH of the 0.1M citrate buffer solution with a solution of 0.1 M HCl; then, instrumental parameters and standard measuring conditions were performed in 0.1 M potassium citrate/HCl buffer, at pH 2; deposition potential and time were -1.7 V and 20 s; start and end potentials were -1.7 and 0.5 V; pulse amplitude and time are were 50 mV and 0.01 s; voltage step, 10 mV and sweep rate 0.05 V/s. The potential of accumulation was usually chosen at -1.7 V and applied for 20 s.

3 RESULTS AND DISCUSSION

3.1 Metal Detection Using DPASV

The calibration curves for the four metals, obtained with the BDD microcell, at pH 2 are presented in Fig.1. The linear model was validated for the four metals, and the detection limits obtained for these four metals are,

respectively, Cd, 0.37nM; Ni, 6.8 nM; Pb, 5.5 nM; and Hg, 2.3 nM. The sensitivity is an important parameter for low detection limits; typically, a higher sensitivity will result in a lower limit of detection. The sensitivities calculated from calibration curves are in decreasing order equal to Pb = 77 mA/M, Ni = 28 mA/M, Cd = 15 mA/M, and Hg = 9.3 mA/M.

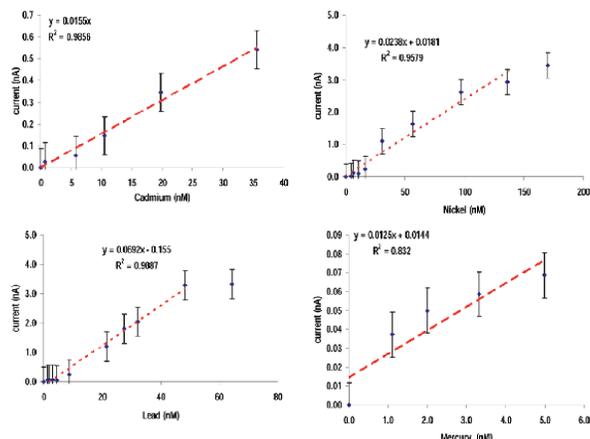


Figure 1: Calibration plots for Cd²⁺, Ni²⁺, Pb²⁺, and Hg²⁺ ions at pH 2 in 0.1 M potassium citrate buffer

To achieve greater detection sensitivity, we used the technique DPASV. This increases the sensitivity by reducing the capacitive current. Standard solutions (Cd²⁺, Ni²⁺, Pb²⁺, Hg²⁺) were prepared to evaluate responses of BDD microcells. These four metals identified as priorities for the Framework Directive (WFD) can be detected simultaneously (see Fig.2).

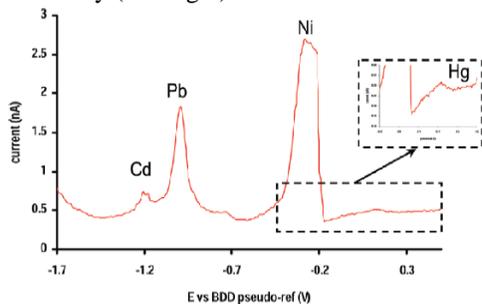
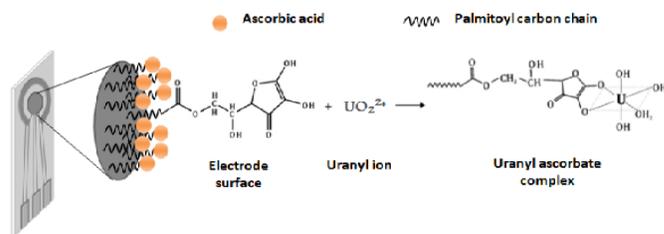


Figure 2: DPASV obtained with the BDD micromachined microcell.

3.2 Uranium detection Using SWV

The uranyl ion, a Lewis acid, has a high affinity for hard donor groups. It is highly oxophilic, and addition of it to ascorbic acid results in the formation of a complex [7]. However the formation of complex depending on concentration of the ligand [8]. (See Scheme 3).



Scheme 3: Tentative view of the interaction of U(VI) ions with immobilized 6-O-palmitoyl-L-ascorbic.

For this detection, we deposited the PAA on BDD electrode by applying cyclic voltammetry in the range -0.8V to +0.8 V, we obtain an electrode modified BDD/ PAA (see Fig.3), after that, and before starting measurements, the electrode was rinsed with distilled water.

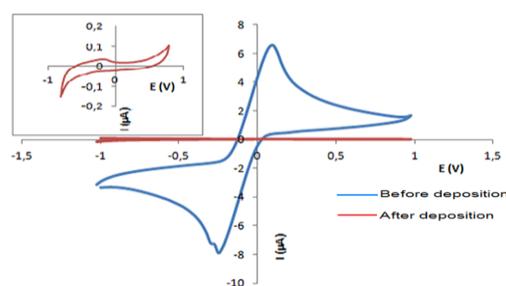


Figure 3: cyclic voltammetry for BDD microcells before and after electrodeposition of 5mM PAA in 10mM Ferri/Ferrocyanide PBS solution (8mM), pH 7.

The SWV parameters, were optimized, potential window, frequency and deposit time were optimized, respectively in the range 0.1 to -0.5 V, 50 Hz, and 20s. A series of experiments were performed in 0.1 M H₃BO₃, covering the pH values 2.85 - 3.4 - 4.30 - 5.67 and 7.18 (see Fig.4). In accordance with previous studies [9,10], the formation of the uranyl-ascorbate complex is favored within the pH range 3.2, 3.9 and under these conditions; it exhibits a maximum stability for about 24 h.

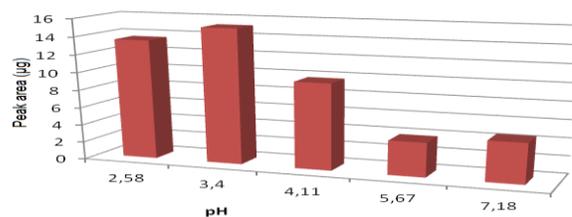


Figure 4: histogram representing effect of the pH of the peak area of uranium.

The most pronounced effect on the intensity of the reduction peak of U(VI) at -0.39 V was observed with respect to the intensity of peak. The uranium peak height increased with increasing values up to $1.62 \mu\text{A}$. The effect of the concentration of PAA was examined over the concentration range 2–5 mM PAA, the optimum concentration was 5mM (see Fig.5).

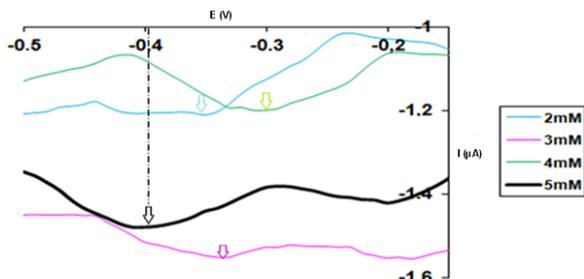


Figure 5: Square wave voltammetry obtained by reduction of U (VI) [$E=-0.39$ V] in $0.1 \text{ M H}_3\text{BO}_3$ at pH 3.4. Electrodeposition in different concentrations of PAA

Uranium U (VI) was detected by SWV after adsorption time of 20s. The reduction peak is obtained at a potential 0.39 V. Calibration curve is obtained in range between $0.5 \mu\text{g/L}$ and $50 \mu\text{g/L}$ with detection limit of $0.5 \mu\text{g/L}$ and a correlation coefficient $r^2 = 0.9978$ (see Fig.6. a). Beyond this range, we observe saturation of the electrode as shown in figure 6 (b).

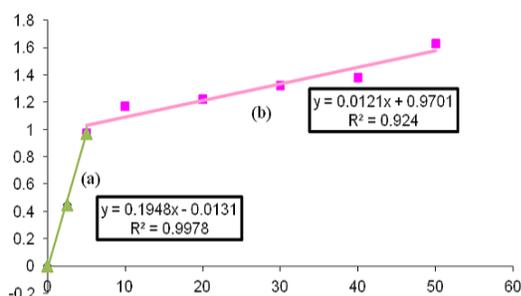


Figure 6: calibration curve corresponding to the response of the BDD/PAA sensors to different concentrations of U (VI).

4 CONCLUSION

The electrochemical microcells were micromachined using a femtosecond laser. We have shown that these microcells not only allow the simultaneous detection of heavy metals in the water to meet the demand of the European Framework Directive on water, but we were able to modify the surface of BDD for the detection of uranium. These microcells can be used for electrochemical analysis not only in water samples from the environmental

applications (natural waters, wastewater and drinking), but also for biological samples. Obviously, some improvements are still possible this microcell: in particular, the potential for accumulation can be optimized, and that they could be inserted in a microfluidic system that should be automated to reduce the accumulation time and increase the sensitivity of the device.

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