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Detection of the neurotoxin, deoxynivalenol, with PANi modified screen-printed electrode

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The polyaniline electrochemical deposited on working electrode of the screen printed electrode has been used for detection of deoxynivalenol (DON), neurotoxin produced by fungi from animal feed. The electrochemical response at DON concentrations from 10^{-9} to 10^{-4}M showed the highst sensitivity around of 10^{-10} M/l measured by cyclic voltammetry. Results highlights that polyaniline is an appropriate mediator making the neurotoxin response at very low concentrations.

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1. Introduction

Sensors continue to have a significant impact in everyday life with applications ranging from food industry, biomedical applications to automotive industry. For each type of analyte there are no universal couple sensing-mediator-electrode and therefore a continuous optimizing and selection of materials combined with micro/nano miniaturization is required. In this respect intensively researches in developing of new sensing materials are underway to create nanosensors that will reduce power consumption, weight and cost [1].

The electrochemical sensors and biosensors even though is one of the oldest research field still continue to draw attention due to new advanced materials for electrodes and sensing elements are developed respectively large interest for applications in food and medicine. The main performances need to be achieved are: fast response, a high sensitivity, low cost and high reliability. In other respect with sensors is to use simple chemical sensing elements with appropriate transducers to detect biological materials instead of biosensors where the sensing element is a biological component often undergoes degradation and limited in repeatability and multiple uses.

Recently on large scale have been developed screen printed electrodes which open multiple alternatives to design simply and low costly electrochemical devices [2]. Also a large series of electroactives and semiconducting polymers where investigated as sensing element due to their specific properties to have redox centers and the response is conducted direct to electrodes through electrons along of their backbones [3].Their combination give rise to a simple concept to design an electrochemical sensors either galvanostatic or amperometric to detect organics and biological analysts, warfare agents up to picomole [4].

Screen-printed electrodes are microminiaturized three -electrode planar electrochemical cells, ready to use either for research and development or for continuous monitoring processes as disposable sensors. In addition a large series of active polymers can be deposited on the working electrode in order to respond to different media as they work as “drop-on sensors”.

To prove this concept has been developed a couple screen-printed electrode- polyaniline (PANi) of the neurotoxin detection. PANi was direct electrodeposited on the working electrode and tested by cyclovoltammetry (CV) at different concentrations (10^{-9}-10^{-4}M) for neurotoxins in buffer solution. The chosen neurotoxin is Deoxynivalenol (DON) also known as Vomitoxin, a mycotoxin released by *Fusarium sp.* which leave and develop in animal feed respective on cereals. DON has important impact in food due to its biochemical action which consists of protein synthesis inhibition at ribosome level or by inhibiting the cell division, especially at children [5]. U.S. Food and Drug Administration have settled the restriction of Vomitoxin at a level of 1ppm. In consequence a simple and reliable chemosensor is required as alternative to analytical methods which take long time and are costly [6].

2. Experimental

2.1 Materials

Monomer: aniline sulfate monohydrate, Alfa Aesar, chemical grade for synthesis

Screen printed electrode (SPE): model DS220 in planar geometry with working and auxiliary electrod, Au; respective Ag/AgCl reference electrod (source: Drop Sense, USA)

Toxin: deoxynivalenol (DON), with different concentrations (from 10^{-9} to 10^{-4}), prepared in phosphate buffer solution at neutral pH by National Research-Development for Biology and Animal Nutrition Institute, Bucharest-Balotesti.

Other: bidistilled water, milipore filters.

2.2 Preparation of chemosensor with PANi

Polyaniline was electrochemical deposited direct on SPE, only on working electrode using a teflon mask cover. Electrolyte: 25 ml aqueous solution of 0.2M aniline sulphate that contained 1.42 g aniline sulphate monomer in 25ml distilled water adjusted to pH=2.2. The electrochemical deposition was performed on working electrode SPE-DS220 by cyclic voltammetry with VoltaLab 4.0 Potentiostatic (from Radiometer Analytical) in a three-electrode cell with reference electrode Ag/AgCl (XR310) and auxiliary electrode, Pt (XM140). A number of 10 cyclic voltammograms (CV) was performed for electrodeposition at RT and scanning rate of 100mV/s in the range -1V to 0.8 V.

SPE coated with PANi on working electrode (SPE-PANi) was washed, dried with nitrogen and kept in normal condition.

2.3 The electrochemical response for SPE-PANi at toxin

SPE –PANi was connected to Voltalab 40 in the usual three electrodes configuration. Being a planar geometry SPE was arranged in horizontal position and the buffer solution with toxin was dripping to cover the active area (drop on sensing method). DON drops in average of 10-15 microliter work as electrolyte in this arrangement and CVs are registered in the range of -1.2-1.2 V at 100 mV/s. The response at oxidation/reduction and sensivity was analyzed related to the concentration of the toxin.

3. Results and discussions

PANi electrodeposited by CV from aniline sulfate is shown in figure 1. Two peaks assigned for oxidation (0.464 V) and reduction (0.215 V) are well defined in the electropolymerizatin PANi of anilinium sulfate. The second reduction peak at -0.65 V corresponds is assigned to the gold response. The anodic current for oxidation increase with number of cycles in the deposition time while the reduction peak remain approximately constant. That shows the electropolymeriztion follow an oxidative route by anilinium sulfate cation. At the end of 15 cycles the density current peak are $I_{oxidation}$ = 207.1 µA/cm^2 respectively $I_{reduction}$ = -194.57 µA/cm^2 at a ratio of 1.02. In this respect the redox centers are in equal concentration distributed along of the PANi chains. The diference between oxidation and reduction potential being 0.249 V this result highlight few features for PANi: 1. If we recall Nernst –Einstein equation [7] for an equilibrium concentration need 0.059 V/n, where n is the number of electrons to reduce the oxidation centers. For the difference of 0.249V need 4 electrons. Based on these assumptions the redox centers are distributed along of the chain and located on bipolaron. 2. If we compare with other reports where PANi was electropolymerized in acidic aqueous solution (1MHCl or $1MH_2SO_4$) with aniline monomers the potentials for oxidation is in the range 0.7-1 V [8-9]. The deposition of polyaniline carried out at the constant potential of maximum 0.75 V for several minutes remain in the emeraldine form (EM). Above of this value PANI changes from the emeraldine to pernigraniline [10-11]. For aniline sulfate the oxidation potential is reduced up to two times leading to a better control to design intrinsic conducting polymers keeping one single form of emeraldine with a given concentration of redox states along of the chain. Moreover the position of the sulfate group induces a well defined distribution of charge located in polarons or bipolarons and in consequence a good sensivity in response to an analyte in a chemosensor.

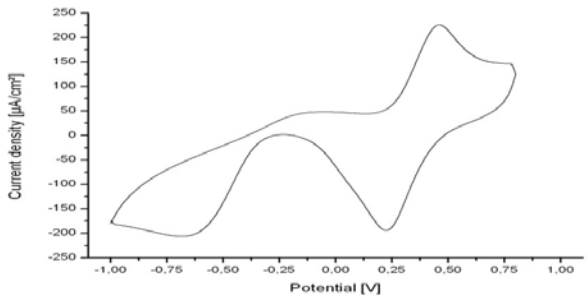

Fig. 1. CV of the electrochemical deposition for polyaniline on Au-SPE .

The response of the SPE-PANi to DON toxin recorded by CV at a scan rate of 100 mV/s from -1V to 1.2V is shown in figure 2 for a concentration of 10^{-6} M/l toxin. Also is drawn for reference the response for toxin at SPE-Au. With SPE-Au there is no response to toxin. For SPE-PANi are observed the specific electroactivity for DON, near the potentials values of 1000mV (the oxidation peak) respectively 400 mV (the reduction peak). In addition there are other two secondary small peaks (oxidation -0.213 V, reduction -0. 624 V) assigned to an intermediate compound which is supposed to be developed at interface Au-PANi as results of gold functionalizing sulfate groups.

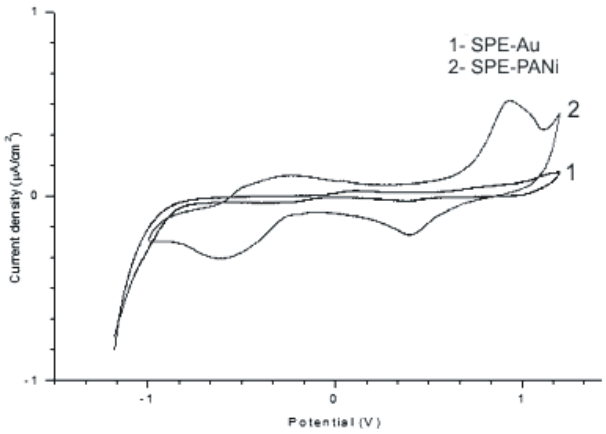

Fig. 2. The CV response to neurotoxin DON on gold screen printed electrode (SPE-Au) respective on SPE-PANi at molar concentration of 10^{-6} M/l.

In Fig. 3 are plotted the current for anodic and cathodic peaks with the concentration. The response on anodic current has dependence described by equation:

$$i_a = i_{a,sat}\left(1 - exp(-kc)\right)$$

With i_{asat}- the anodic curent saturation, c –DON concentration in M/l and k- constant, 36.394 l x mol^{-1}. In the linear part the sensibility for SPE-PANi is:

$$\frac{di_a}{dc}\Big|_{c=0} = 2147.3 \times 10^{-10}\mu A\frac{cm^{-2}l}{mole}$$

The reduction peak has good response at high concentrations having a linear dependence.

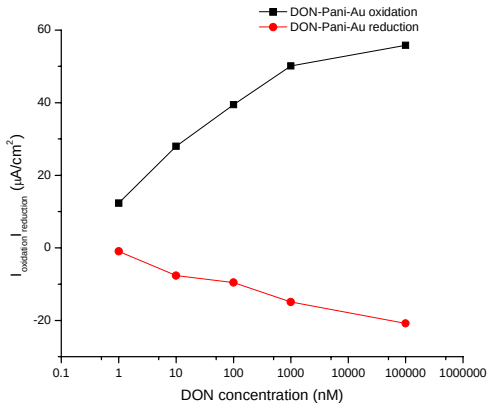

Fig. 3. The response in oxidation and reduction for DON concentrations. The current density recorded for SPE-PANi. The oxidation peak has linear response to very low concentration and reduction peak for high concentration.

4. Conclusions

A simple and effective chemosensor has been developed to detect a neurotoxin produced by fungi in animal feed.SPE-PANi highlight a new direction to detect toxins at very low concentration at nmole order of magnitude**.** PANi electropolymerized from aniline sulfate give rise to ladder polymer structure with bipolaronic conductivity mechanism. Many sensors based on semiconducting polymers are used as mediator or for immobilizing some species that have the role of sensing the analyte component. Experimental results showed that the gold screen printed electrode with electrodeposed PANi gives rise to a good response and a high sensitivity even at very low concentration of Deoxynivalenol in comparison with the simple gold screen printed electrode that presented a lower response at this toxin. Therefore the gold screen printed electrode complexed with electrodeposed PANi could be used for sensing applications even at very low concentration of toxins.

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