# NEW COMPOSITE MATERIALS USED IN THE PHENOL ELECTROANALYSIS. PART I. POLY(AZULENE) / PRUSSIAN BLUE AND PRUSSIAN BLUE / POLY(AZULENE) FILMS

Cecilia LETE,[a*] Stelian LUPU,[b*] Mariana MARIN[a] and Mihaela BADEA[c]

[a] Institute of Physical Chemistry "Ilie Murgulescu", Splaiul Independentei 202, 060021 Bucharest, Roumania
[b] University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science,
Department of Analytical Chemistry and Instrumental Analysis, Polizu Gheorghe 1-5, 011061 Bucharest, Roumania
[c] National Research –Development Institute for Chemistry and Petrochemistry, ICECHIM,
Department of Biotehnology, Splaiul Independentei, 202, 061821 Bucharest, Roumania

The electrochemical preparation and the characterization of inorganic-organic composite materials based on poly(azulene) (PAZ) and Prussian Blue (PB) were presented. The PAZ films were generated by electrochemical polymerisation within two different potential ranges, *i.e.* from -0.6 to 1.2 V and from -0.6 to 1.8 V, respectively. All measurements were performed in 0.1M tetrabutylammonium toluene 4-sulfonate (TBAT4S). The composite materials were prepared in various geometries, PB/PAZ and PAZ/PB, respectively. The voltammetric determination of phenol at these modified electrodes has been carried out in buffered aqueous solution of pH = 6.0 by using square wave voltammetry (SWV). The highest sensitivity of 21.89 µA/nM was obtained for the PB/PAZ composite material.

## INTRODUCTION

Most of phenolic compounds are generated artificially and found in wastewaters of chemical plants, exhaust gases of incinerators, sidestream smoke of cigarettes, etc.[1] Phenolic compounds are harmful to human health due to their toxicity and persistency in the environment. They are a class of polluting chemicals, easily absorbed by animals and human through the skin and mucous membranes. Phenol is used as raw material in the production of dyes, pesticides, surfactants, plasticizers and appears in the effluents of many industries like oil refinery, pharmaceuticals and explosives.[2] The analytical determination of phenolic compounds is therefore important to evaluate the risk of those environmental samples. Several analytical methods, such as spectroscopy,[3,4] gas[5,6] and liquid chromatography,[7,8] calorimetry,[9] fluorimety[10] and electrochemical methods,[11-13]

were used for the determination of phenolic compounds. These methods usually require time-costing, low sensitivity, skilled operators, preconcentration and extraction steps that could increase the risk of samples loss.[14,15] Electrochemical sensors represent promising tools to complete these existing methods, owing to their characteristics such as selectivity, low cost, potential for miniaturization/automation, and for the building of simple flow devices for fast continuous monitoring.[16]

The electrochemical oxidation of phenol in aqueous solution is well known to be affected by the formation of non-conducting polyphenol layers which block the surface of the electrode. This irreversible fouling of the electrodes is a result of the formation of non-conducting/passivating polymeric films derived from electrogenerated phenoxy radicals that appear during electrochemical oxidation of phenol.[17,18] A number of factors have

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* Corresponding author: Tel: +400213167912, fax: +400213121147; E-mail address: celete2002@yahoo.com (C. Lete)
Tel: +40214023886, fax: +400213111796; E-mail address: stelianl@yahoo.com (S. Lupu)

been reported to affect the extent of surface passivation, such as phenol concentration, structure of the phenolic compound and operational conditions. The mechanism of oxidation of phenol and its derivatives at platinum electrode was summarized by Kharlamova, Teodoradze[19] and Hubbard.[20] The generalized mechanistic scheme was suggested to involve electrooxidation, polymerization or combustion of phenol whose occurrence was related to catalyst pretreatment and experimental conditions used. Experimental voltammograms suggested an ECE mechanism.

In this paper, the preparation and the characterisation of various azulene polymeric films and inorganic-organic composite materials are presented. The electrochemical determination of phenol at electrodes modified with these polymeric films and composite materials based on PAZ is also discussed. The modification of the electrode surface by azulene polymeric coatings has eliminated the disadvantage of the electrode surface fouling with insulating polymer films or by

products resulting from phenol derivatives oxidation or reduction.

## RESULTS AND DISCUSSION

### 1. Preparation and characterization of modified electrodes

During the electrochemical oxidation of azulene in 0.1 M TBAT4S-ACN on different potential ranges, (-0.6)- 1.2 V and (-0.6)- 1.8 V, respectively, a continuous growth of the polymer was observed. The anodic peak current increases with the number of potential scans. The cyclic voltammograms for electropolymerization of 1 mM azulene in 0.1 M TBAT4S-ACN on the extended potential range are shown in Fig. 1a. The charging-discharging reactions of PAZ films were studied in monomer free electrolyte solution and the CV response of the PAZ films is depicted in Fig. 1b and Fig. 2b.
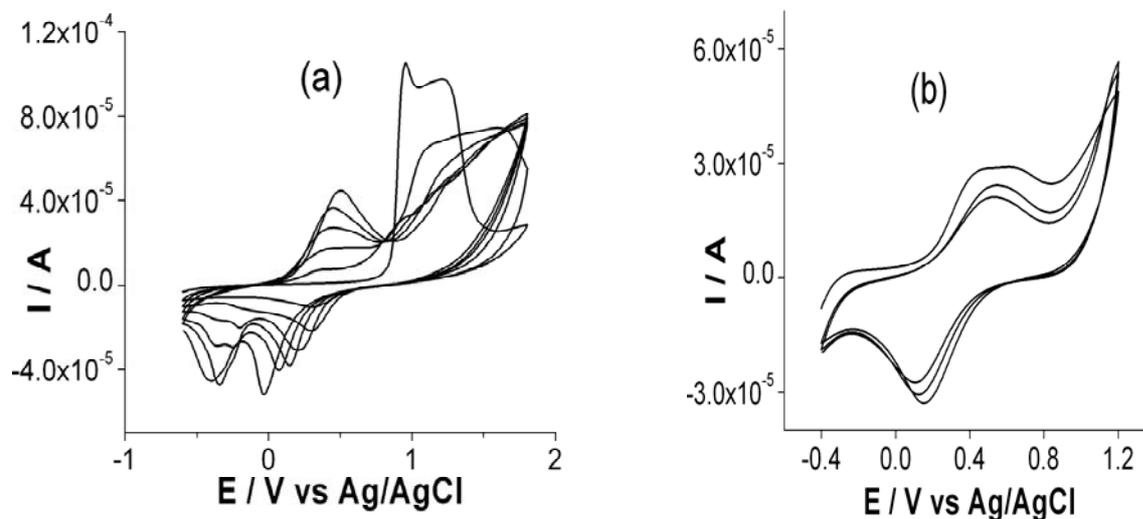


Fig. 1 – a) The cyclic voltammograms for electrodeposition of PAZ from 0.1 M TBAT4S-ACN solution containing 1 mM azulene. The potential scan rate was 50 mV/s on the extended potential range from -0.6 to 1.8V. b) The cyclic voltammograms of Pt/PAZ modified electrode in 0.1 M TBAT4S-ACN monomer free electrolyte solution. Potential scan rate: 50 mV/s.

In Fig. 2 the cyclic voltammograms recorded during electrodeposition of PAZ on the short potential range, *i.e.* (-0.6) – 1.2 V, are shown. A good electroactivity of these PAZ films was observed when they were electrochemically oxidized (p-doping). Some differences can be observed in the cyclic voltammograms of PAZ films synthesized according to both procedures (extended and short potential range). The PAZ films obtained by cycling of the potential on the short potential range, i.e. (-0.6)

– 1.2V (see Fig. 2b), have a lower charging current in comparison to PAZ films obtained by cycling of the potential on the extended potential range (see Fig.1b). From Fig. 1b it can be seen that the polymeric film produces an oxidation peak at 0.5 V and a reduction peak at 0.15 V on the reverse scan, respectively. Fig. 2b shows a reversible redox response with an anodic peak at 0.34 V and a cathodic peak at 0.24 V on the reverse scan, respectively.
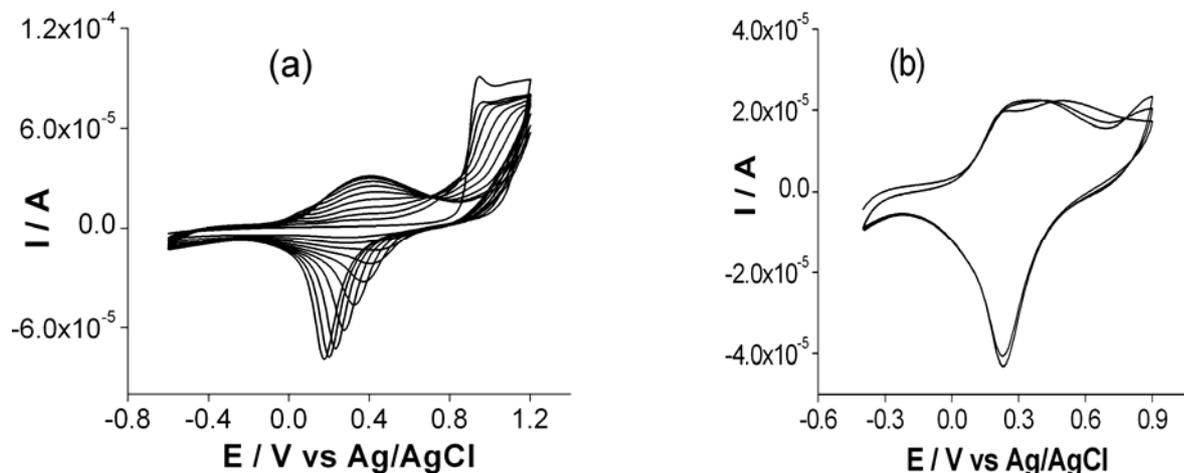
Fig. 2 – a) The cyclic voltammograms for electrodeposition of PAZ from 0.1 M TBAT4S-ACN solution containing 1 mM azulene. Potential scan rate 50 mV/s; short potential range: -0.6 to 1.2V. b) The cyclic voltammograms of Pt/PAZ modified electrode in 0.1 M TBAT4S-ACN monomer free electrolyte solution. Potential scan rate: 50 mV/s.

The PB was electrodeposited onto platinum disk electrode by using the potentiodynamic method, i.e. cycling the electrode potential for 8 cycles from -0.2 to 1.0 V at a scan rate of 50 mV/s in a solution containing 1 mM $FeCl_3$, 1mM $K_3Fe(CN)_6$, 0.1 M KCl and 0.01 M HCl.

The bilayer coatings based on PB and polyazulene films are obtained in a two steps preparation procedure and on various configurations. In the case of the PB/PAZ coating, a PB layer has been first electrodeposited onto the platinum electrode. In the second step, the electrochemical polymerization of azulene onto the Pt/PB modified electrode has been carried out. The cyclic voltammograms for polymerization of 1 mM azulene on Pt/PB modified electrode in a solution containing 0.1 M TBAT4S-ACN are presented in Fig. 3a. The electrochemical response of this modified electrode is characterised by an anodic peak situated at 0.47 V and a cathodic peak at 0.32 V, respectively (see Fig. 3b).
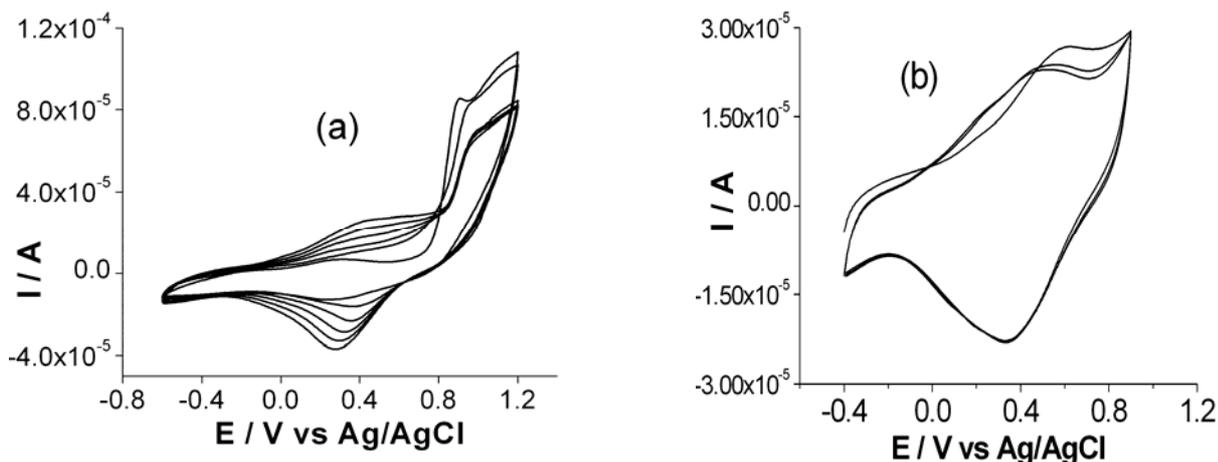


Fig. 3 – a) The cyclic voltammograms for electrodeposition of PAZ on Pt/PB modified electrode from 0.1 M TBAT4S-ACN solution containing 1 mM azulene. Potential scan rate: 50 mV/s; short potential range, -0.6 to 1.2V. b) The cyclic voltammograms of Pt/PB/PAZ modified electrode in 0.1 M TBAT4S-ACN monomer free electrolyte solution. Potential scan rate: 50 mV/s.

The PAZ/PB coatings have been prepared by electrodeposition of PB onto Pt/PAZ modified electrode by cycling the potential between -0.2 and 1.0 V with a scan rate of 50 mV/s. In Fig. 4 are depicted the cyclic voltammograms recorded during electrodeposition of PB onto Pt/PAZ electrode. At the first potential scan one can observe a wide peak at 0.87 V, which decreases for the subsequent scans. In comparison with the formation of PB on the platinum electrode, the typical redox waves corresponding to PB/ES and PB/BG systems are not visible. However, the

presence of an outer PB layer on the surface of the electrode can be observed by simple visual inspection. The resulting modified electrode, denominated as Pt/PAZ/PB, was characterized by cyclic voltammetry in an aqueous solution containing 0.1 M KCl and 0.01 M HCl (see Fig. 4b). The shape of the cyclic voltammogram is not similar to the typical one recorded for Pt/PB modified electrode, suggesting that the inner organic layer does not allow the free motion of

counterions required to maintain electroneutrality. It is well known that the PB films display two redox waves only in potassium ions containing aqueous solutions. For instance, the reduction of PB to ES takes place in the presence of potassium ions and the absence of the characteristic redox wave is due to the PAZ films that hinder the free motion of potassium ions in order to maintain the electroneutrality.
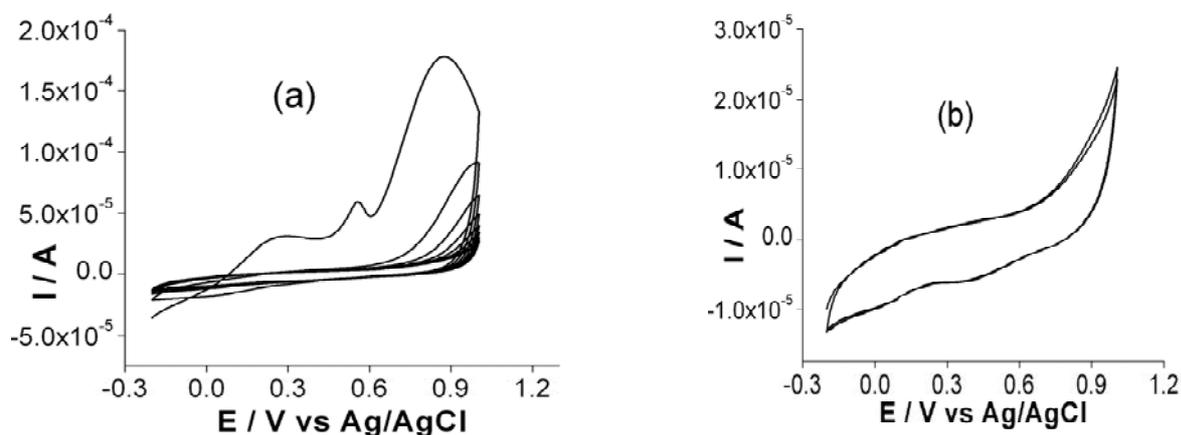


Fig. 4 – a) The cyclic voltammograms for electrodeposition of PB on Pt/PAZ modified electrode from an aqueous solution containing 1 mM $FeCl_3$, 1 mM $K_3Fe(CN)_6$, 0.1 M KCl and 0.01M HCl. Potential scan rate: 50 mV/s. b) The cyclic voltammograms of Pt/PAZ/PB modified electrode in the transfer solution containing 0.1 M KCl and 0.01M HCl. Potential scan rate: 50 mV/s.

## 2. Voltammetric determination of phenol at Pt/PAZ, Pt/PB/PAZ, Pt/PAZ/PB modified electrodes

Each coating, one layer and bilayer, has been characterized in order to asses the potential applications of these modified electrodes as electrochemical sensors for phenol determination. All voltammetric studies were performed in aqueous phosphate buffer solution, by using SWV.

Fig. 5 reports the SWV traces recorded at Pt/PAZ modified electrode for different phenol concentrations and the inset corresponds to the calibration plot, showing the linear dependence of the current intensity with phenol concentration, within the investigated range. This linear relationship exists between $i_p$ and the phenol concentration in the range 20–100 nM ($r^2 = 0.9955$) with a slope of 13.96nA/nM.
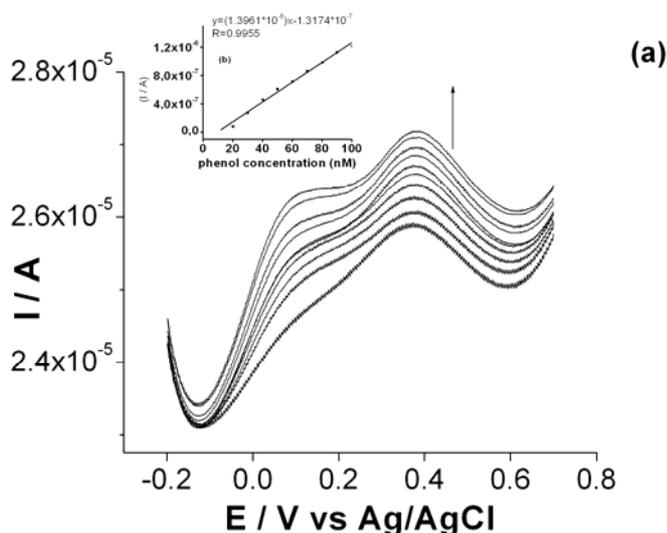


Fig. 5 – a) Square wave voltammograms recorded at Pt/PAZ modified electrode in aqueous 0.1 M phosphate buffer solution of pH = 6 containing various phenol amounts in the range 20 - 100 nM. Pulse amplitude 70 mV, pulse step 2.5 mV, frequency 10 Hz. b) Inset: dependence of square wave anodic peak current on phenol concentration.

The presence of both layers on the surface of platinum electrode improved the analytical performances of these electrochemical sensors owing to special electrochemical features. The organic coating has good permselective properties and assures a stable environment for the inorganic mediator. The presence of the inorganic layer (PB) provides a high concentration of redox centers inside of the film. The organic coating allows favourable electrostatic interactions between the modifying layer and the analyte. The voltammetric determination of phenol at Pt/PB/PAZ and Pt/PAZ/PB modified electrodes has been performed in phosphate buffer solution of pH = 6, by SWV for different phenol concentrations.

Fig. 6 and Fig. 7 show square wave voltammograms for Pt/PB/PAZ and Pt/PAZ/PB modified electrodes used in the determination of phenol for lower phenol concentration ranges, i.e. 10-100 nM and 30-100 nM, respectively. A linear dependence of the anodic peak current corresponding to the oxidation of phenol at 0.15 V has been obtained for each modified electrode, i.e. Pt/PB/PAZ and Pt/PAZ/PB respectively. The corresponding equations are: $I_{pa}(A)=4.0966 \times 10^{-4}+2.1897 \times 10^{-5} C_{phenol}$ (nM) (see inset of Fig. 6) and $I_{pa}(A)=4.4891 \times 10^{-6} + 5.59 \times 10^{-8} C_{phenol}$(nM) (see inset of Fig. 7). According to the obtained sensitivity values, the Pt/PB/PAZ modified electrode displays improved analytical performances than Pt/ PAZ /PB modified electrode.



Fig. 6 – a) Square wave voltammograms recorded at Pt/PB/PAZ modified electrode in aqueous 0.1 M phosphate buffer solution of pH = 6 containing various phenol concentrations in the range 10-100 nM. Pulse amplitude 70 mV, pulse step 2.5 mV, frequency 10 Hz. b) Inset: dependence of square wave anodic peak current on phenol concentration.
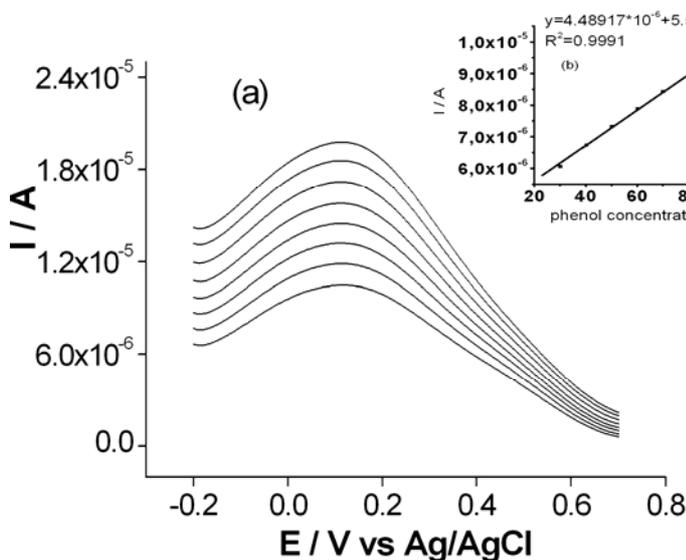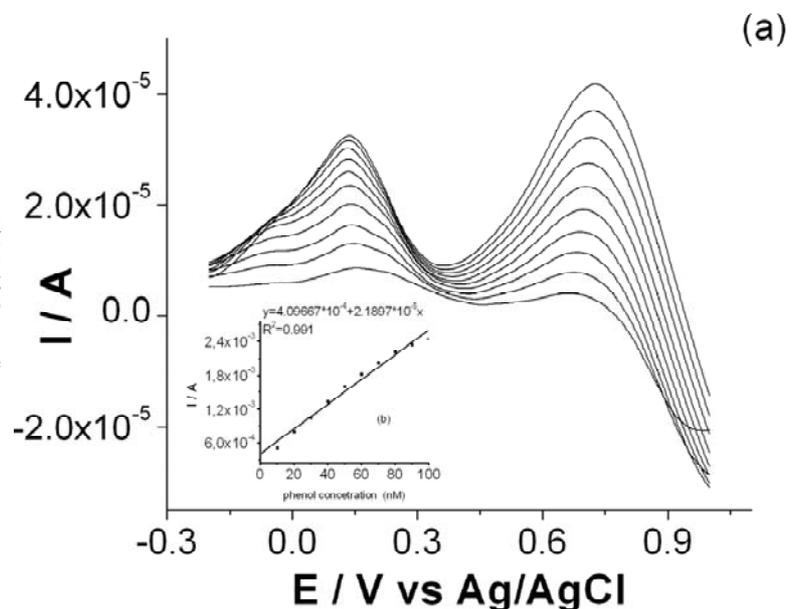


Fig. 7 – a) Square wave voltammograms recorded at Pt/PAZ/PB modified electrode in aqueous 0.1 M phosphate buffer solution of pH = 6 containing various phenol amounts in the range 30-100 nM. Pulse amplitude 70 mV, pulse step 2.5 mV, frequency 10 Hz. b) Inset: dependence of square wave anodic peak current on phenol concentration.

The analytical performances of the composite modified electrode are comparable with those reported in the literature.[21,22]

## EXPERIMENTAL

All chemicals were used without any further purification. The azulene (AZ) was purchased from Fluka. Electrolyte salt used was 0.1M tetrabutylammonium toluene 4-sulfonate (TBAT4S) from Fluka. Doubly distilled water was always used to prepare aqueous solutions.

The electrochemical experiments were carried out with an Autolab potentiostat/galvanostat 302N (Ecochemie) coupled to a PC running the GPES software, using a single-compartment cell with three electrodes, at room temperature. The electrodes used were: a 3-mm diameter Pt disk electrode (Metrohm) as working electrode, a Ag/AgCl as a pseudo-reference electrode (calibrated against ferrocene/ferrocenium $E_{redox}$= 0.48 V) and a platinum wire (Metrohm) as auxiliary electrode. Before each electrochemical measurement the surface of the working electrode was mechanically polished with 1, 0.3, and 0.05 μm alumina powders, and rinsed with doubly distilled water. The solutions were bubbled with high purity argon and a flow of argon was maintained over the solution during the measurements.

The polymerization of azulene was performed in acetonitrile (ACN) containing 0.1 M tetrabutylammonium toluene 4-sulfonate (TBAT4S) and 1 mM monomer by potentiodynamic cycling, in the potential ranges between -0.6 and 1.2V for 3, 6 and 10 cycles or between -0.6 and 1.8V for 3, 6 and 10 cycles, at a potential scan rate of 50 mV/s. Potential ranges and the thickness of the films were chosen based on their voltammetric response during doping characterisation in monomer free solution. The obtained polymeric films were characterized in monomer free solution of 0.1 M TBAT4S-ACN, at 50 mV/s potential scan rate. The thickness of the coating was controlled by the number of potential cycles.

The bilayers films have been obtained electrochemically by a two-step method in different configurations. In the case of the Prussian blue/polyazulene (Pt/PB/PAZ) coating, first a PB layer has been electrodeposited onto a Pt electrode. In the second step, the electrochemical polymerisation of azulene onto the Pt/PB modified electrode has been carried out. The outer layer of polyazulene (PAZ) was obtained by scanning of the electrode potential between -0.6 and 1.8 V at scan rate of 50 mV/s from a solution of acetonitrile containing 0.1 M tetrabutylammonium toluene 4-sulfonate (TBAT4S) and 1 mM azulene. The thickness of the coating was controlled by the number of potential cycles. This modified electrode is referred as to Pt/PB/PAZ. The PAZ/PB coating has been prepared by electropolymerization of azulene in acetonitrile solution and then an outer PB layer was electrodeposited on top of the Pt/PAZ modified electrode. The resulted modified electrode is referred as to Pt/PAZ/PB.

## CONCLUSIONS

In this work a few electrochemical sensors based on organic-inorganic composite materials for determination of phenol were developed. The composite materials were prepared in various geometries, such as: Pt/PAZ, Pt/PB/PAZ and Pt/PAZ/PB. The best sensitivity obtained in determination of phenol was 21.89 μA/nM when platinum electrode was covered with PB/PAZ composite material. The organic-inorganic composite coatings exhibited good electrochemical properties and electrocatalytic activity towards the oxidation of phenol.

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