

VOLTAMMETRIC DETERMINATION OF PHENOL AT PLATINUM ELECTRODES MODIFIED WITH POLYPYRROLE DOPED WITH FERRICYANIDE

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In this work, the electrochemical determination of phenol at platinum electrodes modified with polypyrrole doped with ferricyanide is reported. The modified electrodes were prepared by electrochemical polymerization of pyrrole from aqueous solution by using cyclic voltammetry. The polypyrrole film has been deposited onto Pt electrode surface by potential cycling from (-0.2) V to +1.5 V at a scan rate of 0.1 V/s. The thickness of the polymeric film was controlled by the number of potential cycles. The resulted modified electrode is referred as to Pt/PPy-FeCN. After the deposition of the doped polymer film, the modified electrode was characterized in aqueous solution by using cyclic voltammetry and square wave voltammetry. The electrochemical oxidation of phenol at Pt/PPy-FeCN modified electrode has been investigated in aqueous solution of pH of 2. The oxidation of phenol occurs at a potential value of ca. 0.70 V, which is less positive than that observed at bare Pt electrode. Furthermore, the doped polymer coating eliminates the surface electrode fouling due to phenol oxidation. From tests at different phenol concentrations ranging from 5×10^{-6} M to 1×10^{-4} M, in the presence of 1×10^{-4} M $\text{Cd}(\text{NO}_3)_2$, a linear decrease of the anodic current was obtained. A detection limit of 5×10^{-6} M phenol has been also obtained.

INTRODUCTION

The electrochemical sensors based on modified electrodes are one of the most advancing areas of electroanalytical chemistry. During the last decade several research papers dealing with electrodes modified with conducting organic polymers, such as polyaniline, polypyrrole and polythiophene, have been published.¹⁻³ Conducting polymers can be obtained by electrochemical polymerization of the corresponding monomers. The electrochemical features of conducting polymers allow the incorporation of various anions from the electrolyte solution during the electrochemical polymerization. Organic conducting polymers doped with various anions have been extensively studied due to their improved electrocatalytic, electroreleasing and electrochromic properties. Recently, Eftekhari⁴ reported the preparation and electrochemical characterization of polyaniline films containing ferricyanide. The doped polymer film exhibited potentiometric response towards

ferricyanide ions. The incorporation of various ions in conducting polymer films is based on the electrostatic stabilization and attraction between the positively charged polymer backbone and the negatively charged doping ions. Various experimental procedures for the preparation of inorganic-organic composite material coatings containing organic conducting polymers and cyanometallates have been reported. Polypyrrole⁵, polyaniline,^{6,7} and thiophene derivatives⁸⁻¹⁰ were used as organic modifiers. Among conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been the subject of several studies because of its excellent stability and conducting properties.^{11,12} Moreover, PEDOT coatings can be prepared by electrochemical polymerization in aqueous solution,¹³ which allows the direct incorporation of water soluble anions, like ferricyanide. Recently, a PEDOT coating doped with ferricyanide has been reported.¹⁴ The composite coating has been prepared by a two-step method. First, the PEDOT coating has been

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electrogenerated in aqueous solution by electrochemical polymerization and then the polymer film was doped with ferricyanide ions. The composite modified electrode was used for the electrochemical determination of dopamine.

The contamination of fresh waters with many industrial and natural chemical compounds is one of the key environmental problems facing humanity. Although most of these compounds are present at low concentrations, many of them raise considerable toxicological concerns. Assessing the impact of pollutants in aquatic systems requires improved analytical methods and tools.^{15, 16} Electrochemical sensors based on modified electrodes for organic pollutants determination have attracted a great deal of interest due to their analytical performances, such as low detection limits, selectivity, wide linear response range, and reproducibility. For instance, electrodes modified with conducting polymers films have been used for the electrochemical detection of phenol.¹⁷ The use of the conducting polymers, polyaniline and polypyrrole with a range of different counterions, has resulted in a stable and reproducible response towards phenol oxidation.

In this work, the electrochemical preparation and characterization of polypyrrole (PPy) doped with ferricyanide ions is reported. The composite coating has been prepared by electrochemical polymerization of pyrrole in the presence of ferricyanide ions. The composite modified electrode was investigated in acidic aqueous solutions by using cyclic voltammetry (CV) and square wave voltammetry (SWV). The electrocatalytic activity of the composite coating towards the phenol oxidation has been also investigated. The modified electrode was used for the voltammetric determination of phenol in potable water.

EXPERIMENTAL

All chemicals: $K_3[Fe(CN)_6]$ (Merck), NaCl (Reactivul), HCl (Merck), and pirol (Aldrich), were used without any further purification. Double distilled water was always used to prepare fresh aqueous solutions. The electrochemical experiments were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat (Eco Chemie), equipped with the VA 663 stand (Metrohm), coupled to a PC running the GPES software, using a single-compartment, three-electrode cell, at room temperature. A 2-mm diameter Pt disk electrode (Metrohm) was used as working electrode. A saturated silver-silver chloride electrode was the reference electrode, and a graphite rod (Metrohm) was the auxiliary electrode. Before each electrochemical test, the surface of the working electrode

was polished with 0.3 μm alumina powder to a mirror finish, and rinsed with double distilled water. All the solution used for the electrochemical measurements were bubbled with Ar for 10 minutes and an Ar flow was maintained over the solutions during the experiments.

Deposition procedure of PPy-FeCN composite films

The composite coating has been prepared by electrochemical polymerization from an aqueous solution containing 0.02 M Py and 0.01 M $K_3[Fe(CN)_6]$ as supporting electrolyte. The electrode potential was cycled between -0.2 and 1.5 V at a scan rate of 0.1 V/s. The thickness of the film was controlled by the number of potential cycles. Usually 5 potential scans were performed in order to prepare the composite coating. The resulted modified electrode is referred as to Pt/PPy-FeCN. After the formation of the composite PPy-FeCN coating, the modified electrode was rinsed with doubly distilled water and then immersed in the transfer solution, where it has been characterised by using cyclic voltammetry and square wave voltammetry.

Analytical procedure for phenol determination

The phenol levels in the given sample were assessed using a standard additions protocol in which a known quantity of the sample (typically 9 mL of potable water) is added to the electrolyte solution followed by a series of standard phenol aliquots. Square wave voltammetry was used as the detection methodology. The square wave voltammograms were recorded at Pt/PPy-FeCN after each addition by using the following parameters: frequency 10 Hz, step potential 10 mV, amplitude 50 mV, initial potential -0.2 V, end potential + 1.1 V. Preparation of the sample solution: into 9 mL of potable water were added 1 mL of electrolyte solution with the final concentration of 0.1 M NaCl and 0.01 M HCl. The resulted solution was placed in an electrochemical cell and bubbled with Ar for 10 minutes. An Ar flow was maintained over the solution during the electrochemical measurements. Then, three standard additions of known amounts of phenol were performed. The square wave voltammograms were recorded after each standard addition. Each analytical determination was carried out in 5 replicates through measuring the anodic peak current from square wave voltammograms after subtraction of the blank. For each series a new modified electrode was prepared according to the deposition procedure described above.

RESULTS AND DISCUSSION

Preparation of PPy-FeCN composite coating

The composite coating has been prepared by electrochemical polymerization from an aqueous solution containing 0.02 M Py and 0.01 M $K_3[Fe(CN)_6]$ as supporting electrolyte. The resulted modified electrode is referred as to Pt/PPy-FeCN. The optimum values of the concentrations of potassium ferricyanide have been determined.

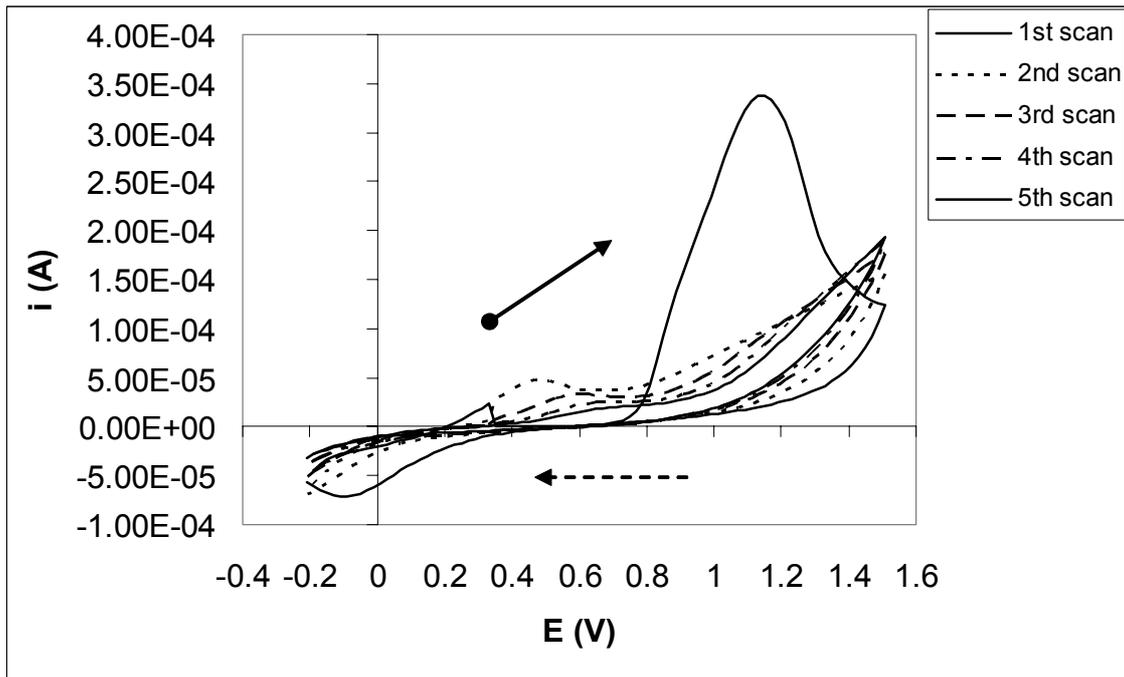


Fig. 1 – Cyclic voltammograms recorded during the electrochemical polymerization of pyrrole at Pt electrode in aqueous solution containing 0.02 M Py and 0.01 M $K_3Fe(CN)_6$. Potential scan rate: 0.1 V/s. The first 5 scans are represented.

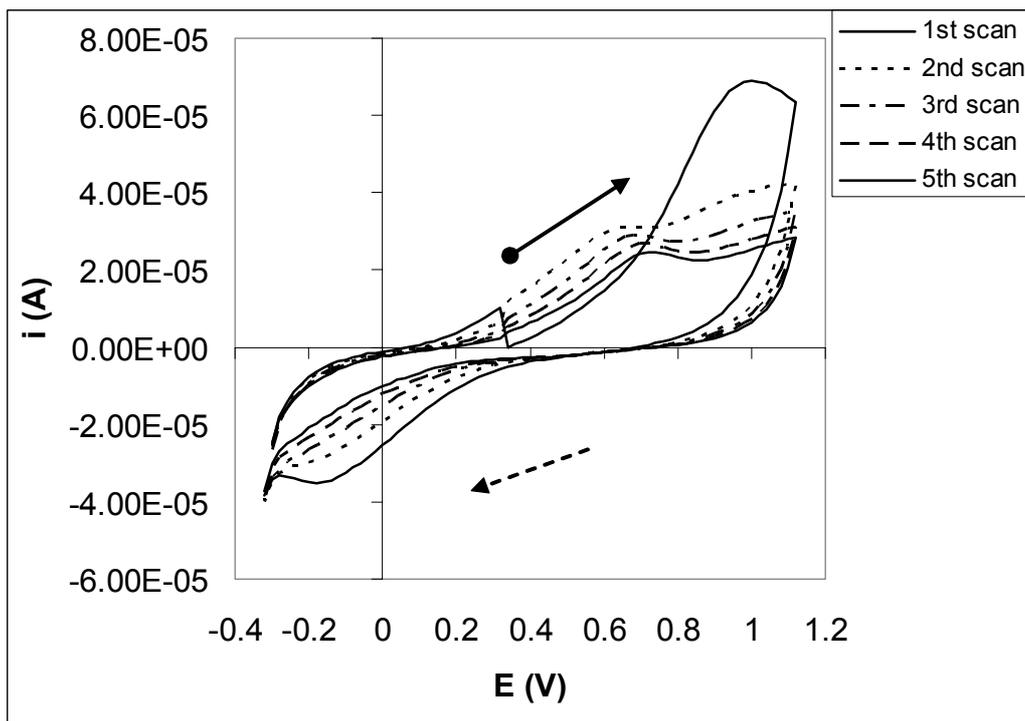


Fig. 2 – Cyclic voltammograms recorded at a Pt/PPy-FeCN modified electrode in a solution containing 0.1 M NaCl and 0.01 M HCl. Potential scan rate: 0.05 V/s. The first 5 scans are depicted.

Fig. 1 shows the cyclic voltammograms recorded during the electrochemical polymerisation of Py in the presence of potassium ferricyanide. In the potential range from 1.0 to 1.3 V the electrochemical polymerisation of Py takes place and therefore the PPy layer is growing on the

electrode surface. During the very first scan, we can observe that the current starts increasing at cca. +1.15 V, indicating the beginning of the deposition process of PPy onto the electrode surface. Due to the presence of ferricyanide ions, the organic polymer is doped with counterions from the

electrolyte solution. The signal of the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ consists of two peaks, an anodic one situated at +0.5 V and a cathodic one at -0.01 V, respectively. The difference between the anodic and cathodic peak potentials suggests a quasi reversible behaviour due to the limited motion of ferricyanide ions into the PPy layer. After the preparation of the ferricyanide-doped PPy coating, the modified electrode was transferred into an aqueous solution containing 0.1 M NaCl and 0.01 M HCl, where the electrode potential was cycled from -0.3 to 1.1 V, at a sweep rate of 0.05 V/s. Fig. 2 reports the cyclic voltammograms corresponding to the first 5 consecutive potential cycles. At the very first scan an anodic peak is observed at +0.9 V that can be ascribed to the oxidation of PPy. For the next scans a redox couple consisting of an anodic peak at +0.6 V and a cathodic peak at -0.02 V could be observed. This redox peaks correspond to the ferricyanide/ferrocyanide ions entrapped inside de PPy matrix. The PPy layer includes ferricyanide ions from the electrolytic solution during its

preparation. These ions are reduced during the potential cycling of the modified electrode in aqueous solution resulting in the formation of ferrocyanide ions into the PPy layer. The anodic and cathodic peak currents decrease slowly during the following potential scans.

Voltammetric determination of phenol at Pt/PPy-FeCN composite modified electrodes

The voltammetric determination of phenol at Pt/PPy-FeCN composite modified electrode has been carried out in aqueous solution containing 0.1 M NaCl and 0.01 M HCl by using cyclic voltammetry and square wave voltammetry. Fig. 3 reports the square wave voltammograms recorded at Pt/PPy-FeCN modified electrode in aqueous solution added with various amounts of phenol. In order to check the response of the electrochemical sensors in the presence of interferences, the solution was spiked with 1×10^{-4} M Cd^{2+} .

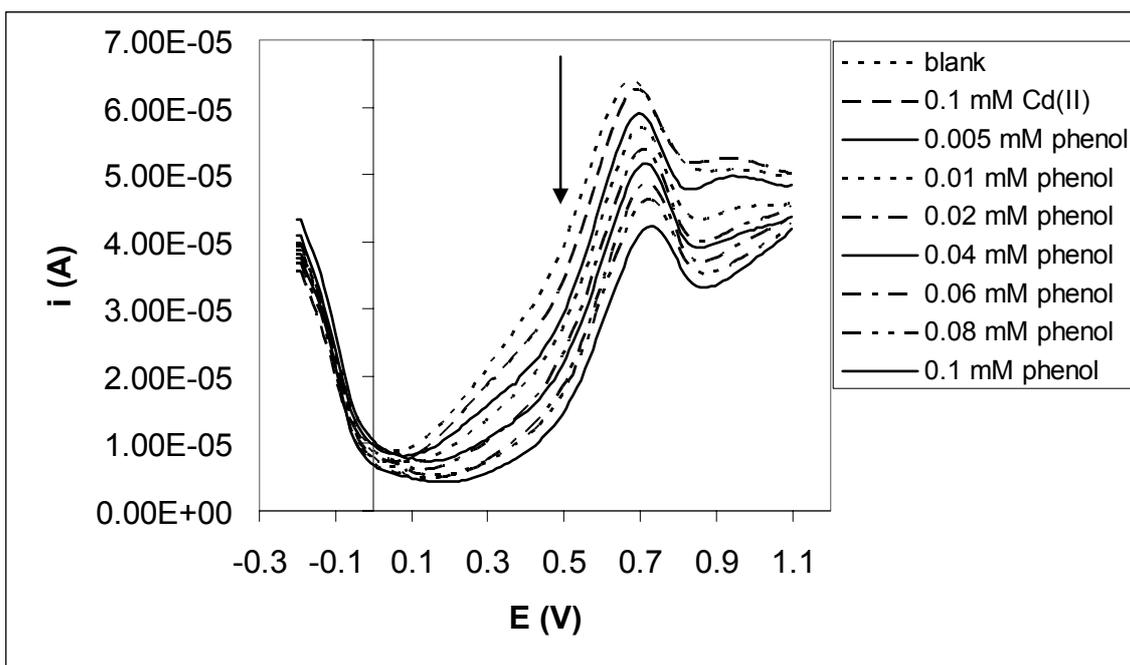


Fig. 3 – Square wave voltammograms recorded at a Pt/PPy-FeCN modified electrode in a solution containing 0.1 M NaCl, 0.01 M HCl, 0.1 mM Cd^{2+} , and various phenol concentrations: 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 mM. Frequency 10 Hz, potential step 10 mV, amplitude 50 mV.

The oxidation of phenol produces an anodic peak situated at +0.75 V, which is shifted towards less positive values with about 300 mV than the anodic peak recorded at bare platinum electrode. This potential difference attests the very good electrocatalytic activity of PPy-FeCN coating

towards the electrochemical oxidation of phenol. The anodic peak current decreases linearly with the increase in phenol concentration. For the sake of comparison, the anodic peak current recorded at bare electrode in the presence of phenol decreases dramatically after the very first scan due to the

formation of an insulating polymer layer onto the electrode surface. For this reason, bare platinum electrodes are not suitable for the voltammetric determination of phenol. Very promising results were obtained when the Pt/PPy-FeCN modified electrode was used for phenol determination. The modified electrode displayed a linear response towards phenol concentrations even in the presence of a high excess of a heavy metal, *i.e.* 1×10^{-4} M Cd^{2+} . From tests at different phenol concentrations ranging from 5×10^{-6} M to 1×10^{-4} M it can be observed that there is a linear dependence of the anodic peak current, according to the equation: $|i_{pa} (\mu\text{A})| = 0.1257 [\text{Phenol}] (\mu\text{M}) + 5.09$, with a correlation coefficient of $r^2 = 0.9756$ (see Fig. 4). The sensitivity of the electrochemical sensor,

computed from the calibration graph, was $0.1257 \mu\text{A}/\mu\text{M}$. A detection limit of $5 \mu\text{M}$, as the lowest concentration value of the linear range, was also obtained. This estimation of the detection limit is due to the decrease of the anodic peak current with phenol concentration, which is different than the usual dependence of the analytical signal on concentration, *i.e.* increase of the analytical signal with the analyte concentration. Furthermore, the calibration graph has been constructed after the subtraction of the blank signal. Due to the fact that the anodic peak current decreases with phenol concentration, the absolute values of the anodic peak currents have been used in the construction of the calibration graph.

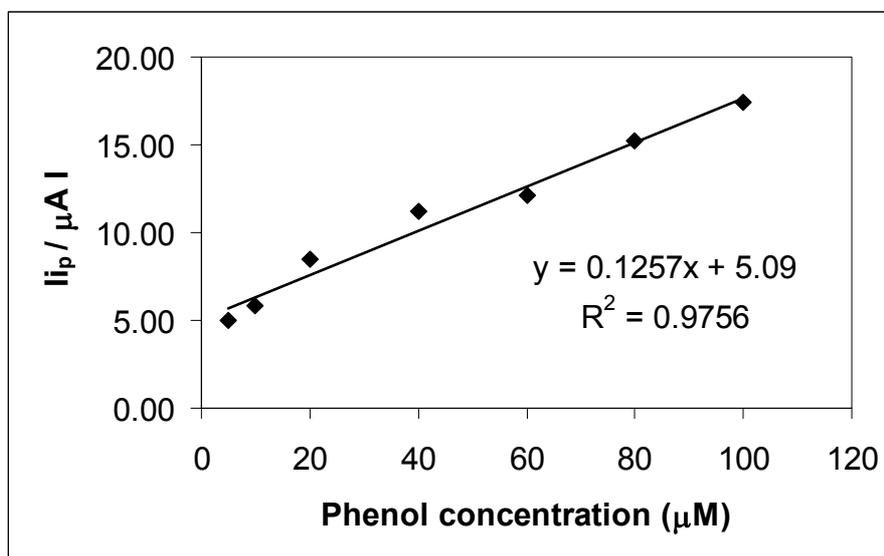


Fig. 4 – Dependence of the anodic peak current from square wave voltammograms on phenol concentration. Experimental conditions as in Fig. 3. On the ordinate axis the absolute values of the anodic peak currents, after subtraction of the blank, are represented.

Analytical performances of the Pt/PPy-FeCN electrochemical sensor

These results indicated that the PPy-FeCN coating exerts a good electrocatalytic effect on phenol oxidation. This behavior clearly demonstrates that the modified electrode exhibit a linear response for low phenol concentrations, which allows its use for phenol electrochemical detection in real samples. To this purpose, the electrochemical determination of phenol in potable water has been investigated. The quantification of phenol in real samples has been performed according to the analytical procedure described in the experimental section. Fig. 5 displays the square wave voltammograms recorded at Pt/PPy-FeCN modified electrode

for the electrochemical determination of phenol in potable water.

The sample water was added with three standard phenol aliquots leading to an increase in the concentration from 5×10^{-6} M to 2×10^{-5} M and the square wave voltammograms were recorded after the introduction of each aliquot. From Fig. 5 it can be seen that the electrochemical oxidation of phenol produces an anodic wave at a potential value of $+0.78$ V, which is almost the same as in the case of synthetic samples. It must be noted that the shape of the square wave voltammograms and the peak positions of different redox processes observed after the introduction of an aliquot of real sample may vary from those recorded in blank electrolyte solution due to the matrix composition.

The anodic peak current decreases linearly with the phenol concentration according to the equation: $|i_{pa} (\mu A)| = 0.2571 [\text{Phenol}] (\mu M) + 8.0$, with a correlation coefficient of $r^2 = 0.9643$ (see inset of Fig. 5). The absolute values of the anodic peak currents, after the subtraction of the blank signal, have been used for the construction of the calibration graph. The phenol concentration was calculated as 2.79 ± 2.2 mg/L (confidence level of

95%), taking in account the dilution factors, with a relative standard deviation ($n=5$) of 5.98%. This value is below the statutory maximum level for phenol in drinking water (3.5 mg/L).¹⁸

The results obtained prove that this new electrochemical sensor may be used for the voltammetric determination of phenol in real samples.

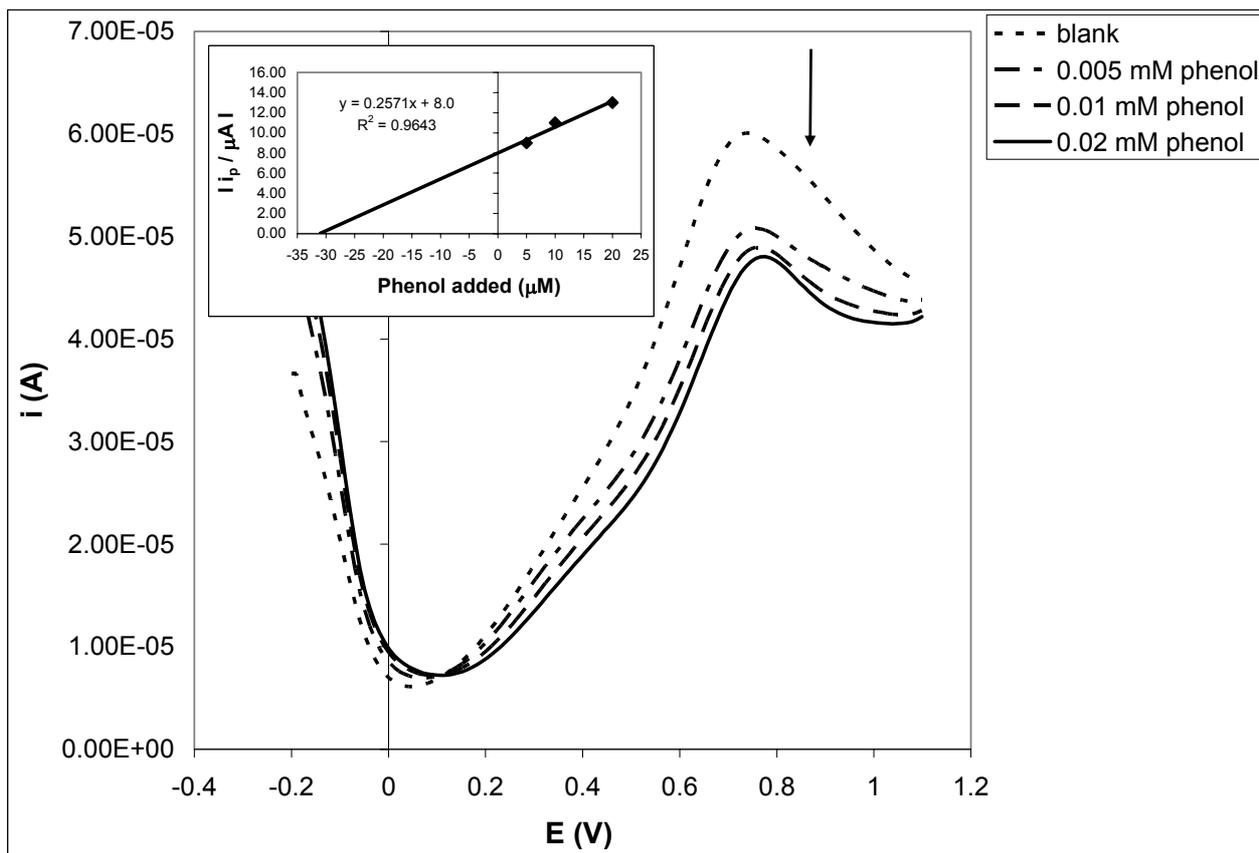


Fig. 5 – Square wave voltammograms recorded at a Pt/PPy-FeCN modified electrode in a solution containing 9 mL potable water sample and 1 mL electrolyte solution. Phenol added: 0.005, 0.01, and 0.02 mM. Frequency 10 Hz, potential step 10 mV, amplitude 50 mV. Inset: Dependence of the absolute values of the anodic peak currents from square wave voltammograms on phenol concentration.

CONCLUSIONS

The PPy-FeCN coating has proved a high electrocatalytic effect towards the phenol oxidation in the presence of heavy metals. A linear response over a wide range of phenol concentrations from 5×10^{-6} to 1×10^{-4} M has been obtained. A detection limit of 5 μM for phenol determination was also obtained. The electrochemical sensor has demonstrated good analytical performances in the analysis of real samples.

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