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VOLTAMMERIC SENSOR FOR NITROPHENOLS BASED ON SCREEN-PRINTED ELECTRODE MODIFIED WITH REDUCED GRAPHENE OXIDE

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Abstract. The electrochemical responses of nitrophenols can be enhanced effectively by using electrochemically reduced graphene oxide at screen-printed carbon electrode (SPCE-ERGO). The influence of the modifier on the electrochemical behavior of hydroquinone, phenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenolat the screen printed carbon electrodes (SPCE) was investigated in phosphate buffer solution at pH 7. The electrode material was printed on transparency film for inkjet devices. Modification of the SPCE with reduced graphene oxide has been significantly increased the sensitivity compared to unmodified electrode. In differential pulse voltammetry (DPV) we observed a significantly increased signal for hydroquinone (25 ppm) from 1.02 µA to 4.11 µA as a result of modification on SPCE. Also it was shown an increase of signal about 4 times for 3-nitrophenol and 4-nitrophenol. In most cases amperometric measurements has shown an increased sensitivity to nitrophenols with modified electrode, specifically for 2-nitrophenol, where sensitivity has been increased 35 times. Simple way of preparing such a sensor, its easy modification, and improvement of signal to nitrophenolsmake this sensor suitable for application. SPCE-ERGO successfully was applied on determination of phenols in waste water.

Keywords: SPCE, sensor, nitrophenols, reduced graphene oxide, waste water

Nitrophenolic compounds are common pollutants in aquatic environments. These compounds are typically toxic and difficult to degrade, comes mainly from the chemical, agricultural, medical and other industries. These compounds have toxic effect on humans, animals, and plants and they give an undesirable taste and odor to drinking water, even at very low concentration. For these reasons, many aromatic nitrocompounds have been included in the environmental legislation

(Chung et al., 2012; Li et al., 2012; Michałowicz & Duda, 2007). Nitrophenols are one of the major and persistent pollutants of the environment. They are considered as primary pollutant components in wastewater due to their high toxicity, high oxygen demand and low biodegradability (Körbahti & Tanyolaç, 2003; Mülazımoğlu & Yılmaz, 2010; Safavi et al., 2007).

Given the harmful effects that nitrophenols cause, many methods have been reported on their determinations. Traditional spectrophotometry and colorimetric methods are easily interfered by related compounds. GC methods can sometimes require relatively expensive reagents and need beneficiation and derivatization before analysis and it cannot be used directly to aqueous samples. HPLC and capillary electrophoresis methods are good alternative methods, but they need high cost to buy columns and waste more organic solvents. Thus, there is a demand for new analytical technique with cheap instrument, low cost, simple operation, time saving and real-time detection for nitrophenols. So, the electrochemical technique has attracted considerable interest due to its suppleness, convenience and low cost, compared to other existing methods (Korkut et al., 2008; Li et al., 2012). In terms of phenols and related compounds, waste treatment and detection are two major research directions. In both fields electrochemical methods are of prime importance (Farrell et al., 1999; Hernandez et al., 2013; Körbahti & Tanyolaç, 2003; Lin et al., 2009; Mülazımoğlu & Yılmaz, 2010; Safavi et al., 2007; Wang et al., 2008; Yang et al., 2013). These methods are based on the direct oxidation or reduction of substrate onto an electrode surface. Screen-printed carbon electrodes (SPCE) are widely used as the working electrode because it shows high stability and is precise in detection. But the demerit of low sensitivity gives the SPCE limitations in practice. Enhancing the electrochemical response, great efforts have been made on SPCE by its treatment and modification (Shan et al., 2002; Thévenot et al., 2001; Zhang & Zheng, 2007). Electrochemical reduction of graphene oxide shows an increase of electronic mobility and electrochemically active surface area (Moraes et al., 2015). Using functionalized graphene also gives good results on detection of different analytes.

In continuation of our recent work, aiming to prepare the electrochemical sensors in order to determine the different analytes (Berisha et al., 2015), we decided to develop a new electrochemical sensor for the determination of nitrophenols. Our research is focused on modification of electrochemical reduced graphene oxide (ERGO) in order to increase the sensitivity of the electrode surface to nitrophenols. The nitrophenols investigated in this work represent most commonly phenols present in the environment and human surroundings that reveal toxic influence towards living organisms, including humans (Girelli et al., 2006; Pan & Kurumada, 2008; Shah & Chen, 2012; Yi et al., 2001). Also, in this research work we have used successfully SPCE-ERGO on determination of nitrophenols in real samples (waste water) and those results are reported.

Materials and methods

The 4-aminoantipyrine, hydroquinone, phenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenolwere obtained from Sigma Aldrich and Carbon/graphite ink GWENT group. The supporting electrolyte, phosphate buffer solution (PBS) 0.1 M pH 7 was prepared by mixing 0.1 M sodium dihydrogen phosphate dihydrate and 0.1 M di-sodium hydrogen phosphate dodecahydrate, obtained from Lachner. All chemicals were of analytical grade. Phenolic compounds solutions were prepared in phosphate buffer solution (pH 7). Redistilled water was used for preparing solutions.

Voltammetric measurements were carried out using a computerized potentiostat and galvanostat (PalmSens, Compact Electrochemical Interfaces) that was connected to a personal computer. The experimental conditions for the voltammetric measurements were controlled with a PSTrace Software.All electrochemical studies were performed at 25 ± 2 °C with a three-electrode assembly with a screen printed carbon electrode (unmodified or modified) as working electrode, an Ag/AgCl/KCl (3 M) reference electrode, and counter electrode of platinum wire. Nitrogen was used for degassing the solutions. A magnetic stirrer provided convection of the solution. A digital 781 pH/Ion Meter Metrohm was used to read the pH of the buffered solutions. UV-VIS Spectrophotometer Helios Alpha was used for phenols reference method of analysis.

Synthesis of graphene oxide (GO)

Graphene oxide was synthesized using Hummer's method mixing 1.5 g graphite, 1.5 g $NaNO_3$ and 69 mL H_2SO_4. In the mixture was added gradually 9 g $KMnO_4$ stirring continuously in ice bath. The solution was let in 22^{o}C for 1h under stirring conditions and after was added 100 mL water and heated to 90^{o}C for 1h. The resulting solution was diluted with 300 mL water and excess potassium permanganate was reduced by addition of 10 mL of hydrogen peroxide 30%. After filtration and washing with HCl, graphene oxide was dried at room temperature.

Screen printed electrode (SPCE) and modification

SPCE were printed in transparent paper for inkjet in dimensions 35 x 3mm using carbon conductive ink. The electrode surface was covered using epoxy resin and electrode contact area was 9 mm^2. The silver paint was used for electrode contact. Electrode was modified with electrochemical reduction of graphene oxide (ERGO) using cyclic voltammetry by cycling of SPCE in graphene oxide solution 0.01 mg/mL in 0.1M phosphate buffer (pH 7) as supporting electrolyte. Modification conditions using cyclic voltammetry were in potential range 0 to -1.5 V with scan rate 50 mV/s and 20 scans.

Analytical procedure

Standard method was used for determination of phenols in water, using distillation method. The distilled water sample was treated with ammonia buffer and 4-aminoantipyrine and was let to stand for 15 min. and measurements were done in UV-VIS spectrophotometer at 510 nm. New electrochemical sensor was used for determination of phenols with standard addition method, 18.00 mL of distilled sample solution and 2.0 mL of phosphate buffer solution was measured in electrochemical cell and after addition of increments of 2-nitrophenol by micropipette.

Results and discussion

Differential pulse voltammetry

Unmodified and modified screen printed carbon electrode (SPCE) was tested on differential pulse voltammetry (DPV) in phosphate buffer solution 0.1 M (pH 7.5). DP voltammograms of plain SPCE and modified with electrochemical reduced graphene oxide (ERGO), comparing them for all nitrophenols used in this investigation are shown in Fig. 1.

In Fig. 1 are shown DPV voltammograms in positive direction of tested nitrophenols in phosphate buffer, and can be seen a difference between them in modified electrode. Generally electrode modified with reduced graphene oxide using electrochemical method has a higher current compared to unmodified because the reduced graphene oxide is good conductive material. During the modification, electrode surface is covered with reduced graphene oxide by reducing oxygen containing groups. During the measurements in DPV was mentioned that nitrophenols interact with modified electrode in different way compared to unmodified one, because of containing unreduced or easy oxidable functional groups. The modified electrode was also tested in negative direction (not shown here), and all nitrophenols show reduction peak around -0.50 V with no significant improvement with ERGO modification compared to phenol, hydroquinone and catechol.

Modified electrode shows better electrochemical response for hydroquinone with increase of peak intensity from 1.02 μA to 4.11 μA and potential shift from 0.14 V to 0.05 V after electrode ERGO modification. In the same manner is increased the electrochemical response to catechol (not shown here). Different view has the DP voltammogram of phenol because two peaks at 0.05 V and 0.35 V are not exposed in comparison to modified electrode where the peaks are very defined and with high intensity.

Electrochemical response of modified electrode to 3-nitrophenol and 4-nitrophenol (Fig. 1D and 1E) was improved with modified electrode around 4 times higher peak intensity around potential 0 V. 2-Nitrophenol DPV didn’t show so difference between modified and unmodified electrode, because of forming intra molecular hydrogen bond between hydroxyl and nitro group.

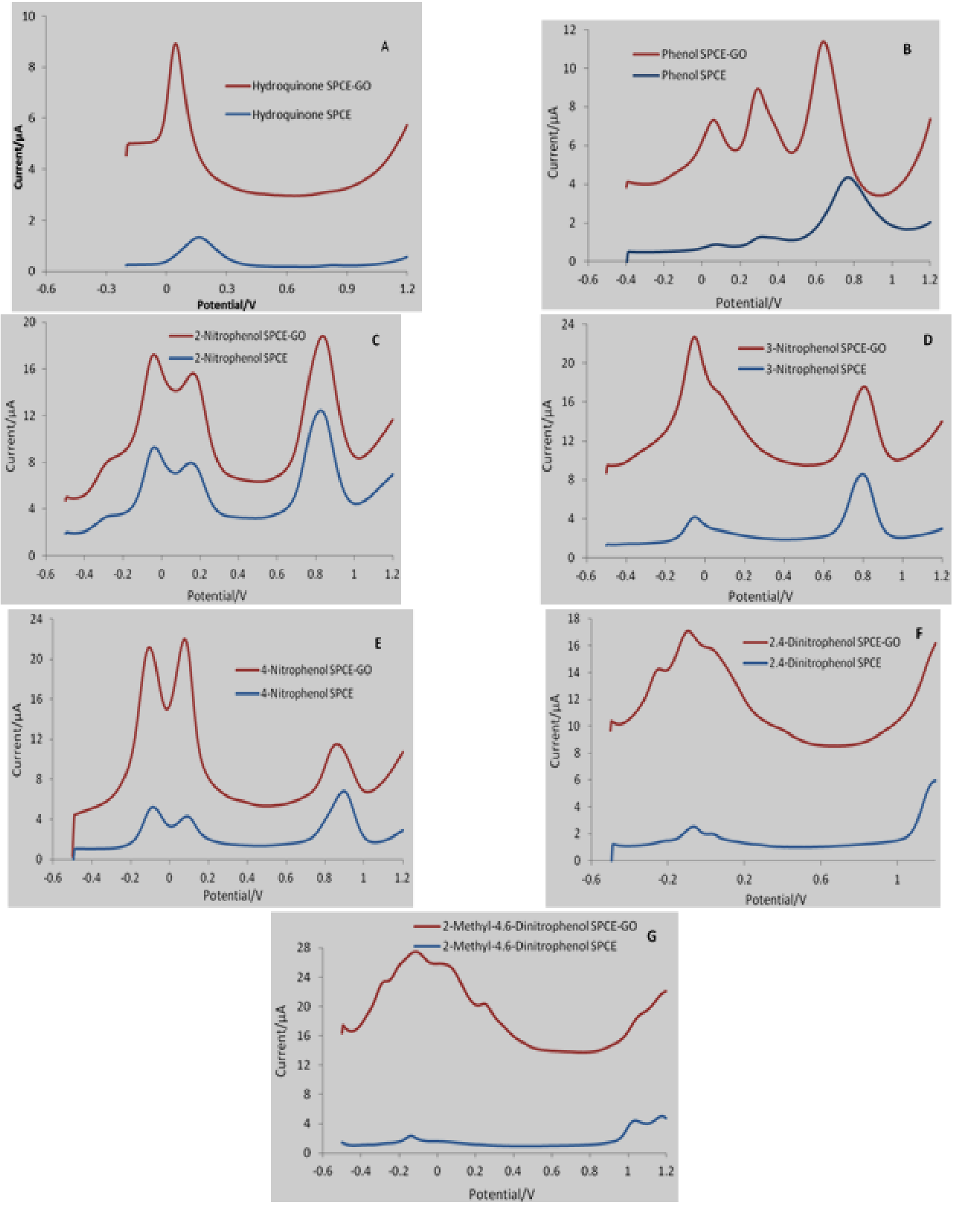

Fig. 1.(l/r: A-G) Differential pulse voltammograms of phenols at plain (blue) and ERGO modified (red) screen-printed carbon electrodes, scan rate 50 mV/s and analyte concentration 25 ppm

Hydrodynamic amperometry

Electrochemical properties of modified electrodes were investigated using hydrodynamic amperometry in different potentials from -400 mV to +400 mV. Sensitivity of electrodes with unit µA/ppm for modified and unmodified electrodes in hydrodynamic amperometry with phosphate buffer as supporting electrolyte pH 7.5, are shown in Fig. 2.

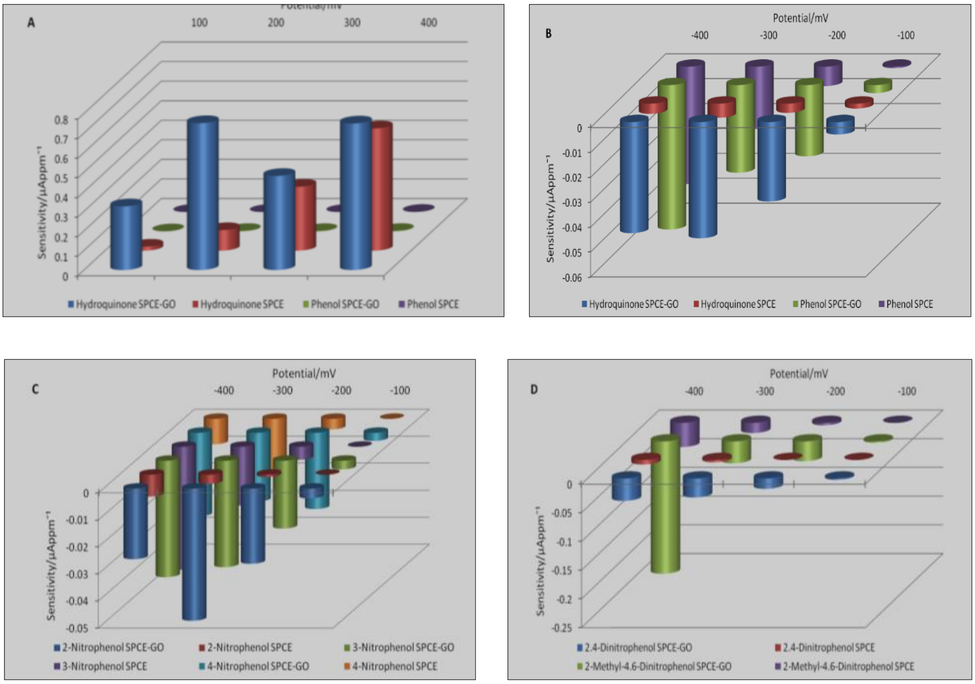

Fig. 2. (l/r: A-D) Electrode response (µA/ppm) to nitrophenols in hydrodynamic amperometry at different operating potential in phosphate buffer pH 7.5

From comparison (Fig. 2) the electrode sensitivity is increased in positive potentials for hydroquinone around 16 times (Fig. 2A), which is expected based on information received from DP voltammograms, especially on operating potential 100 and 200 mV. Also increase of sensitivity is observed in negative potentials for hydroquinone and for phenol, and that increase for hydroquinone is about 11 times at the potential -400 mV (Fig. 2B). In operating potential of -100 mV some of nitrophenols give anodic current response based on interaction of ERGO with nitrophenols. Electrode response to other phenolic compounds was increased at modified electrodes in operating potential of -200 mV. An increase was especially attributed to 2-nitrophenol 35 times (Fig. 2C) and for 2,4-dinitrophenol unmodified electrode didn't give a response (Fig. 2D). During amperometric measurements was observed the adsorption of phenols and was not so appropriate for quantitative measurements because of its low reproducibility.

Phenols determination in waste water

Voltammetric sensor was used for determination of nitrophenols in waste water using standard addition method. 2-Nitrophenol was chosen as standard solution for quantitative determination because the oxidation peak was near oxidation peak at sample solution near 0.80 V which is specific for analyzed nitrophenols. The peak intensity at ~0.80 V was used as signal for quantitative determination of total phenols in water without any treatment and after distillation method used for spectrophotometric determination. Results obtained for total phenols based on reference method are comparable with our new electrochemical electrode modified with ERGO and are shown in Table 1.

Table 1. Waste water results of nitrophenols concentration

Reference method	Voltammetric methods
8.5±0.1	9.2±0.5

Conclusion

In this work we have prepared a new electrochemical sensor for the purpose of electrochemical behavior investigation of nitrophenols and we have achieved this by modifying screen-printed carbon electrodes with reduced graphene oxide. Screen-printed carbon electrodes on transparent laser jet paper modified with electrochemical reduced graphene oxide are suitable for electrochemical investigation of nitrophenols. Using cyclic voltammetry for electrochemical reduction of graphene oxide at screen-printed carbon electrodes is a very simple way of modification and it is successful on improving electrode response to phenolic compounds. SPCE-ERGO modified shows good stability and differential pulse voltammetry is suitable method for determination of phenolic compounds in waste water with standard addition method.

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