

CARBON PASTE ELECTRODES MODIFIED WITH DIATOMITE ADSORBED WITH TOLUIDINE BLUE, USED FOR NITRITE DETECTION IN WATER

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ABSTRACT. This work describes a simple and reliable method for electrochemical determination of nitrite based on carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue (CPE-D-TBO). The electrochemical behavior was investigated using cyclic voltammetry measurements in different experimental conditions (cycling times, scan rates, pH values of supporting electrolyte). The electrochemical parameters of modified electrodes were determined (E^0 , -198 mV vs. Ag|AgCl/KCl_{sat}; ΔE_p , 79 mV vs. Ag|AgCl/KCl_{sat} and $|I_{pa}/I_{pc}| = 1.81$). The modified electrodes CPE-D-AT showed good electrochemical stability. Analytical parameters of the obtained sensors determined using amperometric measurements confirm their possibility to use in real samples (detection limit, 9.10 μ M; sensitivity, 9.88 mA M⁻¹; linear domain, 0.0001-0.1 mM).

Key words: *amperometric sensors, electrodes, diatomite*

INTRODUCTION

Nitrites can contaminate both surface water and the groundwater, particularly as a result of agricultural activities, industrial and due to the oxidation of nitrogen compounds present in various organic materials. Excess nitrites in drinking water can be harmful to health, especially for children and pregnant women (Ghibu, 2008).

Human activity accelerates the pollution of water by using of fertilizers on agricultural land; waste from the fertilizer industry; sewage spills (Brînzei et al., 2005).

Nitrites can cause harmful effects by two mechanisms: (i) it can interact with amines and amides in stomach to form N-nitrosamines, which are carcinogenic; (ii) it can combine with blood pigments forming methaemoglobinemia, resulting lack of oxygen in the tissues (Zhu et al., 2009).

Human exposure to N-nitroso compounds and precursors (nitrate and nitrite) may be derived from exogenous sources, such as water, food and endogenous exposure, resulting in the formation of N-nitroso compounds in the body. Formation of nitrosamines from nitrites can cause cancer and birth of children with congenital problems (Griesenbeck et al., 2010).

Because of their toxicological significance is necessary to determine quality but especially the quantity of nitrites, for monitoring of foods and waters (Miere, 2007). Thus, due to the importance of nitrite in environmental science and food chemistry, a number of analytical methods for detecting nitrites have been developed, such as: electrophoresis, atomic absorption, ion chromatography, high performance liquid chromatography, gas chromatography, etc (Badea et al., 2001; Salimi et al., 2008).

Traditionally nitrite was determined spectrophotometrically by their reaction with sulphanilamide and N-1- naphthylenediamine (Griess reaction). This method requires careful control of acidity for each stage of the process, having carcinogenic effects and can be unreliable due to the interferences present in the sample matrix from the strong oxidants and colored substances. Nitrates were generally reduced to nitrite in a copper-coated cadmium column and then determined spectrophotometrically by the previous Griess reaction. This method required several stages of pre-treatment and a long time. For this, in the last 20 years many analytical methods have been developed, proving to be more rapid, accurate and sensitive than spectrophotometric method (Badea et al., 2001).

Comparing with other methods for nitrite determination, electrochemical methods provide a more rapid response, ease of use, safety and low cost of analysis (Harvey, 2000; Santos et al., 2006).

Regarding the oxidation of nitrite, it implies a very high potential on glassy carbon electrode surface. For this, chemically modified electrodes have been achieved to detect nitrite in order to reduce the overpotential. Electrode surface modification improves the linear domain in nitrite analytical determinations (Zhao et al., 2007).

Diatoms are single-celled plants that live in a hard shell. Diatoms are found in nature both in freshwater and salt water. When plants die their shells sink. Huge amounts of death plants accumulate in time, forming eventually called kieselguhr or rock material easier, known as diatomaceous earth (Yuxin et al., 2007).

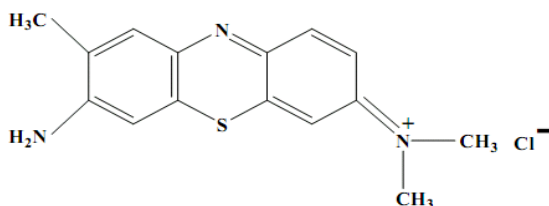
In this context, we obtained a new amperometric sensor based on carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue for nitrite detection in water. The electrochemical behavior of the obtained modified electrodes was characterized using cyclic voltammetric measurements in different experimental conditions (cycling times, scan rates, pH values of supporting electrolyte). The electrocatalytic effect towards nitrite oxidation was tested by cyclic voltammetry and the analytical and kinetic parameters of the obtained sensors were determined using amperometry. The sensors were also applied for nitrite detection in water samples.

EXPERIMENTAL

Materials

Toluidine Blue O (TBO) (Scheme 1) was purchased from Aldrich (Steinheim, Germany). Graphite powder and paraffin oil were obtained from Fluka (Buchs, Switzerland), while sodium nitrite was purchased from Reactivul Bucharest (Romania). $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ were purchased from Merck (Darmstadt, Germany).

All reagents were of analytical grade and used as received. The supporting electrolyte was 0.1 M phosphate buffer solution, obtained by mixing solutions of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in appropriate ratios. When necessary, pH was adjusted in the interval 2-10 using H_3PO_4 or NaOH solutions. The nitrite stock solution used throughout this study was made of 0.1 M NaNO_2 , which was then diluted to reach the desired concentrations.



Scheme 1. Structure of Toluidine blue O (TBO).

Electrochemical measurements

Cyclic voltammetry was performed in a conventional three electrode system. A platinum wire was used as counter electrode, $\text{Ag|AgCl/KCl}_{\text{sat}}$ as reference electrode, and the modified carbon paste electrodes as working ones. All electrochemical experiments were carried out using an Autolab electrochemical analyzer (Autolab-PGSTAT10, Eco Chemie, Utrecht, Netherlands). All measurements were performed at room temperature.

Batch amperometric measurements at various nitrite concentrations were carried out at an applied potential of +880 mV vs. $\text{Ag|AgCl/KCl}_{\text{sat}}$, under magnetic stirring, using 0.1 M phosphate buffer solution as supporting electrolyte. The current-time data were collected using the above-mentioned electrochemical analyzer.

Monitoring pH of the phosphate buffer solutions was made using a HI255 pH-meter (Hanna Instruments, Romania), with a combined glass electrode.

Electrode preparation

100 ml of a 0.01% (w/v) TBO solution in water were magnetic stirred (2 days) with 100 mg of diatomite. The modified material was filtered, washed and dried. 50 mg of the modified adsorbent was mixed with 50 mg graphite powder and 10 μl paraffin oil in order to obtain the modified carbon paste electrodes: CPE-D-TBO.

RESULTS AND DISCUSSION

Figure 1 presents the cyclic voltammograms of carbon paste electrodes modified with pure diatomite (CPE-D) and carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue (CPE-D-TBO), both electrodes being tested in 0.1 M phosphate buffer solution of pH 7. As can be observed, CPE-D-AT electrodes

present a voltammetric response as well-defined peaks, while the CPE-D electrodes don't present a favorable redox response. This behavior proves the adsorption of TBO on diatomite.

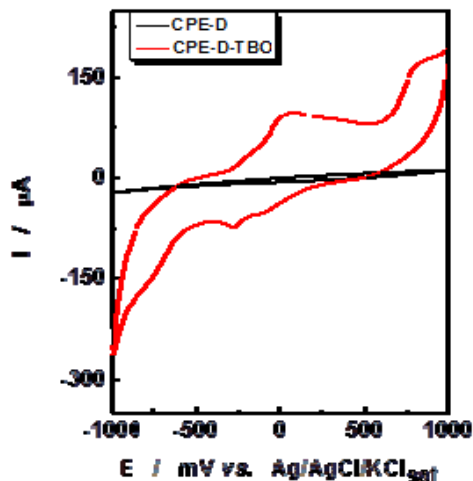


Fig. 1. Cyclic voltammograms for carbon paste electrode modified with CPE-D and CPE-D-TBO. Experimental conditions: starting potential: -1000 mV vs. Ag|AgCl/KCl_{sat}; scan rate, 50 mV s⁻¹; supporting electrolyte, 0.1 M phosphate buffer, pH 7.

The corresponding electrochemical parameters of the CPE-D-AT modified electrodes are: formal standard potential E^0 (defined as average of anodic and cathodic peak potentials), -198 mV vs. Ag|AgCl/KCl_{sat}; ΔE_p (the difference between anodic and cathodic peak potentials), 79 mV vs. Ag|AgCl/KCl_{sat} and $|I_{pa}/I_{pc}| = 1.81$. From the analyses of the obtained parameters can be concluded that voltammetric process is one bielectronic quasi-reversible ($\Delta E_p > 59/2$ mV, $|I_{pa} / I_{pc}| \neq 1$).

Electrochemically stability tests of the investigated systems were carried out under potentiodynamic conditions: the electrode potential of the modified electrodes was cycled in the potential range covering the redox activity of the mediator, at a scan rate of 50 mV s⁻¹, for 25 cycles, in 0.1 M phosphate buffer pH 7. As can be seen in figure 2A, a small increase of peak current intensities took place, while the shape of voltammogram was unchanged.

From dependencies of peak current *versus* cycling time (figure 2B), the kinetics of activation/deactivation reaction was studied. As can be observed, the graphs are linear, the equation obeys a zero order kinetics and it took an activation process, excepting the supporting electrolyte of pH 9 where is a slowly deactivation process. The activation rate constants decreased in the sequence: pH 3 ($122.6 \cdot 10^{-10}$ A s⁻¹) < pH 7 ($23.5 \cdot 10^{-10}$ A s⁻¹) < pH 9 ($6.6 \cdot 10^{-10}$ A s⁻¹).

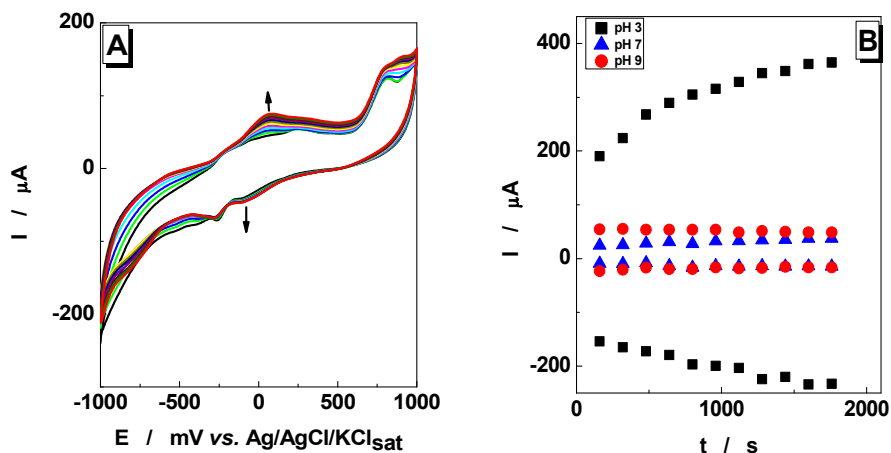


Fig. 2. Cyclic voltammograms corresponding to cycling the CPE-D-TBO electrodes during 20 cycles (A) and dependence of peak current vs. cycling time (B). Experimental conditions: starting potential, -1000 mV vs. Ag|AgCl/KCl_{sat}; potential scan rate, 50 mV s⁻¹; supporting electrolyte, 0.1 M phosphate buffer.

The electrochemical behavior of obtained electrodes was also studied at different scan rates (figure 3A). As expected for redox species attached to the electrode surface, cyclic voltammograms recorded on a large range of potential scan rate (0.01 to 6.4 V s⁻¹) showed a linear dependence of the peak intensity (I_p) versus scan rate (v) (figure 3B).

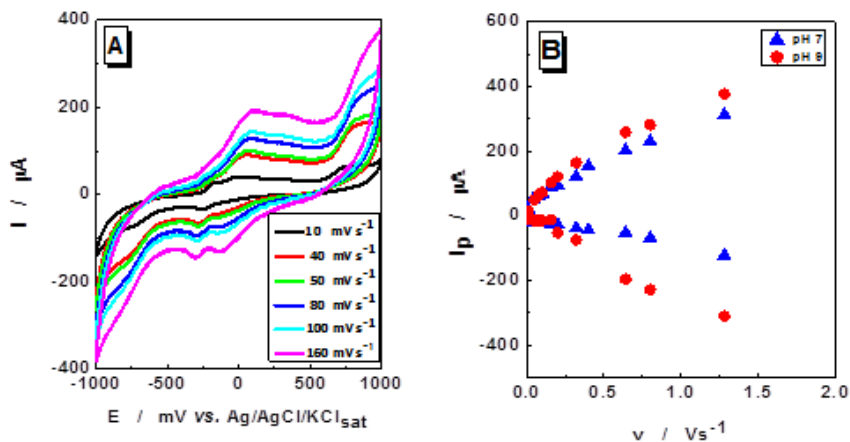


Fig. 3. Cyclic voltammograms obtained at different scan rates (A) and dependence of peak current vs. potential scan rate (B) corresponding to CPE-D-TBO electrodes. Experimental conditions: starting potential, -1000 mV vs. Ag|AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer, pH 7 (A).

The slopes of $\log I$ vs. $\log v$ dependencies were close to the theoretical value one, confirming the existence of adsorbed species and of a kinetic control (Table 1). Deviations observed in some cases could be due to uncompensated ohmic resistance (Zhou et al., 1998) and of mediator diffusion into solution, especially for oxidation process.

Table 1. Linear regression parameters corresponding to $\log I$ vs. $\log v$ dependence of CPE-D-TBO electrodes. Experimental conditions: as in figure 3

| pH | Slope ($A s^{-1}$) | | R / no. exp. points | |
|----|----------------------|-----------------|---------------------|------------|
| | oxidation | reduction | oxidation | reduction |
| 3 | 0.37 ± 0.02 | 0.71 ± 0.03 | 0.983 / 8 | 0.995 / 5 |
| 7 | 0.55 ± 0.01 | 0.71 ± 0.03 | 0.995 / 15 | 0.987 / 12 |
| 9 | 0.64 ± 0.01 | 0.88 ± 0.04 | 0.996 / 11 | 0.991 / 8 |

The heterogeneous electron transfer rate constants were determined, using Laviron's method. The method consists in calculation of the rate constant (k_s) and of transfer coefficient (α) of a redox couple, using cyclic voltammetry measurements performed at different scan rates (Laviron, 1980).

The equations of this method are:

$$E_{pc} - E^{0'} = \frac{RT}{\alpha nF} \times 2.3 \lg \frac{\alpha nF}{RTk_s} + \frac{2.3RT}{\alpha nF} \lg v \quad [V] \quad (1)$$

$$E_{pa} - E^{0'} = \frac{RT}{(1-\alpha)nF} \times 2.3 \lg \frac{(1-\alpha)nF}{RTk_s} + \frac{2.3RT}{(1-\alpha)nF} \lg v \quad [V] \quad (2)$$

where: k_s [s^{-1}] is the heterogeneous electron transfer rate constant, α the transfer coefficient, n the number of exchanged electrons.

From the slope of $(E_p - E^{0'})$ vs. $\lg v$ graph (figure 4), the α coefficient was determined and from intercept, k_s constant. Using equations (1) and (2) and the graph from figure 4, k_s constants and α coefficients were determined at different pH values of supporting electrolyte (Table 2). It can be observed that k_s value obtained at pH 9 is higher than that obtained at pH 7.

Fig. 4. Experimental dependence of $(E_p - E^{0'})$ versus logarithm of the scan rate for CPE-D-TBO electrodes. Experimental conditions: starting potential, -1000 mV vs. $Ag|AgCl|KCl_{sat}$; supporting electrolyte, 0.1 M phosphate buffer (pH 7).

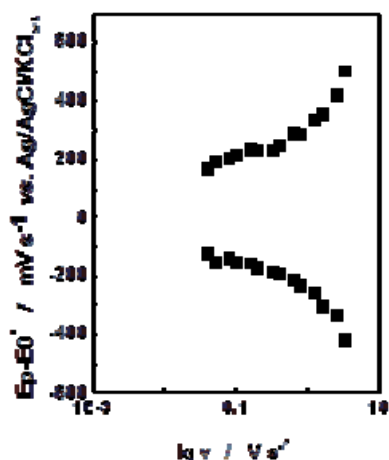


Table 2. Heterogeneous electron transfer rate constants corresponding to CPE-D-TBO electrodes. Experimental conditions: as in figure 4.

| pH | k_s (s ⁻¹) | α | R / no. exp. points | |
|----|--------------------------|----------|---------------------|-----------|
| | | | oxidation | reduction |
| 7 | 3.84 | 0.29 | 0.996 / 4 | 0.982 / 5 |
| 9 | 5.21 | 0.17 | 0.990 / 5 | 0.995 / 5 |

Electrocatalytic activity for nitrite oxidation of modified carbon paste electrode was investigated using cyclic voltammetry. Fig. 5 shows the corresponding cyclic voltammograms of CPE-D-TBO electrode in buffer solution, pH 7, in the absence and in the presence of nitrite of different concentrations. As can be seen, in the presence of nitrite, the oxidation peak current increases significantly, which proves the existence of a favorable electrocatalytic effect.

Electrocatalytic efficiency was estimated using the relation:

$$\frac{[I_p]_{[NO_2] \neq 0} - [I_p]_{[NO_2] = 0}}{[I_p]_{[NO_2] = 0}} \quad (3)$$

where: $[I_p]_{[NO_2] \neq 0}$ and $[I_p]_{[NO_2] = 0}$ are current intensities in the presence and in the absence of nitrite, respectively. The electrocatalytic efficiency estimated at +750 mV vs. Ag|AgCl/KCl_{sat}, for 1mM nitrite, was 282 %. This high value shows the possibility to use these new modified electrodes as amperometric sensors for nitrite detection.

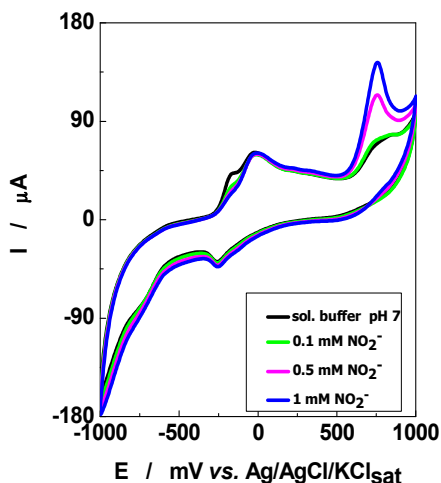


Fig. 5. Electrocatalytic oxidation of nitrite on CPE-D-TBO electrodes. Experimental conditions: starting potential, -1000 mV vs. Ag|AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer, pH 7; scan rate, 10 mV s⁻¹.

Batch amperometric measurements, performed at an applied potential of +880 mV vs. Ag|AgCl/KCl_{sat}, in phosphate buffer solution of pH 7, allowed us determination of analytical characteristics corresponding to the amperometric sensors based on CPE-D-TBO electrodes.

From registration I vs. t , amperometric calibration curve was obtained (Fig 6).

The obtained analytical parameters for these new sensors are: detection limit, 9.10 μM ; sensitivity, 9.88 mA M^{-1} ; linear domain, 0.0001-0.1 mM. These values show possibility to use these amperometric sensors for nitrite detection in real samples.

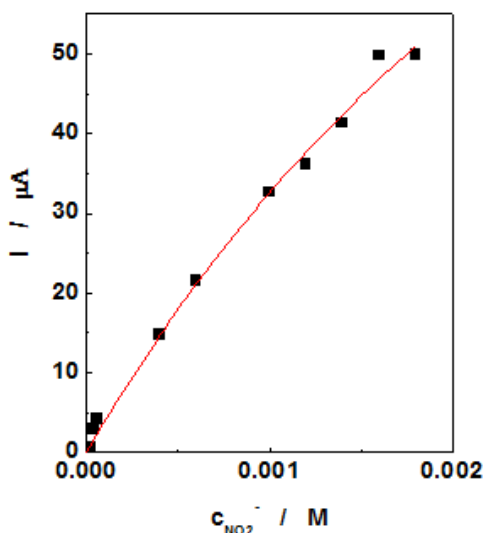


Fig. 6. Calibration curve for nitrite detection using CPE-D-TBO electrodes. Experimental conditions: applied potential, +880 mV vs. Ag|AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer (pH 7).

Thus, the obtained sensors were tested for nitrite detection in real samples of water (surface water from Mediaș, Sibiu county), using the standard addition method. The nitrite concentration obtained using these amperometric sensors was 75 μM , value which is in concordance with that obtained using ion chromatography, 65 μM .

CONCLUSIONS

In this study we developed new nitrite amperometric sensors based on carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue. The nitrite sensors exhibited good analytical characteristics, such as high sensitivity (9.88 mA M^{-1}), low detection limit (9.10 μM), short response time (2 s), and wide concentration range (0.0001-0.1 mM).

The obtained nitrite sensors were used to determine the nitrite concentration in water samples, and the results were comparable with that obtained using ion chromatography. Due to their good analytical performances, these new sensors have potential applications in the environmental monitoring field.

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