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Voltammetric Determination of 5-Amino-6-nitroquinoline at a Carbon Fiber Rod Electrode

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Inexpensive carbon fiber rod electrodes (CFRE) in three diameters of 0.8 mm, 2 mm and 3 mm were used for voltammetric determination of 5-amino-6-nitroquinoline (5A6NQ) based either on its anodic oxidation or cathodic reduction using direct current voltammetry and differential pulse voltammetry. CFRE is based on carbon fiber rod, which consists of lengthwise oriented long carbon fibers coated from outer side by epoxy resin, connected to copper wire by conducting paint. The electrode material is inexpensive, commercially available at very low cost and at various shapes and sizes and its surface is easy to regenerate. Electrochemical behavior of prepared electrodes was examined using typical model redox system potassium ferrocyanide in aqueous supporting electrolytes. The best ratio between signal and noise was attained at CFRE with a 2 mm diameter. Practical applicability of these methods was demonstrated on the determination of 5A6NQ at CFRE-2 mm in model samples of drinking and pond water. CFRE can serve as a good alternative to pencil electrodes or carbon paste electrodes especially in cathodic voltammetry.

Keywords: Carbon fiber rod electrode, Composite carbon electrode, Voltammetry, 5-Amino-6-nitroquinoline.

1. INTRODUCTION

Carbon-based electrodes are currently widely used in electroanalytical chemistry because of their low cost, broad potential windows, rich surface chemistry, low background currents, chemical inertness, and suitability for wide range of demanding applications [1]. Electrochemical properties of carbon electrodes for oxidations and reductions of organic compounds and biologically active molecules in both aqueous and nonaqueous media are often superior to those of noble metals [2]. Over the years, many types of carbon-based working electrodes, modified or unmodified, have been developed and used in various ways in order to improve their performance for voltammetric measurements [3-9]. However, besides the electrodes with excellent electrochemical properties but difficult fabrication, inexpensive and easy-to-made electrodes also find their applications, in spite of their somewhat poorer performance. This is for instance the case of pencil electrode first mentioned in 1989 [10]. Pencil electrodes were used for the determination of various analytes, for example heavy metals [11, 12], caffeine [13], benzo[a]pyrene [14], DNA hybridization [15], etc. Its advantageous low cost and easy preparation are compromised by considerably higher noise and random peak deformations as compared with other electrodes such as carbon paste electrode [16].

The application of carbon fibers in electrochemistry is well-known, as electrodes consisting of one carbon fiber were introduced for *in situ* electrochemical measurement in 1981 [17] and since that time they have been used extensively in electrochemistry, predominantly in applications requiring small measuring volumes such as for *in vivo* monitoring. They have generally diameters in the range of 5–50 μm and are made by heat treatment process of starting polymers (polyacrylonitrile) or asphalt concentrates (petroleum pitch) materials [18]. Furthermore, carbon fibers were used in the preparation of carbon composite electrodes, for example mixing randomly oriented chopped carbon fibers with polymers such as nylon [19, 20].

Carbon fiber rods are made by pultrusion process, in which constant cross-sections carbon fibers are pulled through a resin bath, and gathered together to produce a particular shape in heated die which determines the sectional geometry and finish of the final product. Utilization of carbon fiber rods is generally connected with industrial constructions requiring light but firm materials. They are mainly used in model making. The electrodes made of this material can be classified as composite electrodes. The construction of the electrode from the carbon fiber rod is very simple, involving just the connection of electrical contact to several centimeters long piece of the rod. There have been only a few studies related to electrochemical properties of carbon fiber epoxy composites [21-23] and application as electrochemical detector in HPLC [24].

5-Amino-6-nitroquinoline (5A6NQ) ranks among nitro and aminoderivatives of heterocyclic compounds, which are often mutagenic and carcinogenic [25, 26]. Heterocyclic amines are produced when meat is heated above 180 °C for a long time [27, 28]. They can be found in a cigarette smoke [29] and as products of incineration of fossil fuels [30]. The voltammetric behavior of 5A6NQ at carbon paste electrode was already studied in our previous work [31].

In the presented paper we demonstrate the application of carbon fiber rod electrode (CFRE) in three diameters of 0.8 mm, 2 mm and 3 mm for direct current or differential pulse voltammetric determination of 5-amino-6-nitroquinoline based either on its anodic oxidation or cathodic reduction. Practical applicability of these methods was demonstrated on the determination of 5A6NQ at CFRE-2 mm in model samples of drinking and pond water.

2. MATERIALS AND METHODS

2.1 Apparatus

For voltammetric measurements, a computerized voltammetric analyzer Eco-Tribo Polarograph with software PolarPro 4.0 (all Polaro Sensors, Czech Republic) was used. The three-electrode arrangement with Ag/AgCl reference electrode RAE 113 (Monokrystaly, Czech Republic) filled with 3 M KCl, auxiliary platinum wire electrode, and working CFRE was used. For comparison purposes, the measurements with glassy carbon electrode (GCE) with a 2 mm diameter (Methrohm, Switzerland, type 6.1204.110) were performed.

The pH of the solutions was measured with a pH meter Jenway 4330 with a combined glass electrode (both Jenway, UK).

The stability of the stock solution of 5A6NQ was followed spectrophotometrically using a spectrophotometer Agilent 8453 (Agilent, USA). A microscope camera (Digitus, Taiwan) and a microscope 825072 (Meopta, Czech Republic) were used for microscopic investigation of the CFRE structures. All experiments were carried out at a laboratory temperature.

2.2 Materials

The stock solution (1×10^{-3} mol L^{-1}) of potassium ferrocyanide (Lachema Brno, Czech Republic) was prepared in 1 M KCl (p.a., Lach-Ner, Czech Republic). For obtaining lower concentrations, the stock solution was diluted with 1M KCl. The stock solution (1×10^{-3} mol L^{-1}) of 5-amino-6-nitroquinoline (Aldrich, USA) was obtained by dissolving the exact amount of the analyte in methanol (p.a., Lach-Ner, Czech Republic). Britton-Robinson (BR) buffers were prepared from a solution containing 0.04 M phosphoric acid, 0.04 M acetic acid and 0.04 M boric acid and an appropriate amount of 0.2 M sodium hydroxide. The supporting electrolytes consisting of perchloric acid, sulphuric acid, potassium chloride or sodium hydroxide (0.1 mol L^{-1}) were used. All the chemicals used were of analytical reagent grade and were purchased from Lachema Brno, Czech Republic. All aqueous solutions were prepared using deionized water obtained from MiliQ Plus system (Millipore, USA).

For model samples, drinking water from the public water line in the building of Faculty of Science of the Charles University in Prague was used and the sample of pond water was taken from Milicovsky pond in Prague.

2.3 Carbon fiber rod electrode

The carbon fiber rod electrodes (CFRE, Fig. 1) were produced from carbon fiber rods (RCM Pelikan, Czech Republic) in 0.8 mm, 2 mm and 3 mm diameters and of 1 m length. The electric contact was made of a copper wire which was connected by a conducting paint EL-2 (Elchemco, Czech Republic) to the 5 cm long carbon fiber rod.

For fixing the electrode in the holder compatible with the used instrumentation, a laboratory parafilm M (Pechiney plastic packaging, USA) and a plastic tube were used (Fig. 1D). The surface of the CFRE was renewed mechanically by very fine sandpaper Sianor B (grit 1600, sia Abrasives, Switzerland) and alumina polishing powder (5 μm size, Bioanalytical Systems, Inc., USA) in suspension.

2.4 Procedures

Solutions for voltammetry were prepared by mixing 5 mL of methanolic solution containing the respective amount of the 5A6NQ with 5 mL of BR buffer of chosen pH in volumetric flask and filling to 10 mL with a mixture of methanol and BR buffer of chosen pH (1:1, v/v). Before cathodic voltammetric measurements, the solution in the voltammetric cell was deaerated for 10 min by bubbling with nitrogen.

The solutions for measurement of model samples were prepared by mixing 4 mL of drinking or pond water with 5 mL of methanolic solution containing the respective amount of the 5A6NQ, adding 1 mL of BR buffer of chosen pH and filling to 10 mL with a solution of methanol and BR buffer of chosen pH (1:1, v/v).

Calibration dependences were measured in triplicate and evaluated by a linear regression method. The limit of detection (L_D) was calculated as the amount of 5A6NQ, which gave three times higher signal than the standard deviation (*SD*) of the lowest concentration of the calibration dependence [32].

3. RESULTS AND DISCUSSION

3.1 Carbon fiber rod electrode characterization

The structure of the prepared carbon fiber rod was examined microscopically. The active end of the carbon fiber rod electrode (CFRE), as prepared by the aforementioned procedure, is shown in Fig. 1A. Deliberately destroyed end of carbon fiber rod (Fig. 1B) reveals the structure of the rod, consisting of inner filling made of carbon fibers and outer coating made by epoxy resin. The resin is, besides filling the space between the fibers, forming the layer on the surface of the rod (Fig. 1B, 1C), which is probably responsible for some of its favorable characteristics and for the wall isolation of the carbon fibers from the electrolyte. The photograph of manufactured CFREs ready for measurement is depicted in Fig. 1D.

At first, electrochemical characteristics of prepared CFREs were tested to confirm the proper preparation and function of working electrodes using typical model redox system of $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ in 1M KCl, utilizing cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

For the characterization of the isolation properties of the epoxy resin (Fig. 1C) the DP voltammograms of 1×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ in 1 M KCl were measured with various length (1–20 mm) of the electrode (CFRE-0.8 mm) immersed into the measured solution. The peak height was almost independent of the depth of immersion, thus indicating that the electrode reaction occurs only at the electrochemically active surface at the end of the rod, while the electrode walls are probably well shielded by the layer of epoxy resin.

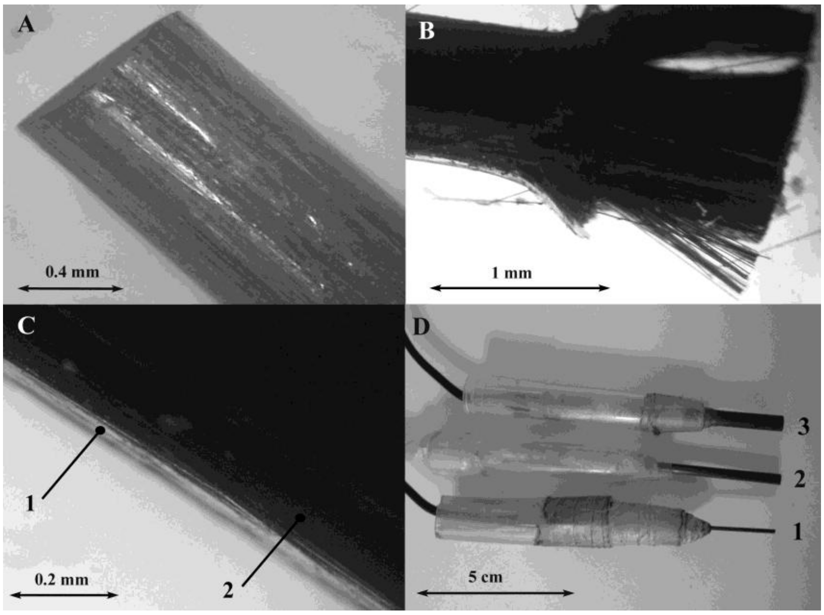


Figure 1. The photograph of the surface of CFRE-0.8 mm (***A***), deliberately destroyed end of carbon fiber rod with a diameter of 0.8 mm (***B***), epoxy resin (***C1***) covering the walls of carbon fiber rod (***C2***), ready to use electrodes: CFRE-0.8 mm (***D1***), CFRE-2 mm (***D2***), CFRE-3 mm (***D3***).

The applicable range of potentials of the prepared CFRE was tested by CV in a solution of NaOH, KCl, $HClO_4$, H_2SO_4, (0.1 M each) and BR buffers (pH 2, 7, 12) and the voltammograms were compared with the supporting electrolyte voltammograms measured on a glassy carbon electrode (GCE) with a diameter of 2 mm.

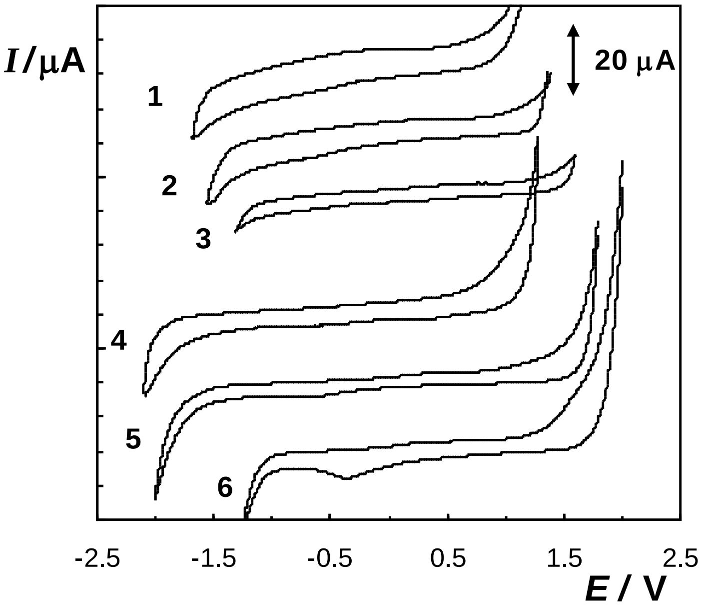


Figure 2. Potential windows of CFRE-0.8 mm in BR buffer pH 12 (***1***), 7 (***2***) and 2 (***3***) compared to those of GCE in BR buffer pH 12 (***4***), 7 (***5***), 2 (***6***), measured by CV, scan rate 20 mV s^{-1}.

The voltammograms in BR buffer are shown in Fig. 2 and it can be seen that CFRE-0.8 mm has practically the same range of potential windows as GCE in anodic area for all tested media and in cathodic area for BR buffer pH 2.

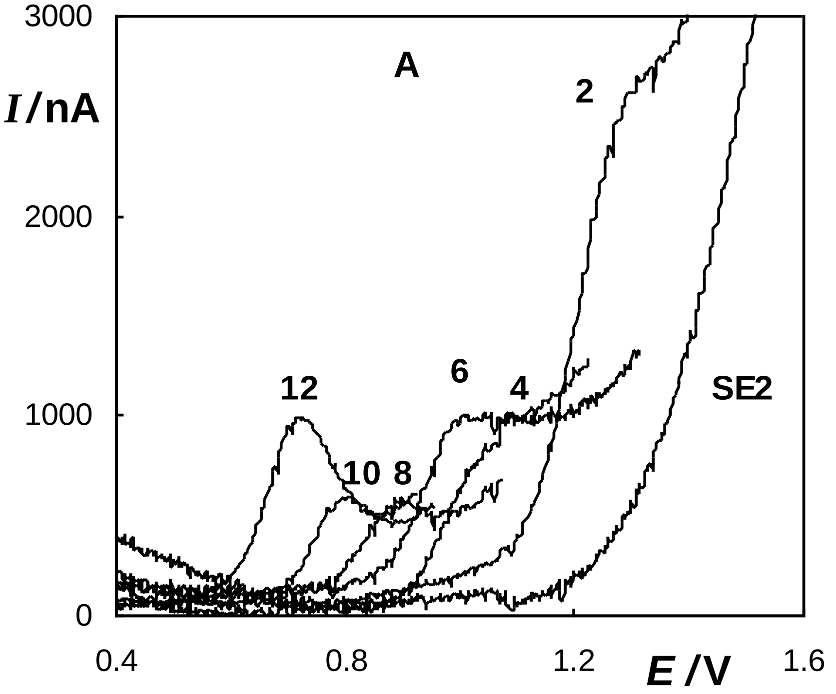
In alkaline medium the potential window of CFRE-0.8 mm is narrower in cathodic area than potential window of GCE. The anodic and cathodic peak potentials of $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ in 1M KCl are almost independent of potential scan rate.

The electrochemical oxidation process of $K_4[Fe(CN)_6]$ is controlled by diffusion at both CFRE and GCE. This was confirmed by direct proportionality observed for the dependence of the peak current on the square root of the scan rate from 2 to 1000 mV s^{-1}. The current height ratio of anodic to cathodic peak (I_a/I_c) remains almost one and peak potential separation ($\Delta E = E_a – E_c$) being 78 mV at scan rate of 100 mV s^{-1}.

3.2 Determination of 5-amino-6-nitroquinoline

After electrochemical characterization of CFRE the possibility of its application for voltammetric determination of 5-amino-6-nitroquinoline (5A6NQ) was investigated. Because of the low solubility of 5A6NQ in water, a mixture of BR buffer with methanol 1:1 (v/v) was used as the supporting electrolyte.

The influence of the BR buffer pH in the range from 2 to 12 was investigated using both differential pulse voltammetry (DPV) and direct current voltammetry (DCV) in the anodic and cathodic potential range at CFRE-0.8 mm, CFRE-2 mm, and CFRE-3 mm.



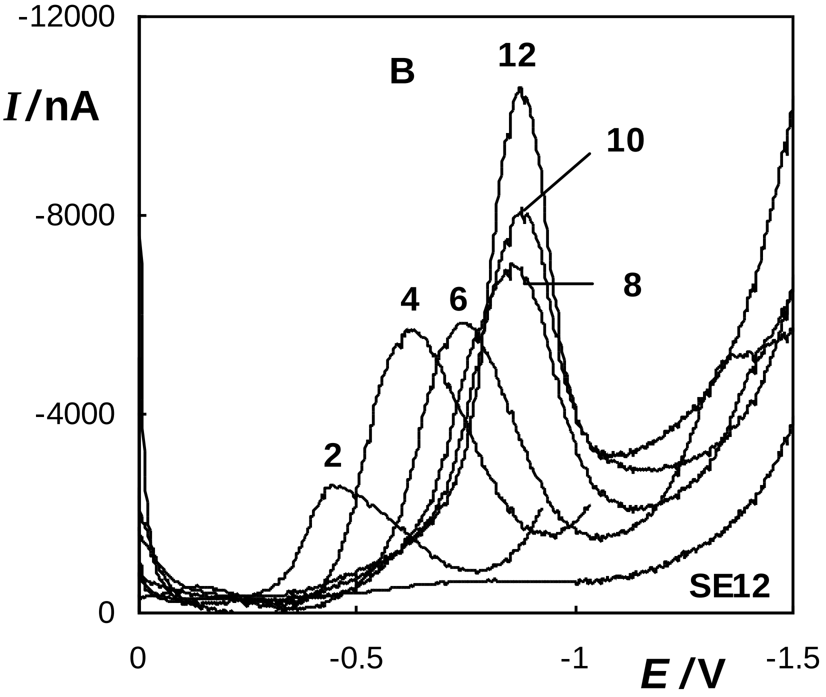


Figure 3. The anodic (***A***) and cathodic (***B***) voltammograms of 5A6NQ ($c = 1 \times 10^{-4}$ mol L^{-1}) measured by DPV at CFRE-2 mm in a BR buffer - methanol mixture (1:1, v/v). Buffer pH corresponds to the number of the curve (***2***–***12***), (***SE2, SE1***2 corresponds to supporting electrolyte: BR buffer pH 2 or pH 12 - methanol (1:1, v/v)). Scan rate 20 mV s^{-1}, pulse width 100 ms, and pulse height 50 mV (***A***) or –50 mV (***B***).

All the electrodes exhibited similar behavior; on the example of CFRE-2 mm (Figure 3A) it can be seen the shift of the 5A6NQ peak potential to the less positive values with increasing pH reflecting the involvement of the protons in the reaction mechanisms. Figure 3B shows the shift of the 5A6NQ cathodic peak potential at CFRE-2 mm to less negative values with decreasing pH, which can be explained by easier reduction of nitro group following the analyte protonation in more acidic medium. BR buffer pH 12 - methanol (1:1, v/v) was chosen as the optimum medium for the measurement of anodic and cathodic 5A6NQ calibration dependences for both DPV and DCV at all electrode sizes due to the highest and the best developed signal. The effect of the electrode surface passivation on the analyte peak current was studied by 20 consecutive measurements of 1×10^{-4} mol L^{-1} 5A6NQ in BR buffer pH 12 - methanol (1:1, v/v) by anodic and cathodic DPV at CFRE-2 mm, without the renewal of the electrode surface. The signal of anodic peak current decreased by 28 % and of cathodic peak current by 3,8 % of original value. Because of the pronounced passivation of CFRE in the case of anodic DPV we have paid attention to the possibility of the renewal of the electrode surface. Although the repeatability of cathodic DPV was much better, we have tried the renewal of electrode surface even in this case to get better results.

The repeatability was calculated from 20 (or from 10 in the case of electrochemical activation) consecutive measurements of 1×10^{-4} mol L^{-1} 5A6NQ by DPV in BR buffer pH 12 - methanol mixture (1:1, v/v) with the renewal of the electrode surface after each measurement. We have tested mechanical renewal by very fine sandpaper (grit 1600) and alumina polishing powder (5 μm size) and in the case of anodic DPV also electrochemical activation of the electrode surface. The variation coefficients of cathodic peak currents were 34 % for sandpaper, 2.2 % for alumina, and of anodic peak currents were 14 % for sandpaper, 5.5 % for alumina. We also tried the electrochemical activation in the supporting electrolyte of BR buffer pH 12 - methanol (1:1, v/v), BR buffer pH 12 and 1 M HNO_3. The best results were obtained in BR buffer pH 12 - methanol (1:1, v/v) for electrode pretreatment for 10 s at the potential of –1.5 V and 10 s at +1.5 V; under these conditions, the variation coefficients reached 9.1 %, which is not better than for mechanical renewal of the electrode surface by alumina powder. It follows from the results that the best way of the electrode surface renewal in both anodic and cathodic DPV is mechanical renewal by alumina powder. The cyclic voltammograms were recorded at various scan rates from 2 to 1000 mV s^{-1} in a mixed BR buffer pH 12 - methanol (1:1, v/v) medium. The oxidation and reduction process of 5A6NQ at CFREs is irreversible and controlled by both diffusion and adsorption, as the direct proportionality was not observed for the dependence of the peak current on the scan rate or on the square root of the scan rate.

The calibration curves were measured under the optimum conditions (BR buffer pH 12 - methanol 1:1, v/v) with mechanical renewal of electrode surface by alumina polishing. The calibration curves were measured in triplicate and evaluated by linear regression method; selected parameters are summarized in Table 1. To verify the linearity of calibration curves, the calibration dependences in a logarithmic form were constructed (log I *vs* log c) and the proximity of their slopes to one shows that all the measured calibration curves for all used electrodes are linear. The lowest limit of detection (L_D) 4.3×10^{-7} mol L^{-1} was obtained for cathodic DPV at CFRE-2 mm. It follows from the comparison of all results at used electrodes that the highest signal to noise ratio was obtained at CFRE-2 mm.

Table 1. The parameters of the calibration straight lines for anodic and cathodic voltammetric determination of 5A6NQ at CFRE (0.8; 2 and 3 mm), BR buffer pH 12 - methanol (1:1 (v/v)) medium.

Method		Concentration range mol L^{-1}	Slope mA L mol^{-1}	Intercept nA	R^{2} [a]	L_D [b] mol L^{-1}
CFRE-0.8 mm						
Anodic	DCV	$0.6 – 10 \times 10^{-5}$	2.6	18.2	0.9960	6.0×10^{-6}
	DPV	$0.6 – 10 \times 10^{-5}$	2.6	-2.1	0.9985	5.1×10^{-6}
Cathodic	DCV	$0.1 – 10 \times 10^{-5}$	-21.3	-18.3	0.9983	1.7×10^{-6}
	DPV	$0.1 – 10 \times 10^{-5}$	-22.8	-152.2	0.9984	1.6×10^{-6}
CFRE-2 mm						
Anodic	DCV	$0.1 – 10 \times 10^{-5}$	22.9	114.2	0.9975	1.6×10^{-6}
	DPV	$0.08 – 10 \times 10^{-5}$	14.5	26.8	0.9987	9.8×10^{-7}
Cathodic	DCV	$0.1 – 10 \times 10^{-5}$	-64.4	-6.9	0.9988	9.5×10^{-7}
	DPV	$0.04 – 10 \times 10^{-5}$	-88.0	-298.3	0.9982	4.3×10^{-7}
CFRE-3 mm						
Anodic	DCV	$0.2 – 10 \times 10^{-5}$	32.4	12.6	0.9991	1.9×10^{-6}
	DPV	$0.1 – 10 \times 10^{-5}$	18.5	87.3	0.9986	1.7×10^{-6}
Cathodic	DCV	$0.1 – 10 \times 10^{-5}$	-159.9	-40.7	0.9981	1.2×10^{-6}
	DPV	$0.06 – 10 \times 10^{-5}$	-199.7	-608.2	0.9976	6.0×10^{-7}

[a] R^2, coefficient of determination; [b] L_D, limit of detection.

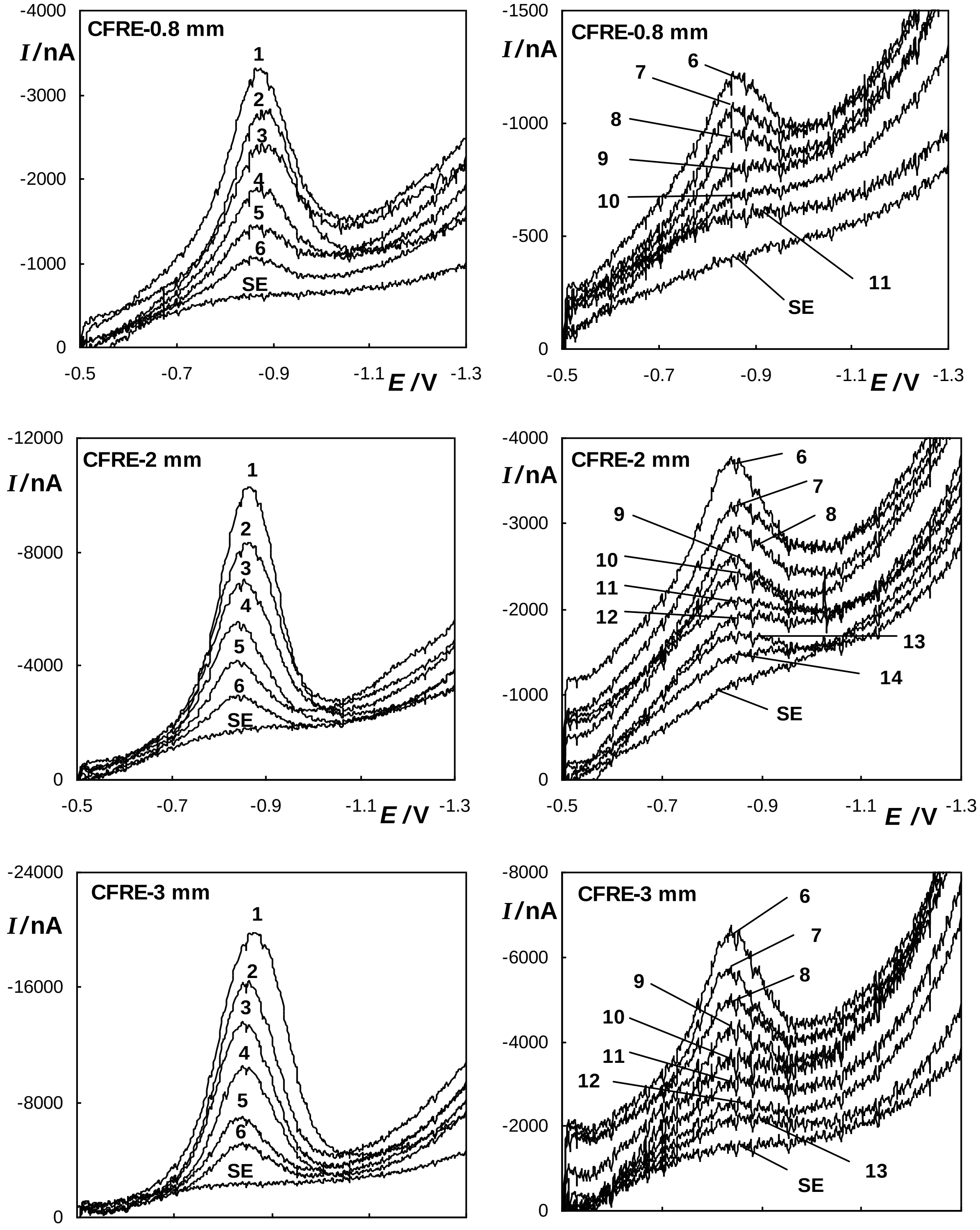


Figure 4. The cathodic voltammograms of 10×10^{-5} (***1***), 8×10^{-5} (***2***), 6×10^{-5} (***3***), 4×10^{-5} (***4***), 2×10^{-5} (***5***), 1×10^{-5} (***6***), 0.8×10^{-5} (***7***), 0.6×10^{-5} (***8***), 0.4×10^{-5} (***9***), 0.2×10^{-5} (***10***), 0.1×10^{-5} (***11***), 0.08×10^{-5} (***12***), 0.06×10^{-5} (***13***), and 0.04×10^{-5} (***14***) mol L^{-1} 5A6NQ, and of (***SE*** - supporting electrolyte) measured by DPV at CFRE-0.8 mm, CFRE-2 mm and CFRE-3 mm in a BR buffer pH 12 - methanol (1:1, v/v). Scan rate 20 mV s^{-1}, pulse width 100 ms, and pulse height – 50 mV.

The practical applicability of the newly developed voltammetric methods was demonstrated by the determination of 5A6NQ in model samples of drinking and pond water. The slopes of the measured calibration dependences for anodic and cathodic DCV and DPV in drinking and pond water correspond to the values obtained in deionized water (Table 2). The obtained limits of detection for anodic voltammetry are slightly higher due to higher noise in model samples. The limits of detection for cathodic voltammetry are quite comparable.

Table 2. The parameters of the calibration straight lines for anodic and cathodic voltammetric determination of 5A6NQ at CFRE-2 mm in model samples of drinking a pond water, supporting electrolyte BR buffer pH 12 - methanol (1:1 (v/v)) medium.

Method		Concentration range mol L^{-1}	Slope mA L mol^{-1}	Intercept nA	$R^{2\,a}$	$L_D{}^b$ mol L^{-1}
drinking water						
Anodic	DCV	0.4 – 10 × 10^{-5}	19.7	83.8	0.9931	3.9 × 10^{-6}
	DPV	0.4 – 10 × 10^{-5}	9.2	-9.6	0.9986	3.6 × 10^{-6}
Cathodic	DCV	0.1 – 10 × 10^{-5}	-65.1	-46.2	0.9986	1.4 × 10^{-6}
	DPV	0.04 – 10 × 10^{-5}	-87.4	-291.5	0.9974	5.3 × 10^{-7}
pond water						
Anodic	DCV	0.4 – 10 × 10^{-5}	21.0	92.0	0.9938	3.8 × 10^{-6}
	DPV	0.2 – 10 × 10^{-5}	11.4	4.2	0.9953	2.1 × 10^{-6}
Cathodic	DCV	0.1 – 10 × 10^{-5}	-65.0	-26.8	0.9961	1.2 × 10^{-6}
	DPV	0.04 – 10 × 10^{-5}	-84.2	-324.5	0.9968	4.8 × 10^{-7}

[a] R^2, coefficient of determination; [b] L_D, limit of detection.

4. CONCLUSION

We have prepared carbon fiber rod electrode (CFRE) in three diameters of 0.8 mm, 2 mm and 3 mm and used these electrodes for voltammetric determination of 5-amino-6-nitroquinoline (5A6NQ). It follows from the results that the best ratio between signal and noise was obtained at CFRE-2 mm, which was used for determination of 5A6NQ in model samples of drinking and pond water. The lowest limit of detection (4.3 × 10^{-7} mol L^{-1}) was obtained for DPV using cathodic reduction of 5A6NQ in BR buffer pH 12 - methanol (1:1, v/v) medium. It follows from the comparison with the determination of 5A6NQ at a carbon paste electrode with a diameter of 2 mm [31] that the limits of detection at CFRE-2 mm are slightly lower than at CPE (3.1 × 10^{-6} mol L^{-1} for DCV and 2.0 × 10^{-6} mol L^{-1} for DPV in supporting electrolyte BR buffer pH 10 - methanol (1:1, v/v)) for anodic voltammetry, but for cathodic voltammetry the limits of detection are significantly lower at CFRE-2 mm than at CPE (1.5 × 10^{-6} mol L^{-1} for DCV and 1.3 × 10^{-6} mol L^{-1} for DPV in supporting electrolyte 0.1 M H_3PO_4 with methanol (1:1, v/v)).

The material for this type of composite electrode used in our work is commercially available at very low cost and at various shapes and sizes. It is applicable as an inexpensive, yet still efficient alternative to other carbon-based electrodes.

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