A novel carbon paste electrode based on nitrogen-doped hydrothermal carbon for electrochemical determination of carbendazim

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Abstract: In this work, a new carbon paste electrode, prepared from nitrogen-doped hydrothermal carbon (CHTCN) was applied for the electrochemical detection and determination of carbendazim fungicide. CHTCN samples with the nominal nitrogen content 0.05–0.5 wt. % in glucose precursor were prepared by simple, low-cost synthesis with the accompanying carbonization to 1273 K. The presence of nitrogen in CHTCN samples was confirmed by elemental analysis. Characterization of CHTCN as material for carbon paste electrode was achieved by cyclic voltammetry measurement of the Fe(CN)₆³⁻/⁴⁻ redox couple. The results showed that best electrochemical response was obtained from the sample with a nominal nitrogen concentration of 0.1 wt. % and with tricresyl phosphate as a binder. During the development of a differential pulse stripping voltammetric method for carbendazim determination applying new electrode, the following experimental parameters were studied: the sort and amount of binding liquid, the effect of pH, accumulation potential and accumulation time. Under optimal conditions, the electrode offered linearity in the wide concentration range from 25 to 490 ng cm⁻³ and an estimated detection limit of 1.21 ng cm⁻³. Moreover, the electrode showed good stability, high selectivity and satisfactory anti-interference ability. Finally, the developed method was successfully applied for the determination of carbendazim traces in spiked tap and river water samples.

Keywords: method development; fungicide; electrochemical determination; stripping voltammetry; tricresyl phosphate.

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INTRODUCTION

Pesticides represent a significant part of the protection of agricultural production. Their application manages the problems with unwanted pests or weeds, but it, unfortunately, constitutes a risk of the environment pollution. Pesticides are generally toxic for living organisms even at low concentrations. Although many pesticides have been forbidden or restricted to use in different regions, many of them are still frequently used for pest or weed control.  

Carbendazim is a systemic benzimidazole fungicide (IUPAC name methyl-1H-benzimidazol-2yl-carbamate) which was regularly used to prevent and cure different diseases of the crop. It was applied to prevent some illnesses on bananas, apples, tomatoes, cereals, etc. It could persist for a long time when applied in the environment and its degradation is rather slow.  

The toxicity of carbendazim is well documented. It shows harmful effects on human health and environment, therefore, its determination is really important.  

Several techniques have been used for quantitative determination of carbendazim, first of all, chromatography, spectrophotometry, spectrofluorimetry, Raman spectroscopy, flow-injection chemiluminescence and enzyme-linked immunosorbent assay (ELISA). On the other hand, the electrochemical methods represent an alternative to these techniques and offer advantages, such as good selectivity, easier sample preparation, faster analysis and sensitivity which could be comparable to chromatography. Several papers were published about voltammetric determination of carbendazim using different unmodified and modified carbon-based electrodes, including also carbon paste-based electrodes.  

Carbon paste electrode (CPE) is generally a mixture of graphite (carbon) powder and liquid binder (e.g., silicone oil (SO), paraffin oil (PO), tricresyl phosphate (TCP)) packed into adequate electrode body. CPEs represent a very popular type of sensors which offers simple laboratory preparation, low price, broad potential window, low background current, unique surface characteristics, usually low toxicity, high sensitivity, and applicability for the monitoring of electrochemically active inorganic and organic environmental pollutants.  

Hydrothermal carbonization (HTC) has been developed recently as a mild and promising strategy to obtain the functional carbonaceous nanostructures from cheap biomass. To convert biomass to carbon, HTC has been considered as an efficient method operated in an environmentally friendly process. The typical HTC carbons are micrometer-sized, spherically shaped particles, which are produced by HTC of soluble, non-structural carbohydrates. Importantly, the versatility of HTC makes it quite easy to achieve heteroatom doping carbon materials. Nitrogen-doped carbon materials have gained an increasing interest in the last decade, mainly because doping carbonaceous materials with nitrogen is an effective way of modifying the surface chemistry of materials and improving
their electrochemical properties.\textsuperscript{34,35} Nitrogen-containing hydrothermal carbons have been prepared from different types of biomasses or derivatives such as chitin, chitosan, glucosamine, microalgae and so on.\textsuperscript{36-38} The nitrogen-free precursors and nitrogen containing molecules such as ovalbumin, glycine, and ethylenediamine have also been employed in the preparation of nitrogen-containing HTC derived carbons.\textsuperscript{39-41} Nitrogen incorporated into carbon materials can not only act as an electron donor due to its five valence electrons which result in a shift of the Fermi level to the valence band but also introduce functional groups containing nitrogen and oxygen atoms.\textsuperscript{42} Hydrothermal carbons doped with nitrogen have been already tested as electrode capacitors and electrocatalyst for oxygen reduction reaction.\textsuperscript{43-45} Strelko et. al\textsuperscript{46} suggested that the influence of nitrogen heteroatoms on the catalytic activity of carbons in electron transfer reactions may be explained on the basis of the suggestion that the insertion of nitrogen atoms into the graphite lattice lowers the band gap, thus producing higher electron (charge) mobility and a lowering of the electron work function at the carbon/liquid (gas) interface, compared with pure carbons.

In our previous work, we have successfully synthesized boron doped carbonized hydrothermal carbon based on glucose as a precursor and applied as a material for carbon paste electrode.\textsuperscript{47} We found that the modified structural and surface characteristics are responsible for good electron transfer property of a carbon paste electrode based on boron-doped samples with a nominal boron concentration range from 0.2 to 0.6 wt. %. Based on these results and literature review we decided to continue to examine the influence of other dopants, especially nitrogen, on properties of hydrothermal carbon and its further application in the field of electrochemistry, especially electroanalysis.

In this work a differential pulse stripping voltammetric (DPSV) method was developed for the determination of carbendazim using a CPE based on newly synthesized carbonized nitrogen-doped hydrothermal carbon (CHTCN) and TCP as a binding liquid. CHTCN samples were synthesized by introducing melamine into glucose precursor solution, to obtain a nominal concentration of nitrogen from 0.05 to 0.5 wt. %. The basic characterization of the new electrodes was done using the cyclic voltammetry of the Fe(CN)$_6^{3-}$	extsuperscript{4-} redox couple. After the DPSV method optimization, the target compound was successfully determined in model solutions, tap- and river water samples.

**EXPERIMENTAL**

**Chemicals**

Methanol, melamine, K$_3$[Fe(CN)$_6$], D(+)-glucose, silicone oil, paraffin oil, tricresyl phosphate, phosphoric, boric and acetic acids, potassium chloride, potassium sulfate, and sodium hydroxide were purchased from Sigma-Aldrich (St. Louise, MO, USA). Deionized water was prepared using a Millipore purification system (Bedford, MA, USA).
Carbendazim (99 % purity) was obtained from Fitofarmacija a.d. (Zemun, Serbia). The stock solution of 333 μg cm\(^{-3}\) concentration was made by dissolving the pesticide in methanol and was kept in dark at –18 °C before analysis. Britton-Robinson buffer solutions were prepared from a stock solution containing 0.04 M phosphoric, boric and acetic acids, respectively by adding 0.2 M sodium hydroxide to obtain the required pH value.

**Preparation of CHTCN samples**

To produce hydrothermal carbons, a water solution of D(+) -glucose (2 M) was prepared and placed into 50 cm\(^3\) Teflon®-lined stainless steel autoclave. Melamine was used as a source of nitrogen and it was added to the precursor solution to obtain the nitrogen concentration of 0.05, 0.1 and 0.5 wt. %. After sealing, the autoclave was heated in a programmable oven for 24 h at 453 K. The obtained black solid powders were abundantly washed with deionized water and alcohol and then dried at 353 K for 24 h. Pyrolysis of CHTCN samples was performed in a flow of high-purity nitrogen up to 1273 K, at the heating rate of 5 K min\(^{-1}\). Obtained samples were marked as CHTCN\(_{0.05}\), CHTCN\(_{0.1}\) and CHTCN\(_{0.5}\). (subscripts denote nominal nitrogen concentration, i.e., concentration in glucose precursor solution).

**Instruments**

The LECO elemental analyser, model CHNS-628, was used for the elemental analysis of CHTCN samples. The morphology of CHTCN was studied by field emission scanning electron microscopy (FESEM) TESCAN Mira3 XMU at 20 kV.

A 797 VA Computrace analyzer (Metrohm) controlled by 797 VA Computrace software version 1.2 was applied for all voltammetric measurements. A three-electrode system included an Ag/AgCl electrode (in saturated KCl) as a reference, platinum wire as auxiliary and different types of CPEs based on CHTCN as working electrode. All electrochemical experiments were carried out in a conventional voltammetric cell (with an operating volume of 10 cm\(^3\)) at room temperature (296±1 K). Before starting a new set of measurements the supporting electrolyte was deaerated by suprapure nitrogen for 5 min.

**Electrode preparation**

CPEs were prepared by hand mixing of 0.25 g CHTCN samples with 0.11 g of binder (TCP, SO or PO) using pestle and mortar, and then packed into the Teflon® holder (2 mm diameter). Prepared CPEs were marked as CPE/CHTCN\(_{0.05}\), CPE/CHTCN\(_{0.1}\) and CPE/CHTCN\(_{0.5}\). Before starting a new set of experiments about 0.5 mm of carbon paste was mechanically squeezed out from the electrode holder and polished on a wet filter paper. During the optimization of the amount of TCP four electrodes were prepared with 0.25 g of CHTCN\(_{0.1}\) and 20, 25, 30 and 40 wt. % of the binder using identical preparation procedure.

**Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and differential pulse stripping voltammetry (DPSV)**

CV experiments were used for preliminary characterization of the working electrodes, including testing of the effect of type and amount of the binding liquids, and also for the investigation of electrode aging. Measurements were performed in 1.0 mM Fe(CN)\(_{6}^{3-}/4-/0.1\) M K\(_2\)SO\(_4\) solution in the potential range from −0.5 to 1.0 V, using scan rate of 50 mV s\(^{-1}\). DPV was used to investigate the effect of pH on the carbendazim oxidation at the CPE/CHTCN\(_{0.1}\) electrode in model solutions containing Britton–Robinson buffer as supporting electrolyte in the pH range from 2.0 to 8.0. DPSV was used for quantitative determination of carbendazim. Its parameters were carefully optimized and were as follows: start potential −0.2 V; end potential 1.2 V; accumulation potential \((E_{acc}) = −0.15\) V; accumulation time \((t_{acc}) = 80\) s and...
The river water sample was collected from river Danube in village Vinča (12 km far from Belgrade). The water samples were filtrated through 0.45 µm filter to remove the suspended particles and storied in a glass bottle at 277 K. Tap water was analyzed without any sample pretreatment. Before analysis, the water samples were spiked with carbendazim (50 ng cm⁻³) and diluted with Britton–Robinson buffer pH 3.0 in the volume ratio 1:1.

RESULTS AND DISCUSSION

Electrode characterization and composition optimization

Results obtained by elemental analysis confirmed the presence of nitrogen in CHTCN samples (Table I). Using melamine as a nitrogen source allows the obtaining of the final nitrogen concentration of 2.8, 3.2 and 4.5 wt. % in carbonized hydrothermal carbons with the initial concentration of nitrogen in glucose precursor solution of 0.05, 0.1 and 0.5 wt. %, respectively.

TABLE I. Summary of the cyclic voltammetric data for Fe(CN)₆³⁻/⁴⁻ redox system at CPE/CHTCNs together with elemental analysis results

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔE_p / mV</th>
<th>iamax / µA</th>
<th>iφ / iφc</th>
<th>C_C / wt. %</th>
<th>C_N / wt. %</th>
<th>C_H / wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE/CHTCN₀.₀₅</td>
<td>384</td>
<td>47</td>
<td>0.866</td>
<td>93.3</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>CPE/CHTCN₀.₁</td>
<td>210</td>
<td>85</td>
<td>0.958</td>
<td>92.6</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>CPE/CHTCN₀.₅</td>
<td>301</td>
<td>33</td>
<td>0.768</td>
<td>90.8</td>
<td>4.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The redox couple of Fe(CN)₆³⁻/⁴⁻ was chosen to characterize the electron transfer properties of CPEs based on different CHTCN samples. Fig. 1 presents cyclic voltammograms of Fe(CN)₆³⁻/⁴⁻ redox couple for three obtained CPE/CHTCN electrodes with TCP as a binder. CPEs based on pure carbonized hydrothermal carbon were excluded from the examination because the previous results showed that poor electrochemical behaviour was obtained independently of the binder type. However, it can be noted that all three CPE/CHTCNs show very well defined the electrochemical response toward Fe(CN)₆³⁻/⁴⁻. In order to clarify the electrochemical response of CPE/CHTCNs better, some derived features are given in Table I. It is obvious that CPE/CHTCN₀.₁ exhibited the smallest...
potential differences between oxidation and reduction peaks ($\Delta E_p$), the highest peak current intensity ($i_{pa}$) and the highest peak current ratio ($i_{pa}/i_{pc}$) of 0.958, suggesting a faster electron transfer kinetics in comparison with other two CPE/CHTCNs.

It can be noticed that there is no linear relationship between the nitrogen content and electrochemical response of examined CPEs. CPE/CHTCNs with lowest and highest nitrogen content have much poorer electrochemical parameters compared to the electrode with the middle value of nitrogen content. Comparison of results for CPE/CHTCN$_{0.1}$ with the results obtained for CPE based on boron-doped carbonized hydrothermal carbon shows that the nominal nitrogen content of 0.1 wt. % provides a CPE with much-improved electrochemical characteristics. Also, these results confirmed suggestion of nitrogen catalytic activity on electron transfer reactions, which originates from higher electron mobility.

Additionally, the examinations of the binder type influence toward Fe(CN)$_6^{3-}/4-$ showed that both other binders SO and PO induced the worsening of CPE/CHTCNs electrochemical behaviour, especially PO comparing to TCP. As an example of that cyclic voltammograms of Fe(CN)$_6^{3-}/4-$ redox couple for CPE/CHTCN$_{0.1}$ are presented in Fig. 2. The examination relating to the binder type influence were also performed with CPE/CHTCN$_{0.05}$ and CPE/CHTCN$_{0.5}$. Unfortunately, any improvement of the electron transfer properties of the examined CPEs was not noticed. All cyclic voltammograms are with well-defined anodic and cathodic peak for the above redox system. The position and intensity of the signals were clearly dependent on the binder type. The advantage of the TCP was evident because it offered the most reversible behaviour, most intense peak current together with the low residual current. Furthermore, $\Delta E_p$, $i_{pa}/i_{pc}$ values for an electrode with SO and PO as binders are 517 mV, 0.912 and 889 mV, 0.746, respectively. Therefore, the TCP was chosen as a binder for the following experiments. For the optimization of TCP content in CPE/CHTCN$_{0.1}$, paste mixtures with 20, 25, and 40 wt. % of TCP were prepared and CV curves of Fe(CN)$_6^{3-}/4-$.

Fig. 2. Cyclic voltammograms of 1 mM Fe(CN)$_6^{3-}/4-$ redox couple in 0.1 M K$_2$SO$_4$ at CPE/CHTCN$_{0.1}$ prepared with the different type of binder: PO, SO or TCP. Potential range from –0.5 to 1.0 V, using scan rate of 50 mV s$^{-1}$. 

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the redox couple, were recorded and compared with the previously obtained CV curve with carbon-to-binder ratio: 0.25 g to 0.11 g, which represents approximately 30 wt. % of TCP. The electrochemical process was most reversible at the CPE/CHTCN₀.₁ with 30 wt. % of TCP, with the acceptable background current. The obtained results showed (Fig. S-1 of the Supplementary material to this paper) that in comparison to CPE/CHTCN₀.₁ with 30 wt. % of TCP, the electrode with 20 wt. % of TCP gave more intense signals, but with very intense background current. On the other hand, an electrode with 25 wt. % of TCP gave significantly lower signal intensity, together with the very favourable background. 40 wt. % of TCP had practically a liquid consistency and it was not possible to conduct measurements with it in current experimental setup.

Based on the above presented results, it was found that the optimal nitrogen content in precursor solution was 0.1 wt. %, for the preparation of a CPE based on nitrogen-doped carbonized hydrothermal carbon. On the other hand, 30 wt. % of TCP was selected as optimal binder liquid content in the mentioned CPE.

Fig. 3 shows SEM images of carbon material CHTCN₀.₁ (a) and CPE based on CHTCN₀.₁ and TCP (b). In general, the morphology of CHTCN₀.₁ is the characteristic morphology for hydrothermal carbons obtained from glucose at a lower temperature, which consists of micrometric spheres with a smooth surface and with the inhomogeneous diameter size, in this case from 0.5 to 3 µm. The image of CPE (Fig. 3b) shows the graphite particles coated with liquid binder and matted, and the cavities which are formed between them.

![SEM images of CHTCN₀.₁ (a) and CPE/CHTCN₀.₁ (b).](image)

**pH-Dependence of carbendazim oxidation**

The effect of pH on the electrochemical response of carbendazim was investigated in the pH range from 2.0 to 8.0 in Britton–Robinson buffer solutions using a DPV method. DPV method was also involved for examination of pH
effect on the electrochemical response of carbendazim for CPE/CHTCN\(_{0.05}\) and CPE/CHTCN\(_{0.5}\). The satisfying electroanalytical responses regarding carbendazim were not obtained for any of the two CPEs since the oxidation peaks were significantly lower in intensity and shifted toward higher potential compared to results obtained for CPE/CHTCN\(_{0.1}\). Consequently, these two electrodes were excluded from further examinations. As shown in Fig. 4, the oxidation peak of carbendazim obtained using CPE/CHTCN\(_{0.1}\) is clearly visible at all pH values, but its intensity and position were clearly dependent on pH. The most intense peak was obtained in acidic media at pH 3.0 (at 0.98 V), therefore this pH was selected for further experiments. The shift of the oxidation peak potential toward negative value with increasing pH from 2 to 6 indicated that the protons are involved in the electrode reaction.

![Fig. 4. DPSV curves of carbendazim (c = 1.3 μg cm\(^{-3}\)) at CPE/CHTCN\(_{0.1}\) in different Britton–Robinson buffer solutions (pH range from 2.0 to 8.0).](image)

**Repeatability and stability of CPE/CHTCN\(_{0.1}\)**

The repeatability and stability of CPE/CHTCN\(_{0.1}\) were also evaluated. The relative standard deviation (RSD) for detection of 125 ng cm\(^{-3}\) carbendazim at pH 3.0 at five independently prepared electrodes was 4.5 %, which shows good repeatability of the CPE/CHTCN\(_{0.1}\). The stability (aging of the electrode) is also an important parameter for the evaluation of the electrode. The electrode surface was covered and stored in the fridge when not in use. After 5 days of storing the electrode gave 96 % of its initial peak current value. 90 % of the initial response still remained after 4 weeks of storage, confirming that the CPE/CHTCN\(_{0.1}\) had also an acceptable storage stability.

Because of the adsorption behaviour of carbendazim at CPE/CHTCN\(_{0.1}\) surface, the electrode can not be reused directly after measurements. It is necessary to renew its surface and then activate it by potential cycling (10 cycles in the range from –0.2 to 1.6 V using scan rate of 250 mV s\(^{-1}\)) in an adequate Britton–Robinson buffer.
**Optimization of DPSV parameters**

The optimal conditions for DPSV determination of carbendazim were carefully selected. It was found that the oxidation peak current intensity changes with the accumulation potential, $E_{acc}$ in the investigated range from 0.15 and 0.55 V. As shown in Fig. 5a, the peak current increased to its maximum at –0.15 V and then started to decrease, so –0.15 V was selected as optimal accumulation potential. When the accumulation time, $t_{acc}$ was changed from 5 to 300 s (Fig. 5b), the oxidation peak current increased gradually to the maximum value at 80 s and then with further increase of the accumulation time, the peak current slightly decreased. Therefore, 80 s was chosen as optimal $t_{acc}$.

![Fig. 5. Optimization of accumulation potential (a) and accumulation time (b) in DPSV of carbendazim ($c = 1.3 \, \mu g \, cm^{-3}$) at pH 3.0.](image)

**Quantitative determination of carbendazim in model solution**

Fig. 6 shows DPSV responses of different concentrations of carbendazim on CPE/CHTCN$_{0.1}$ under the optimal conditions in the concentration range from 25 to 490 ng cm$^{-3}$ (Fig. 6a), together with the corresponding calibration plot (Fig. 6b). Dependence of peak current intensity ($i_p$) on the carbendazim concentration.

![Fig. 6. DPSV determination of carbendazim at CPE/CHTCN$_{0.1}$ in the concentration range from 25 to 490 ng cm$^{-3}$ (a) together with corresponding calibration plot (b).](image)
could be described using the following equation: 
\[ i_p = 1.62128c - 0.0281 \]
with a correlation coefficient of 0.9983. The reproducibility of the analytical response was assessed by comparing the heights of the peak current of seven consecutive recordings at carbendazim concentration level of 125 ng cm\(^{-3}\). The RSD value of 2.9% indicates a relatively good precision of the developed method. The detection limit \((LOD)\) and the quantitation limit \((LOQ)\) were determined using the \(3\sigma/S\) and \(10\sigma/S\) criterion, where \(\sigma\) is the estimated standard deviation of the peak height intensity for the lowest measured concentration (6 measurements) and \(S\) is the slope of the calibration curve. The calculated \(LOD\) and \(LOQ\) were 1.24 and 4.04 ng cm\(^{-3}\), respectively. Considering all above results, it is clear that the proposed electrode can be successfully applied for the quantitative determination of carbendazim in model solution at very low concentration levels.

**Investigation of the interferences**

The interference of some common ions (Na\(^+\), K\(^+\), Ca\(^{2+}\), Ag\(^+\), Cl\(^-\), CO\(_3\)^{2-}, HCO\(_3\)^{−}, and NO\(_3\)^{−}) and pesticides (dimethoate, imidacloprid, tebufenozide and simazine), on the determination of carbendazim, was also tested in this study. Firstly, DPSV signal of carbendazim (125 ng cm\(^{-3}\)) was recorded using the CPE/CHTCN\(_{0.1}\), then either selected ion was added in a concentration that is 50 times higher than carbendazim, or a selected pesticide was added in the same final concentration as carbendazim. The solutions were analyzed by the proposed method and all investigated ions or pesticides neither influenced peak potential nor oxidation peak current intensity of carbendazim significantly.

**Analysis of real samples**

The applicability of the developed voltammetric procedure was also tested for the determination of carbendazim in tap and river water (Danube) samples spiked with 50 ng cm\(^{-3}\) of carbendazim, which was further diluted to 25 ng cm\(^{-3}\) with Britton–Robinson buffer pH 3.0 in 1:1 volume ratio (Fig. 7).

Before spiking, samples did not contain any detectable amount of the analyte. Standard addition method was applied in all determinations (Fig. 7b and d), which were done in triplicate. As can be seen, the matrix from the water samples did not block the electrode surface and did not show voltammetric interferences, which are favourable facts for determination (Fig. 7a and c). Peak height intensities of carbendazim were comparable to the corresponding ones in case of model solutions. The peak potential differs just a slightly from this of the model solution and it has around 0.03 V more positive values. On the other hand, good correlation between the added and found carbendazim amounts in spiked water samples (recovery was 103.70% for tap water and 102.78% for Danube water) and low RSDs (4.1 and 4.3%, respectively) reflected high accuracy and precision of the proposed DPSV method even at such low concentration level.
Fig. 7. Determination of carbendazim in spiked water samples using DPSV: Tap water sample (a) with the corresponding standard addition plot (b) and Danube river water sample (c) with the corresponding standard addition plot (d).

CONCLUSIONS

A novel carbon paste electrode based on simple and low-cost produced, nitrogen-doped hydrothermal carbon was successfully fabricated. Carbonized hydrothermal carbon sample with 0.1 wt. % nominal nitrogen concentration as a carbon component and 30 wt. % of tricresyl phosphate as a liquid binder were the selected components for the preparation of carbon paste electrode with the best electrochemical response toward Fe(CN)$_6^{3/-4}$ redox couple. On the other hand, a differential pulse stripping voltammetric method was developed for the determination of carbendazim fungicide. The method offered linearity in a wide concentration range from 25 to 490 ng cm$^{-3}$ with an estimated low detection limit of 1.21 ng cm$^{-3}$. Several advantageous characteristics of the new electrode such as good stability, high selectivity, and excellent repeatability were also reported. Furthermore, the electrode was successfully applied for the determination of carbendazim traces in spiked tap and river water samples with high precision and recovery. The overall results showed that the nitrogen-doped hydrothermal carbon is a good candidate as a material for the preparation of carbon paste electrodes, which could find broad application in electroanalysis.
SUPPLEMENTARY MATERIAL

Effect of TCP mass fraction in CPE/CHTCN\textsubscript{0.1} on cyclic voltammograms of Fe(CN)\textsubscript{6}\textsuperscript{3-/4-}
redox couple are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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RESULTS

ELEKTROXHEMIJSKO ODRŽIVANJE KARBENZADIMA NOVOM ELEKTRODOM OD UGJENIČNE PASTE BAZIRANE NA AZOTOM DOPIRANOM HIDROTHERMALNOG UGJENIKA

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In this paper, we describe the effect of TCP mass fraction in CPE/CHTCN\textsubscript{0.1} on cyclic voltammograms of Fe(CN)\textsubscript{6}\textsuperscript{3-/4-} redox couple are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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