

Voltammetric determination of MCPA, 4-chloro-*o*-cresol and *o*-cresol in water using a modified carbon paste electrode

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Voltammetric method with use of modified carbon paste electrodes was applied to determining of MCPA herbicide, 4-chloro-*o*-cresol and *o*-cresol in water. All these compounds can be present in waste-water from production of MCPA or in river water. Carbon paste electrode was modified with mesoporous silica SBA-15 or powdered activated carbon Norit SX-2. The results showed that limit of detection for MCPA was 0.7 $\mu\text{mol L}^{-1}$ and 1.3 $\mu\text{mol L}^{-1}$ for Norit SX-2 and SBA-15, respectively. The smaller values of LOD for activated carbon were observed for other applied analytes. The electrode modified by this material used for determination of MCPA was better than electrodes in other works.

Keywords: herbicide, *o*-cresol, MCPA, carbon paste electrode, cyclic voltammetry

1. INTRODUCTION

The development of industry and agriculture focused on intensification of production may cause an increase in environmental pollution. One of the most important group of chemical substances dangerous for human health and ecosystem are hardly biodegradable chlorophenols and chlorocresols. The substances are the intermediates in the production of phenoxy herbicides (MCPA, 2,4-D, mecoprop, dichlorprop).

In the European countries such as Germany, Great Britain, Austria, Russia and Poland MCPA herbicide is one of the most popular active and is applied on large acreage of cereals. In Europe the compound is produced in the scale of thousands of tons per year [1]. The main intermediate for production of MCPA in the world is toxic to animals and humans [2] 4-chloro-*o*-cresol (4Cl2C) formed by chlorination of *o*-cresol (2-C).

The production of phenoxy herbicides may in exceptional cases cause the introduction small amounts of 4Cl2C and 2-C to environment. MCPA produced using the technology based on chlorination of 2-C to 4Cl2C (the most often used technology in the world) contains usually max. 1% of 4Cl2C, which involves the introduction of this substance into the environment. The content level of chlorophenols in technical material is approved by FAO [AGP:CP/312 FAO SPECIFICATIONS FOR PLANT PROTECTION PRODUCTS]. In the present economic reality, it is impossible to resign from the use of chlorophenols in the phenoxy herbicides production, there are only the unique MCPA, mecoprop-P production technologies (Poland) in which the obtained product does not contain chlorophenols, so there are needs to find an effective, quick method of detecting and determination of them in water and waste water.

Many analytical methods can be applied for the analysis of MCPA e.g. spectrophotometric [3-10], NMR spectroscopic [11] and chromatographic techniques [12-15]. Most of these methods are complicated and need sophisticated instrumentation such as HPLC or spectrophotometry. Very cheap method for the determination of herbicides is voltammetry [16-21].

Voltammetry is a very sensitive method for the determination of many traces of organic compounds. Carbon paste electrodes are convenient and often used as working electrodes for the voltammetric measurements because they are easy for modification. The modification consists in adding to the graphite and paraffin oil the third component, e.g. carbon or inorganic materials.

In this paper, we report modification of a carbon paste electrode with a mesoporous silica material (SBA-15) and the powdered activated carbon (Norit SX-2) for the simultaneous determination of MCPA herbicide and its main transformation products 4-chloro-o-cresol and o-cresol.

2. EXPERIMENTAL

2.1. Reagents and solutions

The 2-methyl-4-chlorophenoxyacetic acid (MCPA), o-cresol (2-C) and 4-chloro-o-cresol (4Cl2C) were from Sigma-Aldrich (St. Louis, USA). The acetonitrile (HPLC-grade), sodium sulfate, acetic acid were obtained from Avantor Performance Materials (Gliwice, Poland). All chemicals were of analytical grade. The commercially available mesoporous silica was received from Sigma-Aldrich (SBA-15) and the activated carbon SX-2 was obtained from Norit (The Netherlands). Double distilled water was used throughout all experiments.

2.2. Apparatus

The porous structure characteristics were obtained on the basis of low temperature nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2020 volumetric adsorption analyzer, Norcross, USA). The SEM images were taken to characterization of the electrode modifiers morphology (Philips XL30/LaB6 scanning electron microscope).

The concentrations of the o-cresol, 4-chloro-o-cresol and 2-methyl-4-chlorophenoxyacetic acid in water samples were measured by high-performance liquid chromatography (HPLC) with UV-Vis detector (Shimadzu LC-20, Kyoto, Japan).

All voltammetric measurements were performed using AutoLab PGSTAT 20 (Eco Chemie) electrochemical workstation. The working electrode was carbon paste electrode (CPE), a saturated calomel electrode was used as a reference electrode and platinum wire as an auxiliary electrode. The pH measurement were carried out with Hanna pH 211 microprocessor pH meter.

2.3. Voltammetry

A three-electrode electrochemical cell was employed for all electrochemical measurements. The reference electrode was a saturated calomel electrode and the counter electrode was a platinum wire. The working electrode was a modified carbon paste electrode. Before each analysis, the working electrode was polished with alumina to 0.2 μm thickness, followed by cleaning in an ultrasonic bath in water for 5 min and thorough rinsing with distilled water. The cyclic voltammograms were recorded in a potential range -1.0 to +1.00 V (scan rate 50 mV s^{-1}).

2.4. Preparation of modified CPE

The carbon paste electrode was prepared by hand mixing: paraffin oil and graphite powder (90%, m/m) in a mortar with a pestle. The carbon paste was modified by adding 2.5, 5 or 10% (m/m) of SBA-15 or SX-2. After standing 48 hours a portion of the resulting paste was packed into the electrode cavity of a Teflon tube. The electrode surface could be renewed by simple extraction of a small amount of paste from the tip of the electrode.

3. RESULT AND DISCUSSION

3.1. Characterization of the materials

The physical properties of the materials (CPEs modifiers) were characterized using low temperature nitrogen adsorption–desorption isotherm and SEM techniques. The nitrogen adsorption–desorption isotherms for both the materials were determined at 77 K and the BET surface areas were found to be 517 $\text{m}^2 \text{g}^{-1}$ and 885 $\text{m}^2 \text{g}^{-1}$ for SBA-15 and Norit SX-2, respectively. Figure 1 shows the nitrogen adsorption–desorption isotherms obtained for the investigated samples.

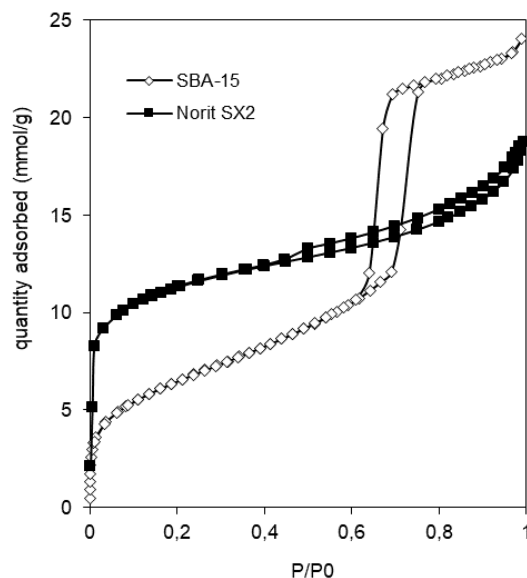


Figure 1. Nitrogen adsorption-desorption isotherms on SBA-15 mesoporous silica and Norit SX2 activated carbon at 77 K.

The values of specific surface areas of the materials, as well as the total pore (V_t) and micropore (V_{mi}) volumes calculated from the adsorption isotherms are presented in Table 1. The measurement results obtained seem consistent with those previously published [22,23].

Table 1. Porous structure parameters obtained from nitrogen adsorption isotherms.

Materials	$S_{BET}, m^2 g^{-1}$	$V_{mi}, cm^3 g^{-1}$	$V_t, cm^3 g^{-1}$
SBA-15	517	0.02	0.830
Norit SX-2	885	0.371	0.616

The SEM images of the CPEs modifiers morphology are shown in Figure 2.

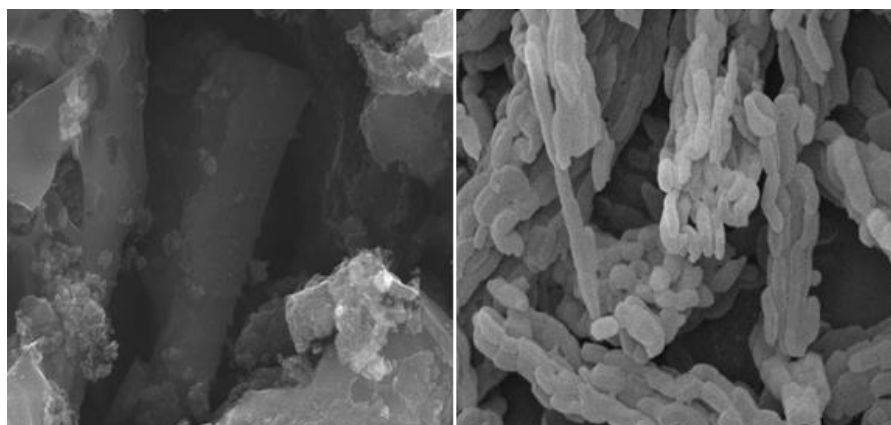


Figure 2. The SEM images (magnification $\times 10,000$) of the Norit SX-2 activated carbon (left) and SBA-15 mesoporous silica (right).

3.2. Chromatography

Separation of the compounds was performed using a Phenomenex Luna C₁₈ (4.6×150 mm, 3 μm) column (Torrance, CA, USA) thermostated at 40°C. The chromatographic measurements were carried out under isocratic conditions; the mobile phase consisted of acetonitrile and water adjusted to pH 3.0 with acetic acid (45/55, v/v); the flow rate was 0.25 mL min⁻¹ and the detection wavelengths were 263, 270 and 274 nm for 2-C, 4Cl2C and MCPA, respectively. A typical chromatogram is shown in Fig. 3. The calibration curves were obtained by plotting peak height against the analyte concentration (0.5 – 100 μmol/L). The limits of detection (LOD) and quantitation (LOQ) were experimentally estimated by analysis of water samples spiked with serially diluted 2-C, 4Cl2C and MCPA standards until the signal-to-noise ratio reached 3 and 6, respectively. The LOD and LOQ as well as the equations for the linear regression lines and correlation coefficients are listed in Table 2.

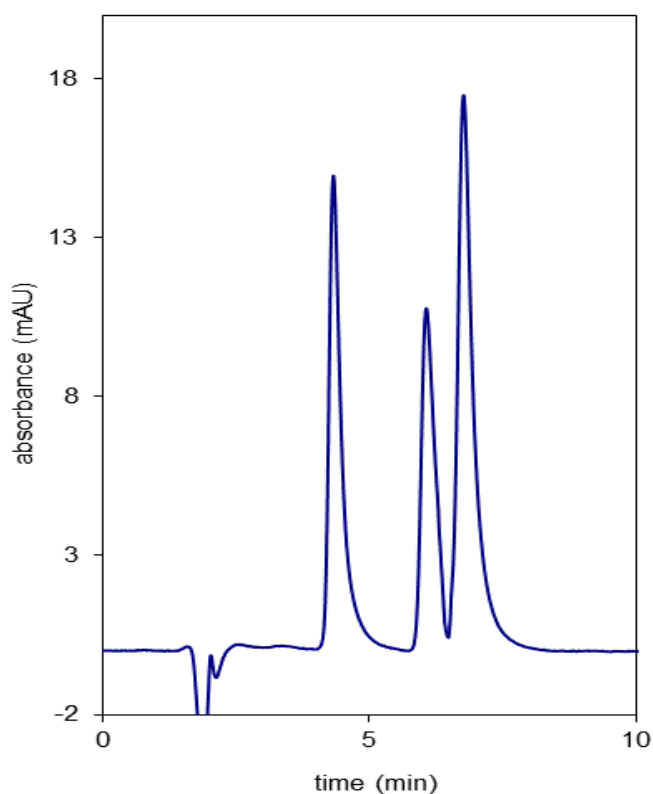


Figure 3. Typical chromatogram of the o-cresol, 4-chloro-o-cresol and MCPA mixture in water recorded at 270 nm; concentration of each compound 10 μmol L⁻¹. Chromatographic conditions as described in text. Peaks: 1 – o-cresol; 2 – 4-chloro-o-cresol; 3 –MCPA

3.3. Electrochemical studies

Before the DPV measurements, the influence of the accumulation time on the peak current was determined. The experiments were conducted at the CPEs containing 5% of the modifiers (SBA-15 or Norit SX-2). Figure 4 shows that for 0.1 mmol L⁻¹ solution of MCPA the peak current increased with the

increasing of accumulation time up to about 3 minutes and then became stable. For the further experiments accumulation time 3 minute was chosen as optimal for all CPEs.

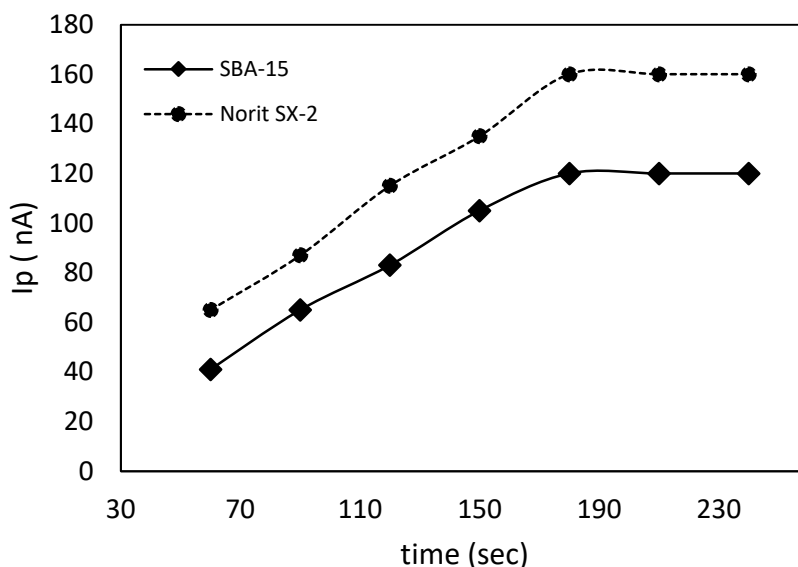


Figure 4. Effect of accumulation time on peak current for 0.1 mmol L⁻¹ MCPA.

In order to study the nature of the electrochemical reaction on modified CPEs the effect of different scan rate in the range from 10 to 150 mVs⁻¹ on the peak current and peak potential was investigated by CV in testing solution. The peak current of analyte increased practically linearly with square root of the scan rate indicating that the oxidation and reduction process on the electrode surface is controlled by diffusion. Also, a plot of the logarithm of peak current versus the logarithm of the scan rate gave a straight line with a slope of 0.46 (theoretical value of 0.5), which is expressed for an ideal reaction of the diffusion-controlled electrode process.

The CV technique was used to develop a voltammetric methodology for determination of the o-cresol, 4-chloro-o-cresol and MCPA in aqueous solutions. Three electrodes containing different amounts of the modifier (2.5, 5 and 10% m/m) were prepared and investigated for their CV signals under identical conditions. The cyclic voltammograms registered for 500 μmol L⁻¹ solutions of o-cresol, 4-chloro-o-cresol and MCPA (in 0.1 mol L⁻¹ Na₂SO₄) using a carbon paste electrode containing 5% by mass of used materials are presented in Fig. 5.

The obtained results showed that the highest peak current value is obtained in the case of o-cresol solution. Both the SBA-15 and Norit SX-2 modifications resulted in an increase in the peak current compared to the unmodified carbon paste electrode. The increasing of the modifier content from 2.5% to 10% resulted with increase in the peak current value for all solutions. An increase in peak current intensity was observed along with an increase in the concentration of the analyte, and the relationships obtained were linear in the range of concentrations from 10 μmol L⁻¹ to 500 μmol L⁻¹ for all modifier contents. The LOD was defined as 3 × standard deviation of the blank signal. The LOD and LOQ as well as the equations for the linear regression lines and correlation coefficients are listed in Table 2.

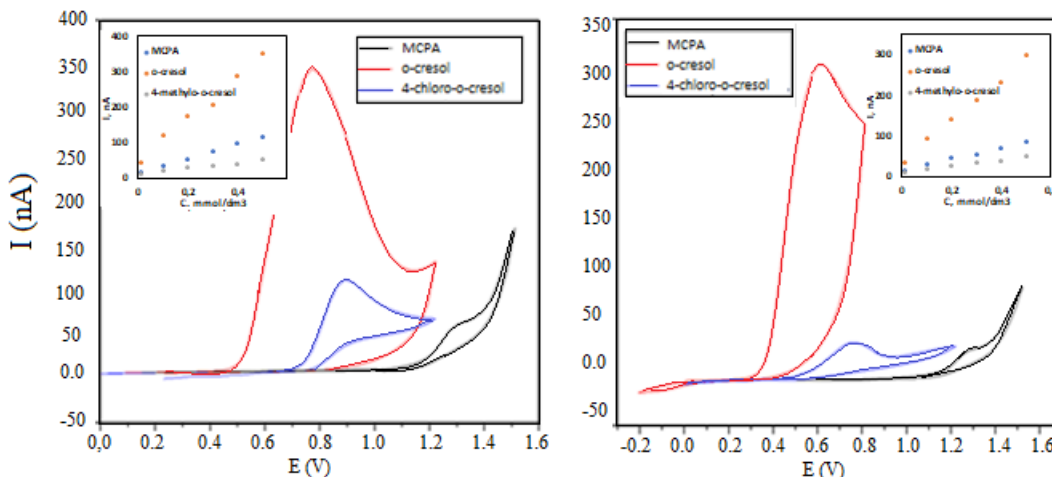


Figure 5. The CV registered for 500 μmol L⁻¹ solutions using carbon paste electrodes containing 5% by mass of tested materials. Modifiers: 1— Norit SX-2, 2— SBA-15

Table 2. Linearity results (n=5)

Analytical method	Linear regression equation	R ²	LOD, μmol L ⁻¹	LOQ, μmol L ⁻¹
MCPA				
HPLC	y = 0.331x + 0.340	R ² = 0.997	0.2	0.5
DPV- Norit SX-2	y = 2.145x + 0.005	R ² = 0.989	0.7	1.4
DPV- SBA-15	y = 2.163x + 0.004	R ² = 0.993	1.3	2.6
o-cresol				
HPLC	y = 0.328x + 0.290	R ² = 0.997	0.2	0.5
DPV- Norit SX-2	y = 4.503x + 0.004	R ² = 0.990	0.5	1.0
DPV- SBA-15	y = 2.876x + 0.007	R ² = 0.986	0.9	1.8
4-chloro-o-cresol				
HPLC	y = 0,204x + 0,112	R ² = 0,999	0.3	0.6
DPV- Norit SX-2	y = 2.054x + 0.015	R ² = 0.993	1.5	3.0
DPV- SBA-15	y = 1.598x + 0.014	R ² = 0.987	1.9	3.8

The limits of detection and quantification observed for CPE modified with Norit SX-2 were 0.7 and 1.4 μmol L⁻¹ for MCPA, while for the CPE with the addition of SBA-15 were 1.3 and 2.6 μmol L⁻¹, respectively. CPE modified with SX-2 activated carbon showed better limits of detection and quantification than the CPE-SBA-15. In each case the modified electrodes were found to be significantly better than the unmodified electrode. However, the sensitivity of the developed electrochemical methods is worse than HPLC methods. Table 3 shows the comparison of the modified CPEs with other electrodes described recently in the literature. The method presented in this work has a comparable or better performance with wide linear range and low detection limit. The advantages of our method are based on simplicity of the electrode preparation.

Table 3. Recently reported electrodes for the determination of used in this paper analytes.

Analyte	Electrode	Modifier	Limit of detection	Ref.
MCPA	Glassy carbon electrode	PANI- β -CD/fMWCNT film*	0.99 $\mu\text{mol L}^{-1}$	[24]
	Glassy carbon electrode	PANI- β -CD/fMWCNT film*	1.06 $\mu\text{mol L}^{-1}$	[25]
	Carbon paste electrode	MnO ₂	0.97 $\mu\text{mol L}^{-1}$	[26]
o-cresol	Screen printed electrode	ZnO**	5.5 nmol L ⁻¹	[27]
4-chloro-o-cresol	Glassy carbon electrode	PANI- β -CD/fMWCNT film*	1.92 $\mu\text{mol L}^{-1}$	[25]
4-chloro-m-cresol	Glassy carbon electrode	-	9.3 $\mu\text{mol L}^{-1}$	[28]

*functionalized multi-walled carbon nanotubes with incorporated β -cyclodextrin and polyaniline film

**screen printed electrode with deposited ZnO nanosheets

3.4. Real samples analysis

The analytical performance of the proposed method was investigated to determine the MCPA, o-cresol and 4-chloro-o-cresol in spiked river water. The water samples were collected in the Vistula river and analyzed without any pre-treatment in the preparation of supporting electrolyte by adding 0.1 mol L⁻¹ Na₂SO₄. One concentration of analytes was investigated and the results are presented in Table 4.

Table 4. Determination of MCPA, o-cresol and 4-chloro-o-cresol in spiked river water samples.

Analytical method	Added, $\mu\text{mol L}^{-1}$	Found \pm SD, $\mu\text{mol L}^{-1}$	Precision, %	Recovery, %
MCPA				
HPLC	10	10.55 \pm 0.12	1.18	105.5
DPV- Norit		9.87 \pm 0.09	0.89	98.70
DPV- SBA-15		9.75 \pm 0.15	0.82	97.50
o-cresol				
HPLC	10	10.47 \pm 0.29	2.80	104.66
DPV- Norit		10.21 \pm 0.04	1.08	102.10
DPV- SBA-15		10.15 \pm 0.05	1.02	101.50
4-chloro-o-cresol				
HPLC	10	9.73 \pm 0.08	0.81	97.27
DPV- Norit		9.89 \pm 0.11	0.90	98.90
DPV- SBA-15		9.68 \pm 0.07	0.87	96.80

Analysis of the results demonstrates the good agreement of the added and found concentrations of the analytes. The recovery was from 96.8 to 105.5%, while the precision, expressed as the relative standard deviation, was in the range of 0.8-2.8%. Moreover, the results were in good agreement with the HPLC method.

4. CONCLUSION

Carbon paste electrodes modified with Norit SX-2 activated carbon and SBA-15 mesoporous silica were applied for the determination of the MCPA herbicide and the main intermediates for its production in aqueous solutions by voltammetric technique. The sensitivity of the methods was correlated with the type of the modifier – the analytical signal was increased with the adsorption capacity of the materials used. The obtained results showed that limits of detection for MCPA were $0.7 \mu\text{mol L}^{-1}$ and $1.3 \mu\text{mol L}^{-1}$ for Norit SX-2 and SBA-15, respectively. The smaller values of LOD obtained for activated carbon compared to mesoporous silica were observed also for other analytes. The proposed electroanalytical method was successfully applied to the determination of MCPA, o-cresol and 4-chloro-o-cresol in river water samples.

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