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SENSITIVITY CHANGE OF THE MODIFIED CARBON PASTE ELECTRODES FOR DETECTION OF CHLORINATED PHENOXYACETIC ACIDS

Arkadiusz Białek[1]*, Katarzyna Skrzypczyńska[2], Krzysztof Kuśmierek[2], Andrzej Świątkowski[2]

[1] Łukasiewicz Research Network – Institute of Industrial Organic Chemistry, 6 Annopol St., 03-236 Warsaw, Poland
[2] Military University of Technology, Institute of Chemistry, 00-908 Warsaw, Poland

Carbon paste electrode (CPE) was modified with F-300 commercial activated carbon or Norit SX-2 powdered activated carbon. CPEs were prepared for detection of 2,4-dichlorophenoxyacetic acid (2,4-D), 2,6-dichlorophenoxyacetic acid (2,6-D) and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T). The electrochemical behavior of these materials was investigated employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The modifier was found to enhance the electroactive surface area and the peak current in comparison to the bare (unmodified) carbon paste electrode. The intensity of the signal increased with the increase in adsorption ability of the modifiers. Compared to the unmodified electrode, all the new paste electrodes showed a much greater sensitivity for detection of chlorinated phenoxyacetic acids in water samples.

Keywords: 2,4-D, 2,6-D, 2,4,6-T, voltammetry, carbon paste electrode, adsorption

1. INTRODUCTION

The synthesis of 2,4-dichlorophenoxyacetic acid herbicide (2,4-D) is based on the reaction of technical 2,4-dichlorophenol (2,4-DCP) with chloroacetic acid, all chlorophenols which are contained in the post chlorination mixture (2-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol) undergo reaction giving as a result a mixture of chlorophenoxyacetic acids containing about 88-95% of 2,4-D acid. Purification of 2,4-D usually is based on the crystallization of sodium salt and enables to obtain pure (98%) 2,4-D sodium salt. Synthesis and purification of 2,4-D gives wastes containing chlorophenoxyacetic acids (4-chlorophenoxyacetic acid, 2,6-dichlorophenoxyacetic acid, 2,4,6-trichlorophenoxyacetic acid), unreacted chlorophenols, glycolic acid and sodium chloride. During crystallization of 2,4-D sodium salt wastes containing chloroorganic compounds – chlorophenoxyacetic acids and chlorophenols in amount of about 9.5% referred to the final product are separated, the main component is 2,6-D isomer (Moszczyński et al., 2008).

About 100,000 tonnes of 2,4-D a year are produced worldwide and about 10% of this herbicide is manufactured in Poland (Moszczyński and Białek, 2011). Difficult to neutralize wastes and contaminants are the most important problem in 2,4-D production technology. In the context of a significant global scale of production of the 2,4-D herbicide, it is interesting to undertake research on the development of fast and selective methods for the detection and determination of individual chlorophenoxyacetic acids (2,4-D, 2,6-D, 2,4,6-T) both in production media and sewage.

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* Corresponding author, e-mail: bialek@ipo.waw.pl

The standard analytical methods used for determination of herbicides including chlorophenoxyacetic acids are separation techniques such as capillary electrophoresis (Chang et al., 2016), gas chromatography (Nollet and Rathore, 2010; Stoytcheva, 2011; Suárez et al., 2018) and high-performance liquid chromatography, in particular HPLC with UV detection (Aulakh et al., 2005; Nollet and Rathore, 2010; Özhan et al., 2005; Stoytcheva, 2011). Although separation methods are used for the determination of herbicides with appropriate limit of detection and sensitivity, they are very expensive which restricts their wider application. Moreover, these methods have limitations related mainly to quite long retention times of individual components, which makes them difficult to apply in online measurements.

Among the non-separative methods used for herbicide measurements, the immunoassay methods including enzyme-linked immunosorbent assay (ELISA) (Clegg et al., 1999; Liu et al., 2018; Matuszczyk et al., 1996; Uthuppu et al., 2015) and microbial biosensors (Chen et al., 2014; Shao et al., 2002; Tucci et al., 2019) are very popular. These methods are widely used for online monitoring of pollutants in the environment, due to the fact that they are relatively low cost, fast and highly sensitive. However, these methods also have some limitations and disadvantages. For example, immunoassays may be limited by the presence of natural inhibitors in the samples, binding of non-specific protein and fact that enzyme reactions are very sensitive to temperature (Nollet and Rathore, 2010). Electrochemical methods do not have such limitations. Voltammetry techniques are quite often used for detection and determination of various pesticides in environmental samples (Barbosa et al., 2019; Ramachandran et al., 2015; Skrzypczyńska et al., 2016; Smarzewska et al., 2017; Stoytcheva, 2011). The described methods are quite precise and fast. The sensitivity of electrochemical methods depends largely on the type and properties of the working electrode – in the case of CPE, it depends on the amount and type of modifier used for its preparation.

The aim of this study was to assess the applicability of modified carbon paste electrodes for detection of chlorinated phenoxyacetic acids, including 2,4-dichlorophenoxyacetic acid (2,4-D), 2,6-dichlorophenoxyacetic acid (2,6-D) and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T).

2. MATERIALS AND METHODS

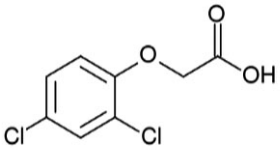
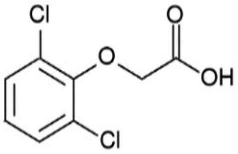
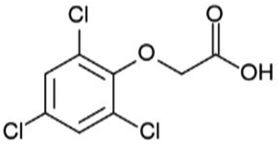
The 2,4-dichlorophenoxyacetic acid (2,4-D), 2,6-dichlorophenoxyacetic acid (2,6-D) and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T) came from Institute of Organic Industrial Chemistry (Warsaw, Poland). The molecular structures and physico-chemical properties of the selected compounds are listed in Table 1. The HPLC-grade acetonitrile and the pure acetic acid, potassium chloride, hydrochloric acid, sodium hydroxide, sodium sulphate and potassium ferrocyanide were obtained from ChemPur (Piekary Śląskie, Poland). Stock standard solutions of 2,4-D, 2,6-D and 2,4,6-T were prepared in 0.1 mol L^{-1} sodium sulfate. The working solutions were prepared daily by dilution with Na_2SO_4 with the same concentration as needed.

The graphite powder (45 μm) and spectroscopic grade paraffin oil were purchased from Sigma Aldrich (St. Louis, USA). As adsorbents/CPE modifiers, the powdered SX-2 (Norit, The Netherlands) and granular F-300 (Chemviron, Belgium) activated carbons were chosen. Prior to use, the materials were dried in an oven at 120 °C to constant weight and stored in a desiccator until use.

The nitrogen adsorption-desorption isotherms were determined using Micromeritics ASAP 2020 series volumetric adsorption analyzer (Norcross, GA, USA).

All voltammetric measurements were carried out using AutoLab PGSTAT 20 coupled with a computer. The measurements were based on the three-electrode system. The working electrode was a modified carbon paste electrode, the reference electrode was a saturated calomel electrode, and the counter electrode was a platinum wire. The measurements were carried out using cyclic and differential pulse voltammetry.

Table 1. Physico-chemical properties of the phenoxyacetic acids

Compound	Chemical structure	Molecular weight	Solubility in water (20 °C), mg L^{-1}
2,4-D		221.04	0.89
2,6-D		221.04	1.558
2,4,6-T		255.48	0.248

The chromatographic measurements (Shimadzu LC-20 series chromatograph, Kyoto, Japan) were carried out under isocratic conditions on a Phenomenex Luna C18, 4.6 × 150 mm, 3 μm column (Torrance, USA) thermostated at 40°C. The mobile phase consisted of water adjusted to pH 3.0 with CH_3COOH and acetonitrile (55/45, v/v); the flow rate was 0.25 mL min^{-1} and the detection wavelengths were 274 and 261 and 278 nm for 2,4-D, 2,6-D and 2,4,6-T, respectively.

The porosity of the selected carbon materials was characterized by low-temperature N_2 adsorption-desorption isotherms measured at 77.4 K. The specific surface areas (S_{BET}) were determined using the Brunauer-Emmett-Teller equation. The total (V_t) and micropore (V_{mi}) volumes were also calculated.

Recent studies have revealed that the properties of the modifier have a significant impact on the peak currents and that there is a positive correlation between the peak current and the specific surface area as well as the adsorption ability of the CPE's modifiers (Kuśmierek et al., 2015; Kuśmierek et al., 2017; Skrzypczyńska et al., 2016). Therefore, the adsorption capacities of the activated carbons for all of the chlorinated phenoxyacetic acids were investigated. All the adsorption experiments were carried out at 25 °C in Erlenmeyer flasks filled with 0.04 L of 2,4-D, 2,6-D or 2,4,6-T solutions (0.1–0.5 mmol L^{-1}). The appropriate amounts of adsorbents (0.03 g) were added and the solutions were agitated at 200 rpm for 8 hours. Then the mixtures were filtered through a filter paper. The filtrates were analyzed for phenoxyacetic acid concentration (C_e) using HPLC method. The adsorption capacities were obtained using the following formula:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

The experiments were carried out in duplicate, and average values were used for further calculations.

The carbon paste electrode was prepared by mixing spectrally pure graphite with a binder (Nujol paraffin oil) in an agate mortar. The modified carbon paste electrode was prepared by mixing in an appropriate amount of graphite, viscous and modifier (10% m/m). The mixture was pounded in a mortar for at least 10 min to produce the final paste. The prepared paste was placed in a desiccator for 72 hours. Then a portion of the paste was placed in an electrode Teflon body.

3. RESULTS AND DISCUSSION

The specific surface areas (S_{BET}) of the materials as well as the total pore volume (V_t) and micropore volume (V_{mi}) calculated from the N_2 adsorption-desorption isotherms are presented in Table 2.

Table 2. Porous structure parameters of the activated carbons

Activated carbon	S_{BET} [m^{2}g^{-1}]	V_{mi} [cm^{3}g^{-1}]	V_t [cm^{3}g^{-1}]
F-300	965	0.40	0.57
SX-2	885	0.37	0.62

The adsorption isotherms of 2,4-D, 2,6-D and 2,4,6-T on the activated carbons from aqueous solutions are presented in Fig. 1.

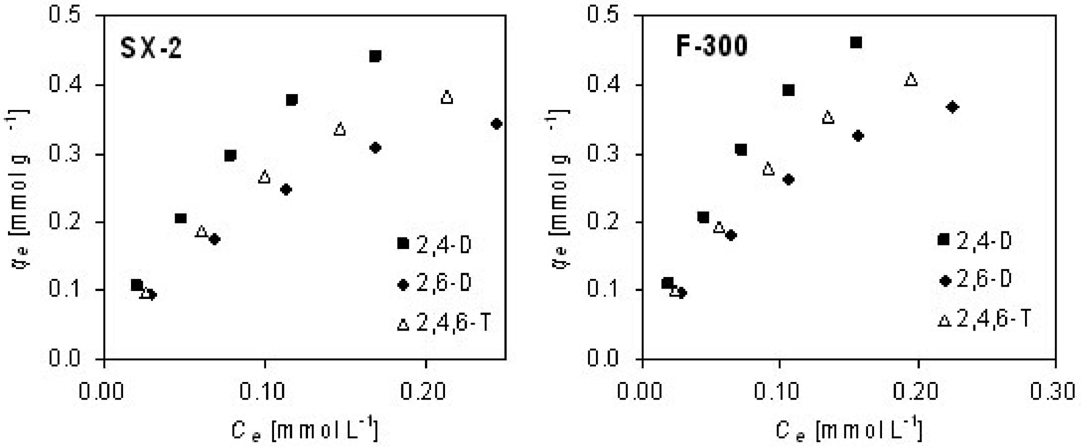


Fig. 1. Adsorption isotherms of 2,4-D, 2,6-D and 2,4,6-T 2,4-D, 2,6-D and 2,4,6-T on the activated carbons

The Freundlich (Freundlich, 1906) (2) and Langmuir (Langmuir, 1916) (3) isotherm models were applied to analyze the experimental data. The equations of the isotherms can be represented as follows:

$$q_{\mathrm{e}} = K_{\mathrm{F}}\, C_{\mathrm{e}}^{1/n} \tag{2}$$

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} b\, C_{\mathrm{e}}}{1 + b\, C_{\mathrm{e}}} \tag{3}$$

All of the isotherm constants were evaluated by a non-linear regression using the OriginPro 7.5 software, and are listed in Table 3.

One can observe that the non-linear regression correlation coefficient values show that equilibrium data obtained for all phenoxyacids were better described by the Langmuir model ($R^2 > 0.99$). The q_m calculated from the Langmuir isotherm equation was found to be 0.865 mmol L^{-1} for 2,4-D, 0.616 mmol L^{-1} for 2,6-D and 0.722 mmol L^{-1} for 2,4,6-T on the F-300 activated carbon, and 0.816 mmol L^{-1} for 2,4-D, 0.556 mmol L^{-1} for 2,6-D and 0.658 mmol L^{-1} for 2,4,6-T on the SX-2 activated carbon. Also the Freundlich (K_{F}) adsorption constants increase in the order: 2,6-D < 2,4,6-T < 2,4-D. The adsorption of 2,4-D, 2,6-D and 2,4,6-T was correlated with the specific surface area of the carbon materials. All of the compounds were adsorbed slightly better on the F-300 activated carbon, which had a larger S_{BET} than the SX-2. Among chlorophenoxy herbicides, the most frequently used compound as the study object is the 2,4-dichlorophenoxyacetic acid (Abdel daiem et al., 2015; Aksu and Kabasakal, 2004; Białek et al.,

Table 3. Parameters of the Freundlich and Langmuir adsorption isotherm models for the chlorinated phenoxyacetic acids

Adsorbate	Freundlich isotherm			Langmuir isotherm		
	K_F	n	R^2	q_m	b	R^2
SX-2						
2,4-D	1.624	1.441	0.981	0.816	7.159	0.996
2,6-D	0.919	1.574	0.979	0.556	6.873	0.992
2,4,6-T	1.160	1.509	0.986	0.658	6.787	0.994
F-300						
2,4-D	1.822	1.423	0.982	0.865	7.422	0.996
2,6-D	1.057	1.534	0.985	0.616	6.789	0.994
2,4,6-T	1.336	1.478	0.989	0.722	6.874	0.995

2016; Białek et al., 2017; Derylo-Marczewska et al., 2019; Doczekalska et al., 2018; Hameed et al., 2009; Kamiński et al., 2014; Kim et al., 2008; Njoku and Hameed, 2011; Ocampo-Pérez et al., 2012; Salman and Hameed, 2010) and the adsorption capacities of 2,4-D onto other activated carbons collected from the literature review are listed in Table 4. To the best of our knowledge, adsorption of 2,6-D and 2,4,6-T has not been described to date. Therefore, unfortunately, it is impossible to compare our results with literature data.

The electrochemical characterization of the carbon paste electrodes (containing 10% of a modifier) was tested in order to estimate their active areas. At first, the electrochemical behavior of potassium ferrocyanide was examined to determine the electroactive surface area of all electrodes. The CV voltammogram of 2 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in 0.1 mol L^{-1} KCl is presented in Fig. 2 (scan rate of 100 mV s^{-1}).

The peak current for a reversible process is described by the Randles–Sevcik equation:

$$i_p = 0.4463\, n_e F A C \left(\frac{nFvD}{RT}\right)^{1/2} \tag{4}$$

The values of the active electrode were found to be equal to 0.0546 and 0.0357 cm^2 for F-300 and SX-2, respectively (Fig. 2).

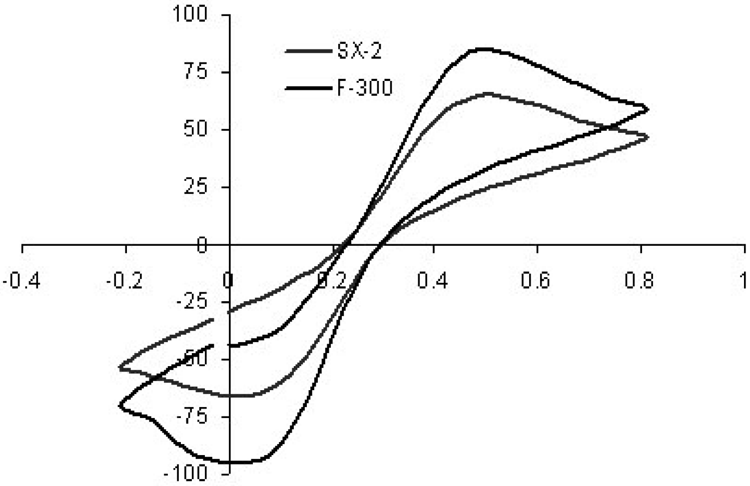


Fig. 2. Cyclic voltammogram of 2.0 mmol L^{-1} potassium ferrocyanide in 0.1 mol L^{-1} KCl

Table 4. Comparison of the 2,4-D adsorption on various activated carbons

Activated carbon	S_{BET} [m^2 g^{-1}]	Adsorption capacity q_m [mmol g^{-1}]	Reference
AC F-300	965	0.865	this study
AC SX-2	885	0.816	this study
AC F-300	731	0.823	Salman and Hameed, 2010
AC WG-12	970	0.827	Białek et al., 2016
AC prepared from data stones	763	1.077	Hameed et al., 2009
AC prepared from corncob	1274	1.358	Njoku and Hameed, 2011
AC Desotec D43/1	1032	1.397	Białek et al., 2017
AC Sorbo Norit	1225	1.490	Abdel daiem et al., 2015
AC Organosorb-10	1049	1.517	Białek et al., 2017
AC Ceca AC40	1201	1.560	Abdel daiem et al., 2015
AC ROW 0.8Supra	1089	1.588	Białek et al., 2017
AC F-400	800	1.860	Kim et al., 2008
AC prepared from willow	1280	2.310	Doczekalska et al., 2018
AC Nuchar WV-H	625	2.514	Aksu and Kabasakal, 2004
AC prepared from miscanthus	1420	2.577	Doczekalska et al., 2018

Then, the effect of the accumulation time on the peak current was examined. The accumulation time was varied from 1 to 10 min and the corresponding current value was measured using one concentration of 2,4-D, 2,6-D and 2,4,6-T solutions. The peak current increased with the increasing of accumulation time up to about 8 min and then became stable. For further research, 8 minutes were selected as the optimal accumulation time.

The effect of scan rate (from 10 mV s^{-1} to 100 mV s^{-1}) on the peak current and peak potential of 2,4-D, 2,6-D and 2,4,6-T were evaluated. The anodic peak current increased as the scan rate increased.

A plot of the oxidation peak currents as a function of the square root of the scan rate is shown in Fig. 3. From the plots of the peak current versus the square root of the scan rate ($\upsilon^{1/2}$), it was found that the peak current is proportional to the square root of the scan rate in the range of 0.01–0.1 V s^{-1} for 2,4-D with an average of 0.998 regression coefficient. The voltammograms of 2,4-6 and 2,4,6-T were recorded at similar conditions. The same trends with increasing scan rate were observed for the compound.

The CVs registered for 0.5 mmol L^{-1} solutions of 2,4-D, 2,6-D and 2,4,6-T (in 0.1 mol L^{-1} Na_2SO_4) using carbon paste electrodes containing 10% by mass of tested modifiers are presented in Fig. 4.

The obtained results showed that the highest peak current value was obtained in the case of 2,4-solution for both carbon modifiers. Both, the F-300 and SX-2 modifications resulted in an increase in the peak current compared to the unmodified carbon paste electrode. 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

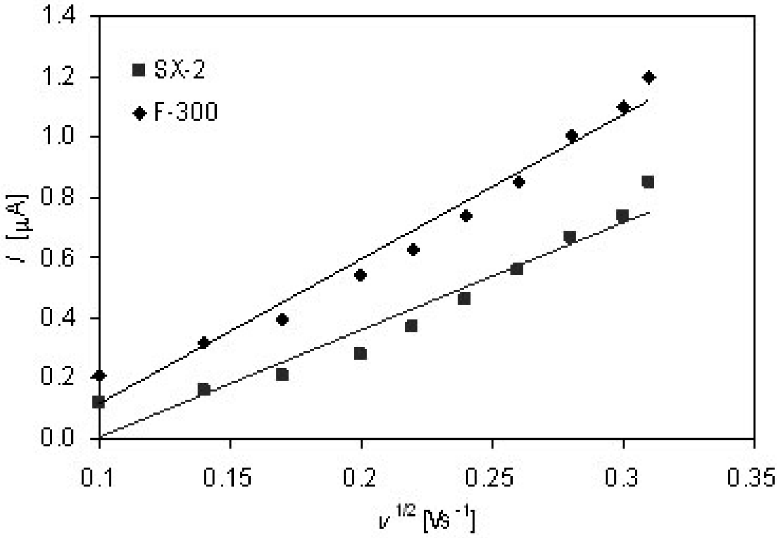


Fig. 3. Plot of I_{pa} versus $\upsilon^{1/2}$ in 2,4-D solution

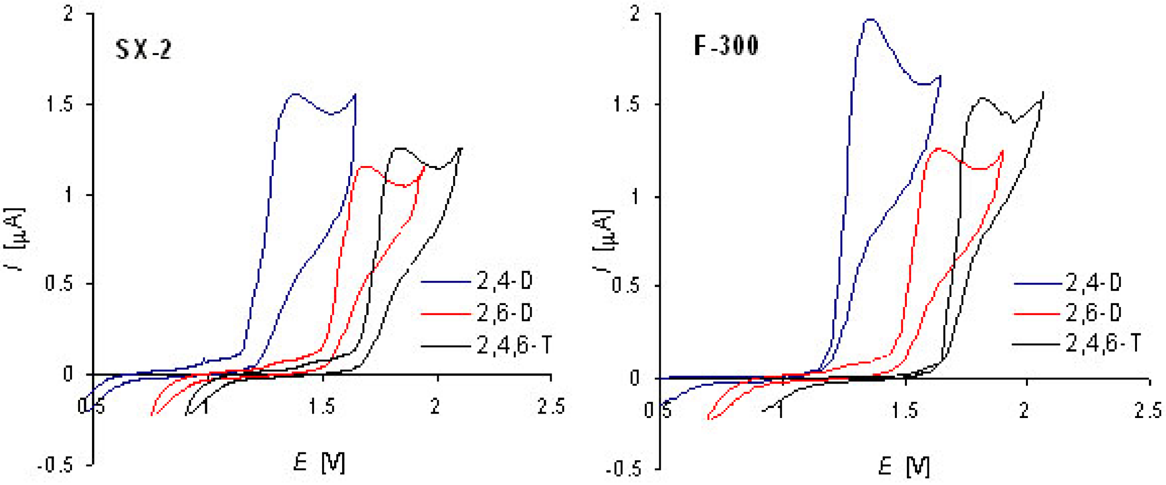


Fig. 4. CV registered for 500 μmol L^{-1} solutions using carbon paste electrodes containing 10% by mass of tested materials (SX-2 and F-300)

the concentration range from 100 μmol L^{-1} to 500 μmol L^{-1}. The limit of detection (LOD), defined as 3 ×standard deviation of the blank signal, was determined and results are listed in Table 5.

The LOD observed for CPE modified with SX-2 activated carbon was 1.14 μmol L^{-1} for 2,4-D, while for the CPE with the addition of F-300 it was 0.98 μmol L^{-1}. CPEs modified with F-300 showed better limits of detection than the CPE SX-2. In each case the modified electrodes were found to be significantly better than the unmodified electrode (LOD for unmodified electrode was about 50 μmol L^{-1} for all solutions).

The results obtained for the modified CPEs were compared with HPLC method – the most commonly used technique for determination of herbicides in aqueous solutions. The calibration curves were obtained by plotting peak height against the analyte concentration (0.5–100 μmol L^{-1}). The limit of detection was experimentally estimated by analysis of aqueous samples spiked with serially diluted 2,4-D, 2,6-D and 2,4,6-T standards until the signal-to-noise ratio reached 3. The LOD, the equations for the linear regression lines as well as correlation coefficients are listed in Table 5. As can be seen, the LOD values are lower than those obtained in electrochemical studies. An unquestionable advantage of voltammetry in comparison to HPLC is its high speed, ease of use and low price of research equipment.

Table 5. Linearity results (n = 3)

Analytical method	Calibration equation ($y = ax + b$)	R^2	LOD [µmol L^{-1}]
2,4-D			
HPLC	$y = 272.7x + 0.945$	0.999	0.37
CPE F-300	$y = 2.425x + 0.281$	0.993	0.98
CPE SX-2	$y = 2.201x + 0.101$	0.999	1.14
2,6-D			
HPLC	$y = 54.159x + 0.27$	0.999	1.84
CPE F-300	$y = 4.302x + 0.311$	0.999	3.25
CPE SX-2	$y = 3.680x + 0.229$	0.998	3.67
2,4,6-T			
HPLC	$y = 85.219x - 0.258$	0.998	1.17
CPE F-300	$y = 3.404x + 0.359$	0.995	2.41
CPE SX-2	$y = 2.951x + 0.336$	0.998	2.67

4. CONCLUSIONS

This paper describes the properties of carbon paste electrodes modified with an addition of two commercial activated carbons (SX-2 and F-300). The sensitivity of the method was correlated with the type of the modifier – the analytical signal was increased with the adsorption capacity of the materials used. The proposed electroanalytical method is applicable for fast detection and preliminary determination of 2,4-dichlorophenoxyacetic acid, 2,6-dichlorophenoxyacetic acid and 2,4,6-trichlorophenoxyacetic acid in real samples (in production media and wastewater).

SYMBOLS

A	area of the electrode, cm^2
b	the Langmuir isotherm constant related to the free energy of adsorption, L $mmol^{-1}$
C	concentration of the probe molecule in the solution
C_0	initial adsorbate concentration, mmol L^{-1}
C_e	final adsorbate concentration, mmol L^{-1}
D	diffusion coefficient of the molecule in solution
I_{pa}	peak current, µA
K_F	the Freundlich isotherm constant, (mmol g^{-1}) (L $mmol^{-1})^{1/n}$
m	mass of adsorbent, g
n	Freundlich isotherm constants or number of replicated measurements
n_e	number of electrons participating in the reaction (equal to 1)

q_e	adsorption capacity, mmol g^{-1}
q_m	Langmuir maximum adsorption capacity, mmol g^{-1}
R^2	correlation coefficient
S_{BET}	specific surface area, $m^2 g^{-1}$
V	the volume of the solution, L
V_{mi}	micropore volume, cm^3 g^{-1}
V_t	total pore volume, cm^3 g^{-1}
v	scan rate (V s^{-1})

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