Nutshells as Modifiers of Carbon Paste Electrodes Used in Detecting Chloroorganic Water Pollutants

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Electrochemical properties of a carbon paste electrode (graphite) modified with hazelnut and walnut shells were investigated. The adsorption of 4-chlorophenol (4-CP) on the studied materials was determined, and the hazelnut shells were found to provide a higher adsorption capacity. The hazelnut and walnut shells were used to modify the carbon paste electrode to detect 4-CP by cyclic voltammetry. Compared to an unmodified electrode, all of the new paste electrodes showed much higher sensitivity in the 4-CP detection.

Keywords: 4-Chlorophenol; Adsorption; Nutshells; Carbon paste electrode; Voltammetry

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INTRODUCTION

Advances in technologies leading to the improvement of the quality of life are often associated with the introduction of processes using environmentally unfriendly chemicals. Therefore, industrial plants can be an important source of environmental pollution (Czaplicka 2004). Over recent decades, the presence of certain compounds with carcinogenic or mutagenic properties in industrial wastewater has become increasingly important for environmental scientists. These substances, even at low levels, can cause harmful effects on the environment and pose a noticeable threat to human health (Gan *et al.* 2016). Among these substances are phenols, especially chlorinated ones, which are widely used as preservatives in the wood industry and as intermediates in the production of pesticides and adhesives (Wei *et al.* 2014). In addition, chlorophenols are resistant to biodegradation due to the presence of chlorine atoms connected to an aromatic ring, which means that they remain in water and soil for a long time (Khanikar and Bhattacharyya 2013).

Due to the toxicity of phenol and its derivatives, their presence in the environment is a serious problem requiring urgent action. For this reason, numerous different methods including biological, chemical, and physical processes have been proposed. Among them, adsorption seems to be the most popular and the most frequently used (Ahmaruzzaman and Sharma 2005; Dąbrowski *et al.* 2005; Hameed *et al.* 2008; Lin *et al.* 2009; Noorimotlagh *et al.* 2015). Therefore, many different adsorbents have been proposed and described. They include activated carbons and other carbonaceous materials, silica materials, and various non-conventional, low-cost materials that have attracted a recent growing interest and popularity. The low-cost sorbents are easily available and disposable without regeneration. They can be classified as natural and biological materials, waste materials including household wastes, industrial wastes, agricultural products, and natural materials including sea materials, soil and ore materials (Lin *et al.* 2009; Soto *et al.* 2011; Zhou *et al.* 2015).

For researchers dealing with the environment, both research and the development of selective and rational methods for the detection and determination of phenols are of increasing importance (Das *et al.* 2014). There are many methods based on chromatographic techniques, capillary electrophoresis (Almeda *et al.* 2007; Fan *et al.* 2015; Saraji and Ghani 2015), and spectroscopy (Mukdasai *et al.* 2016). However, all these techniques have some disadvantages, such as preparation time, high costs, solvents and reagent consumption, and the need for well-trained analysts (Amiri *et al.* 2012). Currently, it is preferable to search for alternative, non-classical methods that could be simple, fast and clean, taking into account, for example, the principles of green chemistry (Gałuszka *et al.* 2013).

In this context, electrochemical sensors, *e.g.*, carbon paste electrodes (CPE), are excellent devices used for initial analysis (Cao *et al.* 2014). They require minimal sample preparation, they are easy to modify, and they are useful for collecting data. In addition, they are sensitive, require a small amount of the sample, and the analysis is carried out quickly and is characterized by high selectivity (Oliveira *et al.* 2014).

There are currently few reports on the determination of chlorophenols by means of sensors due to difficulties and the fact that they have the ability to generate intermediates covering the surface of the electrode with a thin film. As a consequence, the surface of the sensor becomes passivated. In recent years, attention has been focused on alternative cheap adsorbents of natural origin, *i.e.*, biological or mineral (Mojica *et al.* 2007; Gómez *et al.* 2011; Devnani and Satsangee 2013; Elroby 2015; Dar *et al.* 2016). Generally, these materials are easily available. In this work, carbon paste electrodes modified with hazelnut shells (HS) and walnut shells (WS) for the detection of 4-chlorophenol (4-CP) in an aqueous environment are produced.

EXPERIMENTAL

Materials and Research Methodology

The 4-chlorophenol (>99%) used in the electrochemical studies was obtained from Sigma (St. Louis, USA). The hazelnut shells (*Corylus avellana*) and walnut shells (*Juglans regia*) were selected as modifiers of the carbon paste electrodes.

The nutshells were first crushed and then milled in a mixer. Then, they were put through a 2.0 mm sieve and then through a 1.0 mm sieve. In the experiments, fractions with a grain size in the range of 1.0 to 2.0 mm were used (with an average size of about 1.5 mm). Before use, all of the modifiers were thoroughly washed with deionized water and dried in a vacuum oven at 130 °C until they reached a constant weight.

Scanning electron microscope (SEM) photos of these materials were taken at the same magnification using a Philips XL30/LaB6 SEM (Amsterdam, Netherlands). The chemical composition of their surface was also determined using energy dispersive (EDS) X-ray microanalysis. The BET surface area of the nutshells was calculated based on the low temperature N_2 adsorption data obtained using a Gemini 2360 analyzer (Micromeritics, Norcross, GA, USA). For the adsorption and electrochemical studies, the tested materials were stored in a desiccator until they were used.

Sorption of 4-chlorophenol with 0.1 mol/dm^3 of Na_2SO_4 solution on the HS and WS shells was investigated at various initial adsorbate concentrations in the range of 0.05 to 0.5 mmol/dm^3.

The tests were conducted in Erlenmeyer flasks. In the flasks, 0.04 dm^3 of the 4-CP solutions of an appropriate concentration and 1 g of adsorbent (either hazelnut or walnut shell) were introduced. The contents of the flasks were shaken at 200 rpm at 25 °C. After 24 h, the solution samples were filtered and analyzed for 4-chlorophenol content. The adsorbate concentration in the solution was determined spectrophotometrically (Varian, Carry 3E spectrophotometer, Palo Alto, USA).

The adsorption capacity of 4-CP on nutshells (q_e) was calculated from the dependence using Eq. 1,

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

where q_e is the amount of adsorbate adsorbed on the surface of the adsorbents (mmol/g), C_0 is the initial concentration of 4-CP in solution (mmol/dm^3), C_e is the equilibrium concentration after 24 h (mmol/dm^3), V is the volume of the solution (dm^3), and m is the mass of the nutshells (g).

The adsorption kinetic studies were conducted in shaken Erlenmeyer flasks at room temperature for initial 4-CP concentration of 0.2 mmol/dm^3. Samples were continually taken from the solution at given intervals and analysed. The adsorbed 4-CP (q_t, mmol/g) was calculated by following equation,

$$q_t = (C_0 - C_t)V / m \tag{2}$$

where q_t is the amount of 4-CP adsorbed onto adsorbent at time t (mmol/g), C_0 and C_t are the initial concentration (mmol/dm^3) and concentration at time t (mmol/dm^3), respectively, m is the mass of the adsorbent (g), and V is the volume of the solution (dm^3).

From the prepared materials, carbon paste electrodes were made with two content modifiers of 5 wt.% and 10 wt.% in a mixture with graphite. The pastes were prepared by grating a mixture of powdered graphite (Sigma) with the addition of a modifier in an agate mortar, and then adding the appropriate amount of paraffin oil (Nujol) until a homogeneous consistency was obtained. The resulting pastes were conditioned for 72 h in a desiccator. After this time, small portions of the paste were placed in the hollow of a Teflon electrode body, lightly compacted, and then polished on smooth paper to smooth the surface. Voltammetric measurements were collected using an AutoLab analyzer (Eco Chemie B.V., Utrecht, Netherlands) equipped with a PGSTAT 20 potentiometer coupled to a computer with GPES version 4.9 software.

A three-electrode system was used, where the working electrode was a carbon paste electrode, the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum wire. Voltammetric tests were performed for various concentrations of 4-chlorophenol solution (in the range of 0.1 to 0.5 mmol/dm^3) in 0.1 mol/dm^3 sodium sulphate. During all measurements, the following parameters were maintained: the scan rate was 50 mV/s, the potential of the working electrode was 50 mV, the potential pulse amplitude was 25 mV, and the potential step was 5 mV.

RESULTS AND DISCUSSION

Nutshells Characterization

To compare the surface of the shells of both kinds of nuts, SEM (100× magnification) pictures were taken and are shown in Fig. 1. The results of EDS analysis for hazelnut and walnut shells are presented in Table 1. SEM-EDS analyses showed large amounts of C and O (comparable for both analyzed materials), and then about 20 times smaller but also comparable amounts of Ca and K. Other predominant elements in hazelnut shells were S, P, Si, and Mg. Small amounts of Fe and Cu were also found in walnut shells, although these were much higher than their contents in hazelnut shells.

Table 1. EDS Analysis for the Tested CPE Modifiers

Hazelnut shells	Content (wt%)										
	C	O	K	Ca	Mg	S	Cl	Si	P	Fe	Cu
External surface	52.8	41.5	2.27	2.10	0.06	0.12	0.11	0.16	0.07	0.24	0.43
Cross-section	54.9	44.4	0.16	0.04	0.06	-	-	0.06	-	0.07	0.18
Inner surface	51.6	43.2	2.02	1.81	0.10	0.12	0.09	0.18	0.07	0.29	0.39
Walnut shells	Content (wt%)										
	C	O	K	Ca	Mg	S	Cl	Si	P	Fe	Cu
External surface	49.3	43.2	1.20	3.17	0.86	0.16	-	0.08	1.86	-	-
Cross-section	54.8	44.5	0.25	0.17	0.06	-	-	0.05	-	-	0.04
Inner surface	54.7	39.7	1.82	2.23	0.42	0.63	0.14	0.21	0.24	0.02	-

The nutshells were subjected to elemental analysis (Table 2). The results for C and O in the shells of both types of nuts were similar for both test methods (Tables 1 and 2). Some minor differences may have resulted from the differences in the EDS method (surface layer testing) and elemental analysis (for the whole sample mass by the combustion method).

The specific surface areas for hazelnut and walnut shells were 8.5 and 7.1 m^2/g, respectively. These values are low but comparable with the results reported by other authors (Kuśmierek and Świątkowski 2015a; Şencan *et al.* 2015; Tang *et al.* 2017). For example the S_{BET} of the hazelnut shells was 5.92 m^2/g (Şencan *et al.* 2015) and the surface area of the walnut shells ranged from 1.01 to 3.12 m^2/g (Tang *et al.* 2017).

Table 2. Elemental Analysis for the Tested CPE Modifiers

Material	Content (wt.%)			
	C	O	H	N
HS	50.04	43.21	5.89	0.43
WS	48.72	44.51	5.74	0.33

Information on the physicochemical properties of the materials used was presented by Kuśmierek and Świątkowski (2015a). In order to better examine the surface of the hazelnuts and walnuts shells, the water vapor adsorption isotherms were determined (Fig. 2), and on their basis the number of H_2O primary adsorption centers was determined (a_0) using Eq. 3,

$$h / a = (1 / a_0 c) - (1h / a_0) \qquad (3)$$

where h is the equilibrium relative pressure, a is the adsorption (mmol/g), c is the equation constant, and a_0 is the number of primary adsorption centers (mmol/g).

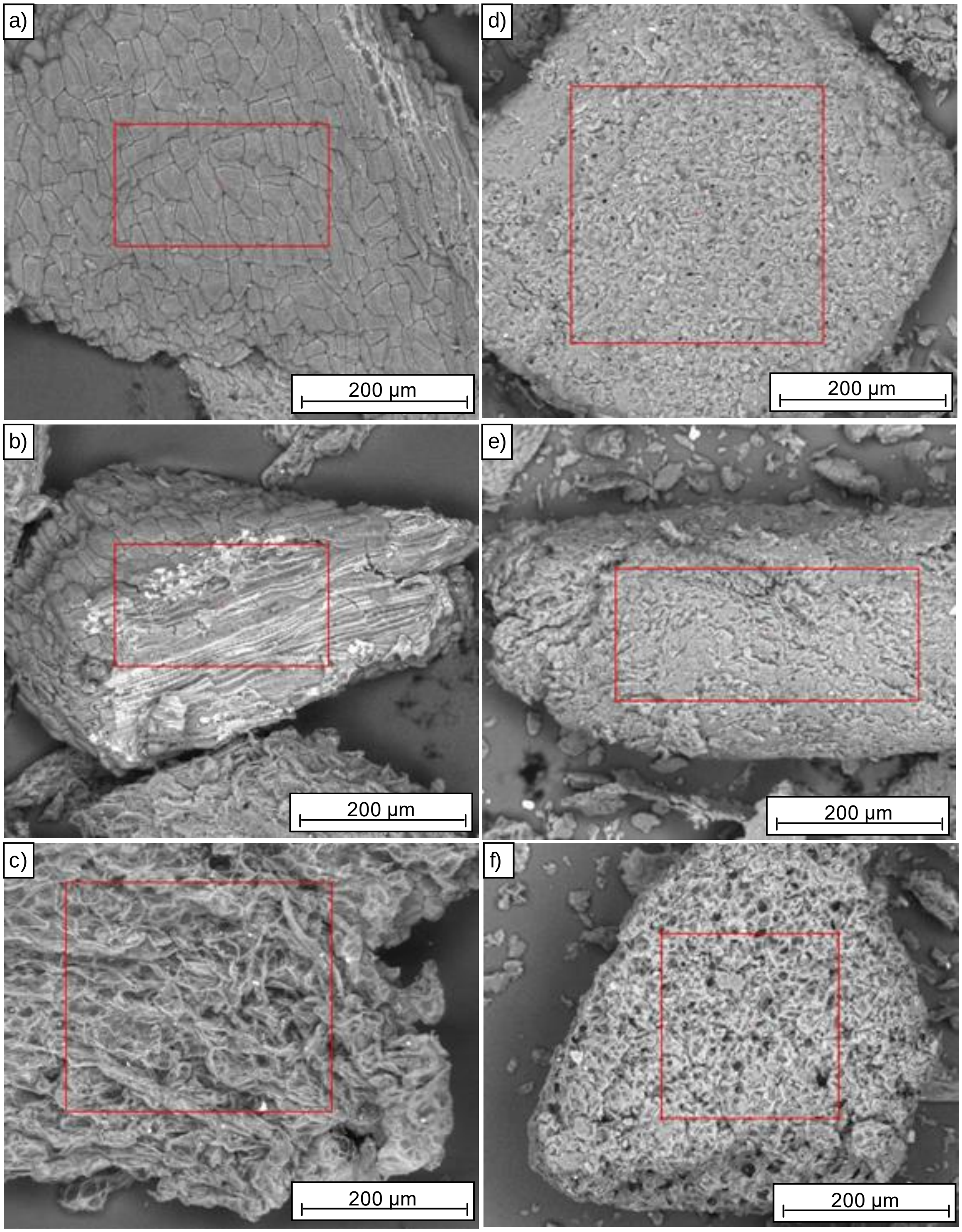

Fig. 1. SEM images of the hazelnut shells: a) external surface; b) cross-section; c) inner surface and walnut shells: d) external surface; e) cross-section; f) inner surface

A detailed procedure is described in Kuśmierek *et al.* (2019). The a_0 values allow the characterization of the degree of polarity of the adsorbent surface to estimate its hydrophilic or hydrophobic character. A slightly higher number of H_2O primary adsorption centers obtained for the WS (12.7 mmol/g) in comparison to the HS (11.9 mmol/g) means the surface of the walnut shells displayed a slightly higher polarity.

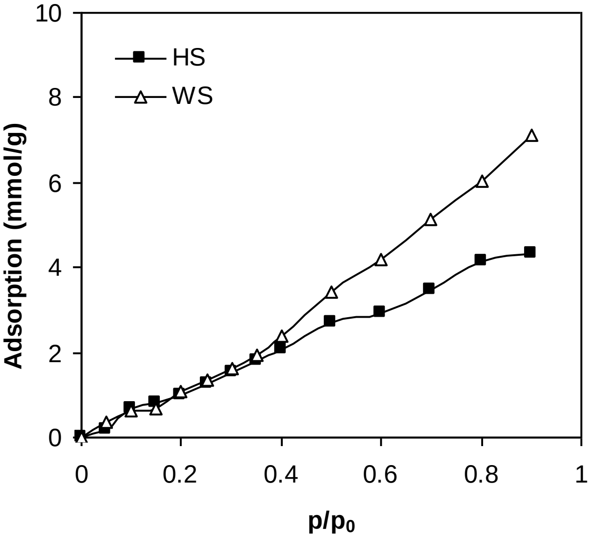

Fig. 2. Isotherms of water adsorption on the hazelnut and walnut shells

Adsorption Studies

The 4-CP adsorption isotherms on the walnut shells and the hazelnuts shells from 0.1 mol/dm^3 of Na_2SO_4 solution are shown in Fig. 3. The higher course of the experimental isotherm for HS compared to WS indicated a better adsorptive capacity of hazelnut shells in relation to 4-CP. In order to more accurately interpret the obtained results, the Langmuir (Eq. 4) and Freundlich isotherms (Eq. 5) were used for their description:

$$q_e = (q_m b C_e) / (1 + bC_e) \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

where q_m is the maximum adsorptive capacity (mmol/g), b is the constant of the Langmuir equation (dm^3/mmol), K_F is the constant of the Freundlich equation [equal to (mmol/g)(dm^3/mmol)$^{1/n}$], and n is the exponent of the equation.

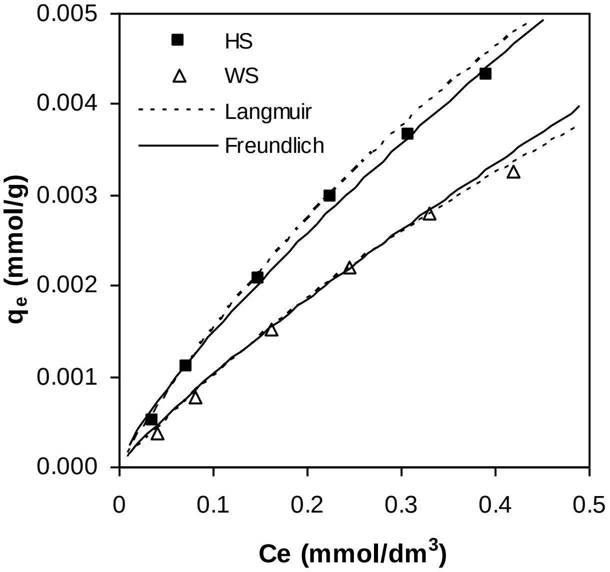

Fig. 3. Adsorption isotherms of 4-chlorophenol onto the hazelnut and walnut shells from 0.1 mol/dm^3 sodium sulphate solution

The constants in Eqs. 4 and 5, shown in Table 3, were determined by curvilinear regression using Origin Pro 7.5 software. Higher q_m and K_F values were obtained for hazelnut shells. Therefore, HS seems to be a better sorbent in relation to 4-chlorophenol than WS probably due to their higher BET surface area in comparison to the walnut shells.

Table 3. The Langmuir and Freundlich Isotherm Equation Parameters for 4-Chlorophenol Sorption on the Hazelnut and Walnut Shells

Adsorbent (modifier)	Langmuir			Freundlich		
	q_m (mmol/g)	b (dm^3/mmol)	R^2	K_F [(mmol/g)(dm^3/mmol)$^{1/n}$]	n	R^2
HS	0.0153	1.381	0.957	0.0108	1.258	0.996
WS	0.0131	0.818	0.961	0.0091	1.175	0.997

The adsorption capacities of HS (0.0153 mmol/g) and WS for 4-CP were essentially comparable with other low-cost adsorbents, including chitosan (0.020 mmol/g) (Li *et al.* 2009), hard coal (0.022 mmol/g) (Kuśmierek *et al.* 2016), and coke breeze (0.023 mmol/g) (Ahmaruzzaman and Sharma 2005).

The 4-CP adsorption was carried out according to the Freundlich model, for which higher values of correlation coefficients R^2 ($\geq$ 0.996) were obtained than for the Langmuir isotherm equation. The good fit obtained for the Freundlich isotherm suggests the heterogeneous nature of the adsorbents surface. The K_F values obtained for 4-CP sorption from solutions of sodium sulphate for the HS [0.0108 (mmol/g)(dm^3/mmol)$^{1/n}$] and the WS [0.0091 (mmol/g)(dm^3/mmol)$^{1/n}$] were higher than for the sorption of 4-CP from water [0.008 (mmol/g)(dm^3/mmol)$^{1/n}$] (Kuśmierek and Świątkowski 2015a). Increased adsorption of 4-CP from inorganic salt solutions compared to water has previously been observed in the case of activated carbons (Hameed *et al.* 2008; Kuśmierek and Świątkowski 2015b). Generally, the adsorption of chlorophenols increases in the presence of an inorganic salt in solution, and it increases further with concentration and ionic strength of the solution. A similar trend was observed in the case of low-cost sorbents, which are wastes of the agri-food industry, on which 2,4,6-trichlorophenol (Kuśmierek *et al.* 2017a,b) and pentachlorophenol (Kuśmierek *et al.* 2018; Wierzbicka *et al.* 2019) were adsorbed.

The adsorption kinetics of the 4-CP onto hazelnut and walnut shells is shown in Fig. 4. In order to better understand the adsorption kinetics of 4-CP on nutshells, the pseudo first-order and pseudo second-order models were tested to fit and evaluate the experimental kinetic data. The pseudo first-order (Lagergren 1898) (Eq. 6) and pseudo second-order (Ho and McKay 1999) (Eq. 7) equations are given as:

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \qquad (6)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (7)$$

where k_1 is the pseudo first-order adsorption rate constant (1/min) and k_2 is the pseudo second-order rate constant (g/mmol·min).

The calculated k_1 rate constants were 0.0228 (R^2 = 0.960) and 0.0217 (R^2 = 0.951) 1/min for HS and WS, respectively. The pseudo second-order rate constants for HS and WS were found to be 9.043 and 8.868 g/mmol·min with high correlation coefficients of 0.993 and 0.994, respectively. The 4-CP was adsorbed slightly faster on the hazelnut shells than on the walnut shells. Based on higher correlation coefficients it can be concluded that the adsorption kinetics of 4-CP could well be approximated more favourably by pseudo second-order kinetic model rather than pseudo first-order kinetic equation. A good fitting of experimental data to pseudo second-order model suggests that the overall rate of adsorption process appears to be controlled by diffusion-related mechanisms.

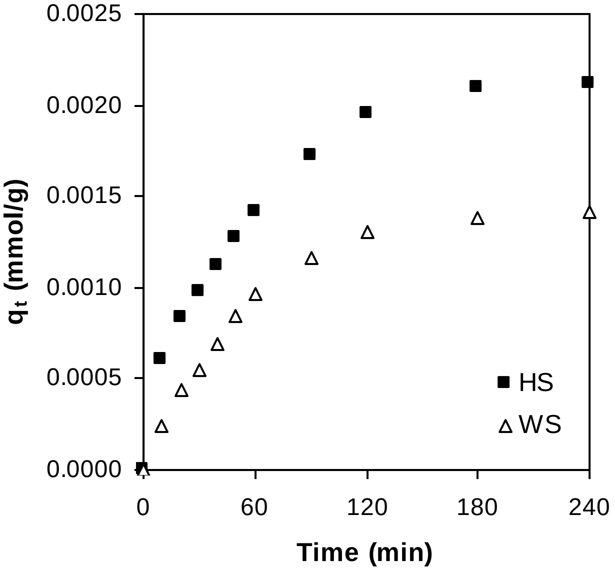

Fig. 4. Adsorption kinetics of 4-chlorophenol (C_0 = 0.2 mmol/dm^3) onto the hazelnut and walnut shells from 0.1 mol/dm^3 sodium sulphate solution

Electrochemical Studies

The first stage of the electrochemical research was the determination of the electroactive surface of the tested electrodes (Apetrei *et al.* 2011; Ganesh and Kumara Swamy 2016). The electrochemical behavior of 2 mmol/dm^3 of potassium ferrocyanide $[Fe(CN)_6]^{3-/4-}$ in 1 mmol/dm^3 of KCl was investigated using cyclic voltammetry (CV). The CV voltammograms are shown in Fig. 5.

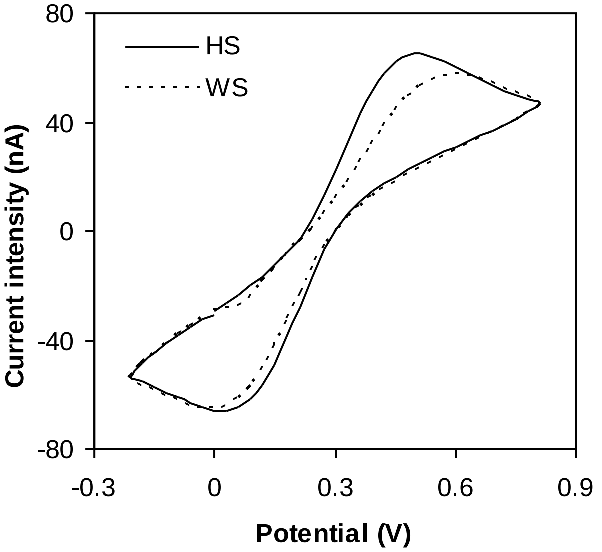

Fig. 5. The CV curves registered in 2 mmol/dm^3 of $[Fe(CN)_6]^{3-/4-}$ solution for CPEs modified with hazelnut and walnut shells (10% m/m)

The peak current for the reversible processes was determined from the Randles-Sevcik Equation, as seen in Eq. 8,

$$I_p = 2.69 \times 10^5 AD^{1/2}n^{3/2}v^{1/2}C \quad (8)$$

where A is the electrode surface (cm^2), n is the number of electrons participating in the reaction, D is the diffusion coefficient, C is the solution concentration (mmol/dm^3), and v is the scanning speed (V/s).

Based on the results obtained from the CV curve, the active surface of the electrode modified with the WS was calculated as 0.123 cm^2, while for the electrode modified with the HS it was calculated as 0.165 cm^2.

Next, the influence of the accumulation time on the peak current of the oxidation of 4-CP in a solution of 0.5 mmol/dm^3 for the CPEs modified with both tested materials was determined. The peak current intensity was found to increase with the accumulation time until 2 min, after which it maintained a constant value (Fig. 6). In further studies the time of accumulation was assumed to be 2 min.

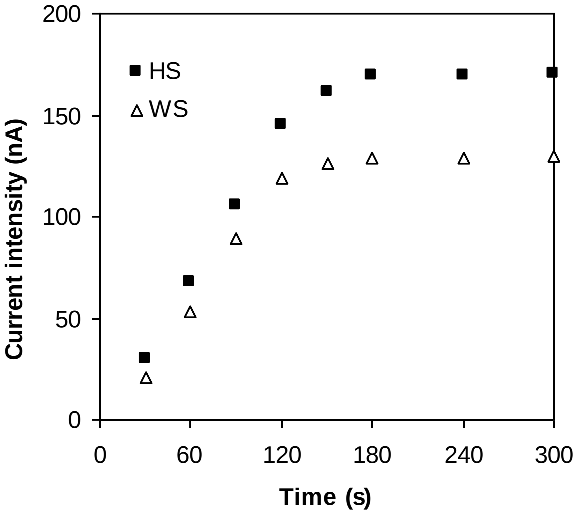

Fig. 6. Effect of accumulation time on the peak current

After accepting all measurement conditions, such as accumulation time and scanning speed, the CV curves were recorded for 4-CP solutions at concentrations of 0.1 to 0.5 mmol/dm^3 using a 5% and 10% addition of the materials tested (CPE modifiers). Example voltammetric curves for five concentrations of 4-CP (from 0.1 to 0.5 mmol/dm^3) recorded using electrodes containing 5 and 10% addition of HS and WS are shown in Fig. 7. Based on the obtained results, *via* linear regression, equations of the calibration curves for individual electrodes were calculated and detection limits (LOD) were determined. The results are shown in Table 4.

Based on data obtained from the CV curves, an increase in peak current was found along with an increased addition of the modifier. This trend was observed for both modifiers. Even a small addition of the modifier clearly improved the electroanalytical properties of the electrode. In comparison to the unmodified electrode (graphite), all new electrodes showed a noticeable higher sensitivity in 4-CP detection. A two-fold increase in material addition (from 5 to 10 wt%) resulted in a 1.5-fold increase in the height of the oxidation peak. The potential for oxidation occurred at about 0.75 ± 0.05 V. Generally, it can be concluded that better effects of the paste electrode modification were observed for the modifier (hazelnut shell) with a higher sorptive capacity in relation to 4-chlorophenol. The LODs observed for CPE modified with HS and WS were better than those observed for the CPEs modified with halloysite materials (Wierzbicka *et al.* 2019). As can be observed in Table 4, greatly increased sensitivity was achieved by including the nutshell material as carbon paste modifier. The increase can be explained as being due to a more open pore structure, allowing material to diffuse more rapidly in the electrode and adsorb more effective. Probably an important role is played here by the surface area of the nutshell materials, that was different (about two times greater) than for the main carbon paste material (graphite powder, S_{BET} = 4 m^2/g). Similar observations regarding the importance of the surface area of CPE modifiers were in previous papers by the authors (Skrzypczyńska *et al.* 2016; Kuśmierek *et al.* 2017c).

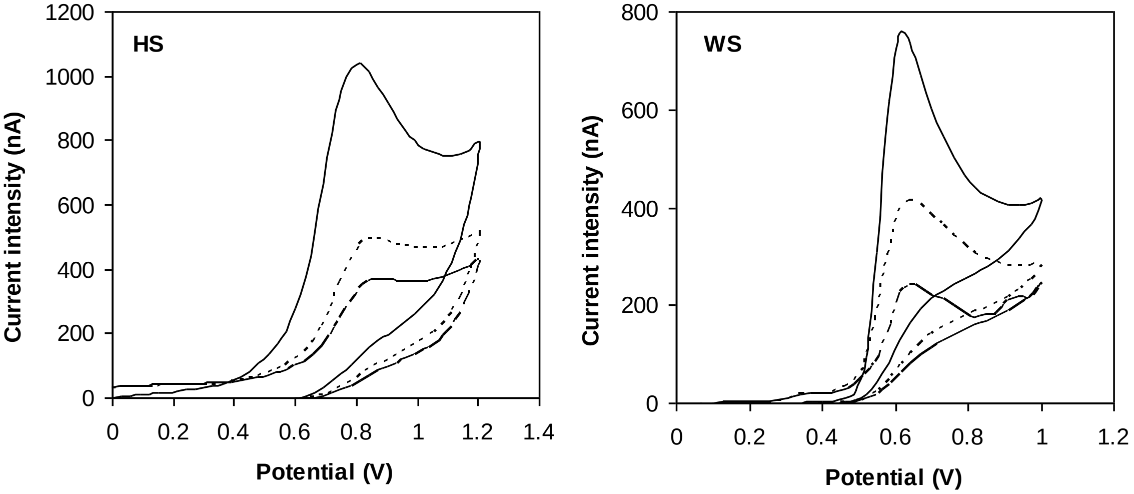

Fig. 7. The CV curves registered for 0.1, 0.3, and 0.5 mmol/dm^3 4-CP for CPEs containing 10% of the modifier content

Table 4. Calibration Results for 4-CP Determination

Material (modifier)	Modifier Content (%)	Equation of a Straight (Calibration) Line	LOD (µmol/dm^3)	R^2
HS	5	$y = 1.180x - 0.036$	8.44	0.979
	10	$y = 1.980x - 0.056$	5.03	0.961
WS	5	$y = 0.990x - 0.047$	10.06	0.982
	10	$y = 1.261x + 0.074$	7.90	0.951
Only graphite	0	$y = 0.155x - 0.004$	63.20	0.945

CONCLUSIONS

1. The use of the graphite paste electrode with walnut shells and hazelnut shells as a modifier increased the current peak oxidation of 4-chlorophenol.
2. Even a small addition of the modifier (5%) noticeably increased the possibilities of chlorophenol determination by means of carbon paste electrodes.
3. Materials with a higher sorptive capacity for the analyte (4-chlorophenol) were better modifiers.

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