

Adsorption and Electrodegradation of Phenoxyacetic Acids on Various Activated Carbons

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Received: 8 January 2020 / Accepted: 4 March 2020 / Published: 10 May 2020

Three kinds of activated carbons: powdered N-SX2, granular F-400 and modified extruded R3ex (N-1800), were used for adsorptive removal and electrochemical degradation in aqueous neutral electrolyte solution of phenoxyacetic acid (PA), 4-chlorophenoxyacetic acid (4-CPA) and 2,4-dichlorophenoxyacetic acid (2,4-D). Electrochemical experiments were carried out after adsorption equilibrium achieving. Adsorption depends on the specific surface area of carbon adsorbent and the number of Cl atoms in the adsorbate molecule. The Langmuir equation and the pseudo-second order model seem to be more useful for describing of adsorption isotherms and kinetics, respectively of all the tested systems. Adsorption on a sediment layer of carbon electrode materials is accompanied with stabilization of stationary potential of the working electrode. During potential cyclisation, the first stages of electrooxidative degradation of the adsorbed molecules can occur with the formation of an electrochemically active benzoquinone/hydroquinone system. The adsorbed molecules and the products of their electrodegradation seem to be responsible for the decrease of electrochemical activity in chloroorganics removal by carbon electrode materials. Simultaneously, the increase of electric double layer capacity of the carbon electrodes can be observed.

Keywords: adsorption; electrodegradation; chlorophenoxyacetic acids; activated carbons; powdered carbon electrodes

1. INTRODUCTION

Halogenated organic pollutants, such as chlorophenoxy herbicides, often present in surface water and sometimes in drinking water, are extremely harmful to human health [1,2]. The limits and guideline values for pesticides in some environmental waters issued by the World Health Organization

have been revived and published [3]. Chloroorganic (e.g. chlorophenoxy herbicides) contamination of waters is a serious threat to living organisms [4]. Their removal from water environments is still interesting and subject-matter topics in literature [5-8]. Firstly adsorption and then electrochemical treatment systems have been evaluated for the removal and degradation of these pollutants in aqueous media. Adsorption on an activated carbon or other materials is one of the most well-established and powerful techniques used for removing chlorophenoxy herbicides [9-17]. Electrochemical treatments, as anodic oxidation or the electro-Fenton process, are the most commonly utilized techniques in order to achieve the destruction of such pollutants [18-21]. Recently, advanced oxidation processes, among them the use of heterogeneous photocatalysis systems by employing semiconductor photocatalyst, have become one of the most promising methods [8,22]. However, in the literature adsorption and electrochemical techniques for chloroorganics removal from water are examined separately. Among chlorophenoxy herbicides, the most frequently used compound as the study object was the 2,4-dichlorophenoxyacetic acid (2,4-D). To the best of our knowledge, a comparison of adsorptive and electrochemical behaviour of phenoxyacetic acids with various numbers of substituted chlorine atoms has not been described.

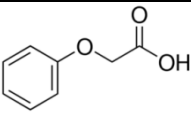
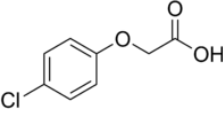
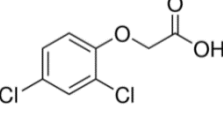
The aim of this work is to study the influences of activated carbons properties and the Cl atoms number in organic molecules on the first stage of their electrochemical destruction, preceded by adsorption on the powder electrode surface. Additionally, in order to recognize the organic removal process, the adsorption ability and kinetics for agitated carbon suspension and stationary electrode bed were compared.

2. EXPERIMENTAL

2.1. Materials

Three external forms of activated carbon – powdered, granular and extruded, were used. The commercial SX2 powdered activated carbon was from Norit (The Netherlands). The granular activated carbon F-400 (Chemviron, Belgium) and the extruded R3ex (Norit, The Netherlands) were grinded and sieved. Previously, the R3ex sample was demineralized using concentrated HF and HCl acids and heat-treated in an argon atmosphere at 1800°C (N-1800) [23]. The adsorbates (and depolarisers), i.e. phenoxyacetic acid (PA), 4-chlorophenoxyacetic acid (4-CPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) as well as electrolyte salt (Na₂SO₄, p.a.) were purchased from Sigma Aldrich. The properties of the tested organics are presented in Table 1. The solutions were freshly prepared with double-distilled water (conductivity 8 μS) and de-aerated with Ar.

Table 1. Properties of the organics (phenoxyacetic acids – PAs) tested

PAs	Molar mass	Structure	Solubility (g dm ⁻³) in water (25°C)	pK _a
PA	152.15		10	3.12
4-CPA	186.59		0.957	3.14
2,4-D	221.04		0.890	2.80

2.2. Activated carbons surface area and porous structure

Carbon porosity was characterized by low-temperature (77 K) N₂ adsorption-desorption, and the relevant isotherms of all samples were determined using the ASAP 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA). Before each adsorption measurement, the samples were heated at 150°C under vacuum.

2.3. Adsorption measurements

2.3.1. Adsorption kinetics

The phenoxyacetic acids (PA, 4-CPA, 2,4-D) were adsorbed on the activated carbons (0.1 g) at 20°C from aqueous electrolyte solutions (100 mL 0.05 mol L⁻¹ Na₂SO₄) containing 1 mmol L⁻¹ concentrations of adsorbates. Adsorption processes were carried out in two independent ways: in an electrochemical cell (without agitation, before cyclisation) and in an Erlenmeyer flask with shaking. The initial, partial (for various contact times) and equilibrium concentration of PAs (in both cases) were measured by HPLC (DAD, Shimadzu LC-20, Kyoto, Japan). The chromatographic analyses were conducted under isocratic conditions on a Phenomenex Luna C18 (4.6 ×150 mm, 3 μm) column (Torrance, CA, USA) operated at 40°C with acetonitrile and water adjusted to pH 3.0 with CH₃COOH (50:50%, v/v). The flow rate was 0.25 mL min⁻¹, and peaks were monitored at λ = 281 nm. On the basis of the obtained results (adsorbate concentration drop with contact time) the kinetic parameters – rate constants, according to the pseudo-first and pseudo-second order models, were calculated.

2.3.2. Adsorption equilibrium

PAs (PA, 4-CPA, 2,4-D) were adsorbed on the activated carbons (50 mg) at 20°C from aqueous electrolyte solutions (50 mL 0.05 mol L⁻¹ Na₂SO₄) containing various concentrations of

adsorbate (from 0.2 to 1.0 mmol L⁻¹). The initial and final/equilibrium concentrations (after 6 h of shaking) of PAs were measured by HPLC in a manner described above (2.3.1).

2.4. Cyclic Voltammetry

Cyclic voltammetric (CV) measurements were carried out using an AUTOLAB (Eco Chemie) electrochemical system equipped with a PGSTAT 10 potentiostat, controlled by the GPES3 software and the three-electrode electrochemical cell presented in one of our earlier papers [24]. A powdered carbon electrode, Pt wire and a saturated calomel electrode (SCE) were used as working, counter and reference electrodes, respectively. The working electrode design is the same as that used and described earlier [24,25]. The carbon sample (100 mg) was placed in an electrode container and drenched with a de-aerated 0.05 mol L⁻¹ Na₂SO₄ solution to obtain a sedimentation layer (3-5 mm thick). The electrolyte solution was then de-aerated. The potentiometric responses (E_{st}) of the carbon electrodes were measured in oxygen-free electrolyte solutions until their values had stabilized (usually after 24 h). All these potentials were measured, and are reported against saturated calomel electrode (SCE). The C_{dl} values for the carbons were determined based on the electric double layer capacity (for $E = 0.4$ V) from first/stabilised cycles. The potential cycling was carried out from -0.3 V to +1.2 V, both for the blank electrolyte and the depolarisers (PAs solutions). The cyclic voltammetric curves were recorded when their shape was reproducible (no change in repeated CV scans). The initial, subsequent (during potential cycling) and final concentrations of PAs were measured by HPLC in a manner described above (2.3.1).

3. RESULT AND DISCUSSION

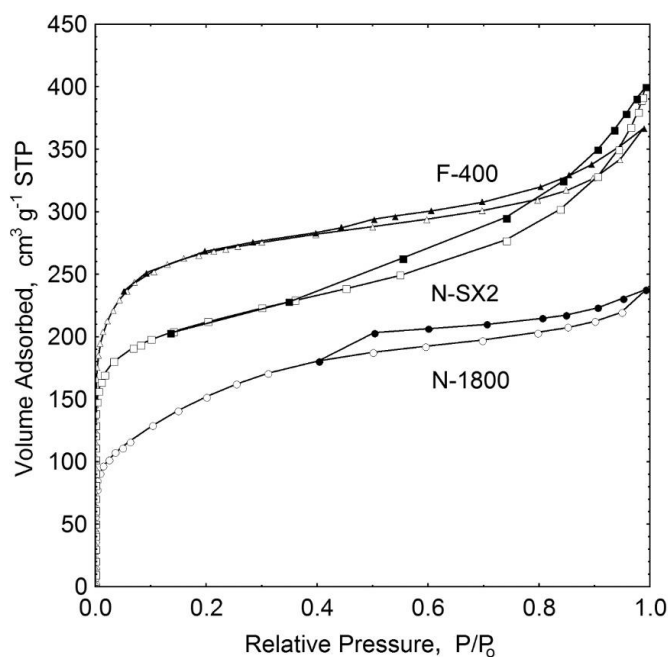


Figure 1. The N₂ adsorption-desorption isotherms (at 77 K) for the activated carbon samples.

For all the tested activated carbons on the basis of the determined N₂ adsorption-desorption isotherms (Fig. 1), the specific surface areas (from BET equation) and porous structure parameters: micropore volumes and mesopore surface areas (V_{mi} and S_{me} , respectively) were calculated using DFT method (Table 2).

The applied carbon materials exhibit differences in the specific surface area (S_{BET}) and micropore volume in order F-400 > N-SX2 > N-1800 (Table 2). These carbons were used as electrode materials for studies of the first stages of electrodegradation of chlorophenoxyacetic acids in neutral aqueous electrolyte solutions.

Table 2. Activated carbons properties

Carbon sample	S_{BET} m ² g ⁻¹	V_{mi} cm ³ g ⁻¹	S_{me} m ² g ⁻¹	E_{st} V vs. SCE	C_{dl} F g ⁻¹
N-SX2	870	0.320	79	0.13	0.73
F-400	995	0.395	63	0.06	1.05
N-1800	550	0.160	61	0.19	0.40

The main differences between them consist in the chlorine atoms number in organic molecules. Firstly, for the assessment of adsorption ability towards the used organics (PAs), the kinetic and equilibrium measurements were carried out. Adsorption kinetics is an important characteristics in order to determine carbon/solution contact time necessary to process equilibrium. The pseudo-first and pseudo-second order models were used for the description of adsorption kinetics [26,27]. Calculated parameters (rate constants, k_1 and k_2) are collected in Table 3. For all adsorbent/adsorbate systems, the pseudo-second order model better described the adsorption kinetics ($R^2 > 0.99$). The adsorption rate decreased with the number of Cl atoms in the adsorbate molecule for all the adsorbents (Table 3).

Table 3. Adsorption kinetics parameters ($C_0 = 1$ mmol L⁻¹, $m = 0.1$ g, $V = 100$ mL, electrolyte concentration = 0.05 mol L⁻¹).

Adsorbent	Adsorbate	Pseudo-first order		Pseudo-second order	
		k_1	R^2	k_2	R^2
		h ⁻¹		g mmol ⁻¹ h ⁻¹	
	PA	0.0038	0.7694	0.3096	0.9932
N-SX2	4-CPA	0.0048	0.8610	0.2862	0.9968
	2,4-D	0.0045	0.8214	0.2739	0.9967
F-400	PA	0.0107	0.9718	0.3801	0.9999
	4-CPA	0.0072	0.9121	0.3066	0.9998
	2,4-D	0.0071	0.8319	0.2776	0.9997
N-1800	PA	0.0120	0.8804	1.2803	0.9997

4-CPA	0.0073	0.9618	1.0214	0.9999
2,4-D	0.0119	0.9254	0.9115	0.9998

The determined adsorption isotherms for all studied systems are shown in Fig. 2. Generally, the adsorption capacity increased with growing specific surface area S_{BET} . For all the adsorbents, the adsorbed quantity depends (growingly) on chlorine number in the adsorbate molecule. Increasing the degree of the Cl content is correlated with the respective increase in the hydrophobicity, molecular mass, and the decrease in the solubility of the compound, which increases the adsorption capacity. Similar results were reported for the adsorption of chlorophenols [28-31].

The experimental isotherms were described according to the Langmuir and Freundlich models [32,33]. The calculated constants of adsorption isotherm for both used equations are presented in Table 4.

Table 4. Adsorption equilibria description (initial adsorbate concentration 0.2 – 1.0 mmol L⁻¹, $m = 0.05$ g, $V = 50$ mL, electrolyte concentration = 0.05 mol L⁻¹)

Adsorbent	Adsorbate	Freundlich isotherm			Langmuir isotherm		
		K_F (mmol g ⁻¹)(L mmol ⁻¹) ^{1/n}	n	R^2	q_m (mmol g ⁻¹)	K_L (L mmol ⁻¹)	R^2
	PA	1.291	2.574	0.9767	1.098	10.434	0.9974
N-SX2	4-CPA	1.424	3.023	0.9722	1.135	18.242	0.9972
	2,4-D	1.518	4.019	0.9899	1.211	36.693	0.9960
F-400	PA	1.707	3.918	0.9971	1.349	32.256	0.9920
	4-CPA	2.116	3.640	0.9770	1.475	50.955	0.9927
	2,4-D	2.354	3.931	0.9909	1.596	74.607	0.9915
N-1800	PA	0.537	1.643	0.9838	0.711	2.032	0.9933
	4-CPA	0.719	1.870	0.9933	0.835	3.005	0.9956
	2,4-D	0.867	1.656	0.9936	1.057	2.355	0.9955

The Freundlich equation constants K_F ((mmol g⁻¹)(L mmol⁻¹)^{1/n}) and n (dimensionless) are indicative parameters of the adsorption strength and the intensity of the adsorption, respectively. The Langmuir equation constants q_m (mmol L⁻¹) is the maximum adsorption capacity, while K_L (L mmol⁻¹) is related to the free energy of the adsorption. One can observe that the linear regression correlation coefficient values show that equilibrium data obtained for all adsorbates were better described by the Langmuir model ($R^2 > 0.99$).

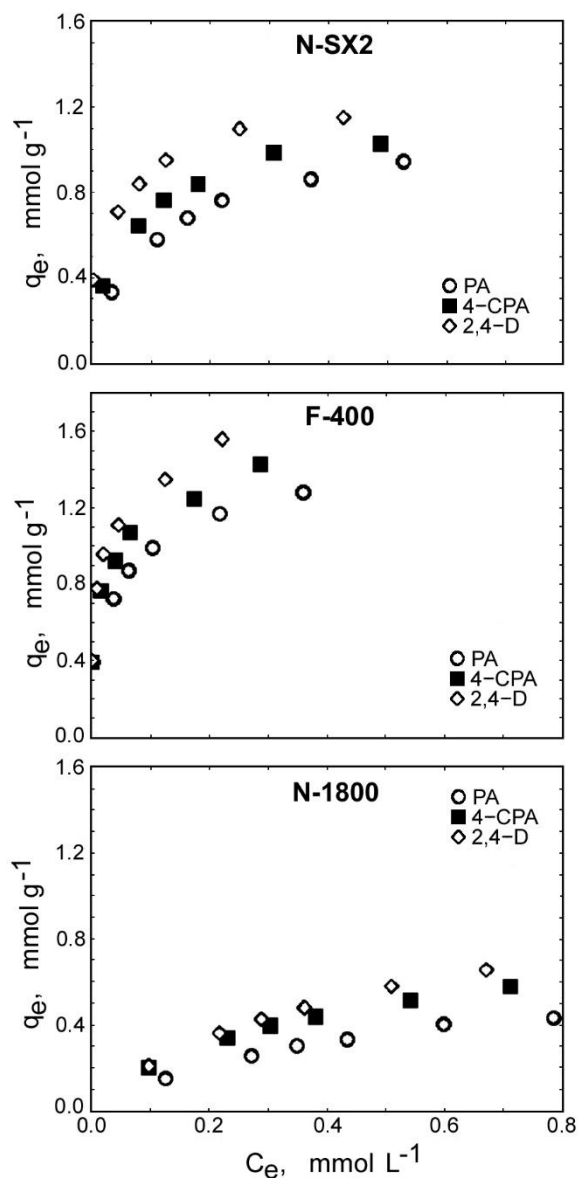


Figure 2. Effect of chlorine substitute on the PAs adsorption of the tested carbon material (adsorption from aqueous solution containing electrolyte - 0.05 mol L⁻¹, initial adsorbate concentration from 0.2 to 1.0 mmol L⁻¹, $m = 0.05$ g, $V = 50$ mL).

The above discussed adsorption results were obtained with the use of agitated suspension of powdered carbon in PAs solution containing electrolyte (0.05 mol L⁻¹ Na₂SO₄). Because the electrochemical measurement with the application of sediment powdered carbon electrodes makes agitations of the solution impossible, the relative decrease of PAs concentration with prolonged contact time between the solution and the carbon bed was determined (Fig. 3). The time of achieving the adsorption equilibrium depends on the kind of electrode material and, despite the different adsorption conditions, their behaviour (relative concentration drop) exhibit similarity (Fig. 3, Table 3).

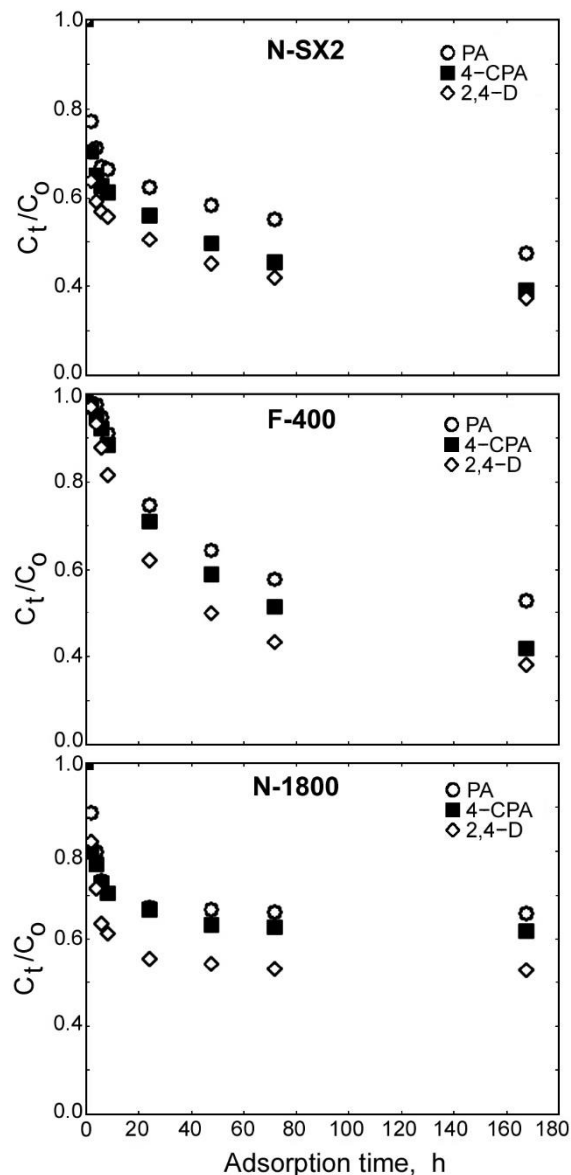


Figure 3. Relative concentration drop of PAs ($C_0 = 1 \text{ mmol L}^{-1}$) in a blank electrolyte solution during adsorption on sediment layer of electrode materials

For all electrochemical systems, the adsorption time preceding the potential cycling was established as 72 hrs, which was in agreement with the time of electrode stationary potential stabilisation. The electrochemical behaviour of all organics (as depolarisers) on carbon electrodes was studied in neutral electrolyte solutions for a sweep rate of 5 mV s^{-1} . In all cases potential cycling was started when the response potential had become stable (after adsorption equilibrium had been achieved). The cyclic voltammograms are shown in Fig. 4. One can only observe changes of the significant high capacitive currents which can mask possible smaller faradaic currents (from charge transfer reaction) [34]. Potential cycling is accompanied by a drop in the depolariser's concentration (Fig. 5). According to our [35] and other [19] former studies, the creation of electrochemically active surface layer of PAs electrooxidation products (in the form of a benzoquinone/hydroquinone system) during potential cycling was attained. It was confirmed by an observation of changes in the electric double layer capacity (C_{dl}) of

electrode after adsorption and long-term potential cycling (Table 5). Analyzing the decrease of PAs concentration during adsorption (Fig. 3) and potential cycling (Fig. 5) one can observe a lowering electrochemical removal for carbon samples with a larger adsorption ability.

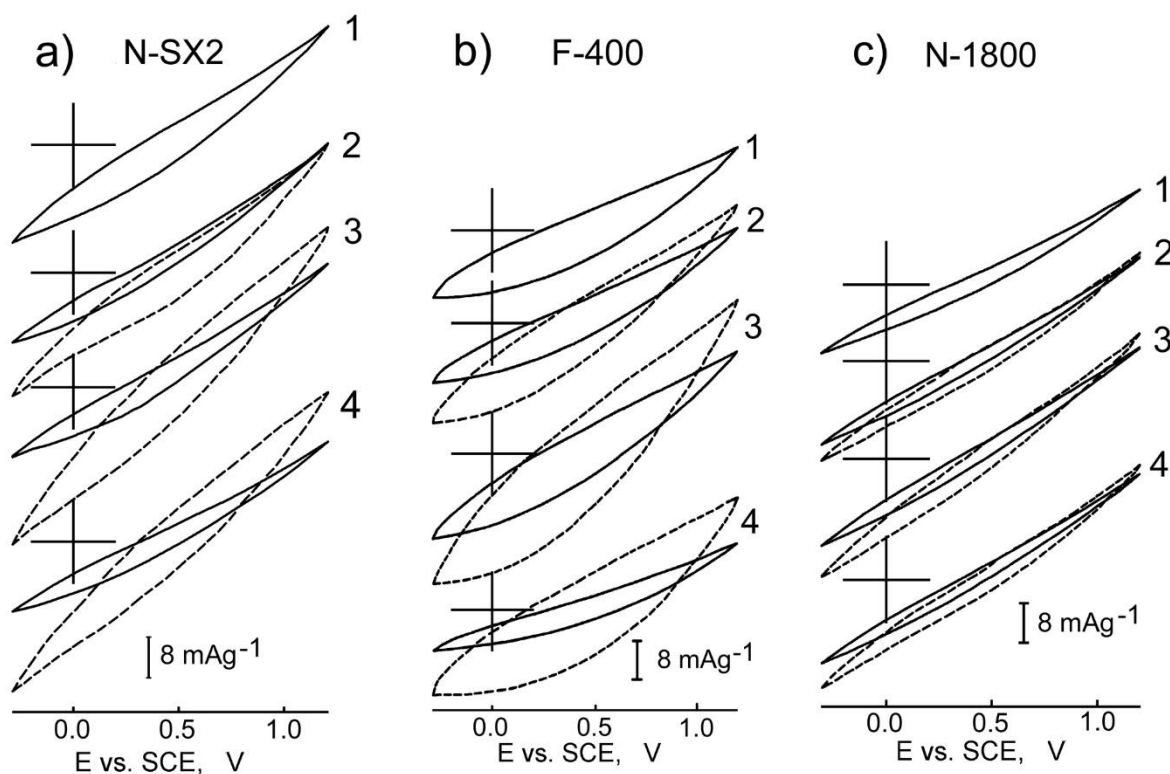


Figure 4. CV curves for carbon materials/(chloro)phenoxacetic acid systems in neutral electrolyte solution: 1- blank ($0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$); 2- PA; 3- 4-CPA; 4- 2,4-D; solid line – first cycle; dashed line – final shape of CV curves. Sweep rate - 5 mV s^{-1}

The relative concentration decrease after 12 days of potential cycling ($ED_{12\text{day}}$) is lower for samples with a higher adsorption capacity (Table 5). Adsorption, in all the tested systems, leads to an increase of stationary potential values (E_{st}) of the used carbon electrode materials (see Tables 1 and 5). In contrary, the electric double layer capacity drops after adsorption, but after potential cycling significantly increases (near two-fold). The behaviour of the tested organics depends on the presence and the number of chlorine atoms in the molecule. With an increase of the Cl number, an enhanced adsorption ability (e.g. q_m in Table 4) and stationary potential (E_{st}) can be observed. A similar regularity was observed for the ability of chlorophenols' adsorption on activated carbons [28-31]. Probably, the adsorbed molecules and the products of their electrodegradation (first stages) caused a decrease of the electrochemical activity in the chloroorganics removal by carbon electrode materials.

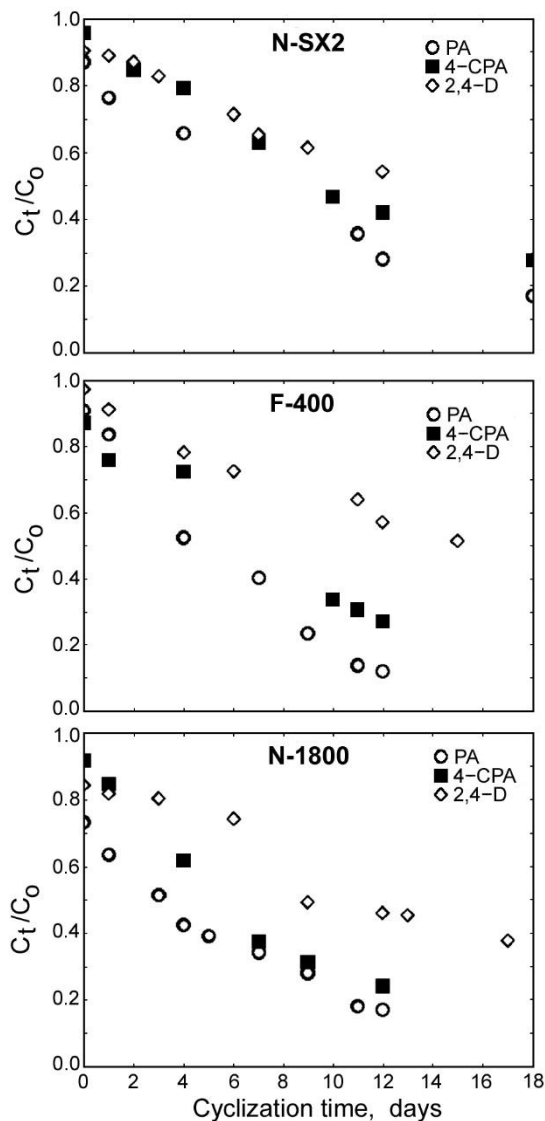


Figure 5. Relative concentration drop of PAs ($C_0 = 1 \text{ mmol L}^{-1}$) in blank electrolyte solution during potential cycling (after 72 h of adsorption)

Table 5 Results of cyclic voltammetry measurements

Sample	PAs	E_{st} V vs. SCE	C_{dl}^* $F \text{ g}^{-1}$	ED_{12day}^{**} %
N-SX2	PA	0.20	0.50/0.92	59.3
	4-CPA	0.28	0.52/1.30	53.8
	2,4-D	0.30	0.40/1.06	36.3
F-400	PA	0.34	0.32/0.48	78.8
	4-CPA	0.35	0.36/0.60	60.0
	2,4-D	0.37	0.32/0.52	40.0
N-1800	PA	0.09	0.84/1.38	68.3
	4-CPA	0.12	0.83/1.10	67.9
	2,4-D	0.30	0.50/1.78	36.4

*Electric double layer capacity (for $E = 0.4 \text{ V}$) from first/stabilised cycles;

**PAs relative concentration drop caused by potential cycling (after adsorption subtraction)

4. CONCLUSION

The enhancement of the chlorine atom number in aromatic ring of phenoxyacetic acid molecules gives an increase in the adsorption quantity of all the tested activated carbon samples. Adsorption amount exhibits proportionality towards the specific surface area of carbon adsorbent for all the used organic compounds. Description of the adsorption equilibrium in all the adsorbent/adsorbate systems seems to be better for the Langmuir equation than for the Freundlich equation. For adsorption kinetics, describing the model of pseudo-second order proved to be more useful for all the tested systems. Adsorption rise with increase of Cl number in adsorbate molecule. Electrodegradation ability of depolarizer falls with decrease Cl number in molecule. During potential cycling the first stages of electrooxidative degradation of the adsorbed molecules can occur with the formation of an electrochemically active benzoquinone/hydroquinone system what leads to observed enhance edl capacity.

ACKNOWLEDGEMENT

The project was funded by a program of the Minister of Science and Higher Education entitled "Regional Initiative of Excellence" from 2019 to 2022 project number 025 / RID / 2018/19, with a financing amount of PLN 12,000,000.

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