Chapter

Influence of Pesticide Properties on Adsorption Capacity and Rate on Activated Carbon from Aqueous Solution

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Abstract

The adsorbate structural properties such as the type, number, and position of substituents on benzene ring of organic compound, as well as a length and arrangement of hydrocarbon chain in a space, exert a significant influence on the adsorption process. The measurements of adsorption equilibria and kinetics of several pesticides belonging to the group of halogenated phenoxyacids differentiated in terms of structural and physicochemical properties were studied in order to characterize the adsorption mechanism and correlate it with the pollutant properties. Regarding a complexity of investigations (capacity and rate) comprising 21 structurally closely related active substances showing the carcinogenic activity on living organisms and relatively long half-life time in the environment, the proposed intensive studies on the removal of pollutants by adsorption process are very important in cognitive and practical terms.

Keywords: pesticide adsorption, activated carbon, adsorption equilibrium, adsorption kinetics

1. Introduction

The improvement of effectiveness of pollutant removal from water and sewage using activated carbons has been a subject of numerous studies. The influence of adsorbate, adsorbent, solution properties, and experiment conditions on adsorption process has been analyzed.

Noteworthy is the impact of adsorbate properties on adsorption process such as solubility, molecule dimension, ability to dissociation, and physicochemical properties. Hydrophobicity which can be expressed by solubility is the main driving force of adsorption process of organics from aqueous solutions on activated carbons. The lower solubility of a pollutant is the highest adsorption on hydrophobic carbon is observed. Additionally, analyzing adsorption of pollutants from aqueous solutions on microporous materials, it is necessary to take into account molecule dimension due to a possible sieve effect. Moreover, the influence of functional groups on adsorbate aromatic ring on the differentiation of adsorptive affinity of organic compounds to activated carbon should be also regarded.

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The influence of adsorbate substituents on adsorption mechanism is similar to that of surface groups of adsorbent. Depending on their nature, they can attract or repel electrons and affect the dispersive interactions between adsorbate aromatic ring and graphene layers of activated carbon. The adsorbate functional groups that are electron donors activate the aromatic ring by moving electrons toward it, and thereby they enhance the interactions between adsorbate molecule and π electrons of adsorbent graphene planes. On the other hand, the deactivating groups as electron acceptors reduce the electron density of aromatic ring; thus, interactions of adsorbate-adsorbent surface are weakened [1–7].

The research on effect of adsorbate properties on adsorption process is an extension of the studies already published in the paper [8]. The pesticides belonging to a group of chloride phenoxyacid derivatives were used as adsorbates in view of their common usage in agriculture and hence a high probability of infiltration to surface and underground waters. Their presence in water affects its quality, worsens its properties, and in some cases makes it unsuitable to consume. These pesticides show a carcinogenic activity on living organisms and a relatively long half-life time in the environment; therefore, the intensive study on their removal by adsorption process is very important for practical applications. The experimental studies include measurements of the adsorption isotherms and concentration rate profiles as well as their interpretation on the basis of the generalized Langmuir (GL) equation for equilibrium data and diffusion models (intraparticle diffusion model (IDM) and pore diffusion model (PDM)) and multi-exponential (m-exp) equation for kinetic data. Based on the obtained results, the correlations between adsorbate structure, its properties, and adsorption uptake and rate were analyzed. The evaluation of the theoretical equilibrium and kinetic equations and models based on a fitting quality and consistency with adsorption mechanism was also made.

2. Experimental

2.1 Materials and methods

The selected adsorbates comprise 21 compounds which are structurally differentiated with regard to the number, position, and type of the functional groups and length and spatial arrangement of the hydrocarbon part in a molecule. Not all of these substances are used as pesticides because of their low biological activity. However, due to complexity of the research issues, it seems to be reasonable to include them as a subject of the investigation.

Table 1 presents the physicochemical properties of the adsorbates collected on the basis of literature data or calculations using computer programs generally available. All the substances are analytical reagent grade purity. The chemical names and abbreviations of them are as follows: 4-chlorophenoxyacetic acid (4-CPA); 2,4-dichlorophenoxyacetic acid (2,4-D); 2,4,5-trichlorophenoxyacetic acid (2,4,5-CPA); 2,4,6-trichlorophenoxyacetic acid (2,4,6-CPA); 4-chloro-3-methylphenoxyacetic acid (4-CMPA); 4-chloro-2-methylphenoxyacetic acid (MCPA); 2,4-dibromophenoxypropionic acid (2,4-BrPA); 2,4,6-tribromophenoxypropionic acid (2,4,6-BrPA); 2-(3-chlorophenoxy)propionic acid (3-CPP); 3-(4-chlorophenoxy)propionic acid (4-CP); 2-(4-chlorophenoxy)propionic acid (4-CPP); 2-(2,4-dichlorophenoxy)propionic acid (2,4-CPP); 2-(2,5-dichlorophenoxy)propionic acid (2,5-CPP); 2-(3,4-dichlorophenoxy)propionic acid (3,4-CPP); 2-(2,4,5-trichlorophenoxy)propionic acid (2,4,5-CPP); 2-(4-chloro-2-methylphenoxy)propionic

Common name	pK$_a$ [9]	Solubility g/dm^3 20–25°C	K$_{ow}$/log D [9]		K$_{ow}$/log P	D$_{min}$ /Å [9]	D$_{max}$ /Å [9]
			pH = 1.81	pH = 10.38			
4-CPA	3.14	0.848 [10]	1.88	−1.63	1.85 [11]	4.33	9.38
2,4-D	2.80	0.682 [10]	2.46	−1.03	2.37 [11]	4.88	9.49
2,4,5-CPA	2.56	0.268 [10]	3.04	−0.42	2.89 [11]	6.22	8.88
2,4,6-CPA	2.57	0.247 [10]	3.04	−0.42	2.89 [11]	5.42	8.84
4-CMPA	3.36	0.650 [12]	2.40	−1.12		5.42	8.96
MCPA	3.36	0.825 [10]	2.40	−1.12	3.25 [13]	5.47	9.52
2,4-BrPA	1.96	0.059 [14]	2.60	−0.70		5.03	9
2,4,6-BrPA	1.50	0.015 [15]	3.12	0.07		5.71	9
3-CPP	3.27	1.200 [16]	2.45	−1.06		5	7.79
4-CP	3.70	0.770 [12]	2.13	−1.39		4.33	9.87
4-CPP	3.27	1.475 [10]	2.45	−1.06		5.22	8.65
2,4-CPP	2.95	0.829 [10]	3.04	−0.46		5.59	9.03
2,5-CPP	2.95	0.181 [14]	3.04	−0.46		5.62	8.63
3,4-CPP	2.94	0.130 [12]	3.04	−0.46		5.5	8.76
2,4,5-CPP	2.70	0.140 [10]	3.62	0.15	3.80 [13]	5.62	9
MCPP	3.47	0.895 [10]	2.97	−0.55	3.13 [13]	5.86	8.64
4-CMPP	3.46	0.690 [15]	2.97	−0.55		5.86	7
CFA	3.37	0.582 [17]	2.89	−0.63	2.84 [13]	4.42	9.14
4-CPB	3.42	0.315 [14]	2.98	−0.54		5.22	9.7
MCPB	3.59	0.048 [10]	3.50	−0.03	3.28 [18]	6.36	9.65
4-CMPB	3.59	0.17 [12]	3.50	−0.03		5.86	9.28

Table 1.
Physicochemical properties of the studied pesticides, where pK$_a$ is the value based on partial charge distribution in a molecule, log D is the octanol-water coefficient at a given pH, log P is the partition coefficient of a compound between octanol and water, and D$_{min}$ and D$_{max}$ are measures between the most distant molecule atoms.

acid (MCPP); 2-(4-chloro-3-methylphenoxy)propionic acid (4-CMPP); 2-(4-chlorophenoxy)-2-methylpropionic acid (CFA); 2-(4-chlorophenoxy)butanoic acid (4-CPB); 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB); and 2-(4-chloro-2-methylphenoxy)butanoic acid (4-CMPB).

The microporous activated carbon F300 was used as adsorbent (S_{BET} = 762 m^2/g, V_t = 0.46 cm^3/g, V_{mic} = 0.28 cm^3/g; pH_{pzc} ∼ 9.8). The characteristics of adsorbent are given in the paper [8]. The methodology of equilibrium and kinetic measurements is also described in the paper [8].

3. Results and discussion

3.1 Adsorption equilibria

3.1.1 Effect of type and number of adsorbate substituents

Substituents on benzene ring of aromatics have a great influence on adsorption process on activated carbon. It is not directly related to their interaction with an adsorbent but mainly with changes in molecular properties of adsorbed compound [19–23]. The crucial factors are the nature of the substituents, number, and their mutual position on benzene ring. In the study the adsorption process of compounds with substituents with electron-acceptor (—Cl, —Br) and electron-donor properties (—CH$_3$) was analyzed. It is well known that substituents affect acid-base properties (pKa), water solubility, hydrophobicity (K$_{ow}$), dipole moment, molecular weight, and spatial dimension in space of an organic compound. In turn, these properties affect a mechanism and a range of adsorption process. Nevertheless, solubility in water and hydrophobicity of substance most often play a superior role in adsorption process.

As pKa values of the studied pesticides are within the range of 1.50–3.70, thus, the buffers of pH = 1.81 or 10.38 were used to prepare the experimental solutions. Thus, the compounds in solutions were nearly undissociated and completely dissociated, respectively. In the case of the compounds of very low solubility, the studies at alkaline pH conditions were carried out. For the systems for which the adsorption process was carried out in acidic solutions, the isotherms both in the standard linear $a = f(c_{eq})$ and reduced coordinates $a = f(c_{eq}/c_s)$ are presented. The second form of presentation allows to study the affinity of a given type of compound to the activated carbon surface without the effect of solubility. In all the pictures, the experimental points and the theoretical isotherms using the generalized Langmuir equation are presented.

In **Figures 1** and **2** the comparison of the adsorption isotherms of chlorophenoxyacetic and chlorophenoxypropionic acid derivatives with a different type and number of substituents on aromatic ring on activated carbon F300 at pH = 1.81 is shown. In the case of phenoxyacetic pesticides, relatively small changes in capacities are observed which can be arranged as follows: 2,4-D ~ 4-CPA > MCPA. The
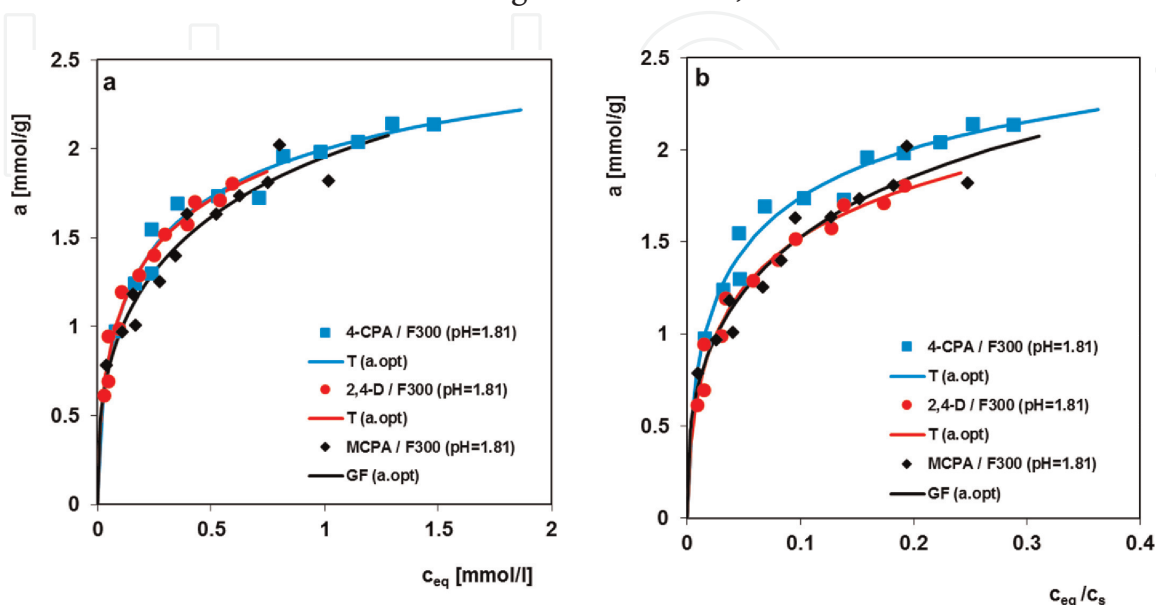

Figure 1.
The 2,4-D; MCPA; and 4-CPA adsorption isotherms on F300, pH = 1.81 in linear (a) and reduced coordinate system (b).
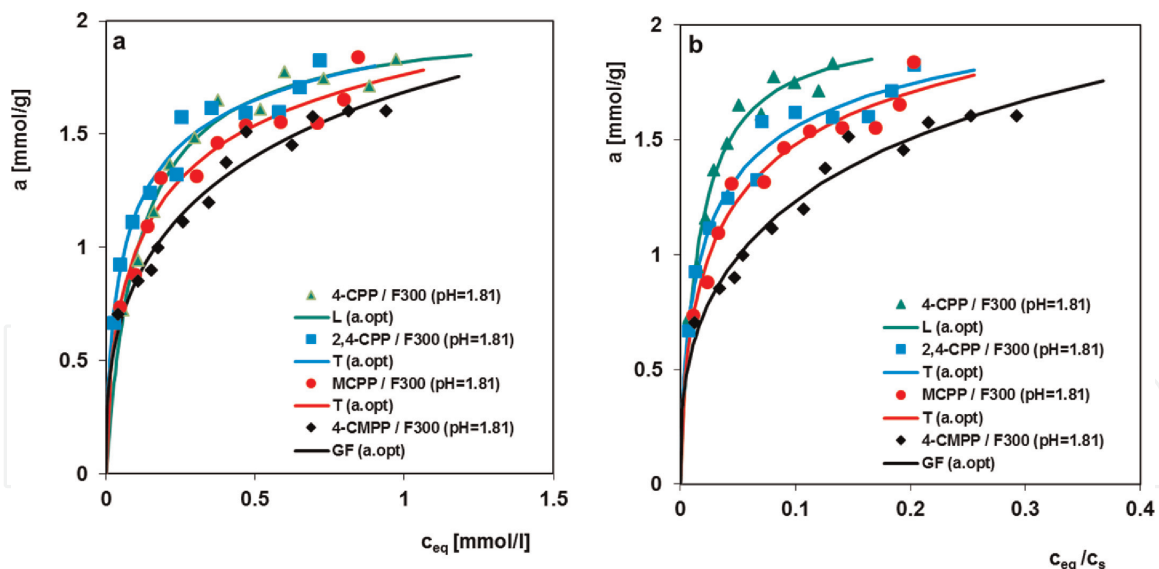
Figure 2.
The 4-CPP; 2,4-CPP; MCPP; and 4-CMPP adsorption isotherms on F300, pH = 1.81 in linear (a) and reduced coordinate system (b).

differences in the course of adsorption isotherms for the phenoxypropionic pesticides are greater. Taking into account their affinity to the carbon F300, it looks as follows: 2,4-CPP ∼ 4-CPP > MCPP > 4-CMPP.

The solubility values were collected from literature, and partition coefficients between octane and water (K_{ow}) were calculated using the Marvin 5.6.0.3 computer program taking into account conditions of adsorption process. For 2,4-D, 4-CPA, and MCPA, the solubilities are equal to 0.682, 0.957, and 0.825 g/dm^3 while log D 2.46, 1.88, and 2.40, respectively. For the phenoxypropionic derivatives, 2,4-CPP, 4-CPP, MCPP, and 4-CMPP, the solubilities are 0.829, 1.475, 0.895, and 0.69 g/dm^3, while the values characterizing hydrophobicity are 3.04, 2.45, 2.97, and 2.97, respectively. As one can see, there is no correlation between solubility/hydrophobicity and the adsorption affinity for the most systems. Analyzing the adsorption isotherms reduced by the solubility parameter, it can be concluded that only in the case of 2,4-D and MCPA, the differences in adsorption result from solubility/hydrophobicity. For other systems, solubility/hydrophobicity is not the only factor determining the effectiveness of adsorption process, and other factors should be considered.

The mechanism of adsorption process is mainly based on the dispersion or donor-acceptor interactions (pH = 1.81, thus both adsorbates and functional groups on active carbon surface are undissociated) and the local repelling electrostatic interactions between positively charged sites on adsorbent surface (as a result of attraction and localization of graphene plane electrons by oxygen functional groups) and a local positive charge in adsorbate molecule (as a result of electron-acceptor properties of chlorine on benzene ring). Generally, the more substituents in a molecule, the greater the local charge and stronger the local electrostatic interactions.

Another aspect concerns a spatial structure of compounds, as the ones with substituents in a para-position have better access to adsorbent micropores. In particular, this applies for halogenophenoxyacetic acids, where the hydrocarbon part is not branched, like in β-halogenophenoxypropionic acids. Therefore, the capacities for 4-CPA and 2,4-D, as well as for 4-CPP and 2,4-CPP, are similar, although comparing the solubility and log D values, one could assume a different situation. A simple explanation is a symmetrical structure of 4-CPA, which means that its molecular volume is smaller than for 2,4-D which enables a better access and

greater packing density in the adsorptive space. In a group of phenoxypropionic acid derivatives, the 4-CPP and 2,4-CPP adsorptions are higher than for MCPP and 4-CMPP. The molecules of all these compounds have at least one ▬Cl group causing a weak deactivation of aromatic ring in the ortho- and para-position and strong deactivation in the meta-position. Consequently, the electron density of benzene ring is decreased, and the interactions of adsorbate-carbon surface are weakened. Moreover, MCPP and 4-CMPP molecules have additional ▬CH_3 group that activates weakly aromatic ring in the ortho- and para-position, resulting in the electrons shift toward the ring. Thus, the interactions of adsorbate ring electrons with π electrons of adsorbent graphene planes are increased. The total effect is a result of at least partial compensation of two types of the functional groups. Therefore, the structural properties of these compounds do not explain clearly the differentiation of their adsorption affinities to activated carbon. An essential factor may be the influence of a position of the electron-acceptor group relative to the electron-donor group on the interactions of adsorbate-adsorbent as well as the steric effect.

In **Figure 3**, the comparison of the adsorption isotherms of chloro- and bromophenoxyacetic derivatives from solutions at pH = 10.38 is presented. The adsorption decreases in the series: 2,4,6-BrPA > 2,4-BrPA > 2,4,6-CPA ∼ 2,4-D > 4-CPA > MCPA. At alkaline conditions the electrostatic interactions are predominant in adsorption mechanism due to dissociated forms of both the adsorbate and the adsorbent functional groups. The repulsive forces between the pesticide anions and negatively charged adsorbent groups appear. However, a halogen with the electron-withdrawing properties on benzene ring decreases the total electron charge of the aromatic ring and shows a local positive charge. The obtained effect results in the creation of local attractive interactions which decrease the electrostatic repulsion between adsorbate and adsorbent. If a degree of halogen substitution increases, the strength of interactions increases, and it leads to stronger adsorption on active carbon. This explanation is true if substituents in a molecule are of the same type, e.g., bromine or chlorine. Comparing the adsorption affinities in the systems with different substituents, it can be observed that the compounds containing bromine show a stronger affinity for the adsorbent surface compared to compounds with chlorine, regardless of a number of substituents in molecule. In the case of MCPA containing a methyl group with electron-donor properties, the weakest adsorption is observed. Increase of the electron density within aromatic ring raises the
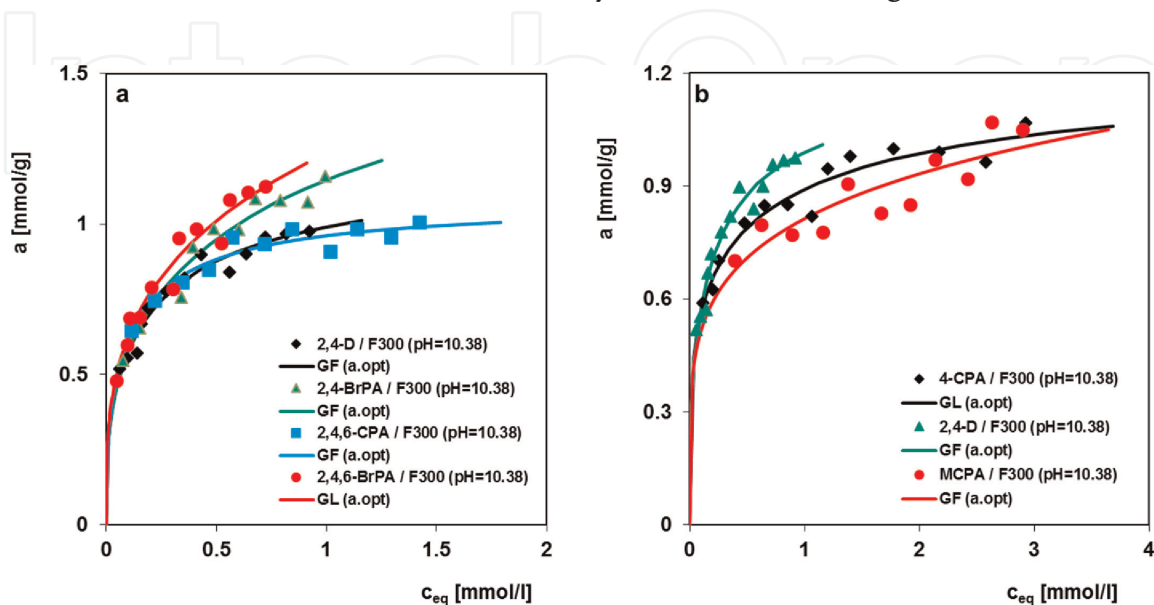

Figure 3.
The 2,4-D; 2,4-BrPA; 2,4,6-CPA; and 2,4,6-BrPA adsorption isotherms on F300, pH = 10.38 (a). The 4-CPA; 2,4-D; and MCPA adsorption isotherms on F300, pH = 10.38 (b).

electrostatic repulsion with the negatively charged surface of the activated carbon. A similar effect is observed in the case of phenoxypropionic acid derivatives with a different halogen substituent in the para-position at acidic pH.

In **Figure 4a** a comparison of the adsorption isotherms for 2,4-D, 2,4,5-CPA, and 2,4,6-CPA, i.e., the compounds with a differentiated number and position of chlorine atoms on benzene ring, is presented. Similar adsorption is observed for 2,4-D and 2,4,6-CPA, whereas for 2,4,5-CPA the process is significantly greater. 2,4-D shows the weakest hydrophobic properties; its molecule contains two chlorine atoms. The other two compounds 2,4,5-CPA and 2,4,6-CPA are characterized by the similar log D values, but they contain three chlorine atoms. Therefore, the differences in adsorption affinity to adsorbent should be attributed to the steric effect. In the group of chlorophenoxypropionic acids differentiated in terms of a number of substituents in a molecule, the adsorbate affinity to the adsorbent active sites increases in the order 2,4,5-CPP > 2,4-CPP > 2,5-CPP > 4-CPP (**Figure 4b**). The octanol/water partition coefficient values (log D) for these compounds at pH = 10.38 are 0.15, −0.46, −0.46, and −1.06, respectively. 2,5-CPP is weakly removed at a given pH than its isomeric form 2,4-CPP although its hydrophobicity should promote the adsorption process. Probably an arrangement of the substituents in 2,5-CPP leads to difficulties in diffusion of the adsorbate molecules into small pores of adsorbent that consequently decreases adsorption.

The comparison of the 4-CMPA and 4-CPA (pH = 10.38) adsorption isotherms (**Figure 5**) shows that removal of the methyl group weakens the adsorption affinity. Similar behavior occurs for their phenoxypropionic and phenoxybutanoic homologs, for which the adsorption of 4-CMPP > 4-CPP and 4-CMPB > 4-CPB (**Figures 6** and **7**). The observed trend fully coincides with the hydrophobicity of pesticides. For the series of 4-CMPA and 4-CPA, log D is −1.12 and −1.63, respectively; for 4-CMPP and 4-CPP, log D is equal to −0.55 and −1.06, respectively, while for 4-CMPB and 4-CPB, this parameter is −0.03 and −0.54, respectively.

3.1.2 Effect of substituent position on aromatic ring

The adsorption affinity of organics depends on a number and type of substituents, as well as on their position on the benzene ring. This is related to the occurrence of the steric and inductive effects of adsorbate. The courses of adsorption
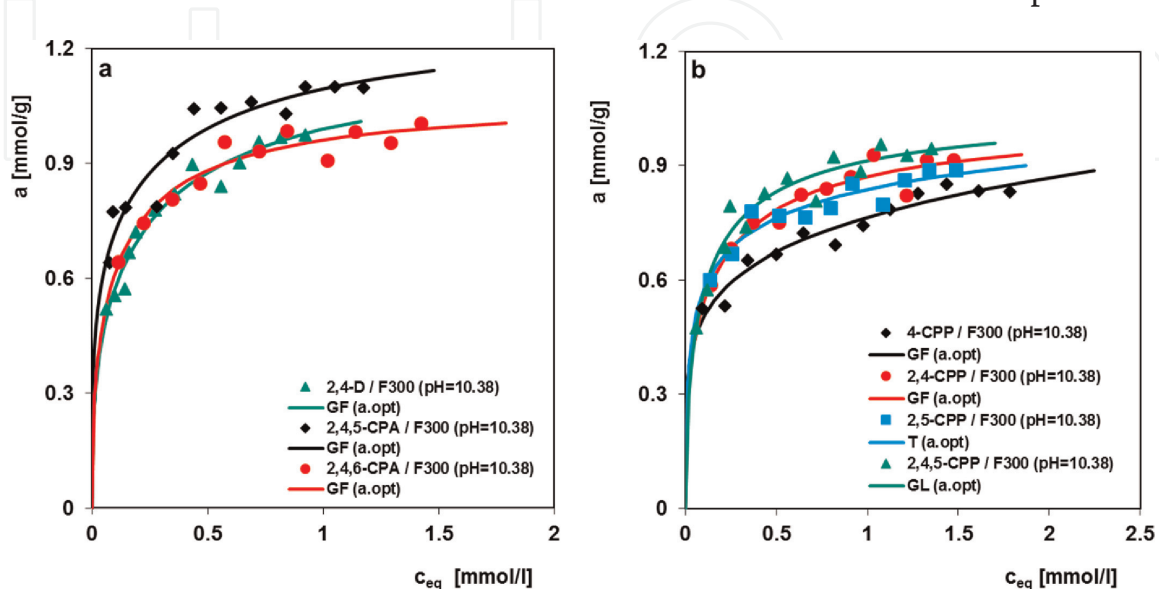

Figure 4.
The 2,4-D; 2,4,5-CPA; and 2,4,6-CPA adsorption isotherms on F300, pH = 10.38 (a). The 4-CPP; 2,4-CPP; 2,5-CPP; and 2,4,5-CPP adsorption isotherms on F300, pH = 10.38 (b).
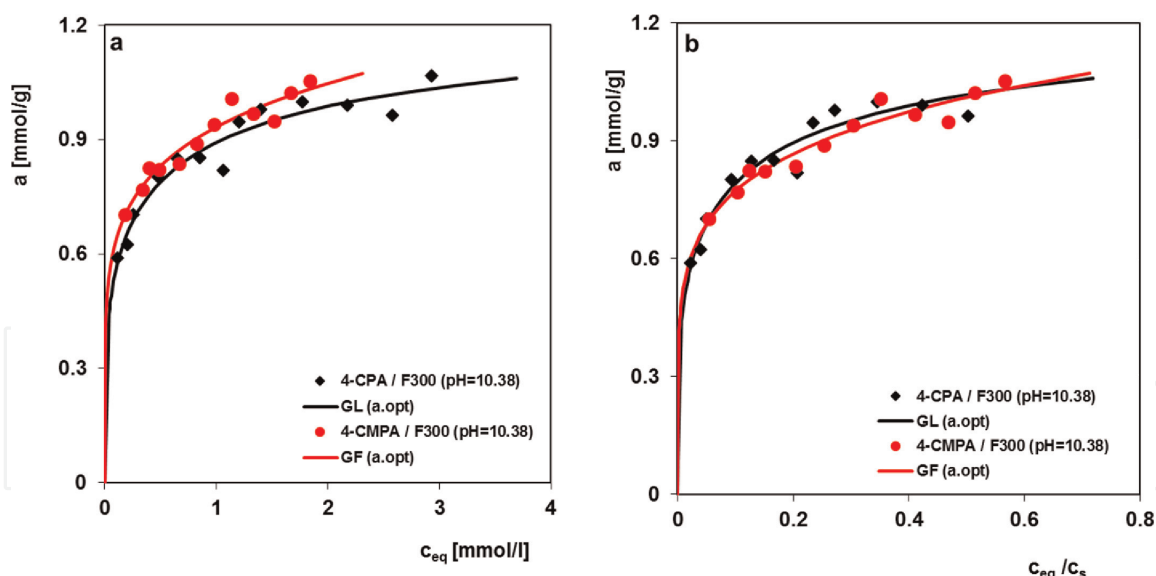
Figure 5.
The 4-CPA and 4-CMPA adsorption isotherms on F300, pH = 10.38 in linear (a) and reduced coordinate system (b).
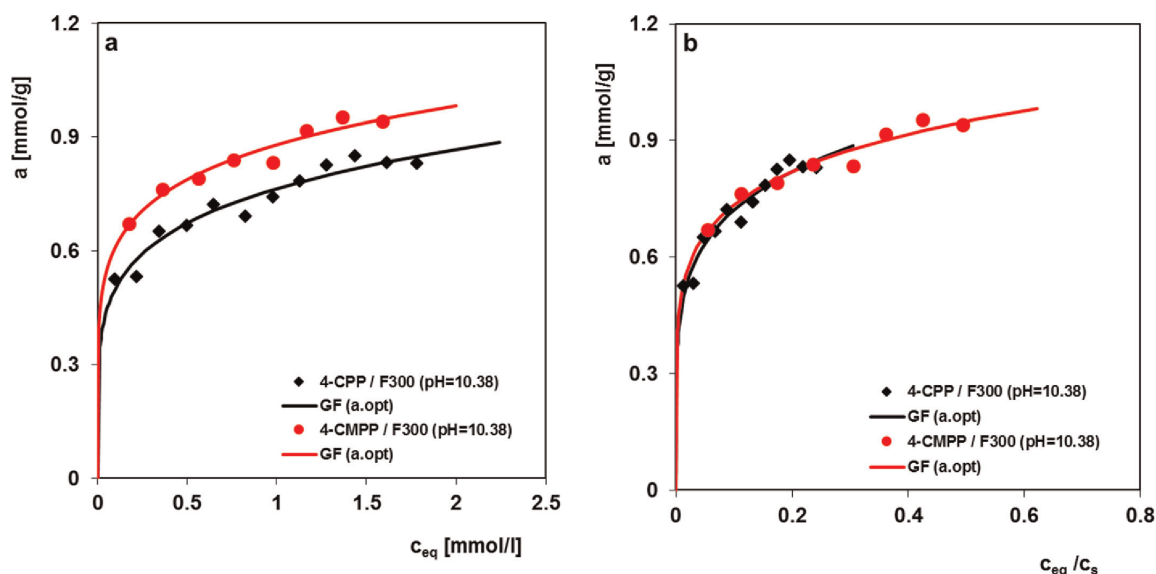

Figure 6.
The 4-CPP and 4-CMPP adsorption isotherms on F300, pH = 10.38 in linear (a) and reduced coordinate system (b).

isotherms measured at alkaline pH for 2,4,5-CPA and 2,4,6-CPA (**Figure 8**) and 2,4-CPP and 2,5-CPP (**Figure 9a**) indicate that the less symmetric distribution of electron charge density in benzene ring is, the stronger adsorption affinity is observed. Therefore, higher affinities for 2,4,5-CPA and 2,4-CPP than for 2,4,6-CPA and 2,5-CPP are found. Analyzing the solubility of these substances, one can say that this parameter is not a main factor controlling the adsorption process.

As results from **Figure 9b** at basic conditions for the isomers of dichlorophenoxypropionic acid, their affinity to the activated carbon increases as follows: 3,4-CPP > 2,4-CPP > 2,5-CPP. The strongly adsorbed compound is characterized by two adjacent chlorine atoms with electron-acceptor properties, causing the overlap of local positive charges in the benzene ring. The negatively charged oxygen groups on the carbon surface interact electrostatically with the positive local charge of the pesticide rings, intensifying the adsorption process. The interactions of other compounds with F300 are disturbed by the steric effect due to the position of
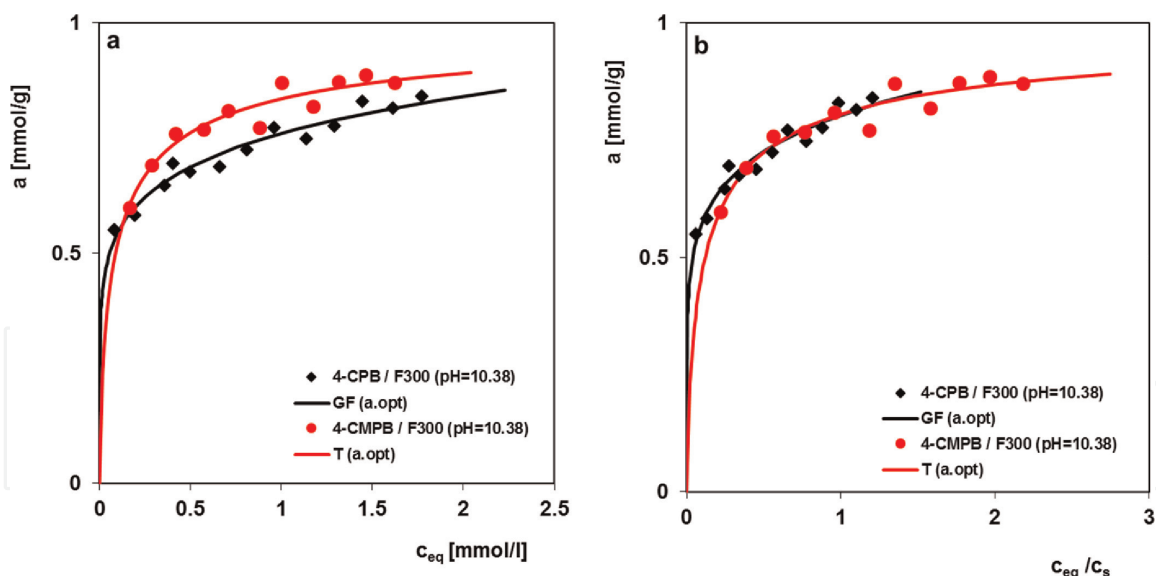
Figure 7.
The 4-CPB and 4-CMPB adsorption isotherms on F300, pH = 10.38 in linear (a) and reduced coordinate system (b).
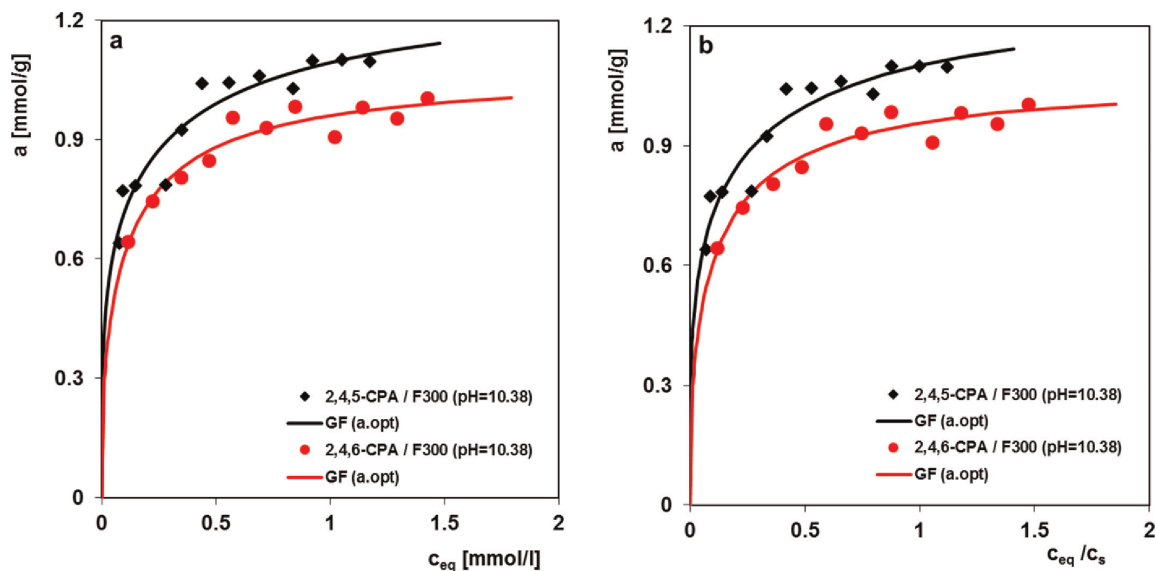

Figure 8.
The 2,4,5-CPA and 2,4,6-CPA adsorption isotherms on F300, pH = 10.38 in linear (a) and reduced coordinate system (b).

substituent at the second carbon in the ring and in the case of 2.5-CPP additionally due to a symmetrical distribution of the σ^+ charge. This explains the differentiation in adsorption of these compounds.

The comparison of the isotherms for 4-CMPP and MCPP at alkaline pH (**Figure 10a**) gives information that a shift of methyl group position on aromatic ring from ortho- to meta-position does not affect adsorption process. The same situation is observed for their homologs from the phenoxybutanoic group; the adsorption affinity of both compounds to activated carbon is similar (**Figure 10b**).

3.1.3 Effect of structure of hydrocarbon chain in adsorbate molecule

To analyze the impact of hydrocarbon chain structure on the adsorption process, the systems with chlorogenic phenoxyacetic derivatives and their homologs—phenoxypropionic and phenoxybutanoic derivatives—were studied. The graphs are grouped with regard to hydrocarbon chain structure, while the aromatic part of
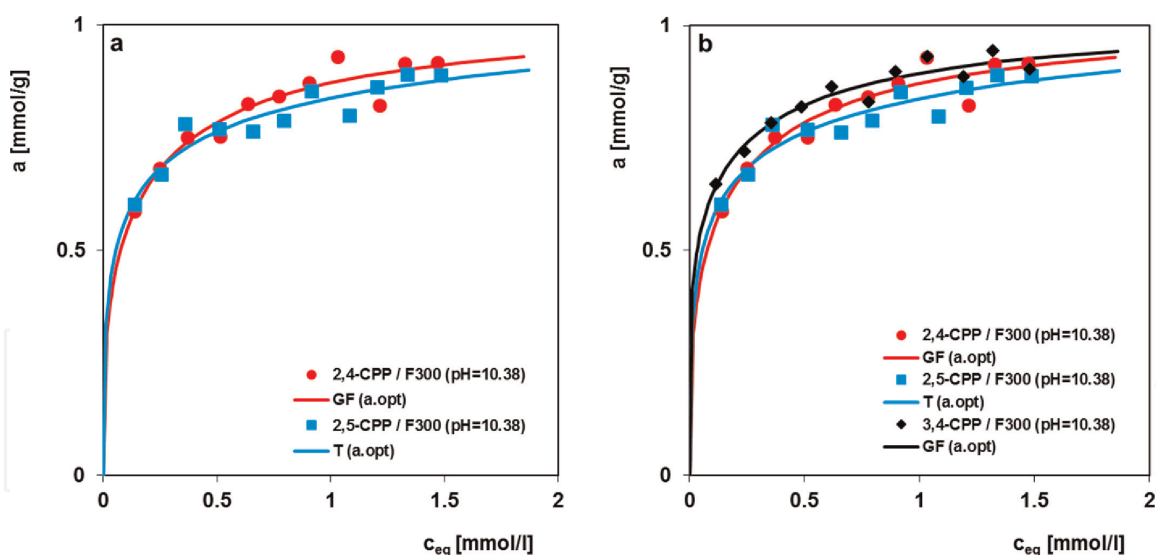
Figure 9.
The 2,4-CPP and 2,5-CPP adsorption isotherms on F300, pH = 10.38 (a). The 2,4-CPP; 2,5-CPP; and 3,4-CPP adsorption isotherms on F300, pH = 10.38 (b).
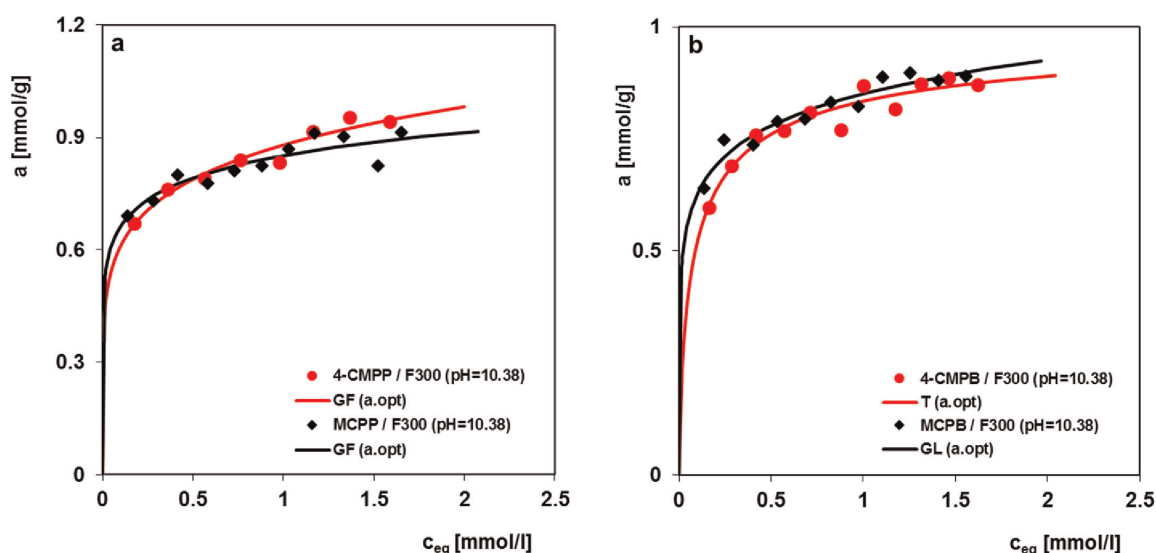

Figure 10.
The 4-CMPP and MCPP adsorption isotherms on F300, pH = 10.38 (a). The 4-CMPB and MCPB adsorption isotherms on F300, pH = 10.38 (b).

molecules is the same. In the case of adsorption processes carried out at pH = 10.38, the adsorption affinities of the studied compounds are as follows: 2,4,5-CPA > 2,4,5-CPP (**Figure 11a**), 2,4-D > 2,4-CPP (**Figure 11b**), MCPP ∼ MCPB (**Figure 12a**), 4-CMPA > 4-CMPP > 4-CMPB (**Figure 12b**), and 4-CPA ∼ 4-CP > 4-CPP ∼ 4-CPB > CFA (**Figure 13**). For the systems for which it was possible to measure the adsorption process at pH = 1.81, the adsorption affinities of pesticides are 2,4-D ∼ 2,4-CPP (**Figure 14**), MCPA > MCPP (**Figure 15**), and 4-CPA > 4-CPP > CFA (**Figure 16**).

Analyzing the coefficient $K_{o/w}$ values, one can say that the adsorption mechanism is more dependent on physicochemical properties of the adsorbates related with their spatial structure of hydrocarbon part rather than on the total hydrophobicity. For example, in the case of pesticides with decreasing adsorptive affinity to activated carbon, 4-CPA, 4-CPP, and CFA at pH = 1.81, $\log D$ is $-1.12 < -0.55 < -0.03$. Relatively smaller influence of the hydrophobicity of these compounds on their adsorption process is confirmed in most cases by the adsorption isotherm course in the reduced coordinates. The above hypothesis is focused on two factors
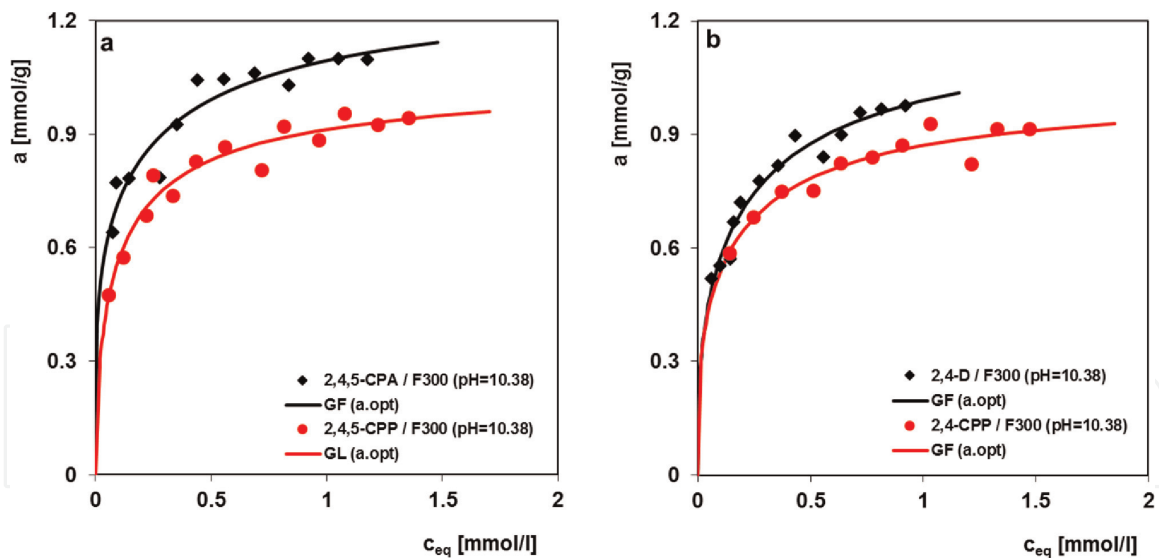
Figure 11.
The 2,4,5 CPA and 2,4,5-CPP adsorption isotherms on F300, pH = 10.38 (a). The 2,4-D and 2,4-CPP adsorption isotherms on F300, pH = 10.38 (b).
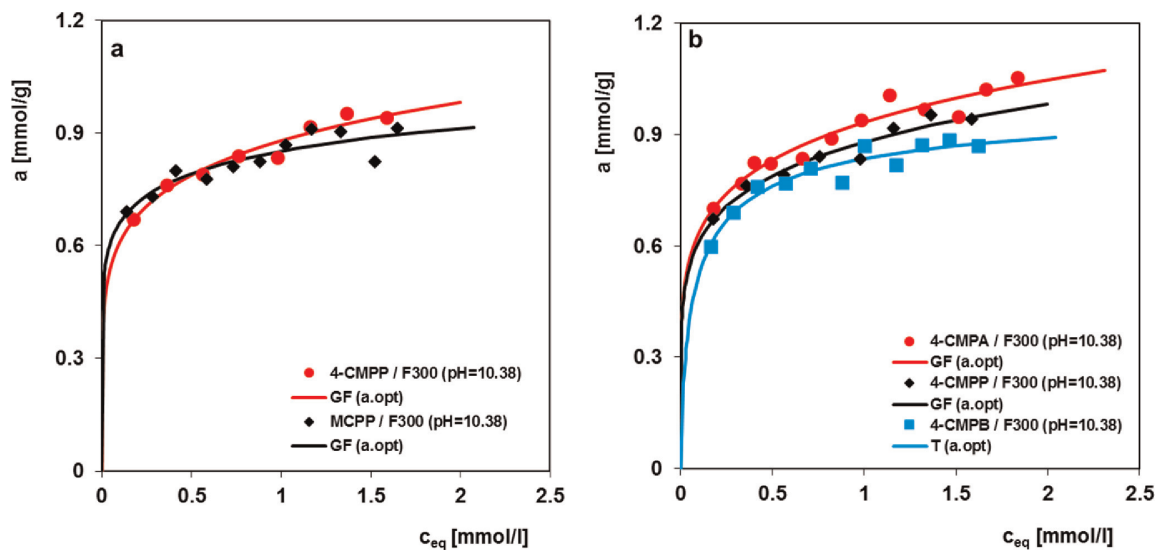

Figure 12.
The MCPP and MCPB adsorption isotherms on F300, pH = 10.38 (a). The 4-CMPA; 4-CMPP; and 4-CMPB adsorption isotherms on F300, pH = 10.38 (b).

related with a hydrocarbon chain structure of halogen phenoxycarboxylic derivatives: a number of carbons forming a hydrocarbon chain and arrangement of carbons in a chain. Considerations on adsorption of the pesticides with different number of aliphatic carbon atoms are concerned on phenoxyacetic, phenoxypropionic, and phenoxybutanoic derivatives. In the case of phenoxypropionic and phenoxybutanoic derivatives, the hydrocarbon parts form branched chains. Merely 4-CP has an unbranched chain. 4-CP and its phenoxyacetic homolog 4-CPA were used to compare the adsorption affinity of adsorbates with unbranched hydrocarbon chain (**Figure 13a**). The other compounds which form the homologous series were used to analyze the adsorption of molecules with different number of carbons in a branched aliphatic chain. On the basis of adsorption isotherms of the abovementioned pesticides, one can conclude that a number of carbon atoms in unbranched hydrocarbon chain do not affect the adsorbate affinity to the activated carbon surface. The increase of a number of carbon atoms in branched hydrocarbon chain for the most homologous series results in a decrease in adsorption or occasionally does not affect it at all. These
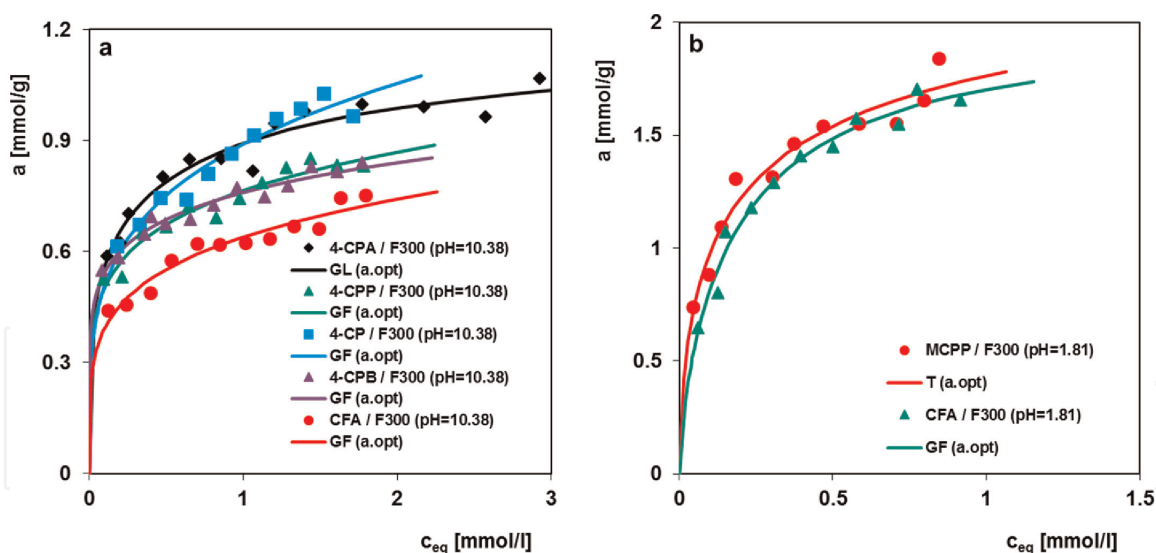
Figure 13.
The 4-CPA; 4-CPP; 4-CP; 4-CPB; and CFA adsorption isotherms on F300, pH = 10.38 (a). The MCPP and CFA adsorption isotherms on F300, pH = 1.81 (b).
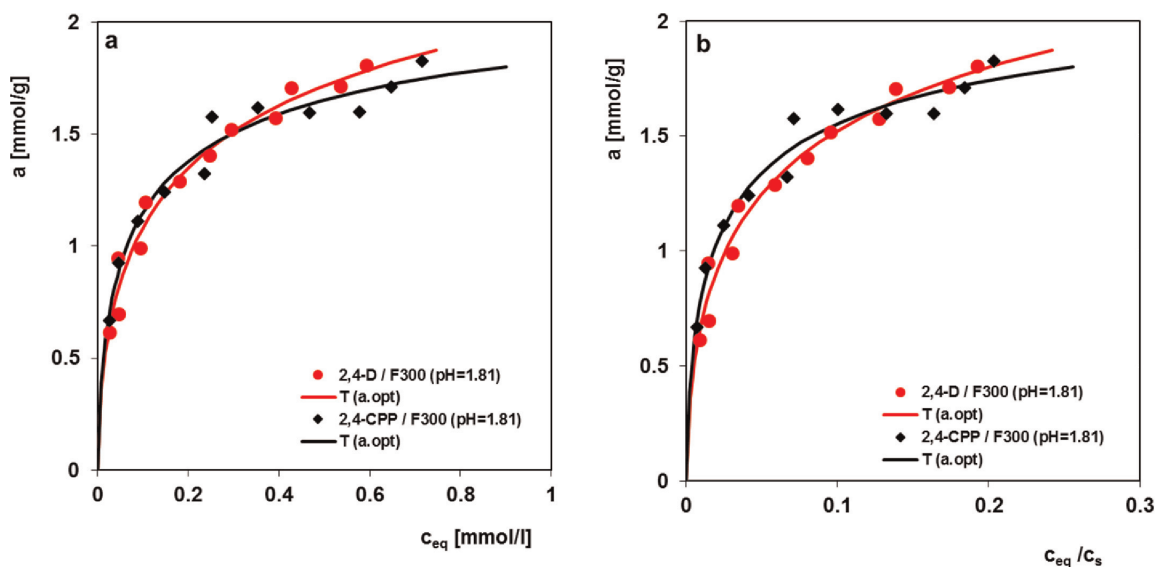

Figure 14.
The 2,4-D and 2,4-CPP adsorption isotherms on F300, pH = 1.81 in linear (a) and reduced coordinate system (b).

observations apply to the adsorption systems studied at acidic and basic conditions. According to the Lundelius principle, the more developed structure of compounds from the same homologous series, the greater adsorption should occur [16]. The lack of compliance of the obtained results with the Lundelius principle indicates that there are also other factors. The adsorbent is characterized by a microporous structure with the highest contribution of pores with a diameter of 4.5–9 Å. Minimal diameter of the compounds calculated using the Marvin Space 5.6.0.3 program is in the range of 4.33–6.36 Å, while their maximal diameter is in the range of 7–9.87 Å. Thus, smaller adsorbent micropores may have been inaccessible especially for the homologs with the highest molecular sizes. CFA and 4-CPB are hydrocarbon chain isomers (**Figure 13a**), and they differ in an order of the respective aliphatic carbon atoms. This in turn is related with the differences in spatial structure of the molecules. Adsorption capacity for 4-CPB is higher than for CFA, which results from stronger adsorption of the substance with less branched aliphatic part. The comparison of the 4-CP and 4-CPP adsorption (**Figure 13**) confirms the thesis that
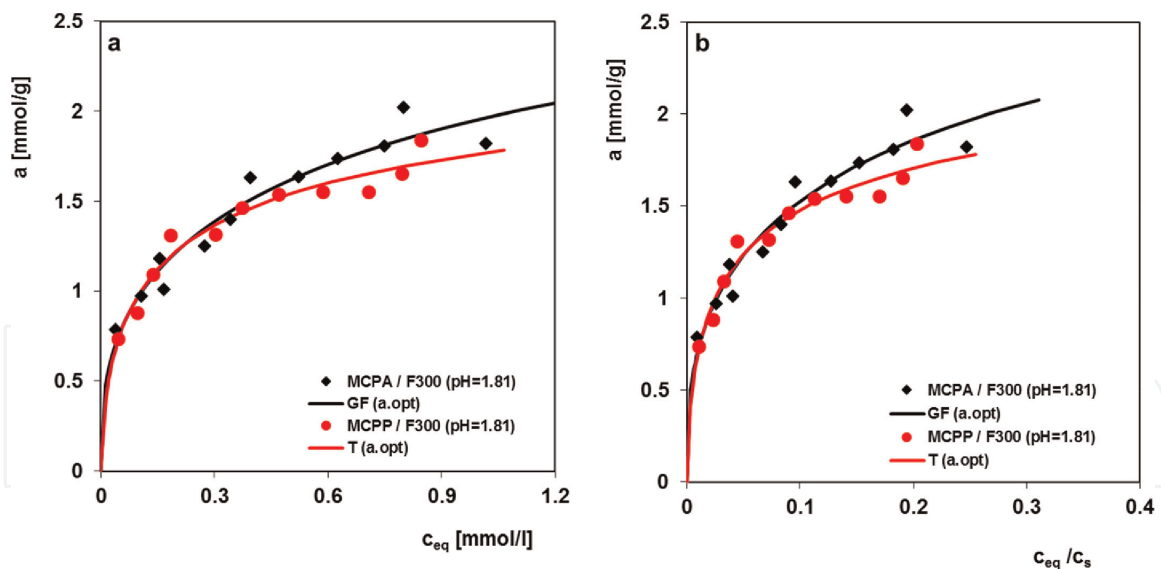
Figure 15.
The MCPA and MCPP adsorption isotherms on F300, pH = 1.81 in linear (a) and reduced coordinate system (b).
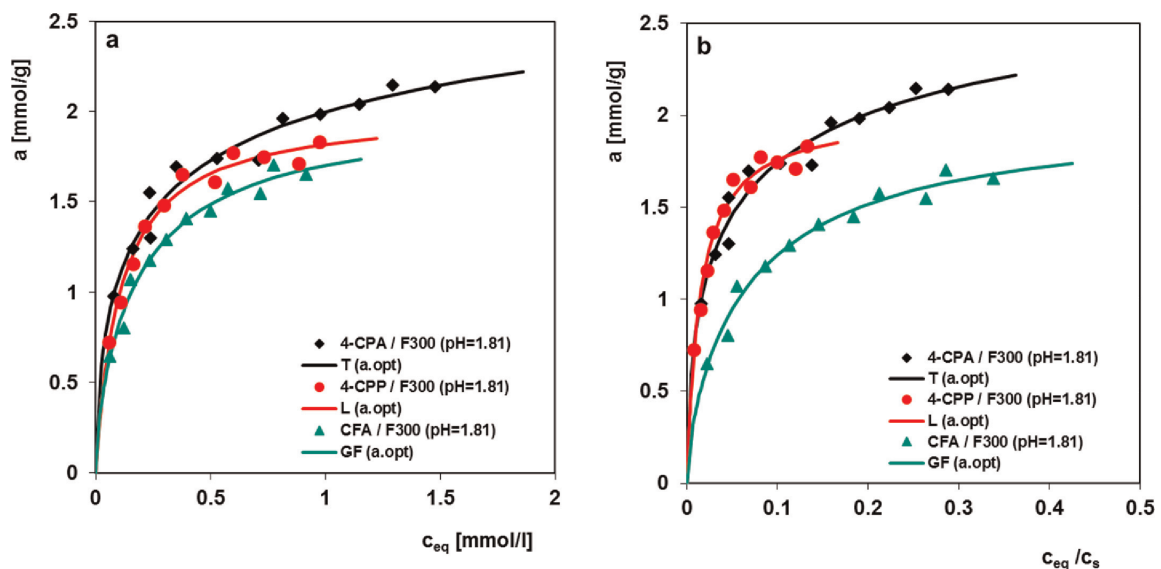

Figure 16.
The 4-CPA; 4-CPP; and CFA adsorption isotherms on F300, pH = 1.81 in linear (a) and reduced coordinate system (b).

hydrocarbon part linearity enables better adsorption. Linearity of the compound structure is related with poorer solubility compared to its branched isomer. Therefore, stronger adsorption of 4-CP compared to 4-CPP is mainly due to their solubility differentiation as evidenced by the overlapping isotherms in the reduced coordinates. Among the pesticides there are also structural isomers differentiated with regard to both phenolic and hydrocarbon part. This applies to CFA and MCPP for which the CFA adsorption is weaker (**Figure 13b**). The isopropyl group as the side branch of hydrocarbon chain has decisive influence on limiting the adsorbate-adsorbent interactions.

3.2 Analysis of experimental isotherms by means of the GL isotherm

All the studied experimental systems were analyzed by the generalized Langmuir isotherm equation (GL) [24–26] that for the specific values of heterogeneity parameters are reduced to four equations: Langmuir (L, m = n = 1), Langmuir-

Freundlich (LF, $0 < m = n \leq 1$), generalized Freundlich (GF, $0 < m \leq 1$, $n = 1$), and Tóth isotherm (T, $m = 1$, $0 < n \leq 1$). These isotherms were obtained from the global integral equation assuming that the Langmuir isotherm is a local one. In the optimization procedure, a method of the minimal sum of square deviations of adsorption values was used assuming the limitation of adsorption capacity ($a_m \leq 20$ mmol/g) and the equilibrium constant K ($K \leq 10^5$ l/mmol). **Table 2** presents the parameters of this equation, the correlation coefficients R^2, and standard deviations SD(a).

The parameters for two systems correspond to the simple L isotherm equation which is characteristic for energetically homogeneous system. For the other

System, pH (type of isotherm)	a_m	m	n	log K	R^2	SD(a)
4-CPA/F300, pH 1.81 (T)	3.34	1	0.40	1.59	0.957	0.087
4-CPA/F300, pH 10.38 (GL)	1.25	0.25	0.78	−0.35	0.940	0.043
2,4-D/F300, pH 1.81 (T)	3.69	1	0.35	1.81	0.968	0.079
2,4-D/F300, pH 10.38 (GF)	1.19	0.35	1	0.14	0.960	0.035
2,4,5-CPA/F300, pH 10.38 (GF)	1.29	0.25	1	0.01	0.907	0.054
2,4,6-CPA/F300, pH 10.38 (GF)	1.07	0.38	1	0.46	0.923	0.036
4-CMPA/F300, pH 10.38 (GF)	15.11	0.17	1	−7.25	0.936	0.030
MCPA/F300, pH 1.81 (GF)	3.09	0.34	1	−0.45	0.937	0.110
MCPA/F300, pH 10.38 (GF)	20	0.20	1	−7.04	0.766	0.064
2,4-BrPA/F300, pH 10.38 (GF)	1.83	0.33	1	−0.49	0.957	0.046
2,4,6-BrPA/F300, pH 10.38 (GL)	20	0.32	0.29	−3.71	0.949	0.056
3-CPP/F300, pH 1.81 (L)	1.92	1	1	0.93	0.948	0.082
4-CP/F300, pH 10.38 (GF)	20	0.24	1	−5.53	0.955	0.033
4-CPP/F300, pH 1.81 (L)	2.02	1	1	0.96	0.977	0.058
4-CPP/F300, pH 10.38 (GF)	20	0.18	1	−7.73	0.939	0.031
2,4-CPP/F300, pH 1.81 (T)	2.41	1	0.48	1.79	0.96	0.081
2,4-CPP/F300, pH 10.38 (GF)	1.02	0.32	1	0.181	0.916	0.035
2,5-CPP/F300, pH 10.38 (T)	1.32	1	0.29	2.94	0.896	0.032
3,4-CPP/F300, pH 10.38 (GF)	1.03	0.22	1	0.05	0.937	0.026
2,4,5-CPP/F300, pH 10.38 (GL)	1.07	0.56	0.75	0.83	0.942	0.041
MCPP/F300, pH 1.81 (T)	2.83	1	0.40	1.67	0.951	0.083
MCPP/F300, pH 10.38 (GF)	1.12	0.11	1	−1	0.822	0.034
4-CMPP/F300, pH 1.81 (GF)	2.60	0.34	1	−0.41	0.961	0.070
4-CMPP/F300, pH 10.38 (GF)	12.90	0.16	1	−7.35	0.949	0.026
CFA/F300, pH 1.81 (GF)	2.02	0.66	1	0.53	0.995	0.061
CFA/F300, pH 10.38 (GF)	20	0.21	1	−7.03	0.928	0.030
4-CPB/F300, pH 10.38 (GF)	10.42	0.15	1	−7.81	0.952	0.022
MCPB/F300, pH 10.38 (GL)	4.65	0.45	0.08	5	0.934	0.025
4-CMPB/F300, pH 10.38 (T)	1.02	1	0.59	1.54	0.923	0.027

Table 2.
Values of parameters of the generalized Langmuir equation characterizing the experimental systems.

systems, satisfying optimization using the T and GF equations or the general form of the GL isotherm was obtained. The GL equation corresponds to the quasi-Gaussian function of adsorption energy distribution; the heterogeneity parameters characterize the extension of this function toward the higher (*m < 1*) and lower (*n < 1*) adsorption energies (if *m ≠ n*, the energy distribution is asymmetrical, *m* the smaller and *n* the greater heterogeneity). The Tóth equation is represented by the asymmetrical quasi-Gaussian function of the adsorption energy that is extended toward low energies, whereas the GF isotherm corresponds to the exponential function with the characteristic minimal energy. The applied equations show slightly different behavior in the area of low and high adsorption. For low concentrations, only the T isotherm reduces itself to the Henry's equation, while the other isotherms to the classic Freundlich equation. In the range of high concentrations, all the equations show typical Langmuir behavior; however, the GF equation reaches the maximum adsorption most quickly. For many experimental systems, in limited ranges of concentration and adsorption, various types of isotherms may exhibit similar behavior; hence, they can describe the same data well. Unequivocal selection of the model can be made on the basis of precise experimental data in a wide range of concentrations and adsorptions (required range depends on the system heterogeneity). In the case of experimental systems, the choice of theoretical adsorption isotherm should be considered as approximate one because it is based on the standard deviation values obtained in the optimization procedure within a limited measurement range and with relatively large scattering of experimental points (adsorbent inhomogeneity).

Analyzing the heterogeneity parameters which characterize the experimental systems, one can conclude that in most cases they achieve values much lower than one. It indicates a significant impact of the energetic heterogeneity. Attention should be paid to high values of the adsorption capacity for several experimental systems. In the case of experimental isotherms with a narrow range of relative adsorption *θ*, the adsorption optimization method by using the adsorption capacity limit (20 mmol/g—reaching this value or even a lower value of 10 mmol/l indicates that the determined capacity is unrealistic; consequently the value of the constant K is not also reliable) leads to the achievement of minimal *SD* for high values of the parameter a_m. The best results for the generalized Freundlich isotherm were obtained due to the specific features of this equation. **Figure 17** presents the results of model calculations for dependence of the isotherm slope in logarithmic coordinates (*φ = lna/lnθ*) as a function of the surface coverage *θ* for the GL and GF equations. For the GL equation, it can be described [25, 26] as

$$\varphi = \frac{d\ln a}{d\ln c_{eq}} = \frac{m}{1 + (Kc)^n} = m\left(1 - \theta^{n/m}\right) \tag{1}$$

Analyzing the calculated curves, one can observe the different nature of the GF equation in relation to the other isotherms being special cases of the GL isotherm. For the LF equation (*m = n = 0.5*), the slope *φ* is always a linear function of the relative adsorption (**Figure 17a**); for other types of GL isotherm, a shift of the slope always takes place at lower values of the coverage than for GF. The GF equation shows the weakest initial slope of the dependence *φ* on the coverage. Additionally, the stability ranges of slope *φ* strongly depend on a value of the heterogeneity parameter *m*; for the systems with high heterogeneity (*m = 0.2*), this area clearly increases (**Figure 17b**). In particular, for *m = 0.2* the slope remains almost constant —a decrease of 5% occurs until relative adsorption of 0.55 is achieved, while for *θ < 04* a shift of the slope does not exceed 1%.
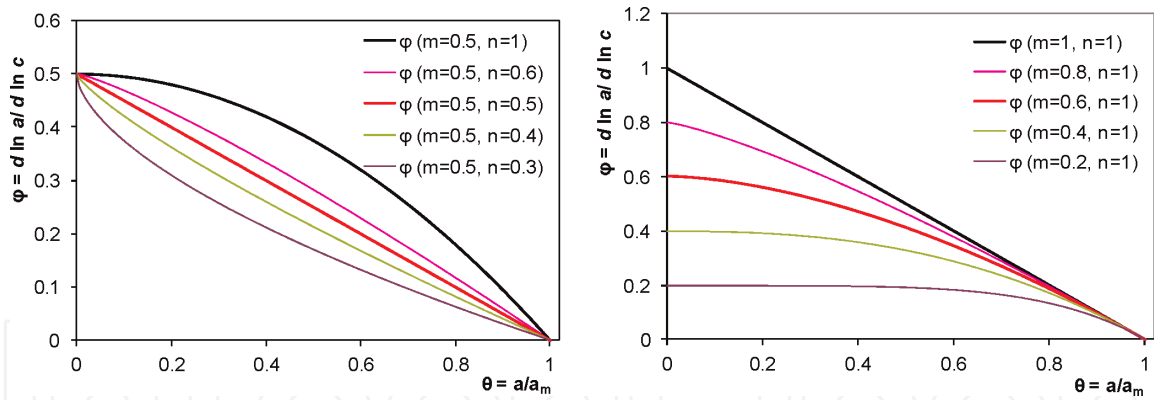
Figure 17.
Model dependencies of the adsorption isotherm slope in logarithmic coordinates, φ = lna/dlnθ, as a function of surface coverage θ for the GL (left side) and GF (right side) equations for various values of the heterogeneity parameters m *and* n.

The above observations are confirmed by the results of model calculations presented in **Figure 18** as the dependences of relative slope $\varphi/\varphi_{\theta\,=\,0}$ as a function of surface coverage θ for the GL type equation and the dependences of surface coverage θ corresponding to the specific relative slope φ. A distinguish type of variability of these dependences for the GF equation is observed in comparison to the other GL isotherms. It means that in the case of GF isotherm a widest range of the steady slope φ corresponding de facto the Freundlich isotherm is followed by a rapid change of isotherm character into a typical isotherm with the adsorption *plateau*. Many of the experimental systems exhibit typical behavior for the Freundlich isotherm—despite existence of the adsorption limitations (due to the limited pore volume). This behavior perfectly explains the above analysis. Other factors affecting such behavior comprise a multilayered nature of some isotherms and intermolecular interactions in the surface phase (it can lead to the increase of the linearity range φ—especially for the LF or Tóth isotherms) [26].

Referring to a general problem of accuracy of the determination of adsorption isotherm parameters, it should be emphasized that a key problem is to determine the adsorption capacity a_m that for every optimization is in fact the extrapolated value and as a result the most susceptible to error. Simultaneously, the error in a_m determination is transferred to other parameters. For the experimental data in a range of low adsorption, it is possible to achieve a relatively high accuracy of determination of the heterogeneity parameter m and the aggregated value (corresponding to an adsorption coefficient in the Freundlich equation), $\ln k_F \approx m$
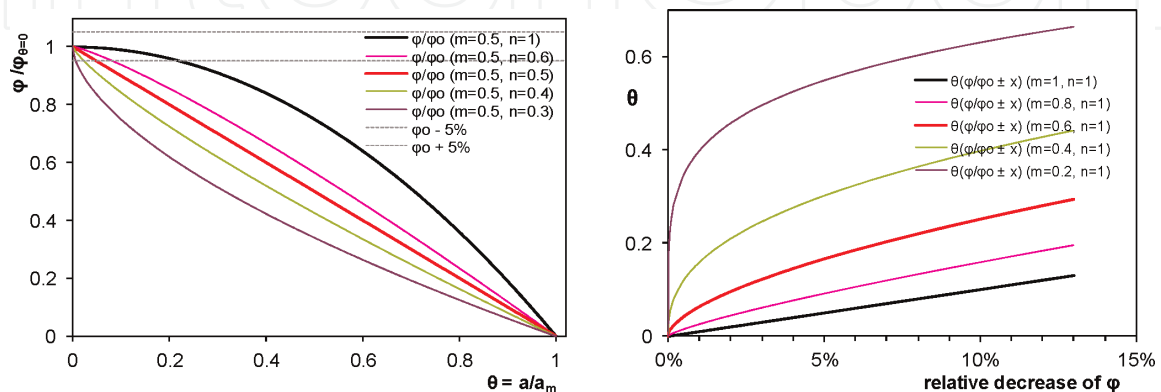

Figure 18.
Model dependences of relative slope φ/φ$_{\theta\,=\,0}$ *as a function of surface coverage θ for the GL equation at various values of heterogeneity parameters* m *and* n *(left side, the deviations φ ± 5% are marked) and model dependences of the surface coverage θ corresponding to relative shift of slope φ for the GF equation (right side).*

ln$K$ + lna_m. Unfortunately, the accuracy of determination of the adsorption equilibrium constant ln$K$ depends not only on lna_m but also on a value of m (error of a_m determination increases for small m because ln$K$ = [(m ln$K$ + lna_m)-lna_m]/m). When the adsorption data can be described well by the Freundlich isotherm (no systematic deviations from linearity in the logarithmic coordinates), this means that there are not points in the experimental data from which a reliable value a_m could be calculated. It would be possible only if the experimental isotherm shows a change of the slope in the logarithmic coordinates. On the other hand, a greater accuracy of the determination of the adsorption capacity a_m and heterogeneity parameter n can be obtained mainly for the data in a range of high adsorption.

It should be stated that a fully reliable optimization of the theoretical model can be obtained if the experimental data are distributed evenly in a range of both low and high concentration/adsorption regions. It is important that the range of relative adsorption is symmetrical in relation to θ = 0.5 (e.g., from the point of view of isotherm parameter analysis, the range θ = 0.1–0.9 is much better than 0.01–0.1 or 0.9–0.99). Unfortunately, the measurements in both ranges are burdened with a relatively large experimental errors—for low concentrations a problem is related to the apparatus quality (e.g., the signal noises), and for high ones, the main barrier is a necessity of dilution preparation (or necessity of changing the measurement method) and slight changes in solution concentration due to adsorption near to a saturation point of the surface phase with the adsorbate.

3.3 Adsorption kinetics

In order to investigate an effect of the adsorbate properties on adsorption rate, the measurements of adsorption kinetics for selected systems were conducted. As the activated carbon is characterized by high porosity, it seemed reasonable to include diffusion effects in a kinetic description. The Crank model (intraparticle diffusion model) in a standard form as well as in a simplified one is a fundamental model of intraparticle diffusion process. The full IDM model takes into account the changes of adsorbate concentration during adsorption process and a spherical shape of adsorbent particles with a radius r [27]:

$$F = 1 - 6 \cdot (1 - u_{eq}) \sum_{n=1}^{\infty} \frac{\exp\left(-p_n^2 \cdot \frac{Dt}{r^2}\right)}{9 \cdot u_{eq} + (1 - u_{eq})^2 \cdot p_n^2}, \quad \tan p_n = \frac{3p_n}{\left[3 + \left(\frac{1}{u_{eq}} - 1\right)p_n^2\right]} \quad (2)$$

where u_{eq} is the relative adsorbate uptake at equilibrium, F is the adsorption progress, p_n is the non-zero roots of $\tan p_n$ function, D is the effective diffusion coefficient, and r is the adsorbent particle radius.

However, for the analyzed experimental kinetics, the full IDM equation describes the data very poorly (the curves and points are marked as "Crank" in **Figure 19**). The Crank model analysis for MCPP/F300 at pH = 2 was chosen and presented as representative for all experimental systems; the quality of optimization of all of them was very similar. If effective concentration of the adsorbate in a surface layer is different than in a volume phase, it can be assumed that u_{eq} is also a fitting parameter. If concentration during adsorption process remains almost constant, u_{eq} is close to 0, and then one gets a simplified form of the Crank model [8, 28–30]:

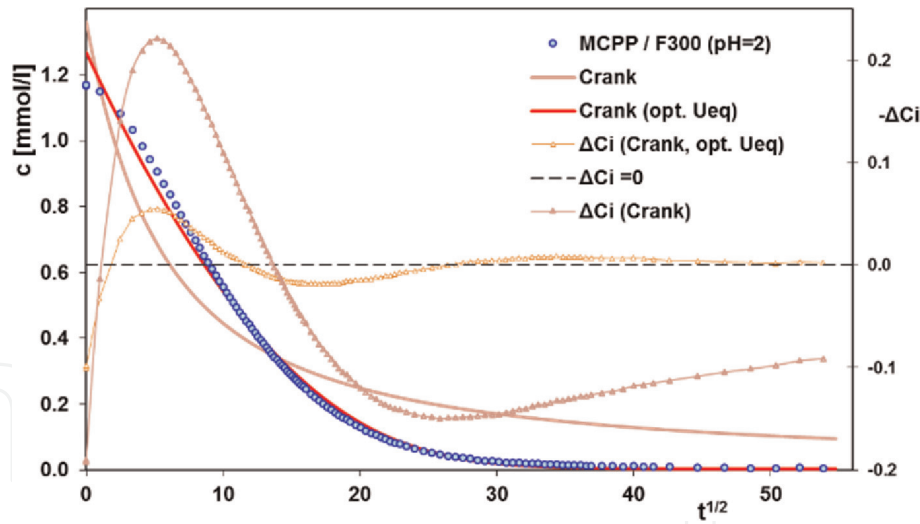$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(\frac{-\pi^2 n^2 Dt}{r^2}\right) \quad (3)$$

Figure 19.
The comparison of the optimization using the Crank model (Crank) and the optimization neglecting a relation of a parameter u_{eq} of the Crank model with concentration change during adsorption process (Crank, opt. U_{eq}) for the MCPP adsorption data on F300 at pH = 2. The figure shows deviations for both optimizations (triangles).

As one can see, the adsorption data can be described quite satisfactorily by using the simplified form of Crank model. It should be assumed that as a result of the rapid initial adsorption stage, the outer part of the granules becomes an adsorbate reservoir providing constant conditions for adsorbate penetration inside the granules. The standard deviation of concentration for the simplified Crank model decreased 3–5 times compared to the full IDM model. In turn, the obtained values of parameter D/r^2 of the order 10^{-3}–10^{-5} are acceptable, while those determined on the basis of the full model IDM were unsatisfactory. Nevertheless, nonlinearity of experimental data in the initial range in $c \sim t^{1/2}$ coordinates (linearity is the fundamental assumption of all variants of the Crank model) proves that this model is not suitable for the description of the adsorption process for the studied systems

In practice, a somewhat better choice was the McKay model (pore diffusion model) [31]. It additionally takes into account a resistance during adsorbate transfer through adsorbent surface layer and assumes that the adsorbate evenly penetrates the granules, and a clear boundary between an area in which adsorption equilibrium is established, and the one without adsorbate is formed:

$$\frac{dF}{d\tau_s} = \frac{3(1 - u_{eq} \cdot F) \cdot (1 - F)^{\frac{1}{3}}}{1 - B \cdot (1 - F)^{\frac{1}{3}}} = \frac{3x\left[1 - u_{eq}(1 - x^3)\right]}{1 - Bx} \tag{4}$$

$$\tau_s u_{eq} = \frac{1}{6}\left\{\left(2B - \frac{1}{X}\right) \cdot ln\left[\left|\frac{x^3 + X^3}{1 + X^3}\right|\right] + \frac{3}{X} ln\left[\left|\frac{x + X}{1 + X}\right|\right]\right\} \\ + \frac{1}{X \cdot \sqrt{3}} \cdot \left\{arc \tan\left(\frac{2 - X}{X \cdot \sqrt{3}}\right) - arc \tan\left(\frac{2 \cdot x - X}{X \cdot \sqrt{3}}\right)\right\} \tag{5}$$

Here, $x = (1 - F)^{\frac{1}{3}}$ is an auxiliary variable; $X = \left(\frac{1}{1 - u_{eq}}\right)^{\frac{1}{3}}$ is the parameter; and $B = 1 - B_i$, B_i is the Biot number, where $B_i = K_f r / D_p$, K_f is the external mass transfer coefficient, D_p, is the effective pore diffusion coefficient, and τ_s is the dimensionless model time, where $\tau_s = c_0 / (\rho_t a_{eq}) \cdot (D_p / r^2) \cdot t$ and ρ_t is the particle density.

As shown in **Figure 20**, the McKay model describes quite well the kinetics of experimental systems in the initial range, and it does not exhibit the same feature as the IDM model. The initial part of curve is a characteristic for typical adsorption
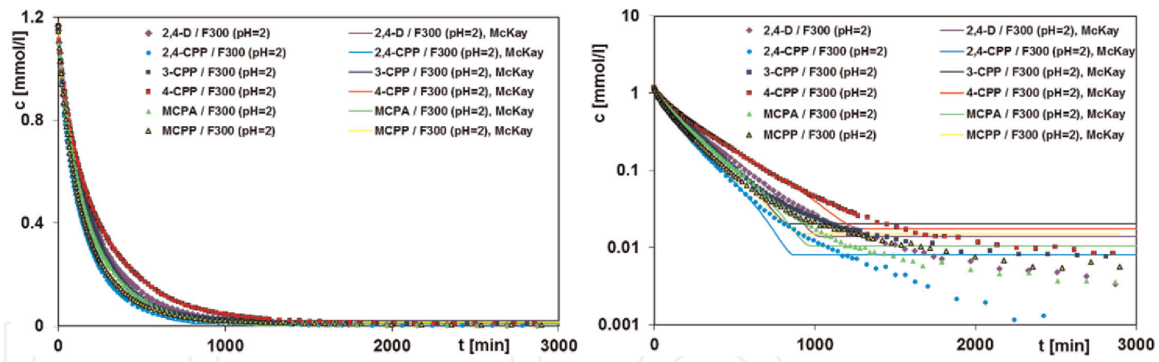
Figure 20.
Comparison of the optimization procedure using the McKay model to the adsorption pesticides data on F300 at pH = 2.

systems. However, in the subsequent stage of experiment, one can see significant discrepancies between the model and data, because this model predicts that the system comes to equilibrium after a finite time (curve bend corresponds to reaching the equilibrium state). It is reflected in the increase of the standard deviations with time, inversely to the IDM model. It should be added that obtaining an acceptable optimization using the McKay model was associated with treating a parameter u_{eq} (total adsorbate loss from solution) as the optimized parameter regardless of equilibrium concentration, the same assumption as for the simplified Crank model.

Very good results in the analysis of the kinetic data were obtained for the multi-exponential equation (**Figure 21**). This equation describes kinetics as an independent parallel series of first-order processes or approximation of follow-up processes [8, 32–34]. Generally, the multi-exponential equation characterizes well enough the experimental systems with a heterogenous pore structure or a complex pore system with differentiated pore distribution. A mathematical form of the multi-exponential equation is as follows:

$$F = 1 - \sum_{i=1}^{n} f_i exp\,(-k_i t), \; \sum_{i=1}^{n} f_i = 1 \qquad (6)$$

where n is the number of exponential terms and the coefficient f_i (i = 1, 2, …, n) is the fraction of adsorbed equilibrium amount corresponding to the adsorption process characterized by the rate coefficient k_i.

Both the experimental and optimized concentration profiles for the studied systems are presented in two coordinate systems: the relative concentration (c/c_o) ~ time (t) and relative concentration (c/c_o) ~ square root of time ($t^{1/2}$). The latter form of presentation allows precisely to depict the fit quality in a broad range of measured concentrations.
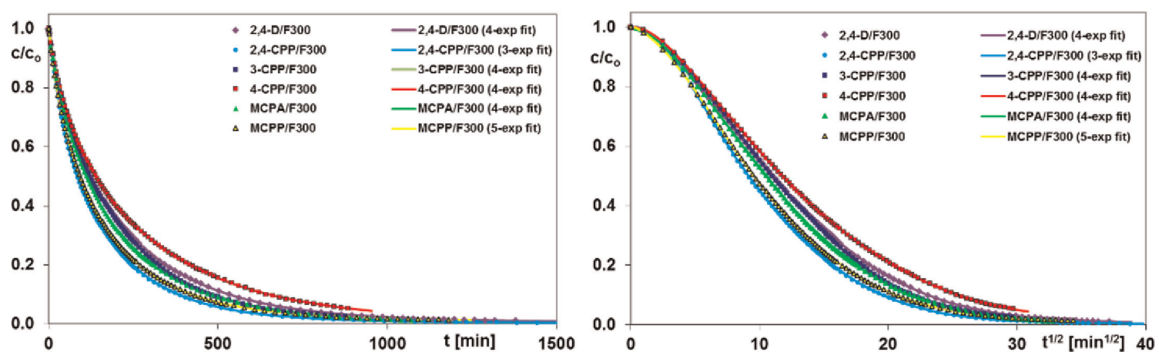

Figure 21.
Comparison of the optimization using the multi-exponential equation to the experimental data in the coordinates: relative concentration c/c_o ~ time and c/c_o ~ time$^{1/2}$.
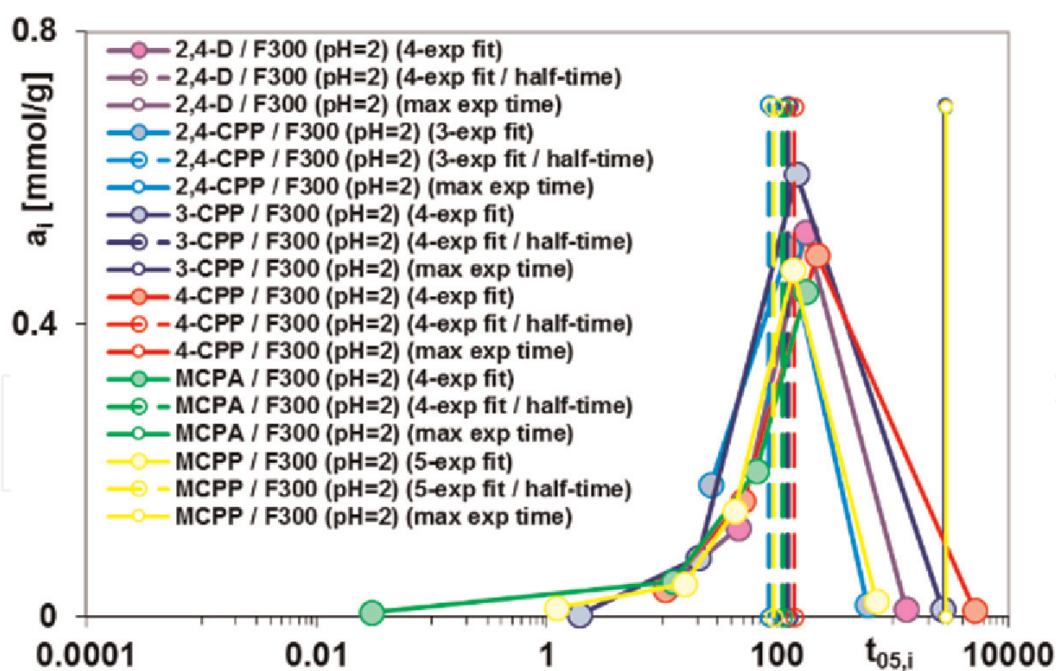
Figure 22.
Distributions of adsorbed amounts versus adsorption half-times determined from the multi-exponential equation.

Analyzing the values of adsorption half-time and time needed to reach a nearby equilibrium state, one can state that the kinetics of studied pesticides on a given type of carbon material is relatively slow as a result of the micropore predominant contribution in the adsorbent structure. The kinetic curves for the selected adsorbates can be set from the fastest to the slowest ones in order: 2,4-CPP > MCPP > MCPA > 3-CPP > 2,4-D > 4-CPP. The differences are not very significant, but it is clearly noticeable that adsorption of compounds with hydrocarbon chain of propionic acid is faster compared to their homologs of acetic acid, i.e., 2,4-CPP > 2,4-D and MCPP > MCPA. This is undoubtedly a result of the increase of the hydrophobic interactions between the adsorbate and activated carbon surface ($pH_{pzc} \sim 9.8$). These interactions along with dispersive ones are the main mechanism of adsorption process in aqueous systems at fixed pH = 2. One can say that in the case of these pairs of compounds, differences in a length of the hydrocarbon chain (a molecule dimension as well) do not affect differentiation of the diffusion rate in the microporous structure of activated carbon. Completely reverse trend in the adsorption capacity for these compounds determined on the basis of equilibrium isotherms was observed. The shorter hydrocarbon chain of adsorbate, the greater adsorption capacity for a given compound due to possibility of greater packing in the adsorbent structure.

Additionally a comparison of the adsorption kinetics for the studied systems is presented as spectrum of m-exp optimized parameters in the coordinate system: the adsorbed amounts a_i versus the adsorption half-times $t_{05,i}$, for respective exponential terms (**Figure 22**). The spectra are similar in shape and consist of 3–5 terms depending on differentiation in the rate of particular stages of the adsorption process. The faster the kinetics, the greater the adsorbed amounts ai for the lower adsorption 26 half-times $t_{05,i}$ and larger corresponding rate coefficients.

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