

# Dependence of Sorption of Phenoxyacetic Herbicides on Their Physico-Chemical Properties

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## Abstract

The purpose of this study is to assess the efficiency of removal of phenoxyacetic pesticides from water by means of activated carbon sorption. The sorbents used in this study (WD-extra, CWZ-22, NP-5) were produced by GRYFSKAND, Ltd., Hajnowka.

The first step of the study was the steady-state test of the suitability of selected sorbents in herbicide removal. The steady-state test was conducted according to the Chemviron Carbon methodology. Its aim was to determine the Freundlich isotherm and sorption capacity, and to select the best sorbent in static conditions.

The residual concentration of the contaminant in the filtrate was determined using relevant analytical techniques. Also, the concentration of phenoxyacetic acid was identified by TLC and HPLC methods.

On the basis of the results obtained it was concluded that the best sorbents of phenoxyacetic acid from water in steady-state conditions are CWZ-22 and NP-5. No significant difference was noticed in the removal process of the whole group of phenoxyacetic acids by sorption.

**Keywords:** sorption, activated carbon, herbicides, pesticides, Freundlich isotherm

## Introduction

The question of water protection against agricultural pollutions is very complex and has not been solved so far. Pesticides have been detected in all kinds of water circulating in nature: in atmospheric waters, surface and underground waters. Many countries have undertaken special research programmes to reduce the influence of pesticides on drinking water. The presence of pesticides in natural waters in such countries as the USA, Canada, Hungary, India, Russia, Germany, Greece, France, Switzerland, Poland, and also in the Baltic Sea and the North Sea has been proven many times [1, 3, 5, 6, 7, 8, 9]. (Tables 1-2) For the last few years the concentration of compounds belonging to the phenoxyacid group has been

observed to increase. An alarming fact is that these compounds are more and more often detected in shallow or even deep underground waters.

Concentration of marked pesticides in Polish surface waters reaches a level as high as 290 µg/l. The following compounds are detected most often and in the largest quantities: lindan, DDT (which has not been used for many years now) simazina and atrazina, chlorofenwinfos and fenitroton, 2,4-D, MCPA, MCPP. The presence of pesticides in surface waters in the Zulawy Wislane region has been described many times by Zelechowska and Makowski. [9] Additionally, our own research has confirmed the presence of phenoxyacid herbicides (2,4-D, MCPA, MCPP) in the surface waters of the northern-eastern region - in the Supraśl, Białka, Narew and Biebrza rivers.

Research into the pollution of the Baltic Sea, which

Table 1. The level of herbicides in polluted surface waters.

Name of herbicide	Concentration [ $\mu\text{g/l}$ ]		
	Waters from drainage systems intensively used for agriculture	Waters polluted with sewage	Safe waters according to the former CMEA
	Maximum	Maximum	
2,4-D	150.0	120.0	1.0
MCPA	200.0	120.0	0.5
MCPP	200.0	100.0	-
2,4-DP	50.0	45.0	-

Source: Tabulated on the basis of this study and [7, 8].

Table 2. The presence of pesticides in drinking water.

Pesticide	Concentration [ $\mu\text{g/l}$ ]		Percentage of results higher than admissible		
	max	average	Poland	EEC	WHO
2,4-D	30	7.14	14.4	14.4	0.0
MCPA	25	6.14	14.1	14.1	0.6
2,4-DP	10	3.84	6.0	6.0	1.1
MCPP	15	3.89	7.9	7.9	3.0
Atrazyna	3	0.58	28.1	28.1	0.0
Simazina	10	0.80	21.1	21.1	0.0
Linuron	3	1.43	3.0	3.0	0.4
Chlorofeninfos	12.2	0.98	10.9	10.9	-

Source: Tabulated on the basis of [7, 8].

has been carried out under the Helsinki Convention, has proved the pollution of the sea by pesticides. The study carried out in Poland (1992-1995) as part of environmental monitoring has shown the changes of concentrations of pesticides in the Zalew Wislany. The study has been stimulated by the presence of the selected chloroorganic compounds in herring muscles. Phenoxyacetic acid herbicides are in the Red List of the Helsinki Committee enumerating substances whose inflow to seas should be reduced by 50%.

We have comparatively little reliable information on the presence of pesticides in underground waters in Poland. A reconnaissance research carried out by the Institute of Protection of Plants has proved the presence of 27 compounds. In shallow underground waters (depth of water less than 4 m) the most often present compound was atrazina in quantities up to half a dozen  $\mu\text{g/l}$ . The examination of wells carried out during the period of intensive pesticides usage showed their presence in 305 country-wells in the Lublin Region. Examination of ground waters in the Poznan Region has also confirmed the presence of pesticide compounds. [6]

There is an inseparable connection between the presence of pesticides in natural waters and their presence in drinking water. Even relatively small quantities of pesticides cause changes of organoleptic characteristics of water. A feature disqualifying polluted water is its very specific smell caused by different substances and deterio-

rated taste. Pesticides can make water smell of earth, mould, chlorine, onion, etc. Some compounds cause white turbidity, yellow tinge, foaming.

Acceptable concentrations of pesticides in drinkable water were tightened following the introduction (Sept., 2000) of new standards for drinkable water. The amount of a single pesticide compound cannot exceed 0.1  $\mu\text{g/l}$  while all of the pesticides - 0.5  $\mu\text{g/l}$ . It should be mentioned at this point that these strict standards follow the directives of the European Union. There is consequently the need to intensify potable water treatment. Additionally, special attention should be given to subsequent stages of the removal of organic compound residue, including pesticide residue.

Pesticides in natural waters, especially surface waters, undergo physico-chemical and biochemical changes. These changes may lead to partial removal of the pesticides which, in turn, is a very arduous process, mainly because the pesticides are so varied and undergo detoxication in different ways. Another problem is the fact that the transient products can be more dangerous than the substrate. Technological methods of removing pesticides from water include:

- oxygenation with strong oxidants, i.e. with chlorine, ozone, hydrogen peroxide, potassium permanganate,
- photochemical exposure to UV rays,
- biochemical decomposition by means of biofilter, activated sludge and soil microorganisms,
- mechanical, i.e. filtration, rotation, sedimentation,
- coagulation with aluminium sulphate, iron sulphate, iron chloride,
- adsorption on natural and artificial materials, i.e. peat, clays, bentonite, humus, ionite, active carbons, zeolite, and others.

Judging from the above-discussed methods of removing pesticides and possibilities of their implementation it is unquestionable that sorption on active carbon should be included in the treatment of all surface waters. This is why research into the removal of phenoxyacetic acids using the method of sorption on active carbons has been undertaken.

## Experimental

Experiments in steady-state conditions were carried out according to the methodology of the American company Chemviron Carbon used in Belgium, Germany, France, Italy, England, the USA, and Poland [4]. The aim of the experiments was to draw the adsorption isotherms which would enable a comparison of the degree of sorption of different adsorbents.

Degassed granular carbon was washed with distilled water and dried; next it was crushed in mortar and dried in an electric drier at a temperature of 150°C for 3 hours until solid. Carbon in this form was separated into fractions of different weight: 0.01, 0.02, 0.05, 0.1, 0.25, 0.5 and 1.0 g on every 100 ml of the solution. Representative samples of the sorbent were added to cone-shaped cobs with glass plug containing a working herbicide solution. The cobs were shaken in electric shaker type 358 at a constant amplitude of 9 twitches for 4 hrs and then were left for 24 hrs in order to reach full sorption equilib-

Table 3. The physico-chemical parameters of the carbons examined.

Parameter	Carbon		
	WD-extra	CWZ-22	NP-5
Active Surface [m <sup>2</sup> /g]	950-1050	800-950	1300-1500
Pore Volume [cm <sup>3</sup> /g]	0.85-0.95	1.5-2.0	min 0.7
Granulation [mm]	1.0-1.5	1-4	0.75-1.2
Dechloration Capacity [cm]	4-5	10-15	5-8
Methylene Number [cm <sup>3</sup> ]	22	22-29	min 40
Iodic Number [mg/g]	900-1000	800-1000	1390
Phenol Number [%]	4-5	4-5	-
Mechanical Strength [%]	90	92-96	95-97
Grindability [%]	3.0	1.5-3.0	0.3

rium. Afterwards, the samples were double-filtered through soft filter paper. The first and the last portion of the filtrates were rejected. Next the concentration of the pollutant in the filtrate was determined with an appropriate analytical technique [2].

The concentration of herbicides in the samples was established in two ways: using the direct method of HPLC (High Performance Liquid Chromatography) and TLC (Thin Layer Chromatography), and an indirect method of TOC [2]. The TLC analysis was conducted in accordance with the Polish Standards. The analysis is applied when the amount of specific substances in water 2,4-D, MCPA, MCPP exceeds 0.001 mg/l. The marking method requires that phenoxyacetic acids are extracted from the samples by means of diethyl ether and their amount is measured by means of TLC method. The visual method of comparison is used to determine the amount of herbicides; the size and intensity of stains of different substances in samples are compared to appropriate patterns.

The phenoxyacetic acid derivatives were also marked by means of HPLC method. Biologically active substances 2,4-D, MCPA and MCPP were extracted from water samples of 1000 ml by Solid Phase Extraction (SPE) technique; 300 mg of Carbopack B packing was used. After the elution and concentration of extracts, the active substances were separated and marked with HPLC technique in the reversed phase system (RP).

Because of analytical requirements and for a better comparison of sorbents the following concentrations of working solutions were applied:

- 2, 4-D = 130 mg/l

- MCPA = 100 mg/l

- MCPP = 150 mg/l

The herbicide sorption was conducted on carbons type WD-extra, CWZ-22, and NP-5 produced by GRYF-SKAND, Ltd., Hajnowka. They are used for the treatment of water solutions, specifically for the treatment of drinkable water in big water treatment plants, and in small installations containing organic traps. Thanks to their large active surface and well developed structure, they remove organic pollutants from water effectively. These carbons are made of different raw materials: WD-extra made from hard coal, CWZ-22 from wood, NP-5 from coconut shells. Table 3 presents physico-chemical parameters of the carbons examined.

## Results and Discussion

The herbicides chosen for sorption in static conditions have similar chemical composition. They differ in the molecule size, ligands, physico-chemical properties, and, especially, solubility, which can influence the process of sorption. What is more, MCPP acid, as opposed to MCPA, 2,4-D, is an active chiral enantiomer R.

It was possible to describe the sorption of the applied adsorbates on all active carbons by means of the equation of the Freundlich adsorption isotherm:

$$A = k \cdot c^{1/n}$$

The constants  $k$  and  $1/n$  were fixed by means of minimal squares with the help of statistical computer programme STATISTICA; next the range of error in those constants was determined. The values of the parameters  $k$  and  $1/n$  and also correlation  $R$  coefficients of different adsorbates are presented in Tables 4-6.

Schemes 1-9 show the isotherms of adsorption of the herbicides examined on domestic carbons. The curves depend on different course of adsorption in the range of low concentrations. This results from competitive character of the dissolved substance and the solvent working against the adsorbate surface. According to the Giles classification, basically, two groups of isotherms were obtained: S and L. Group S includes isotherms of systems in which the solvent undergoes strong sorption, that is to say it competes with the adsorbed dissolved substance. The isotherms shape testifies also to the fact that the adsorbate particle may be placed vertically or at an angle in the active centre of the adsorbent. Group L is connected with the flat arrangement of aromatic rings of a particle.

Table 4. The coefficients of the Freundlich adsorption isotherms of phenoxyacetic acid herbicides on carbon NP-5.

Coefficient	Phenoxyacetic compound		
	2,4-D	MCPA	MCPP
$k$	0.695	0.0001	0.0004
$1/n$	1.942	3.690	3.145
$R$	0.984	0.951	0.967

Source: Tabulated on the basis of this study

Table 5. The coefficients of the Freundlich adsorption isotherms of phenoxyacetic acid herbicides on carbon CWZ-22.

Coefficient	Phenoxyacetic compound		
	2,4-D	MCPA	MCP
k	21.416	39.830	22.840
1/n	0.653	0.061	0.357
R	0.974	0.998	0.777

Source: Tabulated on the basis of this study

Table 6. The coefficients of the Freundlich adsorption isotherms of phenoxyacetic acid herbicides on carbon WD-extra.

Coefficient	Phenoxyacetic compound		
	2,4-D	MCPA	MCP
k	0.0097	9.117	0.026
1/n	2.321	0.366	1.761
R	0.888	0.938	0.768

Source: Tabulated on the basis of this study

The knowledge of the 1/n parameter value from the Freundlich equation allows us to determine the intensity of adsorption of a particular substance from the water phase on active carbon, whereas the value of the constant k shows the sorption capacity of the sorbent. The higher the coefficient k value the greater the sorption capacity. The constants 1/n of the Freundlich equation are the isotherms; direction coefficients, and they equal the tangent of the angle of inclination of the lines in the logarithmic coordinate system. Consequently, the higher the 1/n value, the more intensive the sorption.

Judging from the above experiments it can be stated that the process of sorption of phenoxyacetic acid compounds is similar for the whole group. No substantial differences were noticed in detoxication of the substances previously discussed. This phenomenon could be described by means of Freundlich adsorption isotherm (Figs. 7-9) for the whole group of phenoxyacid compounds on each type of sorbent:

$$\begin{aligned} \text{WD-extra } A &= 4.0 c^{0.76} \quad R = 0.66 \\ \text{CWZ-22 } A &= 42.53 c^{0.35} \quad R = 0.51 \\ \text{NP-5 } A &= 45.96 c^{0.49} \quad R = 0.60 \end{aligned}$$

On the basis of the Roller table of the terminal values of the correlation R coefficient it can be claimed that, because as many as 45 variables were considered, the above equations are crucial. It is an important observation because in future it will be possible, judging from the behaviour of just one phenoxyacid compound, to draw preliminary conclusions about the rest of the phenoxyacid group subjected to sorption during the water treatment process. In this way the study of the process of sorption will be more cost-effective and less time-consuming.

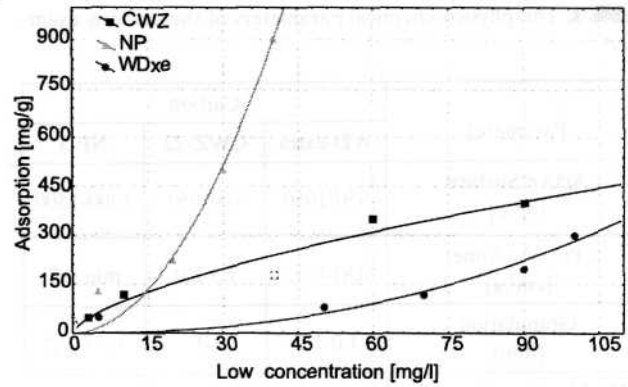


Fig. 1. The Freundlich adsorption isotherm of 2,4-D from Aminopielik D water solution.

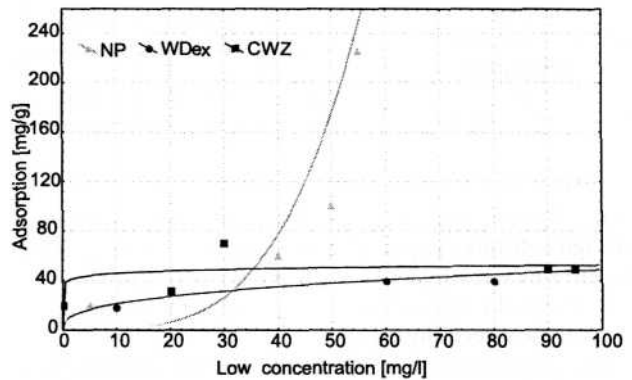
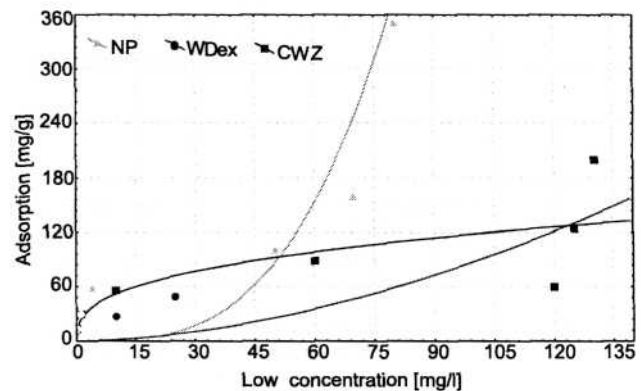


Fig. 2. The Freundlich adsorption isotherm of MCPA from Chwastox trio water solution.

Fig. 3. The Freundlich adsorption isotherm of MCPP from Chwastox trio water solution.



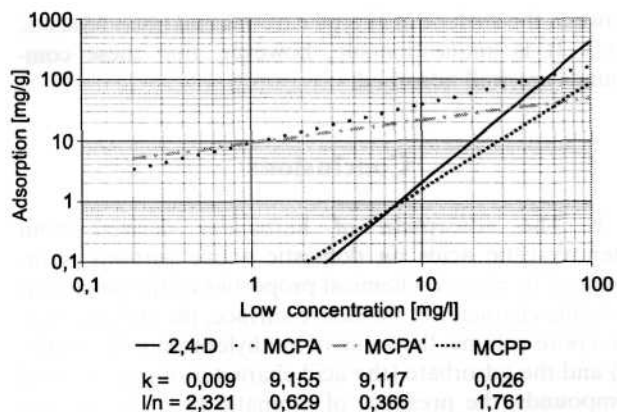


Fig. 4. The comparison of the adsorption isotherms of phenoxyacetic acids on carbon WD extra.

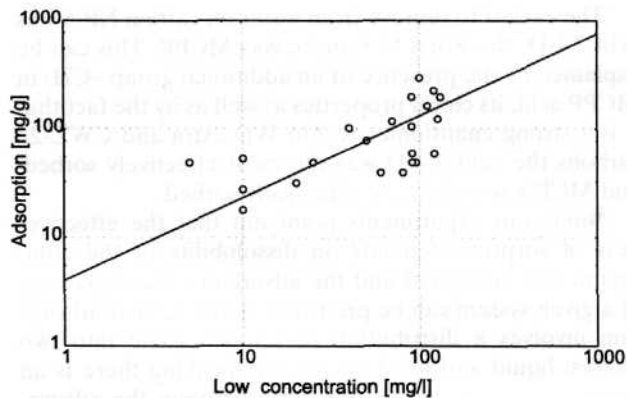


Fig. 7. The Freundlich adsorption isotherm of phenoxyacetic acid derivative on carbon WD-extra:  $y = 4 x^{0.76}$   $R=0.66$ .

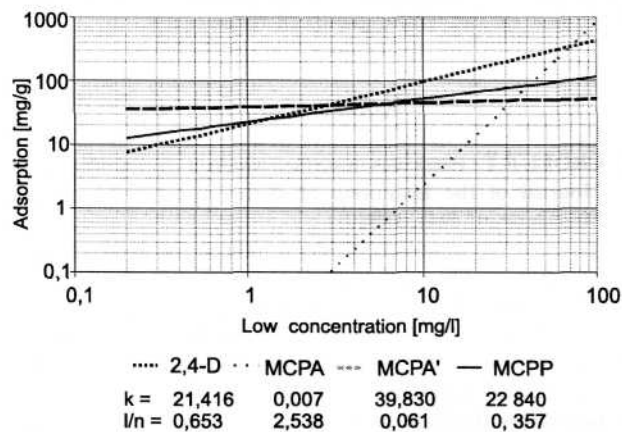


Fig. 5. The comparison of the adsorption isotherms of phenoxyacetic acids on carbon CWZ 22.

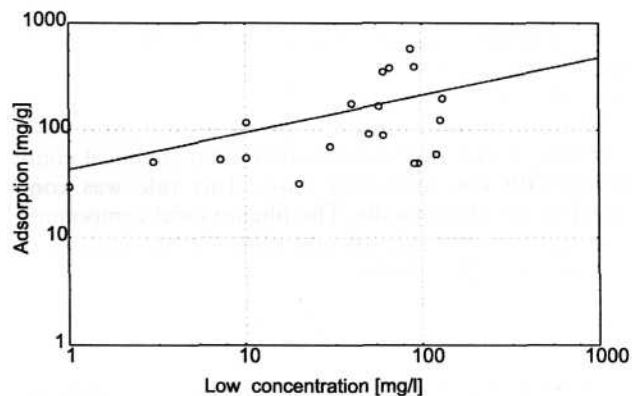


Fig. 8. The Freundlich adsorption isotherm of phenoxyacetic acid derivative on carbon CWZ-22:  $y = 42.53 x^{0.349}$   $R=0.513$ .

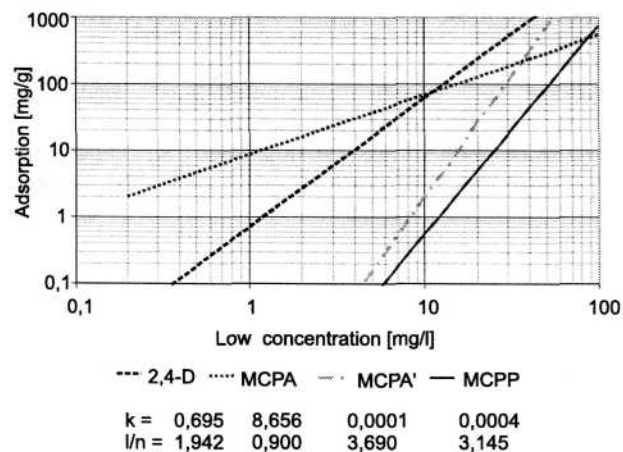


Fig. 6. The comparison of the adsorption isotherms of phenoxyacetic acids on carbon NP-5.

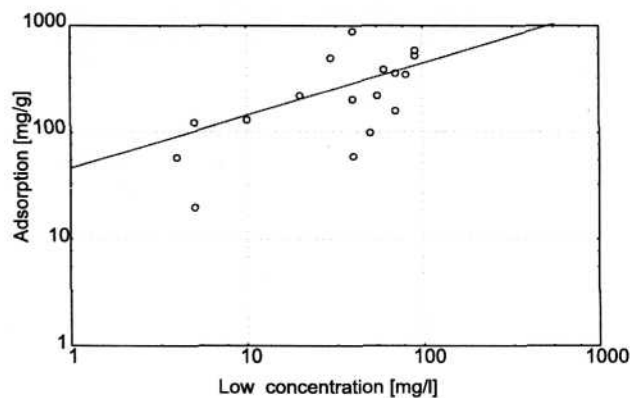


Fig. 9. The Freundlich adsorption isotherm of phenoxyacetic acid derivative on carbon NP-5:  $y = 45.958 x^{0.495}$   $R=0.600$ .

The easiest to remove from water on carbon NP-5 was acid 2,4-D, the worst to remove was MCPP. This can be explained by the presence of an additional group  $-\text{CH}_3$  in MCPP acid, its chiral properties as well as by the fact that it is a strong enantiomer R. On WD-extra and CWZ-22 carbons the acid 2,4-D was the most effectively sorbed, and MCPA was the least effectively sorbed.

Numerous experiments point out that the effectiveness of sorption depends on dissolubility of the compound, the adsorbent and the adsorbate. The behaviour of a given system can be predicted assuming that adsorption involves a distribution of the adsorbate into two phases: liquid and solid. Generally speaking there is an inversely proportional dependence between the adsorption of a given substance and its solubility in the solvent. Namely, the less soluble the substance, the more likely it is to be adsorbed.

The above remarks fully reflect the results of the experiment: the least soluble compound, i.e. acid 2,4-D had the highest capacity of sorption. Dissolubility of the compounds examined can be ordered as follows:



The exemplary values of sorption capacity of carbon NP-5 at equilibrium concentration 10 mg/l are: 2,4-D - 70 mg/g; MCPA - 2 mg/g; MCPP - 0.5 mg/g.

Similarly, substances with high molecular mass have a tendency to be stronger adsorbed than chemical compounds with low molecular mass. This rule was confirmed in our experiments. The phenoxyacid compounds examined can be ordered according to the increasing molecular weight as follows:



It is known that surface functional groups behaving as volumetric compounds take part in the adsorbate-adsorbent interaction. The chemical composition of the active carbon surface in an essential way influences its following properties: adsorption capacity, electrochemical, hydrophilic-hydrophobic, acidic-basic, oxydo-reduction, catalytic, and others. In the case of ordinary active carbons the presence of oxygen on the surface has a decisive influence on its chemical properties. The carbons examined were activated with water vapour at over 850°C, which proves that groups of alkaline character were formed on their surface. These are the so called H type carbons, which adsorb acids from water solutions. According to previous studies it is quite difficult to assess the quality of basic / alkaline functional groups of H type carbons. It is difficult to predict the kind of interaction

between the surface of H type carbons and phenoxyacetic acids. It is unquestionable, however, that these compounds are well adsorbed.

## Conclusions

1. The adsorption of herbicides derived from phenoxyacetic acids on domestic active carbons is influenced by physico-chemical properties of the adsorbent (alkaline character of the active surface, the surface area, total pore volume, the value of methylene an iodine number) and the adsorbate (the acid character of phenoxyacid compounds, the presence of aromatic ring, dissociation constant, dissolubility, molecular mass) as well as the parameters of the process conducted (active carbon mass).

2. It is indispensable to analyse the Freundlich adsorption isotherm coefficients to assess the optimum amount of the active carbon for herbicide detoxication.

3. Carbon NP-5 proved to be the best sorbent for the process of removal of phenoxyacetic acids from water.

4. On the basis of the adsorption of one phenoxyacetic compound it is justifiable to draw conclusions about the adsorption of the whole group of these acids.

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