



Removal of selected carbamate pesticides (pro sulfocarb) from aqueous solutions using sorption on WG-12 activated carbon

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ABSTRACT

This article presents a study of removing carbamate insecticides (pro sulfocarb) from aqueous solutions by adsorption on carbon sorbent WG-12. Static tests were carried out, and the author's IZO computer application performed the analysis. It is ideal for studying adsorption by generating Freundlich, Langmuir, and Brunauer–Emmett–Teller (BET) isotherm equations in classical and linear forms. In addition, the application made it possible, based on simplified equations of adsorption dynamics, to calculate the operating time of the bed. Based on the generated isotherms and the values of the coefficients R^2 and S representing the quality of the model fit to the measurement points, it can be concluded that the process of adsorption of pro sulfocarb on WG-12 carbon is best described by the BET isotherm ($R^2 = 0.98$ and $S = 5.3E-4$). According to the Gils classification, an S-type isotherm was obtained, corresponding to adsorption, where adsorbate–adsorbent interactions and adsorbate–adsorbate interactions occur. Thus, cooperative adsorption of molecules can be observed. According to Branauer's type II classification, a group of isotherms was obtained, indicating the physical adsorption of multilayers. Depending on the change in the velocity of the medium flow through the bed v_p in the range from 5 to 25 m/h and the change in the height of the adsorbent bed H_z in the range from 5 to 10 cm, calculated from the balance equation, the duration of the pro sulfocarb adsorption process varies from about 1.7 to about 17 y.

Keywords: Sorption; Pesticide; Carbamate; Pro sulfocarb; Isotherm; IZO application

1. Introduction

In recent years, more and more attention has been paid to the principles of sustainable development in various areas of life. As a result of these activities, the concept of sustainability is gradually being introduced into many fields of environmental engineering. In addition, the challenge facing environmental engineering today is solving a wide range of technical problems and integrating social, economic, and economic aspects. It also applies to the issues of water and wastewater management, including treatment technologies

water and the application of high-efficiency methods of removing micropollutants.

Among the identified micropollutants in natural waters, pesticides are a significant group [1]. It is mainly related to the widespread use of chemical pesticides in agriculture to achieve higher and better-quality yields [2,3]. Pesticides play an important role in increasing the efficiency of agricultural production by destroying weeds, fungi, mites, insects, and rodents and reducing plant diseases that attack the crops in question [4,5]. The number of plant protection products used worldwide is constantly increasing. In Poland in 2021, there are 2,543 registered preparations based on 235 active

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substances [6]. With the proliferation of pesticides, the main concern is the impact on human and animal health, and more and more attention is focused on the effects of pesticides on the environment [7,8]. Their toxicity to living organisms varies widely, depending on the organism under environmental conditions and the pesticide's type, form, application method, persistence (persistence), and bioaccumulation ability that can lead to biological multiplication of pesticides' impact through their food chain absorption [9].

This article presents a study of removing carbamate pesticides from aqueous solutions by adsorption on a carbon sorbent. The analysis was performed in the author's IZO computer application. According to Freundlich, Langmuir, and Brunauer–Emmett–Teller (BET), it is ideal for studying the adsorption process by generating adsorption isotherms in classical and linear forms. In addition, the application made it possible, based on simplified equations of adsorption dynamics, to calculate the operating time of the bed.

1.1. Isotherms and modeling of the adsorption process

Most commonly, widely used isotherm models describing experimental data - Langmuir isotherm (1918), Freundlich isotherm (1894), BET (1938) - are used to evaluate the maximum saturation capacity of the adsorbent and determine the sorption mechanism [5,6,10–12].

The most common equation used for mathematical analysis of the adsorption process on energetically heterogeneous surfaces and microporous adsorbents is the experimental equation of adsorption isotherm, according to Freundlich:

$$a = x_m \cdot C_r^{1/n} \quad (1)$$

The value of x_m parameter varies in a wide range and shows the adsorption capacity of the sorbent at equilibrium concentration in the solution. A higher value of the x_m coefficient corresponds to a higher adsorption capacity. On the other hand, the value of the n parameter allows for assessing the adsorption intensity of a given substance on activated carbon from an aqueous solution. The more intensive process of adsorption, the higher value of n . The Freundlich isotherm cannot be applied at low concentrations, where the isotherm is linear ($n = 1$). It also cannot be used at high concentrations because, according to the Freundlich equation, the amount of adsorbed substance can increase indefinitely along with the equilibrium concentration increase. But in reality, the adsorbent becomes saturated. Within the range of average equilibrium concentration values, the Freundlich isotherm allows for obtaining good results. Within this range, the course of Freundlich isotherm corresponds to Langmuir isotherm.

According to Langmuir's theory, adsorbate molecules strike the surface of the adsorbent, forming a monolayer on the surface. The molecules interact with adsorption sites, while they do not interact or weakly interact with each other-the chances of adsorption increase with the available free surface area. However, adsorbed molecules are also subject to desorption phenomena. The phenomena mentioned above are affected by several factors, the most important

of which are the magnitude of the energy and the temperature of adsorption. In addition, with increased pressure, the number of impacts of molecules on the surface increases. At the same time, with the number of adsorbed molecules, the number of vacancies on the surface of the adsorbent decreases. Under the assumptions of Langmuir theory, there is no possibility of multilayer formation, and the surface is homogeneous, that is, energetically homogeneous (there is a constancy of adsorption energy), and lateral interactions can be neglected. Langmuir's theory applies isotherm equation:

$$a = x_m \cdot \left[\frac{(K_L \cdot C_r)}{(1 + K_L \cdot C_r)} \right] \quad (2)$$

The Langmuir model is ineffective when sorbate molecules on the adsorbent surface often form a multilayer system. In 1938, Stephan Brunauer, Paul Emmett, and Edward Teller developed the monolayer adsorption model considering the possibility of additional interaction between molecules. Langmuir's theory is more applicable for chemisorption, while BET theory is more applicable for physical adsorption on a non-microporous surface. The BET isotherm can be written as:

$$a = x_m \cdot \frac{(K_B \cdot C_r)}{[(1 - C_r)(1 + K_B - 1)C_r]} \quad (3)$$

In considering practical applications, it is always necessary to determine the duration of the adsorption process in a bed filled with, for example, granular activated carbon operating in a flow (dynamic) system. In this case, certain simplifying conditions should be assumed for both the adsorbent bed and the adsorbed medium, that is, the adsorbent layer is homogeneous. It has the same porosity in each cross-section. As a result of flow and hydraulic diffusion, mass transport of the adsorbate on the surface of the bed grains occurs, and constant values of the mass penetration coefficient during the process and the amount of adsorption across the grain cross-section are assumed. Conversely, the medium is assumed to be incompressible, and the volume output is assumed to be constant over time. For such conditions, the operating time of the adsorption bed t (h) can be most simply estimated based on a simplified mass balance equation for the adsorbent layer:

$$t = x_m \times H_z \times r_n \times v_p \times \Delta C^{-1} \quad (4)$$

For the maximum saturation capacity x_m (kg/kg), the height H_z (m) and bulk density r_n (kg/m³), the difference in input and output concentration ΔC (kg/m³) and the flow velocity v_p (m/h). In the literature, one can find other equations extended based on Eq. (4) that allow calculating the duration of the adsorption process in a flow system. Nevertheless, they require knowledge of other parameters, among them external and internal mass transfer coefficient, mass penetration modulus, hydraulic diffusion coefficient, height and migration rate of the adsorption front [6,12–15].

2. Material and methods

2.1. Sorbate

On the basis of literature data and own studies, carbamate pesticides that most often occur in drinking water at the highest concentration were selected as representative sorbate [1–5]. As thiocarbamate herbicide, prosulfocarb (PSC, $(C_3H_7)_2NC(O)SCH_2C_6H_5$, S-benzyl dipropylcarbamothioate) is mainly used in winter cereals. Some vapor pressures data of PSC reported in the previous literature indicated that PSC could exist in both gas and particulate phases in the atmosphere [16]. Except for being volatile in the atmosphere, PSC could also be distributed to the different environmental media, such as water, soil and sediment. PSC exists in aqueous system and has a long half-life in water with the fugacity model [17,18]. Therefore, PSC may cause potential threat to organisms. It may be as toxic to human and animals as the molinate mentioned above and the removal of PSC is an essential problem to be figured out. Individual pure active substance prosulfocarb was applied. Technical grade prosulfocarb of $99.9\% \pm 0.2\%$ purity obtained from the Institute of Industrial Organic Chemistry in Poland was used as sorbate. A sample solution of pesticide has been prepared by dissolving 1 g of pesticide in 10 cm^3 of acetone and then diluted to 1 dm^3 with doubly distilled deionised water. The toxicological parameters of prosulfocarb are given in Table 1.

2.2. Sorbent

The sorbent is made of special low-ash coal and binder. It is designed for water treatment. Due to its high specific surface area and developed pore structure, it has high efficiency in removing organic pollutants. The surface area and the porous properties, such as the pore size, the pore volume, the porosity, and the skeletal density, are shown in Table 2. Scanning electron microscope photos of WG-12 are given in Fig. 1.

2.3. Sorption procedure

Static studies were conducted following the methodology of Chemviron Carbon (European Operations of Calgon

Carbon Corporation, Parc Industriel de Feluy, Zone C, B-7181 Feluy, Belgium) and literature data [19–24]. Based on these analyses, adsorption isotherms were plotted, making it possible to determine the sorption mechanism. After degassing, washing with distilled water and drying, the

Table 2
Characteristics of WG-12 sorbent [20]

Total surface area	m^2/g	1,000
Micropore volume	cm^3/g	0.81
Mesopore's surface area	m^2/g	54
Total pore volume	cm^3/g	0.90
Granulation	mm	0.75–1.5
Dechlorination	cm	5
Methylene blue	cm^3	30
Iodine number	mg/g	1,000
Hardness	%	95–97
Grindability	%	0.3

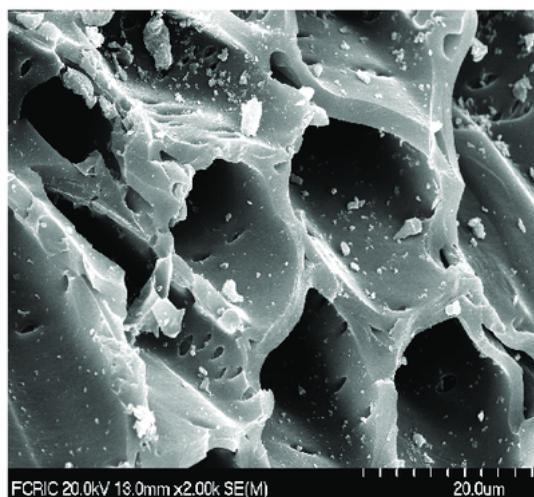


Fig. 1. Scanning electron microscope photos of WG-12.

Table 1
Toxicological parameters of prosulfocarb [19]

Active substance	Prosulfocarb
BFC (dm^3/kg)	Low limit
LD_{50} (mg/kg) mammals	5,000
LC_{50} (mg/dm^3) fish	91
DT_{50}^a (d)	38.4
$Kfoc^b$ (cm^3/g)	1,367–2,339
EC_{50}^c (mg/dm^3)	96
CT_{50} (d)	1.7

BFC – Bioaccumulation factor; LD_{50} – Lethal dose

^aSoil degradation half-life DT_{50} ; substances with $DT_{50} > 20$ are considered to be stable;

^bSoil adsorption and mobility coefficients $Kfoc$ are defined as the ratio of the active substance in the soil to the concentration of the substance in the equilibrium water phase: if $< 500 \text{ mL}/\text{g}$, substance is considered to be elutable;

^c EC_{50} – Toxicity determined as toxin effective concentration in the environment, which effects 50% of *Daphnia magna* population.

sorbent was crushed with a ball mortar and dried in an oven at 150°C for 4 h to a constant mass. From the material thus obtained, weights of 1, 1.5, 2, 4, 6, 10, and 25 mg/100 mL of solution were used. The sorbent samples were added to flasks containing a prosulfocarb solution of 5 mg/dm³. The flasks were shaken for 24 h and allowed to stand for 48 h to achieve complete sorption equilibrium.

Based on the results obtained, the adsorption process was analyzed using the author's IZO program [25] for calculating the values of adsorption isotherm coefficients and adsorption bed running time, presented in detail with free download (freeware application) on the website at [http://app.ros.edu.pl]. Based on the values of the parameters of the independent variables shown in Fig. 2 (initial concentration C_0 , equilibrium concentration C_r , mass of adsorbent m , volume of solution V), the application allows calculating the values of the parameters of the resulting variables, that is, the coefficients of adsorption isotherms according to Freundlich (1), Langmuir (2) and BET (3) theories. In addition, the program allows estimating the operating time of the adsorption bed based on Eq. (4) and other formulas found in the literature [2]. The calculation of the values of the coefficients of adsorption isotherms is realized on the method of transformation of Eqs. (1)–(3) to the form of linear functions. The Freundlich isotherm Eq. (1) is transformed to the form $\ln(a) = \ln(b_1) + b_2 \cdot \ln(C_r)$. The coefficients of isotherm (1) are calculated from the equations $x_m = \exp(b_1)$, while $n = b_2$. Linearization of the Langmuir isotherm involves transforming (2) to the form $1/a = b_1 + b_2 \cdot 1/C_r$. The coefficients of the isotherm (2) are calculated from the equations $x_m = 1/b_1$, and $K_L = b_1/b_2$. The BET isotherm (3) application also transforms to a linear function form $C_r/[a(1 - C_r)] = b_1 + b_2 \cdot C_r$. The isotherm coefficients (3) values are calculated from the equations $x_m = 1/(b_1 + b_2)$ and $K_B = 1 + b_2 \cdot 1/b_1$. The coefficients b_1 and b_2 presented in the equations of linear adsorption isotherms are calculated by least-squares approximation. The application presents the quality of fit of the approximated linear function to a set of measurement points by calculating the value of the coefficient of determination R^2 and the standard error of fit S .

2.4. Analytical procedure

Analytical studies were carried out at the Plant Protection Institute—National Research Institute using a waters liquid chromatograph apparatus and AB SCIEX mass spectrometer using validated test procedures for the determination

of pesticide residues in wastewater and plant material [26]. Chromatographic analysis (Fig. 3) was performed using an Eksigent Ultra LC-100 liquid chromatograph (Eksigent Technologies, Dublin, CA, USA) coupled to a QTRAP 6500 mass spectrometer (AB SCIEX Instruments, Foster City, CA, USA). Separation of analytes was performed on a Kinetex C18 column (100 mm × 2.1 mm, 2.6 μm) maintained at 40°C. The volume of the injected sample was 10 μL. The mobile phase was 0.5% formic acid solution with 2 mmol ammonium formate in water (phase A) and in methanol (phase B). Analysis was carried out using gradient elution, with the following program: 0–1 min 1% phase B; 1–13 min 1% to 90% phase B; 13–23 min 90% phase B; 23–25 min 90% to 1% B; and 25–30 min 1% phase B. Detection was carried out using electrospray ionization in the positive ion formation mode characterized by the following parameters: voltage applied to the electrode (IS) 5,000 V; ion source temperature 400°C; sputtering assist gas pressure 60 psi; auxiliary gas 50 psi; and shielding gas 30 psi. Nitrogen was used as sputtering gas, auxiliary gas and shielding gas. The optimized parameters of instrumental analysis in the mode of monitoring multiple fragmentation reactions in parallel (MRM) for prosulfocarb are given in Tables 3 and 4. To ensure the reliability of the results, validation was carried out based on

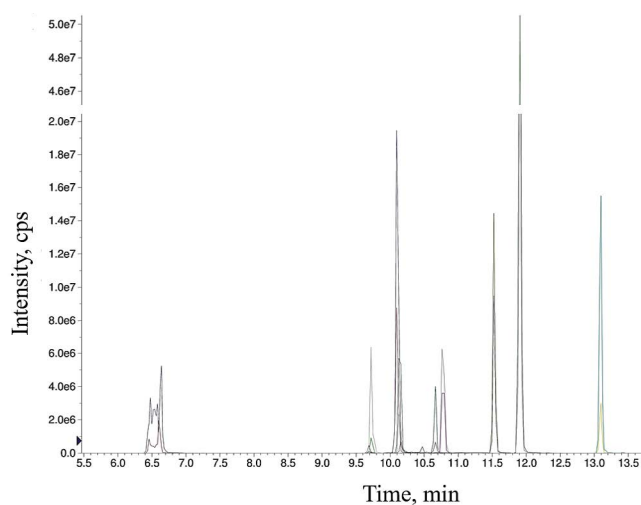


Fig. 3. Chromatogram of a mixture of standards with a concentration of 0.50 mg/dm³.

Input data table					
Initial concentration C_0 [mg/L]	Equilibrium concentration C_r [mg/L]	Adsorbent mass m [g]	Volume of solution V [L]	Concentration difference x [mg/L]	Adsorption capacity a [mg/g]
5.000E+000	8.102E-001	1.000E-003	1.000E-001	4.190E+000	4.190E+002
5.000E+000	7.522E-001	1.500E-003	1.000E-001	4.248E+000	2.832E+002
5.000E+000	6.548E-001	2.000E-003	1.000E-001	4.345E+000	2.173E+002
5.000E+000	4.457E-001	4.000E-003	1.000E-001	4.554E+000	1.139E+002
5.000E+000	2.916E-001	6.000E-003	1.000E-001	4.708E+000	7.847E+001
5.000E+000	1.681E-001	1.000E-002	1.000E-001	4.832E+000	4.832E+001
5.000E+000	3.230E-002	2.500E-002	1.000E-001	4.968E+000	1.987E+001

Fig. 2. IZO application – layout of the table of values of independent and outcome variables.

Table 3
Optimized LC-MS/MS system operating parameters for prosulfocarb

Retention time (min)	Quantitative/qualitative determination				
	Fragmentation reaction (m/z)	CE (V)	CXP (V)	DP (V)	EP (V)
11.55	252.1 > 91	35	10	66	10
	Qualitative determination				
	Fragmentation reaction (m/z)	CE (V)	CXP (V)		
	252.1 > 128.1	17	6		

DP – Declustering potential; EP – Entrance potential; CE – Collision energy; CXP – Collision cell exit potential

Table 4
Validation parameters of the method

Validation parameters	Coefficient of determination R^2	
0.001	Recovery	97
	Relative standard deviation	10
0.05	Recovery	96
	Relative standard deviation	6
0.5	Recovery	99
	Relative standard deviation	6
10	Recovery	102
	Relative standard deviation	13
100	Recovery	104
	Relative standard deviation	5
Extended measurement uncertainty		13
Matrix effect		12

the SANTE/11945/2015 guide. During the validation process, parameters such as linearity, recovery, precision, limit of detection (LOD), limit of quantification (LOQ), matrix effect and expanded uncertainty of the method (U) were determined. Precision calculated as relative standard deviation was less than 22%. The effluent and plant matrix effects for most compounds did not significantly affect the attenuation or amplification of signals.

In the analyzed concentration range (0.0001–0.30 mg/dm³), satisfactory linearity of the method was achieved with a

determination coefficient of $R^2 > 0.99$. The LOQ was set equal to 0.001 mg/dm³, and the LOD was set at 0.00003 mg/dm³. The expanded measurement uncertainty averaged between 8% and 22%.

3. Results and discussion

3.1. Static sorption

The results of the static adsorption process of prosulfocarb on the carbon sorbent are shown in Table 5 and Figs. 4 & 5.

The values shown in Fig. 4 were entered into the IZO application - Fig. 2. The program calculated the values of the coefficients of linear and classical adsorption isotherm equations according to Freundlich (1), Langmuir (2), and BET (3) and generated graphs (Fig. 5). In addition, the application presented the quality of the model fit to the measurement points by deriving the values of the coefficient of determination R^2 and the standard error of fit S (Table 5).

Fig. 5 shows the adsorption isotherms of prosulfocarb on the carbon sorbent used as a function of the adsorbed by unit mass of the adsorbent from the equilibrium concentration of the adsorbate (prosulfocarb) in aqueous solution. Based on the plotted isotherms and the coefficients R^2 and S values, it can be concluded that the process of prosulfocarb sorption on WG-12 carbon is best described by the BET isotherm ($R^2 = 0.98$). According to the Gils classification type S , an isotherm was obtained, corresponding to adsorption, where adsorbate–adsorbent interactions take place and

Table 5
Values of linear coefficients and classical adsorption isotherms of prosulfocarb according to Freundlich, Langmuir, and Brunauer–Emmett–Teller for WG-12 carbon and quality of approximation

Isotherm	Equation					
	Linear			Classical		
	Coefficient	Value	R^2	S	Coefficient	Value
Freundlich	b_1	5.76	0.91	3.4E-1	k	317.4
	b_2	8.918E-1			n	1.121
Langmuir	b_1	4.586E-3	0.95	4.3E-3	x_m	218.1
	b_2	1.520E-3			K_L	3.016
Brunauer–Emmett–Teller	b_1	1.906E-3	0.98	5.3E-4	x_m	77.95
	b_2	1.092E-2			K_B	6.732

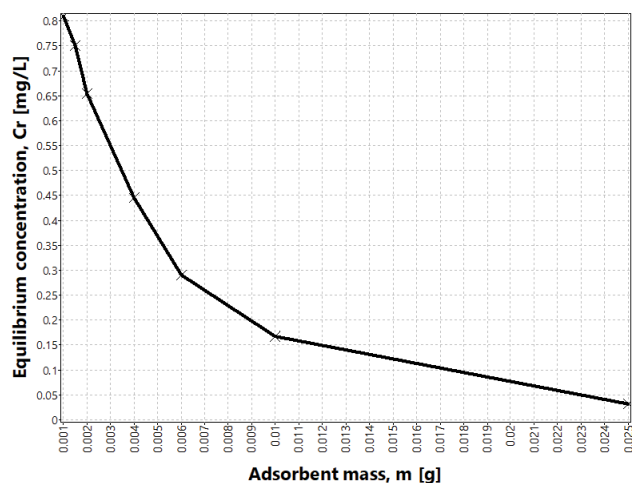


Fig. 4. IZO application - effect of changing the adsorbent dose m (g) on the change in the value of equilibrium concentration C_e (mg/dm^3) in the process of static adsorption of prosulfocarb using WG-12 adsorbent.

adsorbate–adsorbate interactions. Thus, we can observe the cooperative adsorption of molecules. According to Branauer's type II classification, a group of isotherms was obtained, indicating the physical adsorption of multilayers. According to this theory, an adsorbate particle hitting an occupied site does not leave it immediately. A short-lived adsorption complex is formed. Increasing pressure reduces the number of active sites occupied by a single adsorbate molecule as double, triple adsorption complexes are formed [27–30].

Piekarski et al. [20] studied an adsorption process of aldrin on selected materials including waste and carbon. The research used three sorbents: two activated carbons NP and WG-12 and compost from sewage sludge as a low-cost sorbent. The adsorption process of aldrin on NP5, WG-12 activated carbons, and compost is similarly described by the Freundlich, Langmuir, and BET isotherms. The investigated adsorbents are characterized by a heterogeneous surface, and reactions occur in monolayer during adsorption along with additional interactions. That results in the multilayer adsorption effect. One group of isotherms was obtained according to the Giles classification: L. This group includes isotherms of systems in which there is no high competitive interaction of solvent particles when the adsorbate populates active sites on the surface. In such a case, the planar arrangement of the aromatic ring of particles fills functional areas of the adsorbent. At the same time, the highest sorption capacity of the adsorbent at the equilibrium concentration was observed for WG-12 active carbon, for which the adsorbate concentration in the adsorbent monolayer, based on the BET isotherm, was approximately $x_m = 636.3$ g/kg.

Alcione Aparecida de Almeida Alvesa studied the kinetics, equilibrium, and thermodynamic parameters of the adsorption of the pesticides carbaryl, methomyl, and carbofuran on activated carbon. In this case, the Langmuir–Freundlich isotherm model most accurately described the adsorption kinetics [31]. Satisfactory results for the removal of the pesticide carbofuran on carbon derived from rice straw agricultural waste were obtained by Salman and Al-Saad

[32]. Similar results were obtained by Salman et al. [33], who studied the sorption of insecticide carbofuran from an aqueous solution onto activated carbon derived from palm oil fronds. The mechanism of the prosulfocarb degradation process was also studied by Bo et al. [34]. Ozimek and Dąbrowski [35] studied the removal of pesticides and polychlorinated biphenyls from municipal wastewater by reed beds in a constructed wetland.

3.2. Dynamic sorption modeling

The adsorption dynamics, in mathematical terms, uses the equations of sorption statics and kinetics, as well as the mass balance of the adsorbate. While the statics of adsorption are represented by simple adsorption isotherms, concerning adsorption kinetics, complicated equations of the flow of the medium outside the adsorbent molecule and saturation equations of the activated carbon molecule are used. Therefore, a good solution is to use approximate equations of adsorption dynamics, which relate to the temporal-spatial distribution of adsorbate in the adsorbent bed. In this case, the independent variable parameters relate to the adsorbent (diameter, grain porosity, porosity, and bulk density) and the adsorptive (initial and assumed final concentration, temperature, and flow rate). In turn, the most critical parameters of the resulting variables are mass transfer coefficients, the adsorption front's height and migration rate, and the adsorption bed's operating time [15].

Based on the best fit expressed by the values of the coefficient of determination $R^2 = 0.98$ and the standard error of fit $S = 5.3E-4$ (Table 5), the BET isotherm was used to calculate the duration of the adsorption process. The adsorbate concentration in the adsorbent layer was assumed to be $x_m = 77.95$ g/kg. The bulk density of the WG-12 carbon bed is $\rho_n = 476$ kg/m³. It was also assumed that prosulfocarb is completely retained in the bed, that is, its concentration is reduced from $C_0 = 5$ mg/m³ (the concentration found in surface water $C_0 = 5$ $\mu\text{g}/\text{dm}^3$) to a value of $C_e = 0$ mg/m³. Depending on the change in the velocity of the medium flow through the bed v_p in the range from 5 to 25 m/h and the change in the height of the adsorbent bed H_c in the range from 5 to 10 cm, using the transformed mass balance Eq. (4), the calculated duration of the prosulfocarb adsorption process varies from about 1.7 y to about 17 y (Fig. 6).

4. Summary

This paper presents a study on applying a carbamate pesticide (prosulfocarb) adsorption process on carbon sorbent WG-12. Static tests were carried out, and the author's IZO computer application performed the analysis. According to Freundlich, Langmuir, and BET in classical and linear forms, it is ideal for studying the adsorption process by generating adsorption isotherms. In addition, the application made it possible, based on simplified equations of adsorption dynamics, to calculate the operating time of the bed. Based on the plotted isotherms and the coefficients R^2 and S values, it can be concluded that the process of prosulfocarb sorption on WG-12 carbon is best described by the BET isotherm ($R^2 = 0.98$). According to the Giles classification, an S-type isotherm was obtained, which corresponds to

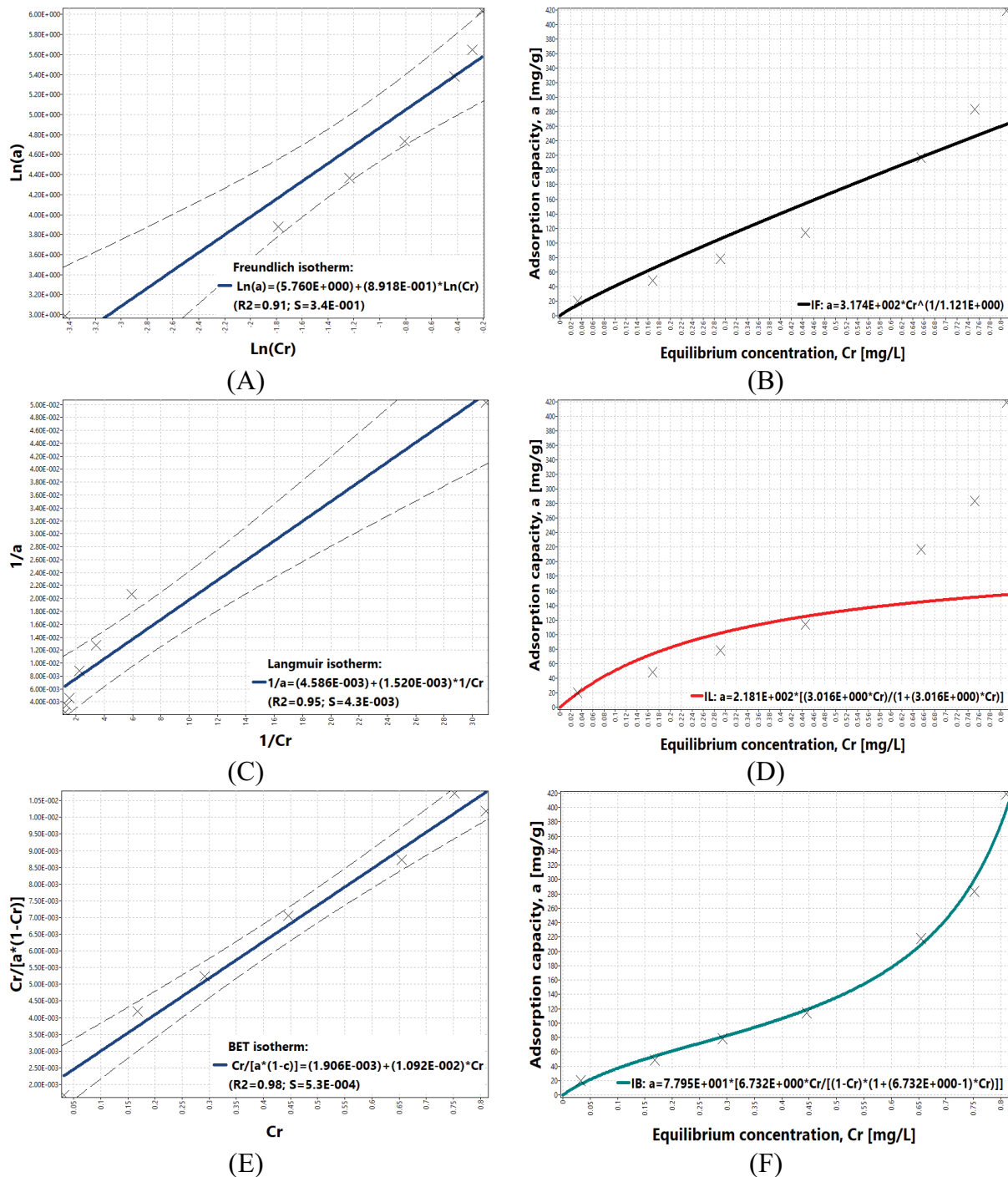


Fig. 5. IZO application - prosulfocarb adsorption isotherms according to Freundlich (linear A, classical B) and Langmuir (linear C, classical D) and Brunauer–Emmett–Teller (linear E, classical F) for WG-12 carbon.

adsorption in which adsorbate–adsorbent interactions take place and adsorbate–adsorbate interactions. Thus, we can observe the cooperative adsorption of molecules. According to Brunauer’s type II classification, a group of isotherms was obtained, indicating the physical adsorption of multilayers. The duration of the prosulfocarb adsorption process varies from about 1.7 to about 17 y depending on the variation of the selected parameters of the independent variables,

that is, the flow velocity v_p in the range of 5 to 25 m/h and the height of the activated carbon bed H_z in the range of 5 to 10 cm. Based on the estimated operating time of the bed and the assumed removal efficiency of the selected pesticide, it can be concluded that the selected activated carbon can provide a protective barrier to pesticide migration. However, in the future, for economic reasons, new cheaper adsorbents made from waste materials should be sought.

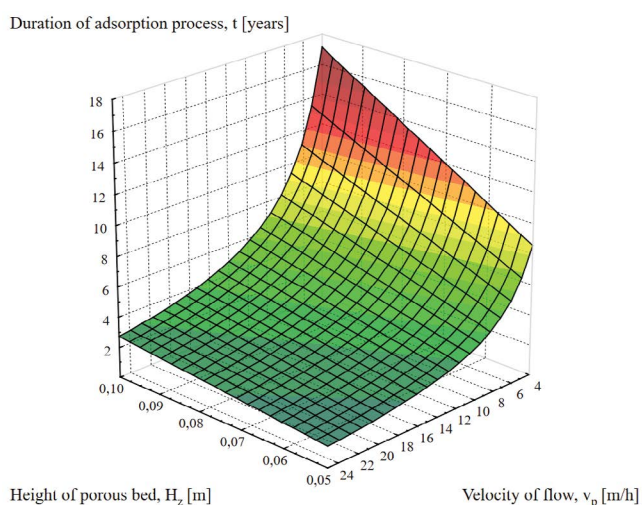


Fig. 6. IZO application - change in the duration of prosulfocarb adsorption process t (y) on WG-12 bed depending on the change in its height H_z (m) and the value of flow velocity v_p (m/h).

Symbols

a	—	Adsorption capacity, mg/g
b_1, b_2	—	Adsorption isotherm coefficients, —
BFC	—	Bioaccumulation factor, dm/kg ³
CE	—	Collision energy, V
C_0	—	Initial concentration, mg/dm ³
C_r	—	Equilibrium concentration, mg/dm ³
CXP	—	Collision cell exit potential, V
DT ₅₀	—	Half-life, d
DP	—	Declustering potential, V
EC ₅₀	—	Effective concentration, mg/dm ³
EP	—	Entrance potential, V
H_z	—	Height of porous, m
K_B	—	Adsorption isotherm coefficient according to Brunauer–Emmett–Teller, —
Kfoc	—	Soil adsorption and mobility coefficient, cm/g ³
K_L	—	Coefficient of adsorption isotherm according to Langmuir, —
LD ₅₀	—	Lethal dose, mg/kg
LC	—	Lethal concentration, mg/dm ³
m	—	Adsorbent mass, g
n	—	Coefficient of adsorption isotherm according to Freundlich, —
R^2	—	Coefficient of determination, —
S	—	Standard error of fit, —
t	—	Duration of the adsorption process, h
V	—	Volume of solution, dm ³
v_p	—	Velocity of flow, m/h
x	—	Concentration difference, mg/dm ³
x_m	—	Maximum saturation capacity, kg/kg
ΔC	—	Difference in input and output concentrations, kg/m ³
r_n	—	Bulk density, kg/m ³

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References

- [1] K. Ignatowicz, Sorption process for migration reduction of pesticides from graveyards, Arch. Environ. Prot., 34 (2008) 143–149.
- [2] K. Ignatowicz, Metals content chosen for environmental component monitoring in graveyards, Fresenius Environ. Bull., 20 (2011) 270–273.
- [3] K. Ignatowicz, Occurrence study of agro-chemical pollutants in waters of Suprasl catchment, Arch. Environ. Prot., 35 (2009) 69–77.
- [4] K. Ignatowicz, Pesticide waste burials in the area of Podlaskie Province, Rocznik Ochrona Środowiska, 10 (2008) 545–555.
- [5] A. Derylo-Marczewska, M. Blachnio, A.W. Marczewski, M. Seczkowska, B. Tarasiuk, Phenoxycarb pesticide adsorption on activated carbon – equilibrium and kinetics, Chemosphere, 214 (2019) 349–360.
- [6] K. Ignatowicz, Hexachlorocyclohexane (HCH) isomers adsorption from water solution using natural sorbent, Desal. Water Treat., 134 (2018) 1420–1428.
- [7] A. Ascherio, H. Chen, M.G. Weisskopf, E. O'Reilly, M.L. McCullough, E.E. Calle, M.A. Schwarzschild, M.J. Thun, Pesticide exposure and risk for Parkinson's disease, Ann. Neurol., 60 (2006) 197–203.
- [8] S.M. Bradberry, S.A. Cage, A.T. Proudfoot, J.A. Vale, Poisoning due to pyrethroids, Toxicol. Rev., 24 (2005) 93–106.
- [9] M.S. Akash, S.D. Supowit, R.U. Halden, Fate of Neonicotinoid Pesticides During Wastewater and Wetland Treatment, Assessing Transformation Products of Chemicals by Non-Target and Suspect Screening – Strategies and Workflows, 1 (2016) 121–131.
- [10] K.-L. Chang, J.-H. Lin, S.-T. Chen, Adsorption studies on the removal of pesticides (carbofuran) using activated carbon from rice straw agricultural waste, World Acad. Sci. Eng. Technol., Int. J. Agric. Biosyst. Eng., 5 (2011) 210–213.
- [11] J. Choma, M. Jaroniec, E.A. Ustinov, Adsorptive characterization of activated carbons with highly developed porosity, Ochrona Środowiska, 26 (2004) 3–7.
- [12] K. Ignatowicz, J. Piekarski, I. Skoczko, J. Piekutin, Analysis of simplified equations of adsorption dynamics of HCH, Desal. Water Treat., 57 (2016) 1420–1428.
- [13] K. Ignatowicz, Selection of sorbent for removing pesticides during water treatment, J. Hazard. Mater., 169 (2009) 953–957.
- [14] K. Kuśmierk, K. Bieniek, L. Dąbek, A. Świątkowski, Adsorption of halogenophenols from aqueous solutions on activated carbon, Rocznik Ochrona Środowiska, 19 (2017) 355–369.
- [15] J. Piekarski, Numeric Modelling of Filtration and Sorption Process, Monografia, Wydawnictwo Politechniki Koszalińskiej, 2009.
- [16] A. Muñoz, E.M. Borrás, T. Ródenas, H.A. Vera, Pedersen atmospheric oxidation of a thiocarbamate herbicide used in winter cereals, Environ. Sci. Technol., 52 (2018) 9136–9144.
- [17] V.C. Cysneiros, A.L. Pelissari, S.A. Machado, A. Figueiredo-Filho, H.C. David, Cluster and discriminant analyses for stem volume modelling of tree species groups in an amazon rainforest, J. Trop. For. Sci., 29 (2017) 325–333.
- [18] S. Ahmet, M. Soylak, Equilibrium and thermodynamic studies of stearic acid adsorption on Celtek clay, J. Serb. Chem. Soc., 72 (2007) 485–494.
- [19] <https://pubchem.ncbi.nlm.nih.gov/compound/Prosulfocarb>
- [20] J. Piekarski, K. Ignatowicz, T. Dąbrowski, Application of an adsorption process on selected materials, including waste as a barrier to the pesticide penetration into the environment, Materials, 15 (2022) 4680, doi: 10.3390/ma15134680.
- [21] J.A. Rodríguez-Liébana, A. Peña, Differences in the sorption kinetics of various non-ionisable pesticides in a limited number of agricultural soils from the Mediterranean Basin, J. Environ. Manage., 276 (2020) 111336, doi: 10.1016/j.jenvman.2020.111336.

- [22] J. Piekarski, T. Dąbrowski, K. Ignatowicz, Effect of bed height on efficiency of adsorption of odors from sewage sludge using modified biochars from organic waste materials as an adsorbent, *Desal. Water Treat.*, 218 (2021) 252–259.
- [23] A.M. Hassan, M. Abed El-Moteleb, M.A. Ismael, Removal of lindane and malathion from wastewater by activated carbon prepared from apricot stone, *Assiut Univ. Bull. Environ.*, 12 (2009) 56–62.
- [24] J.S. Chin-Pampillo, M. Masis-Mora, K. Ruiz-Hidalgo, E. Carazo-Rojas, C.E. Rodríguez-Rodríguez, Removal of carbofuran is not affected by co-application of chlorpyrifos in a coconut fiber/compost based biomixture after aging or pre-exposure, *J. Environ. Sci.*, 46 (2016) 182–189.
- [25] J. Piekarski, K. Ignatowicz, T. Dąbrowski, Analysis of selected methods use for calculation of the coefficients of adsorption isotherms and simplified equations of adsorption dynamics with the use of IZO application, *Materials*, 14 (2021) 4192, doi: 10.3390/ma14154192.
- [26] K. Ignatowicz, J. Łozowicki, B. Łozowicka, J. Piekarski, Treatment of agricultural wastewater containing pesticides by hydrophytic method as a preliminary method of water recovery, *Energies*, 16 (2023) 660, doi: 10.3390/en16020660.
- [27] N. Narayanan, S. Gupta, V.T. Gajbhiye, K.M. Manjaiah, Optimization of isotherm models for pesticide sorption on biopolymer-nanoclay composite by error analysis, *Chemosphere*, 173 (2017) 502–511.
- [28] R. Kodešová, M. Kočárek, V. Kodeš, O. Drábek, J. Kozák, K. Hejtmánková, Pesticide adsorption in relation to soil properties and soil type distribution in regional scale, *J. Hazard. Mater.*, 186 (2011) 540–550.
- [29] J.M. Salman, Batch study for insecticide carbofuran adsorption onto palm-oil-fronds-activated carbon, *J. Chem.*, 2013 (2012), doi: 10.1155/2013/630371.
- [30] Kogut, J. Piekarski, K. Ignatowicz, Start-up of biogas plant with inoculating sludge application, *Rocznik Ochrona Środowiska*, 16 (2014) 534–545.
- [31] A.A. de Almeida Alvesa, A. Dervanoski da Luz, A.R. Müller Tones, T. Campos Martins Nonato, G.L. de Oliveira Ruiz, M.L. Sens, Removal of carbamate insecticides from drinking water through a fixed bed column of granular activated carbon: a thermodynamic, kinetic and equilibrium study of multicomponent adsorption, *Desal. Water Treat.*, 108 (2018) 171–182.
- [32] J.M. Salman, K. Al-Saad, Batch study for herbicide bentazon adsorption onto palm oil fronds activated carbon, *Int. J. Chem. Sci.*, 10 (2012) 731–740.
- [33] J.M. Salman, F.M. Fabid, A.A. Muhammed Adsorption of carbofuran insecticide from aqueous solution using commercial activated carbon, *Int. J. Chem. Sci.*, 9 (2011) 557–564.
- [34] X. Bo, J. Sun, Q. Mei, B. Wei, Z. An, D. Han, Z. Li, J. Xie, J. Zhan, M. He, Degradation of prosulfocarb by hydroxyl radicals in gas and aqueous phase: mechanisms, kinetics and toxicity, *Ecotoxicol. Environ. Saf.*, 191 (2020) 110175, doi: 10.1016/j.ecoenv.2020.110175.
- [35] T. Ozimek, W. Dąbrowski, Removal of pesticides and polychlorinated biphenyls from municipal wastewater by reed beds in a constructed wetland, *J. Life Sci.*, 8 (2014) 563–569.