

Application of selected carbamate pesticides from aqueous solution using coconut sorbents

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ABSTRACT

This paper presents a study of the removal of carbamate insecticides (pirimicarb) from aqueous solutions by adsorption on coconut sorbent. Static studies were carried out and the analysis was performed on the author's computer application IZO (<http://app.ros.edu.pl>), which is an ideal solution for studying the adsorption process by generating adsorption isotherms according to Freundlich, Langmuir and Brunauer–Emmett–Teller in classical and linear forms. Moreover, the application allowed calculation of the working time of the adsorption bed based on simplified adsorption dynamics equations. Based on the isotherms plotted and the values of R^2 and S coefficients, it can be concluded that the process of pirimicarb sorption on coconut coal is best described by Langmuir ($R^2 = 1$) and Freundlich ($R^2 = 0.99$) isotherms. A group of isotherms according to Giles classification type L was obtained. Depending on the variation of the medium flow rate through the bed v_p in the range of 5–25 m/h and the variation of the height of the adsorbent bed H_z in the range of 5–10 cm, the calculated duration of the pirimicarb adsorption process varies from 6 to 56 y.

Keywords: Sorption; Pesticide; Carbamate; Isotherm; IZO app

1. Introduction

Among the identified pollutants present in waters, pesticides constitute a significant group. This is mainly associated with the extensive use of chemical plant protection products in agriculture to produce more abundant and better-quality crops [1–3]. Pesticides play an important role in increasing the quality and efficiency of agricultural production by destroying weeds, fungi, mites, insects and rodents and reducing plant diseases that attack the crops [4,5]. The number of plant protection products used in the world is constantly increasing. In Poland, in 2021, 2543 preparations are registered, based on 235 active substances. In 2009, Directive 2009/128/EC on the sustainable use of pesticides was adopted aiming to reduce environmental and health risks while maintaining crop productivity

and improving control of pesticide use and distribution. The 20 May 2020 report on the implementation of the Directive showed that although the Member States had made progress in implementing the Directive, only less than a third of them had completed the review of their National Action Plans by the regulatory deadline. Most of the countries that have reviewed their NAPs have failed to address the deficiencies identified by the Commission. As part of the European Green Deal, and in particular the Farm-to-Fork and Biodiversity Strategies, the Commission will take action to reduce the use of chemical pesticides and their risks by 50% by 2030, including the use of more dangerous pesticides.

In addition to the benefits, the use of pesticides is also associated with many adverse effects. The toxicity of

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pesticides to living organisms varies widely, depending on the organism itself and the type, form and manner of application of the pesticide, persistence (persistence), bio-accumulation ability that can lead to biological multiplication of the effects of pesticides by their absorption through the food chain. Residues of plant protection products are found in crops and animals, soil and water, as well as in the human body. Special attention should be paid to the problem of protecting waters from pesticide contamination. The occurrence of pesticides has been found in all types of water circulating in the ecosystem – surface and groundwater and precipitation [6–9]. The presence of such a large number of pesticide contaminants in water makes the search for more and more effective and economical methods of their disposal. One of the methods used to remove pesticides from water is sorption.

This paper presents a study of the removal of carbamate insecticides from aqueous solutions by adsorption on coconut sorbent. The analysis was carried out in the author's computer application IZO, which is an ideal solution for studying the adsorption process by generating adsorption isotherms according to Freundlich, Langmuir and Brunauer–Emmett–Teller (BET) in classical and linear forms. Moreover, the application enabled the calculation of working time of the bed based on simplified equations of adsorption dynamics.

2. Isotherms and modelling of the adsorption process

To evaluate the maximum saturation capacity of an adsorbent and to determine the sorption mechanism, the most commonly used isotherm models describing the experimental data – isotherm Langmuir (1918), Freundlich (1894), BET (1938) [9–13].

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

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

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 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 [14,15]. But in reality, adsorbent becomes saturated. Within the range of average values of equilibrium concentration, the Freundlich isotherm allows obtaining good results. Within this range, the course of Freundlich isotherm corresponds to Langmuir isotherm.

Langmuir isotherm is the basic isotherm of adsorption. It assumes that the adsorbate can form a so-called monolayer of molecules on the surface of the adsorbent, interacting with adsorption sites (“vertical” interactions) and not interacting (or weakly interacting) with each other (“horizontal” interactions). The adsorbate molecules present in the liquid phase impinge on the surface – the probability of their adsorption increases with the available free surface area. The adsorbed molecules have a certain probability of desorption. Both probabilities depend on the temperature and the magnitude of the adsorption energy. As the pressure increases, the frequency of particles hitting the surface increases, and the available surface area decreases with the amount of adsorbed particles [7,14,16]. The assumptions of the equation include: impossibility of multilayer formation, constancy of adsorption energy (energetically homogeneous surface, that is, homogeneous), and negligibility of lateral interactions. Langmuir theory applies isotherm equation in the form:

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

The sorbate molecules often form a multilayer system, hence the Langmuir model loses validity. In 1938, Stephan Brunauer Paul Emmett and Edward Teller developed the model taking into account the possibility of additional interactions between molecules [17,18]. The Langmuir isotherm is more applicable for chemisorption, while the BET isotherm is more applicable for physical sorption on a non-microporous surface. The BET isotherm can be written as:

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

When considering the modeling of the adsorption process on granular activated carbon, some simplifying assumptions are made. The flowing medium is incompressible, the volume flux is constant in time, while the bed is homogeneous and has the same porosity value in each cross section. Moreover, the mass penetration coefficient during the process is constant, the adsorption volume across the grain cross-section is the same, the mass transport of adsorbate along the bed is realized by flow and hydraulic diffusion [10,14,19].

The running time of the adsorption bed can be calculated based on the developed mass balance equation for an adsorbent layer with height H_z (m) and bulk density ρ_n (kg/m³), difference of input and output concentration ΔC (kg/m³) and flow velocity v_p (m/h):

$$t_s = x_m \cdot \rho_n \cdot \frac{H_z}{(v_p \cdot \Delta C)} \quad (4)$$

In literature, one can find simplified equation according to Zuchowicki, Zabezinski and Tikhonov (ZZT) or according to Bohart–Adams (BA) equation [10,14,20].

The relation according to ZZT follows from the equation of kinetics of non-stationary external diffusion for the

adsorption system described by the Langmuir equation and is expressed by the formula [7,10,14]:

$$t_s = x_m \cdot \rho_n \cdot (v_p \cdot C_0)^{-1} \left\{ H_z - v_p \cdot k_e^{-1} [\ln(C_0 \cdot C_e) - 1] \right\} \quad (5)$$

In this equation, the value of the external mass transfer coefficient k_e (s^{-1}) is calculated from the value of the averaged diffusion coefficient D (m^2/s), the layer porosity ε_w (–) and the average adsorbent grain diameter d (mm).

Equation according to BA (6) similarly to Eq. (5) relates to the adsorption isotherm only through the value of adsorbate concentration in the monolayer x_m [7,10,14]:

$$t_s = x_m \cdot \rho_n \cdot (v_p \cdot C_0)^{-1} \left\{ H_z - v_p \cdot k_e^{-1} [\ln(C_0 \cdot C_e - 1) + \ln(C_0 \cdot C_e) - 1] \right\} \quad (6)$$

3. Material and methods

3.1. Sorbate

Based on literature data and our own studies, carbamate insecticides, which are most commonly found in drinking water at the highest concentrations, were selected as representative sorbates. [1–5,16,19,21,22] It is a systemic insecticide with contact, stomach and respiratory effects. It is used selectively against aphids in agriculture and horticulture. The LD₅₀ for mammals is 150 mg/kg. The individual pure active ingredient pirimicarb was used. Technical pirimicarb of 99.9% ± 0.2% purity obtained from the Analytical Department of the Institute of Industrial Organic Chemistry in Poland was used as sorbate. The sample solution of the insecticide was prepared by dissolving 1 g of the pesticide in 10 cm³ of acetone and then diluted to a volume of 1 dm³ with double distilled deionized water.

3.2. Sorbent

The sorbent was produced from waste materials – coconut shells by steam activation and seeding of appropriate grain class of activated carbon (Fig. 1). It is a high grade sorbent characterized by high specific surface area. The BET surface area, porous properties such as pore size, pore volume, porosity and skeletal density are shown in Table 1. The porosity, total pore volume, average pore diameter and surface area of the sorbent samples are measured by nitrogen adsorption isotherm at 77 K. The samples are first treated for possible degassing at 473 K for 3 h. The surface area is determined by the BET method from the N₂ adsorption isotherm data.

3.3. Sorption procedure

The studies under static conditions were conducted according to the methodology of the American company Chemviron Carbon and literature data [7,10,11,14,23–25]. They were aimed at plotting adsorption isotherms, thanks to which it is possible to determine the mechanism of sorption, determine the sorption capacity under given conditions. The sorbent, after degassing, washing with distilled water and drying, was crushed with a ball mortar and dried in

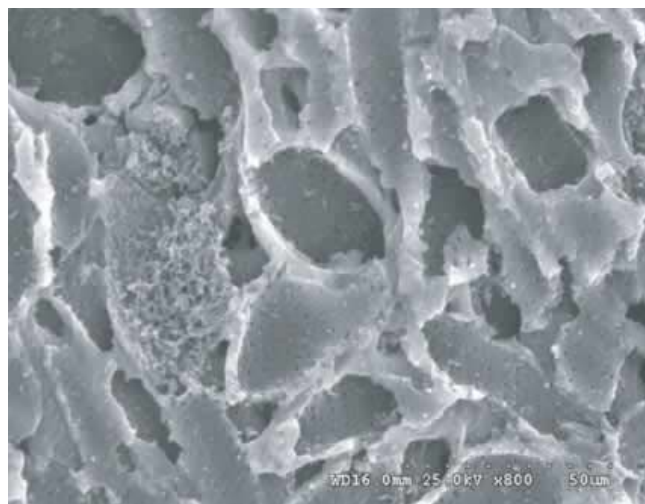


Fig. 1. Scanning electron microscope photos of coconut sorbent.

Table 1
Porous properties of coconut sorbent

BET surface area, m ² /g	1,840
Total surface area, m ² /g	1,360
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	0.75–1.2
Dechlorination, cm	5–8
Methylene blue, cm ³	40 min
Iodine number, mg/g	1,390
Hardness, %	95–97
Grindability, %	0.3

an electric dryer at 150°C for 3 h to a constant mass. From the material thus obtained, weights of 0.003, 0.004, 0.005, 0.007, 0.01, 0.015, 0.025 and 0.050 g were prepared for each 100 cm³ of solution. The prepared sorbent samples were added to conical flasks containing 5 mg/dm³ pesticide solution. The vessels were shaken on a shaker at a constant amplitude of vibration for a period of 24 h, after which they were left for 48 h to obtain full sorption equilibrium. After this time, the samples were subjected to double filtration using soft tissue filters. The first and last portions of the filtrate were discarded. The concentration of contaminants in the filtrate was then determined according to current methodology.

The analysis of the adsorption process was performed on the basis of the obtained results using the IZO program [14]. The application consists of two modules, enabling calculation of coefficients and modeling of adsorption isotherms according to Freundlich, Langmuir and BET on the basis of measured data and calculation of adsorption bed working time based on formulas found in the literature [7,9–13]. The program calculates the coefficient values of adsorption isotherms using the linearization method. In the case of Freundlich isotherm, the transformation of

the graph $a = x_m \cdot C_r^n$ to the form $\ln(a) = \ln(b_1) + b_2 \cdot \ln(C_r)$ is performed. Hence, the coefficient values $x_m = \text{Exp}(b_1)$, while $n = b_2$. Linearization of the Langmuir isotherm $a = x_m \cdot [(K_L \cdot C_r) / (1 + K_L \cdot C_r)]$ involves transformation to the form $a^{-1} = b_1 + b_2 \cdot C_r^{-1}$, whence the values of the coefficients $x_m = b_1^{-1}$, while $K_L = b_1 \cdot b_2^{-1}$. BET isotherm of the form $a = x_m \cdot (K_B \cdot C_r) \cdot [(1 - C_r) \cdot (1 + (K_B - 1) \cdot C_r)]^{-1}$ the program transforms to the form $C_r \cdot [a \cdot (1 - C_r)]^{-1} = b_1 + b_2 \cdot C_r$, hence the values of the coefficients $x_m = (b_1 + b_2)^{-1}$ and $K_B = 1 + b_2 \cdot b_1^{-1}$. The coefficients b_1 and b_2 are calculated by linear approximation using the method of least squares. The program uses Lazarus add-on modules to calculate the quality of the least squares approximation, deriving values for the coefficient of determination R^2 and the standard error of the fit S . The coefficient of determination R^2 is defined as the quotient of the sum of the squares of the deviations and the sum of the squares of the errors, describing the extent to which the variation in the data is explained by the fitted curve. The value of R^2 ranges from 0 to 1, with an increase in value to 1 indicating a better fit.

3.4. Analytical procedure

Pirimicarb concentrations was determined in collected samples in accordance with obligatory methodology using gas chromatograph AGILENT equipped with ECD and NPD detector. The injector temperature was 210°C and the flow rate of helium was 1.0 cm³/min. The column DB (35 m length·0.32 mm i.d.·0.5 mm film thickness) temperature was set at 120°C for 2 min and increased at a rate of 13°C/min to 190°C. The temperature was finally increased to 295°C and maintained isothermally for 20 min [1,3,7,10,11,26,27].

In order to maintain credibility of the results, validation based on the SANTE/11945/2015 transmitter was conducted. During the validation process the following parameters were determined: linearity, recovery, precision, limit of detection (LOD), limit of quantification (LOQ), matrix effect (ME) and uncertainty (U). The applied method ensured satisfying recovery (R) for all isomers within 92%–99% range. Precision calculated as relative standard deviation (RSD) was below 22%. For the majority of compounds, the matrix effect did not have a substantial impact on decreasing or increasing the signals and was within –13% and 12% range. In the analyzed concentration range, a satisfactory linearity of the $R^2 > 0,999$ correlation coefficient method was obtained. LOQ was determined at 0.1 µg/L, whereas LOD was established at 0.03 µg/L. The extended uncertainty of measurements was on average between 8% and 22%.

4. Results and discussion

4.1. N₂ adsorption data

Fig. 2 shows the nitrogen adsorption/desorption isotherm data for a coconut sorbent at 77 K. The isotherm is type I among six isotherm categories according to the IUPAC (International Union of Pure and Applied Chemistry) classification. Type I isotherms indicate high adsorption in the low relative pressure range, that is, they apply to sorbents with significantly developed micropores

(pores with linear dimensions smaller than 1 nm). In the region of medium and high relative pressures the isotherm has a course almost parallel to the y abscissa axis, which indicates that mesopores (pores with dimensions from 2 to 50 nm) are poorly developed or absent. In the case of the coconut sorbent studied, it can be assumed that there are well-developed micropores and poorly developed mesopores. The type I isotherm applies to microporous solids and is concave with respect to the relative pressure axis P/P_s , and the adsorption volume approaches the limiting value with time P/P_s 1. Here P_s represents the saturation pressure of the adsorbate. The very steep region at low P/P_s is due to the filling of very narrow pores and the limiting uptake depends on the available volume of the micropores rather than the inner surface [7,9,10]. The breakthrough curves for coconut sorbent are completely reversible over the entire P/P_s range, that is, they have no hysteresis. To obtain a more realistic appearance of PSD, the NLDFT reports (pore volume, V , cm³/g) were derived by normalizing the pore volume to the pore size interval (differential volume, dV/d , cm³/g nm), and the PSD results are shown in Fig. 3. The NLDFT method shows only two peaks in the PSD curve at the pore radius of 1.20 and 1.67 nm, and the micropore region lies between 0.1 and 2.4 nm. Therefore, it can be said that the coconut sorbent is highly microporous.

4.2. Static sorption

The results of static adsorption process of pirimicarb on coconut sorbent are shown in Tables 2 and 3 and Fig. 4.

The values presented in Table 2 were entered into the IZO application [11,14]. Using the application, the values of coefficients of linear and classical equations of adsorption isotherms according to Freundlich, Langmuir and BET were calculated and their graphs were generated (Fig. 4). With the application, a measure of the quality of the model fit was simultaneously calculated by deriving

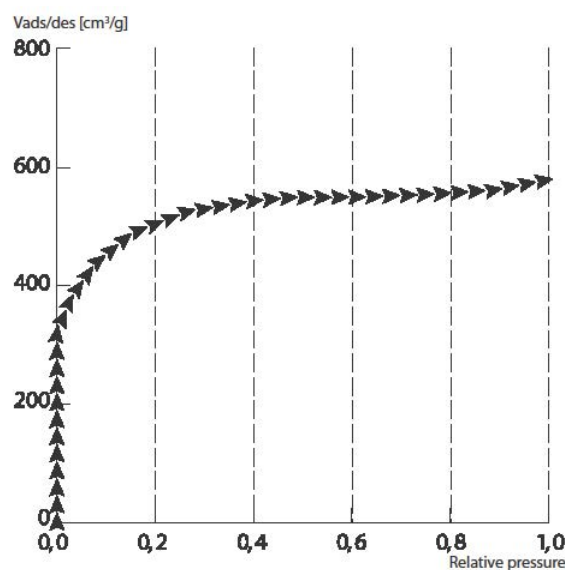


Fig. 2. Adsorption/desorption isotherm of N₂ on coconut sorbent.

the values of the coefficient of determination R^2 and the standard error of fit S (Table 3).

Fig. 4 plots the adsorption isotherms of pirimicarb on the used coconut sorbent as a function of adsorbed by unit mass of adsorbent from the equilibrium concentration of adsorbate (pirimicarb) in aqueous solution. The shape and arrangement of the curves are related to the different course of adsorption in the low concentration range, which is due to the competitive nature of solute and solvent interactions with the adsorbate surface. A group of isotherms was obtained according to Giles' classification: L. Group L includes isotherms of systems in which there is no strong competitive interaction from the solvent particles when the adsorbate occupies the active sites on the surface. In this case, the active centers of the coconut sorbent are filled by the planar arrangement of the aromatic ring of the pirimicarb molecule [7,9,10].

From the plotted isotherms (Fig. 4) and the values of R^2 and S coefficients (Table 3), it can be concluded that the sorption process of pirimicarb on coconut carbon is best described by Langmuir ($R^2 = 1$) and Freundlich ($R^2 = 0.99$) isotherms. The scanning electron microscope image and the mathematical description show that the studied sorbent is probably characterized by a homogeneous surface and

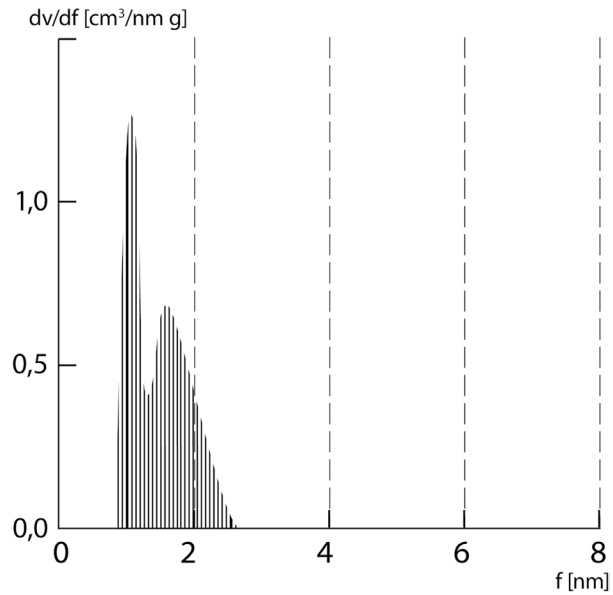


Fig. 3. The pore size distribution of coconut sorbent for the NLDFT method.

Table 2

Results of the effect of varying the adsorbent dose m (g) on changing the equilibrium C_r concentration values (mg/dm³) in the static adsorption of pirimicarb using coconut adsorbent

Sample no.	Initial concentration	Volume	Sorbent mass	Equilibrium concentration
	C_0	V	m	C_r
	(mg/dm ³)	(dm ³)	(g)	(mg/dm ³)
1	5.00	1.0E-1	3.0E-003	6.997E-001
2			4.0E-003	5.395E-001
3			5.0E-003	3.603E-001
4			7.0E-003	2.332E-001
5			1.0E-002	1.460E-001
6			1.5E-002	9.100E-002
7			2.5E-002	5.200E-002
8			5.0E-002	2.541E-002

Table 3

Values of linear coefficients and classical adsorption isotherms of pirimicarb by Freundlich, Langmuir for coconut coal and quality of approximation

Adsorbent	Isotherm	Equation					
		Linear				Classical	
		Coefficient	Value	R^2	S	Coefficient	Value
Coconut carbon	Freundlich	a	5.301	0.99	8.8E-2	x_m	200.5
		b	7.862E-1			n	1.272
	Langmuir	a	3.891E-3	1.00	3.8E-4	x_m	257.0
		b	2.449E-3			K_L	1.589
	BET	a	1.033E-3	0.94	1.3E-3	x_m	49.66
		b	1.910E-2			K_B	19.50

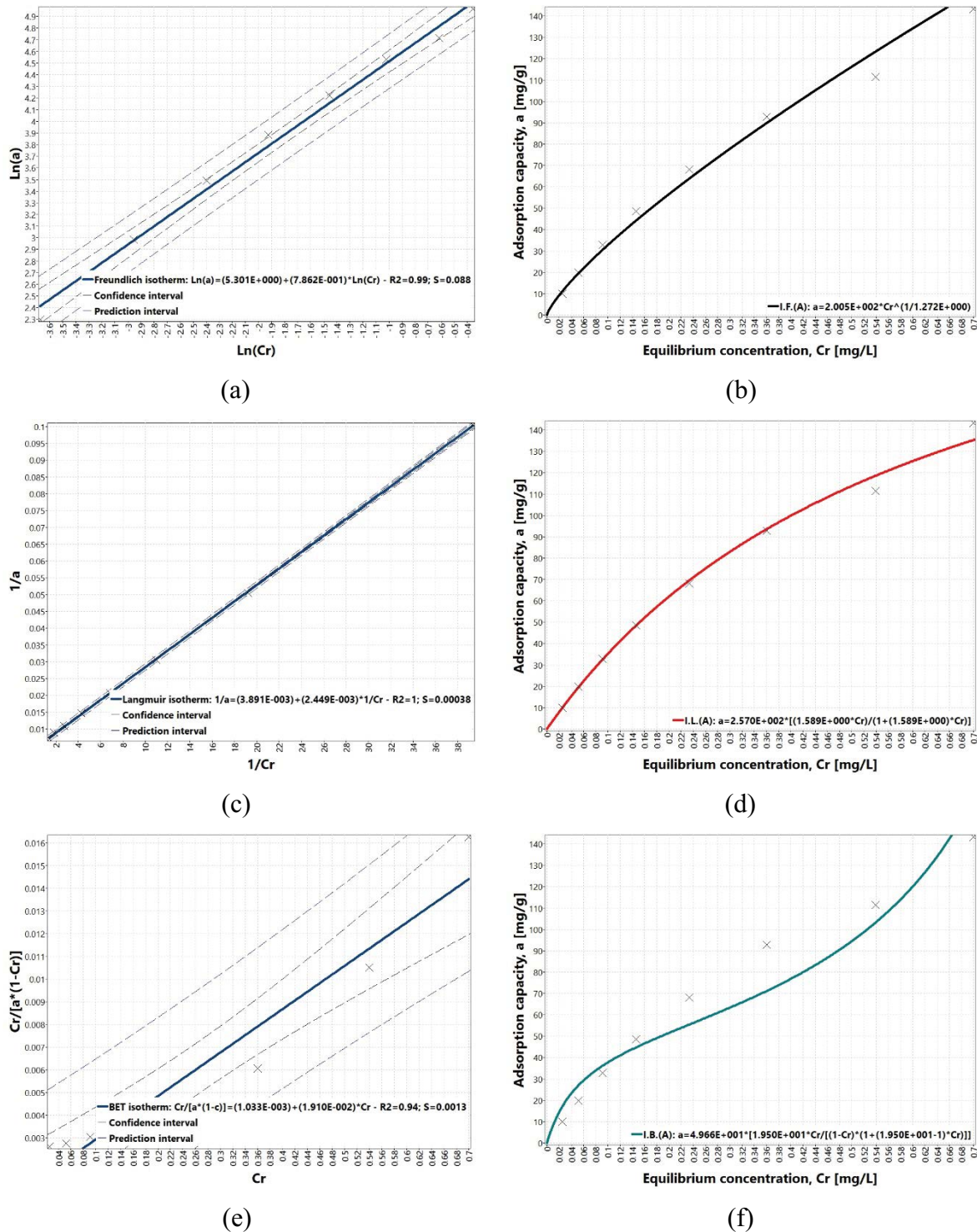


Fig. 4. Plots of pirimicarb adsorption isotherms by Freundlich (linear A, classical B) and Langmuir (linear C, classical D) and BET (linear E, classical F) for coconut coal.

that during sorption reactions occur only in the monolayer. However, additional interactions giving the effect of multi-layer sorption are also possible. Similar results were obtained by Salman [26], who studied the sorption of insecticide, carbofuran from aqueous solution onto activated carbon

derived from palm oil fronds. Alcione Aparecida de Almeida Alvesa [27] studied the kinetics, equilibrium and thermodynamic parameters of adsorption of the pesticides carbaryl, methomyl and carbofuran on activated carbon. The adsorption statics was most accurately described by the Langmuir

– Freundlich isotherm model. Satisfactory results for the removal of the pesticide carbofuran on carbon from Rice Straw Agricultural Waste were obtained by Chang et al. [8].

4.3. Modeling of dynamic sorption

The adsorption process has to be considered taking into account the kinetic aspect, which in terms of mathematical modeling is represented by the equations of flow of the medium outside the particle and the equations of saturation of the activated carbon particle. Another aspect is the adsorption statics expressed by adsorption isotherms. On the other hand, the dynamics of adsorption in mathematical description is constituted by the kinetics and statics of adsorption and the mass balance of adsorbate. The approximate equations of adsorption dynamics relate to the spatio-temporal distribution of adsorbate in the sorption bed. The most important parameters of the resulting variables are the averaged diffusion coefficient, the mass penetration modulus, the hydraulic diffusion coefficient, the external and internal mass transfer coefficients, the overall mass transfer coefficient, the height and migration rate of the adsorption front, and the operating time of the adsorption bed. On the other hand, the independent variable parameters are grain diameter, grain porosity, layer porosity, bulk density, initial concentration, flow velocity, medium temperature, and adsorption isotherm coefficients [7,10,14,28–31].

Therefore, in determining the duration of the adsorption process, the adsorbate concentration in the adsorbent monolayer was assumed to be $x_m = 257$ g/kg based on Langmuir isotherm. The bulk density of the coconut charcoal bed of $\rho_n = 476$ kg/m³ was also assumed. Complete retention of pirimicarb in the bed, that is, reduction of its concentration from $C_0 = 5$ mg/m³ (concentration found in surface water $C_0 = 5$ µg/L) to the final value $C_e = 0$ mg/m³ was assumed. Depending on the variation of the medium flow velocity through the bed v_p in the range of 5 to 25 m/h and the variation of the adsorbent bed height H_z in the range of 5 to 10 cm, using the transformed mass balance equation (1), the calculated duration of the pirimicarb adsorption process varies from about 6 y to about 56 y (Fig. 5).

5. Summary

This paper presents a study on the application of the adsorption process of carbamate pesticides (pirimicarb) on a sorbent made from waste material – coconut shells. Static studies have been carried out and the analysis has been performed in the author's computer application IZO, which is an ideal solution for studying the adsorption process by generating adsorption isotherms according to Freundlich, Langmuir and BET in classical and linear forms. Moreover, the application allowed the calculation of working time of the adsorption bed based on simplified adsorption dynamics equations. Based on the plotted isotherms and the values of R^2 and S coefficients, it can be concluded that the process of pirimicarb sorption on coconut coal is best described by Langmuir ($R^2 = 1$) and Freundlich ($R^2 = 0.99$) isotherms. A group of isotherms according to the Giles classification type L was obtained. In this case, the active centers of the

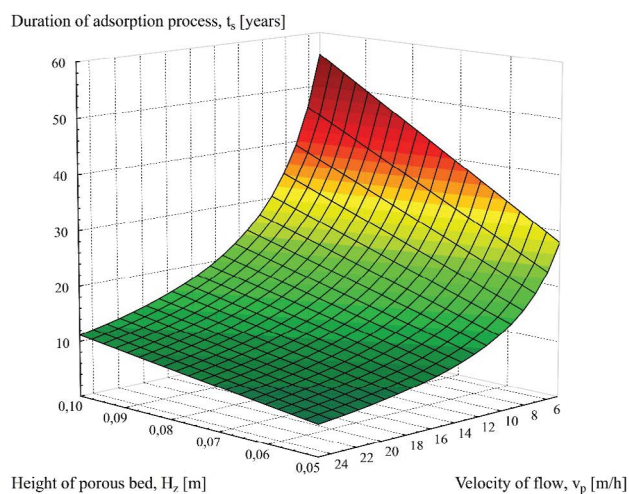


Fig. 5. Graph of the variation of the duration of pirimicarb adsorption process t_s (y) on coconut sorbent bed as a function of the variation of its height H_z (m) and the value of flow velocity v_p (m/h).

adsorbent are filled by the flat arrangement of the aromatic ring of the particle. The investigated adsorbent is characterized by a homogeneous surface, and during adsorption reactions take place mainly in the monolayer. Depending on the variation of the medium flow rate through the bed v_p in the range of 5 to 25 m/h and the variation of the adsorbent bed height H_z in the range of 5 to 10 cm, the calculated duration of the pirimicarb adsorption process varies from about 6 to about 56 y. Analyzing the bed working time and the assumed pesticide removal efficiency, it can be concluded that new cheaper sorbents made from waste materials should be sought in the future.

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