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THE ADSORPTION OF PENDIMETHALIN BY PEATS AND LAKES BOTTOM SEDIMENTS

ADSORPCJA PENDIMETALINY NA TORFACH I OSADACH DENNYCH JEZIOR

Abstract: The paper presents results of an experimental research on the influence of the adsorbent type on the adsorption of pendimethalin and water/peat index and water/bottom sediment index (K_d and K_{OC}). The research was carried out in a laboratory using samples of bottom sediment and peat of various organic carbon contents. The experiment involved herbicide of Panida 330 EC containing 330 g of pendimethalin in 1 dm³ of preparation.

According to the research, there is a strong relationship between adsorption and time emulsion of pesticide remains in contact with peat and bottom sediment samples. Additionally, results indicate that adsorption of pendimethalin involves two phases. The first phase is fast and non-linear, whereas the second one slow and linear. The 24 hour contact and 10 hour contact in the case of an increased content of adsorbent by 150 % between herbicide emulsion and peat/bottom sediment samples enabled to reach an adsorption equilibrium in the active substance. The content of organic carbon in peat and bottom sediment samples was decisive as regards time of non-linear phase of pendimethalin adsorption.

Keywords: herbicide, adsorption, peat, lake bottom sediment

Introduction

For many years, despite numerous controversies related to their negative impact on the environment, crop protection chemicals have been the most effective and modern

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method of counteracting threats to the yield from biotic factors [1]. Due to their common application and long half-time in the natural environment, remains of those chemicals can now be found in all segments of the natural environment, including water, soil, bottom sediments, air, plants and living organisms [2]. Apart from its direct threat, the accumulation of pesticides in the environment promotes their movement inside and between ecosystems. A natural storage of all types of contamination in ecosystems, including pesticides, is soil. Adsorption of pesticides by soil plays an important role in their transport and movement in the environment. It is assumed that the sorption of xenobiotics involves various mechanisms, *eg* formation of hydrogen bonds – weak surface interactions or strong ionic interactions [3]. In the case of pesticides, Gevao et al [4] have distinguished van der Waals interactions, π -electron interactions and covalent bonds.

According to the literature, the process of pesticides adsorption involves two phases [5–8]. The first one is a macroscopic process (macro sorption) which includes surface sorption. For those processes the equilibrium constant is reached relatively fast. The second phase requires longer contact between pesticide and soil, and involves a microscopic process (micro sorption), related to diffusion of pesticides into inner active layers. Contamination is either enclosed in 3D structure of macromolecules of the organic matter or in interpocket space of clay minerals.

The research aimed at defining the influence of different types of adsorbent of various organic carbon content on kinetics of pendimethalin adsorption – an active substance in the Panida 330 EC preparation, and determining water/peat and water/bottom sediment indices (K_d and K_{OC}) for the linear phase (micro sorption) of the process.

Material and methods

The experiment used Panida 330 EC herbicide (*emulsifiable concentrate*) which contained pendimethalin as a biologically active substance (Fig. 1).

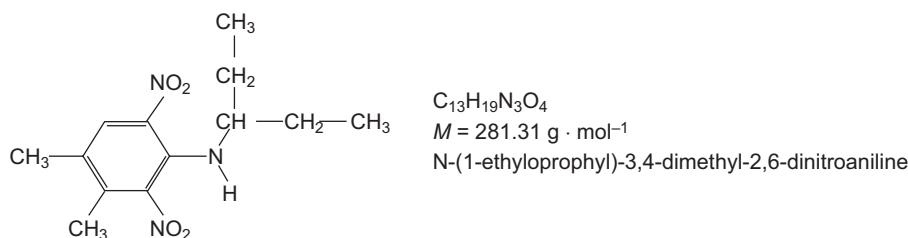


Fig. 1. Structural formula of pendimethalin

It is a selective soil-applied herbicide which migrates into a plant through its roots and leaves preventing mitotic division of cells and growth of weed seedlings. The herbicide is commonly used to eradicate weeds from a number of crops [9–11].

The research on adsorption of dinitroaniline derivative used lyophilised samples of bottom sediments from lake Kociolek (sample O1) and lake Sniadowo (sample O2) and dry surface samples of peat from Jablonka fen (sample T1) and Pod Dolnym Plajem fen

(sample T2). In all samples examined the content of water did not exceed 12 %. Lakes Kociolek and Smiadowo, situated in West Pomerania, are lobelia lakes of volatile morphometric parameters. Jablonka fen situated in the Orawsko-Nowotarska basin, whereas Pod Dolnym Plajem fen in the Babiogorski National Park. In both fens, soil has undergone different pedogenic processes. The following assessments were made in the analysed soils: pH (by potentiometric method in H₂O and 1 mol · dm⁻³ KCl solution), organic carbon and total nitrogen content on LECO CNS 2000 apparatus. Physico-chemical properties of the both adsorbents are presented in Tables 1 and 2. The content of organic carbon was the main criterion for selecting samples of bottom sediment and peat.

Table 1

Physico-chemical properties of peat samples

Physico-chemical properties Peat samples	Geographical location	pH		C _{org}	N _{tot}	C _{org} /N _{tot}
		H ₂ O	KCl	[g · kg ⁻¹]		
Jablonka fen (T1)	N 49°29'54.4" E 19°40'51.6"	5.8	5.1	344	20.0	17.2
Pod Dolnym Plajem fen (T2)	N 49°35'43.5" E 19°30'15.1"	6.3	5.7	264	22.6	11.5

Table 2

Physico-chemical properties of bottom sediment samples

Physico-chemical properties Bottom sediment samples	Geographical location	pH		C _{org}	N _{tot}	C _{org} /N _{tot}
		H ₂ O	KCl	[g · kg ⁻¹]		
Lake Kociolek (O1)	N 53°56'30" E 16°41'	4.4	3.8	220	16.0	13.7
Lake Smiadowo (O2)	N 51°37' E 16°34'	5.0	4.5	118	11.0	10.8

Pendimethalin adsorption tests were performed at 20 °C in dynamic conditions, where the ratio of peat/bottom sediment mass to the volume of the solution was: 1:10 for sample T2 (2.5 g peat + 25 cm³ pendimethalin solution), and 1:25 for samples O1, O2 and T1 (1.0 g peat/bottom sediment + 25 cm³ pendimethalin solution). While preparing samples, 2.5 g of sample T2 and 1.0 g of O1, O2 and T1 were placed on a laboratory scales. Samples were weighted in conical flasks with cut of 50 cm³. 25 cm³ pendimethalin solution of 0.2 mg · cm⁻³ was added to the experimental material. For each peat/bottom sediment sample ten (10) measurement points were prepared in three consecutive series. The samples were closed with corks and mixed in laboratory shakers. After shaking, the samples were centrifuged at each time point for 5 minutes at 4000 rev · min⁻¹, and the pendimethalin solution underwent extraction with chloroform (5 cm³) and spectrophotometric analysis was applied to measure the value of

absorbance at wavelength of 430 nm. The quantitative interpretation of the active substance tested was performed using a rating curve.

The examining of the pendimethalin adsorption kinetics in peat/bottom sediment samples involved measurements after 0, 5, 15, 30, 45, 60, 90, 120, 180, 540 and 1440 minutes of contact between the pendimethalin solution and the above mentioned adsorbents.

While taking into consideration the difference between the initial concentration (C_0) and equilibrium concentration (C_r), and the volume of the solution and the mass of peat/bottom sediment samples, calculations were made to determine the adsorption (x/m) of pendimethalin in peat and bottom sediment samples analysed according to formula (1) [8]:

$$\frac{x}{m} = \frac{V \cdot (C_0 - C_r)}{m} \quad (1)$$

where: x – mass of adsorber in peat/bottom sediment [mg],

m – mass of peat/bottom sediment [g],

V – volume of solution used for measurement [dm^3],

C_0 – concentration of component in initial solution [$\text{mg} \cdot \text{dm}^{-3}$],

C_r – concentration of component in adsorption equilibrium solution [$\text{mg} \cdot \text{dm}^{-3}$].

The experimental values of adsorption and equilibrium concentration were used to calculate (dispersion) water/peat and water/bottom sediment ratios, K_d and K_{OC} respectively, while taking into consideration the content of organic carbon in adsorbents for the active substance (a.s.). K_d and K_{OC} for the analysed pendimethalin peat/sediment system were calculated for the linear phase (micro sorption) of the adsorption process. The analysis times for bottom sediments, peat sample from Jablonka fen and peat sample from Pod Dolnym Plajem fen were respectively 24 and 10 hours for the adsorption process concerned. The value of K_d was calculated based on formula (2) [12, 14]:

$$K_d = \frac{\text{mg a.s./kg adsorbent}}{\text{mg a.s./dm}^3 \text{ water}} \quad (2)$$

Resulting values of K_d are translated into K_{OC} according to equation (3) [13, 14]:

$$K_{OC} = \frac{K_d \cdot 100\%}{C\%} \quad (3)$$

Results

The relationship between adsorption of pendimethalin and contact time is presented in Fig. 2. Resulting curves show changes of the pendimethalin adsorption rate. Regardless the peat/bottom sediment system used, the geometry of curves indicates relationship between the parameters and a clear dual phase (non-linear and linear) adsorption process.

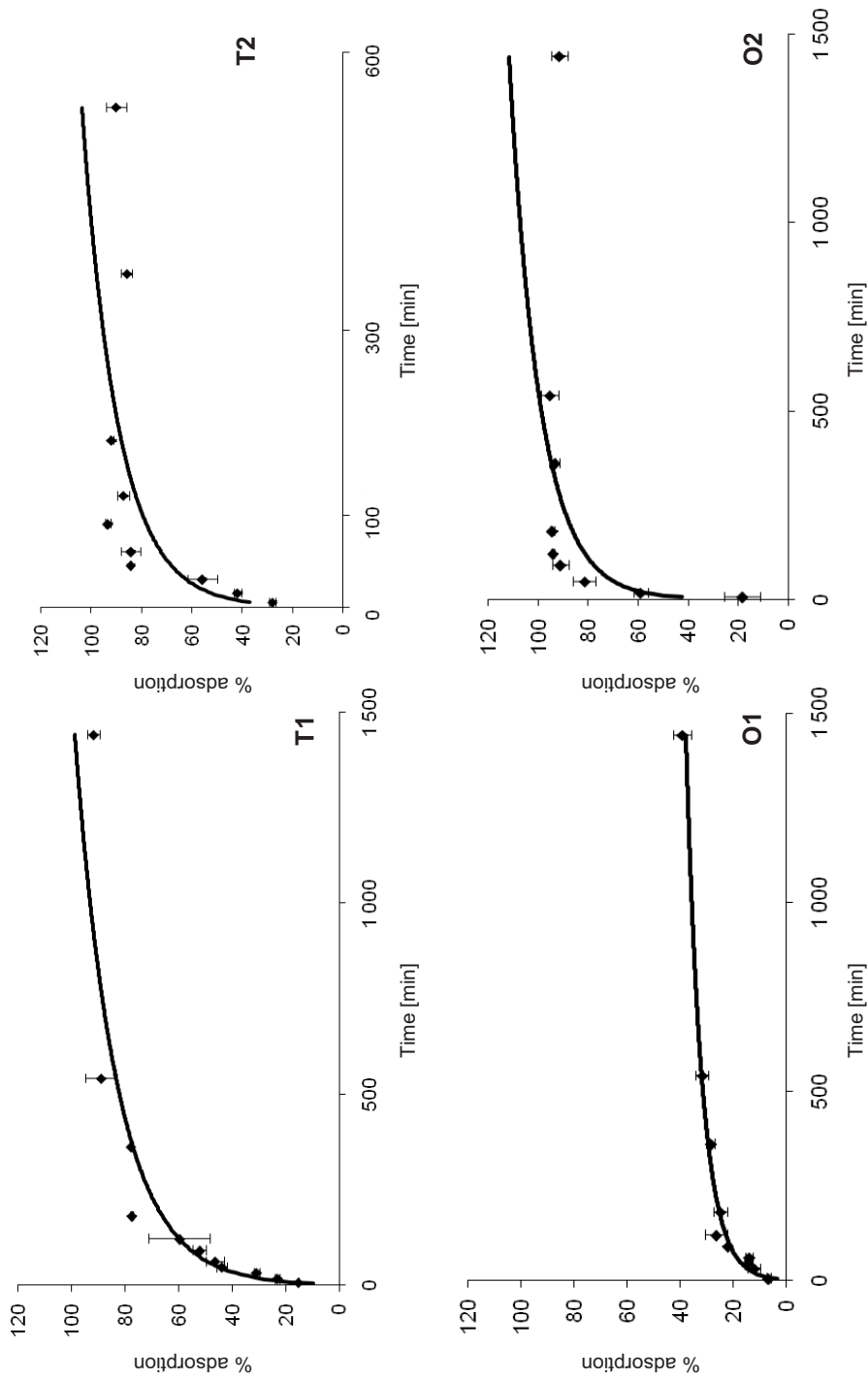


Fig. 2. Kinetics of pendimethalin adsorption in peat samples (T1, T2) and bottom sediments samples (O1, O2)

Depending on the type of adsorbent (peat, bottom sediment), the linear relationship between the volume of herbicide adsorbed and time of contact with adsorbent is reached in 60 to 180 minutes. The linear phase is reached much faster for samples of bottom sediments: from 90 minutes in the case of O2 sample of the lowest organic carbon content ($C_{\text{org}} = 118 \text{ g} \cdot \text{kg}^{-1}$) to 120 minutes in the case of O1 sample ($C_{\text{org}} = 220 \text{ g} \cdot \text{kg}^{-1}$). The non-linear phase of the pendimethalin adsorption was significantly prolonged to 180 minutes for sample T1 of $344 \text{ g} \cdot \text{kg}^{-1}$ organic carbon content. In the case of T2, the quantity of adsorbent was increased to 2.5 g which resulted in reaching the linear phase of the process much faster, namely in just 60 minutes.

According to the analysis, pendimethalin shows significant adsorption capacity. In the case of bottom sediment samples, the highest adsorption values ($4.01\text{--}4.20 \text{ mg} \cdot \text{g}^{-1}$), for the linear phase of the process, were recorded for sample O2. Between 90 to 1440 minutes were sufficient to adsorb $91.07 \pm 3.24 \%$ to $95.45 \pm 3.44 \%$ of the active substance applied. Adsorption of pendimethalin in bottom sediment samples was not correlated with the content of organic carbon. Sample O1 showed nearly 100 % higher organic carbon content in comparison with sample O2; x/m values were significantly lower. The linear adsorption phase involved adsorption of $24.73 \pm 2.78 \%$ to $39.45 \pm 3.48 \%$ of pendimethalin, and adsorption was at the level of $x/m = 1.08\text{--}1.72 \text{ mg} \cdot \text{g}^{-1}$.

The peat samples used showed considerable pendimethalin adsorption capacity. During the linear phase, sample T1 adsorbed $77.66 \pm 0.53 \%$ to $91.86 \pm 0.53 \%$ of the active substance within 180 to 1440 minutes. For the time span concerned, pendimethalin adsorption values calculated varies from 3.41 to $4.05 \text{ mg} \cdot \text{g}^{-1}$. The volume of adsorbent used for testing has significant influence on the effectiveness of the adsorption process, in particular during the initial non-linear phase. Pendimethalin adsorption results obtained for the increased dose of the adsorbent in sample T2 were from 0.49 to $1.65 \text{ mg} \cdot \text{g}^{-1}$. In the linear phase, the adsorption of substance analysed was from $84.44 \pm 2.53 \%$ to $93.46 \pm 1.05 \%$ per every 2.5 g of sample T2. An increased dose of the adsorbent shortened the non-linear phase of the process and expedited reaching the adsorption equilibrium. As regards peat samples, a major relationship was determined between the adsorption process and the content of organic carbon. For sample T1 of increased organic carbon content ($C_{\text{org}} = 344 \text{ g} \cdot \text{kg}^{-1}$), x/m values of pendimethalin were by 22.89 to 59.43 % higher if compared with pendimethalin x/m for sample T2 ($C_{\text{org}} = 264 \text{ g} \cdot \text{kg}^{-1}$).

Table 3

Values of water/peat and water/bottom sediment pendimethalin indices (K_d , K_{oc})

Sampling points location	K_d	K_{oc}
	[$\text{dm}^3 \cdot \text{kg}^{-1}$]	
Lake Kociolek (O1)	16.0	73
Lake Smiadowo (O2)	267.1	2271
Jablonka fen (T1)	282.2	820
Pod Dolnym Plajem fen (T2)	9.7	90

According to data presented in Table 3, we can see that the highest value of K_d was obtained for sample T1 of the highest organic carbon content, whereas sample O2, of the lowest organic carbon content, showed the highest K_{OC} . No relationship was determined between the value of those adsorption indices and organic carbon content in adsorbent samples.

Conclusions

1. The research shows that there is a direct relationship between adsorption and the time herbicide emulsion remains in contact with peat and bottom sediment samples.
2. Adsorption of pendimethalin contained in Panida 330 EC involves two phases: macro adsorption – a non-linear phase in which the equilibrium is achieved relatively fast, and micro adsorption – a linear phase in which reaching the equilibrium takes more time.
3. The 24 hour contact and 10 hour contact in the case of increased content of adsorbent by 150 % between herbicide emulsion and peat/bottom sediment samples led to an adsorption equilibrium in the active substance.
4. The content of organic carbon in peat and bottom sediment samples was decisive as regards time of the non-linear phase of pendimethalin adsorption.

Acknowledgments

Research project co-financed by Polish Ministry of Science and Higher Education 3968/P01/2010/38.

References

- [1] Banaszekiewicz T. Chemiczne środki ochrony roślin, zagadnienia ogólne (Crop protection chemicals, general issues). Olsztyn: Wyd Uniwersytetu Warmińsko-Mazurskiego; 2003.
- [2] Różański L. Przemiany pestycydów w organizmach żywych i środowisku (Transformation of pesticides in living organisms and the environment). Warszawa: PWRiL; 1998.
- [3] Zbyszewski R, Buszewski B. Chem Inż Ekol. 2000;7:1289-1299.
- [4] Geva B, Semple KT, Jones KC. Environ Pollut. 2000;108:3-14.
DOI: 10.1016/S0269-7491(99)00197-9.
- [5] Szperliński Z. Ocena procesu sorpcji pestycydów na podstawie właściwości gleb w aspekcie ochrony wód (Assessment of pesticide sorption based on properties of soil and protection of water resources). Prace Naukowe Budownictwa Politechniki Warszawskiej. Warszawa: Wyd Politechniki Warszawskiej; 1981.
- [6] Wybieralski J, Muliński Z. Pestycydy (Pesticides). 1985;4:11-25.
- [7] Oleszczuk P. Ecol Chem Eng. 2007;14(S2):185-198.
- [8] Włodarczyk M, Siwek H, Wybieralski J, Waszak M. Przem Chem (Chemical Industry). 2009;88:590-593.
- [9] Praczyk T. Diagnostyka Uszkodzeń Herbicydowych Roślin Rolniczych (Diagnosing Herbicide Defects in Crops). Poznań: PWRiL; 2003.
- [10] Anyszka Z, Golina J, Łykowski W. Prog Plant Prot/Post Ochr Rośl. 2011;51(3):1335-1339.
- [11] Włodarczyk M, Matuszak R, Muszyńska A, Maciejuk M. Przem Chem (Chemical Industry). 2011;90:1072-1075.
- [12] Sadowski J. Prog Plant Prot/Post Ochr Rośl. 1996;36(2):280-282.
- [13] Karickhoff SW. J Hydraul Eng. 1984;6:707-735. DOI: 10.1061/(ASCE)0733-9429(1984)110:6(707).
- [14] Włodarczyk M, Wybieralski J. Ecol Techn (Ecology and Technology), 2006;1(79):16-22.

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Abstrakt: Przedstawiono wyniki badań doświadczalnych nad wpływem rodzaju adsorbentu na szybkość adsorpcji pendimetaliny oraz wartość współczynników podziału woda/torf oraz woda/osad denny (K_d i K_{OC}). Badania przeprowadzono w warunkach laboratoryjnych z zastosowaniem próbek osadów dennych i torfów o różnej zawartości węgla organicznego. W doświadczeniu wykorzystano herbicyd Panida 330 EC zawierający 330 g pendimetaliny w 1 dm³ preparatu.

Badania wykazały, że istnieje ścisła zależność adsorpcji od czasu kontaktu emulsji pestycydu z próbkami torfów i osadów dennych. Uzyskane wyniki wskazują ponadto, że adsorpcja pendimetaliny zachodzi w dwóch etapach. Pierwszy etap jest szybki – nieliniowy, drugi wolny – liniowy. 24-godzinny czas kontaktu, a w przypadku zwiększenia ilości adsorbentu o 150 %, 10-godzinny czas kontaktu emulsji herbicydu z próbkami torfów/osadów dennych umożliwił osiągnięcie stanu równowagi adsorpcyjnej badanej substancji aktywnej. Zawartość węgla organicznego w próbkach torfowych i osadów dennych miała decydujący wpływ na czas trwania nieliniowego etapu adsorpcji pendimetaliny.

Słowa kluczowe: herbicyd, adsorpcja, torfy, osady denne jezior