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Application of energetic willow (*Salix viminalis*) for biosorption of soil contaminated with chloroorganic pesticides

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ABSTRACT

The paper presents the results of an experiment on the evaluation of the usefulness of the basket willow (*Salix viminalis*) for the phytoremediation of a sorption substrate composed of soil and stabilized dairy sludge – vermicompost contaminated with pesticides. Preliminary studies confirmed the usefulness of a mixture of soil and stabilized dairy sludge for creating a sorption screen around the waste dump. In the experiments, the mallow was planted in plots with an area of 0.3 m^2 filled with the abovementioned mixture. The vegetation season lasted from spring to late autumn 2018. After the plant acclimatization period, a mixture of organochlorine pesticides was introduced to the plot at regular intervals. At the same time, samples of soil, as well as ground and underground parts of plants, were collected. In the samples, the concentration of pesticides was determined in accordance with the current methodology, with the use of GC/MS/MS/MS 4000 gas chromatograph connected with a mass spectrophotometer and AGILENT gas chromatograph with the use of ECD and NPD columns. The obtained results allow us to conclude that mallow can be used for reclamation of soils contaminated with pesticides, and first of all for prolonging the life of the sorption barrier around the waste dumps.

Keywords: Pesticides; Sorption; Phytoremediation; Basket willow *(Salix viminalis)*; Vermicompost; Bioremediation

1. Introduction

The effects of storing toxic substances, even after the liquidation of a waste dump, will be visible for many years in both soil and water [1–4]. Therefore, it is necessary to look for ways to reduce the migration of pesticides in the environment and to implement new ideas. In this regard, it seemed reasonable to conduct research on the application of the sorption process on selected natural and waste materials as a screen for the permeation of pesticides and metals (which are components of pesticides) to the environment in order to reduce their migration from the remaining waste dumps and warehouses [1–3]. An additional element used on energy plants to limit the migration of contaminants is phytoremediation. The success of the phytoextraction method depends mainly on the choice of the appropriate plant species [5–9]. Desired features enabling plant application include fast growth, production of large biomass in a short period of time, developed root system, greater tolerance to contamination, high capacity to accumulate toxins especially in ground parts, resistance to diseases, pests and weather fluctuations. All the given features are present in energy plants, which are represented by basket willow (*Salix viminalis*). The species has no special soil requirements and can therefore be grown on chemically contaminated land where the production of consumer crops is not desirable. Basket willow (*Salix viminalis*) is used for energy purposes as a fuel, for the production of particleboards.

An additional factor involved in the degradation of pesticides is soil fungi. There are at least two reasons for the high activity of soil fungi. The first one is higher resistance to some vegetation conditions in comparison with other

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soil microorganisms, while the second one is the activity of enzymes produced by them in relation to organic compounds found in the soil. The soil microorganisms with the highest effectiveness in pesticide degradation are the *Penicillium, Aspergillus, Fusarium* and *Trichoderma* types of fungi [9,10].

The aim of the study was to determine the usefulness of basket willow (*Salix viminalis*) for phytoremediation of a sorption substrate (composed of soil and vermicompost) contaminated with pesticides, as well as to determine the mycological composition of the substrate. In the future, this will allow to use a sorption screen around the waste dump, which will limit the migration of pesticides to the environment, and the energy plants grown on it will extend the life of the sorbent through phytoremediation and appropriate strains of fungi, and will also allow to eliminate the pesticides accumulated in ground parts by combustion.

2. Materials and methods

2.1. Sorbate

On the basis of literature data and own studies, chloroorganic pesticides that most often occur in drinking water near graveyards at the highest concentration were selected as representative sorbate [1–3]. Individual pure active substance isomers α-HCH, β-HCH, γ-HCH (lindane) and DDT were applied. Technical grade γ-HCH of 99.8% ± 0.2%, α-HCH of 99.8% ± 0.3%, β-HCH of 99.8% ± 0.2%, DDT 99.8% ± 0.3% purity obtained from Institute of Industrial Organic Chemistry Analytical Department in Poland were used as sorbate. A sample solution of pesticide has been prepared by dissolving 1 g of pesticide in 10 mL of methanol and then diluted to 1 L with doubly distilled deionised water.

2.2. Sorbent

As sorbent, the vermicompost made from municipal sewage sludge after aerobic stabilization was applied. The characteristics of the compost are given in Table 1, on Figs. 1 and 2. The used waste products comply with the requirements of the ordinance of the Minister of the Environment concerning agricultural usage of municipal sewage sludge [11].

2.3. Sorption procedure

Studies under static conditions were performed in accordance to the methodology applied in Belgium, Germany, France, Italy, England, the USA, Poland and other [1–3,9]. From such material test portions were prepared with the mass of 0.001, 0.002; 0.005; 0.01; 0.025 g for each 100 mL of solution. Representative sorbent samples were added to conical flasks containing pesticide solution with 10 mg/L concentration. The flasks were shaken on a vortex mixer with a constant vibration amplitude for 24 h, then they were left for 24 h in order to obtain full sorption balance. After that time, the samples underwent double filtration using soft tissue drains. Sorption process analysis was conducted on the basis of the obtained results (using Statistica software). Freundlich isotherms were estimated as non-linear models with the method of the smallest squares with the use of Gauss–Newton algorithm.

2.4. Phytoremediation procedure

The research on phytoremediation of sorption material was carried out in the conditions of a vase experiment. The experiment scheme included a control vase and a basic vase to which organochlorine pesticides were supplied. The preliminary studies [8,9] confirmed the usefulness of the mixture of soil taken from the vicinity of the waste dump and vermicompost to make a sorption screen around the waste dump.

In the experiment, basket willow (*Salix viminalis*) was planted in vases of 0.3 m^2 surface area and volume of 90 dm^3 filled with sorbent (Fig. 3). The vegetation season lasted from spring to late autumn 2018. After the acclimatization period, a mixture of chemically pure organochlorine pesticides (ΣHCH, DDT) was continuously introduced into the plot (imitating surface inflow). During the research season, 5 mg of each active substance was applied per vase. After the

Table 1
Vermicompost's characteristic

Properties of compost						
Manurial (mg/kg_{dm})						
Ca	Mg	Nog	N–NH_4^+	Pog	C	K
20.2	4.2	8.1	0.2	6.1	265.8	2.2
Metal (mg/kg_{dm})						
Pb	Cu	Cd	Cr	Ni	Zn	Hg
53.4	67.1	8.3	316.3	8.5	1,231	1.2
Permissible standard						
500	800	10	500	100	2,500	5
Other (%)						
pH	Hydration		Dry mass		Organic matter	
5.88	46.0		54.0		54.0	

Fig. 1. Compost prism with *Eisenia fetida.*

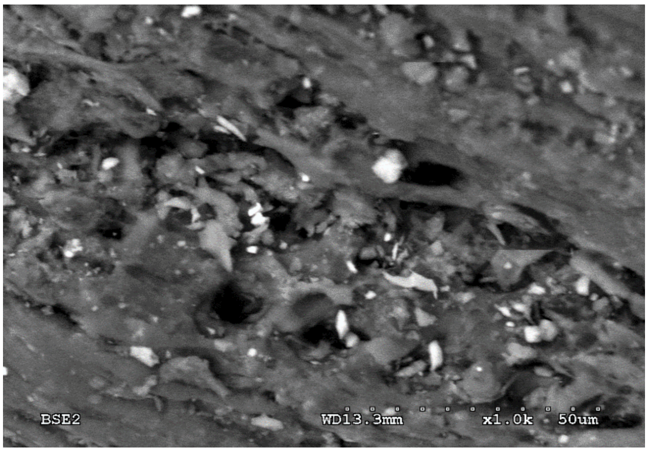

Fig. 2. Scanning electron microscope (SEM) images of vermicompost.

harvest, soil and both ground and underground parts of the plants were sampled [8,9].

2.5. Analytical procedure

α-HCH, β-HCH, γ-HCH and DDT concentrations were 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 mL/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 [1–3,8,9].

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 was below 22%. For the majority of compounds, the ME 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%.

Fig. 3. Basket willow (*Salix viminalis*).

3. Results and discussion

The sorption process was also described with Freundlich equations: $A = kc^{1/n}$. Following curve was achieved $A_F = 440.7\ c^{0.3}$ for vermicompost at correlation coefficient of $R^2 = 0.95$. Freundlich equation presents the most information. Knowledge of $1/n$ parameter value in the Freundlich equation allows to assess the adsorption intensity of particular substance in water phase on sorbate, whereas the value of constant k determines the sorption value with equilibrium concentration in the solution. Higher value of k coefficient relates to bigger sorption capacity. In the conducted research, k indicator value of 440.7 was obtained, which confirms vermicompost's usefulness in applying it as sorption screen for removing chloroorganic pesticides around a pesticide waste site. $1/n$ constant in Freundlich equation is isotherm directional coefficient, equal to tangent of angle slope of a line in a logarithmic coordinate system. Due to this, the higher $1/n$ value, the more intensive sorption process [2,11].

The obtained results of own research confirm the observations of Borkowska and Wardzińska [6] that basket willow (*Salix viminalis*) as a long-term, multi-use species is

Table 2
Mean concentration pesticides in basket willow *(Salix viminalis)*

Pesticide (mg/kg sm)	Limit detection	Control test			Test 1–3		
		Soil	*Salix viminalis*		Soil	*Salix viminalis*	
			Stem	Leaves		Stem	Leaves
ΣHCH	0,001	0.061 ± 0.004	0.001 ± 0.0001	0.006 ± 0.0003	0.143 ± 0.005	0.003 ± 0.0001	0.002 ± 0.0001
DDT	0,005	0.182 ± 0.012	0.003 ± 0.0001	0.002 ± 0.0001	0.375 ± 0.007	0.009 ± 0.0005	0.003 ± 0.0001

Table 3
Fungi species in the sorption subsoil or solum

No	Fungi	Fungi quantity
1	*Acremonium potronii* Vuill.	10
2	*Chrysosporium pannorum* (Link) Hughes	42
3	*Cladosporium cladosporioides* (Fres.) de Vries	1
4	*Fusarium sacchari* (Butler) W. Gams	2
5	*Helicosporium vegetum* Nees	1
6	*Mortierella alpina* Peyronel	1
7	*Mortierella humilis* Linnem.	2
8	*Oidiodendron tenuissimum* (Peck) Hughes	17
9	*Paecilomyces carneus* Duche & Haim	2
10	*Penicillium fellutanum* Biourge	7
11	*Penicillium citreonigrum* Dierck	7
12	*Penicillium daleae* Zaleski	9
13	*Penicillium decumbens* Thom	16
14	*Penicillium glabrum* Westling	12
15	*Penicillium lividum* Westling	12
16	*Phoma oculo-hominis* Punithalingam	3
17	*Scopulariopsis brevicaulis* Bain	3
18	*Trichoderma koningii* Oudem.	17
19	*Trichophyton tonsurans* Malmsten	3
20	*Wardomyces humicola* Henneb. & Barron	25
	Total	197

characterized by high harvest potential despite low soil and climatic requirements. Already in the first year of the experiment, the plants showed a large growth of ground parts. The possibility of obtaining a high harvest allows us to propose basket willow (*Salix viminalis*) as one of the plant species for reclamation of chemically degraded areas, and in this case of phytoremediation of pesticides from a sorption barrier.

Studies of Lunney et al. [12] were to compare the ability of five plant varieties to mobilize and phytoremediation DDT and its metabolites. The potential and limitations of phytoremediation for removal of pesticides in the environment have been reviewed by Chaudhry et al. [13].

As shown by Antonkiewicz et al. [5], the high harvest potential of basket willow (*Salix viminalis*) on the soil with varied heavy metal contamination testifies to its substantial resistance and quick adaptation to the conditions of contaminated soils. Own research also confirmed the observations made by Borkowska and Wardzińska [6], Xia and Ma [14], and Keri Henderson et al. [15] that the harvest of basket willow (*Salix viminalis*) is higher on a substrate enriched with vermicompost than on mineral soil. This concerned both plant height and harvest biomass (Fig. 3).

In addition to its high harvest potential, the mallow has a good potential for pesticide uptake from the substrate. The collected samples of the substrate showed several times greater concentration of absorbed pesticides in the soil mixed with vermicompost (0.002–0.009 mg kg d m.) than in the soil itself (0.001–0.003 mg kg d m.). A similar relationship was found in the samples of ground parts of basket willow (*Salix viminalis*). The leaves and stems of the plant cultivated on the sorption substrate accumulated more pesticides. Higher toxin concentrations were found in stems (DDT 0.009, HCH 0.003 mg kg d m.) than in leaves (DDT 0.003, HCH 0.002 mg kg d m.) of basket willow (*Salix viminalis*) regardless of the substrate on which it was grown.

On the basis of a conducted mycological test, 20 species of fungi were isolated on sorption substrate. Among them, the species occurring in the largest number were determined (Table 3). The results were similar to those obtained by Wagner and Dixon [16] and Mietkiewsk et al. [17], who determined the fungi present in pesticide waste. Species found to be dominant were, among others: *Penicillium* and *Trichoderma*, which are responsible for the degradation of pesticides in soil, and *Chrysosporium*, *Wardomyces* and *Oidiodendron* [8–10].

4. Conclusion

The obtained results of the exploratory research allow us to assume that basket willow (*Salix viminalis*) may be used for phytoremediation of soils contaminated with pesticides, and above all for prolonging the life of the sorption barrier around the waste dump. A more abundant harvest of basket willow *(Salix viminalis*) on a substrate enriched with vermicompost than on mineral soil makes it possible to predict the obtaining of large biomass for energy purposes, and thus the elimination of accumulated pesticides by subsequent combustion. These studies require to be continued and an experiment in the vicinity of the existing waste dump should be conducted.

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