Chapter 7

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Compost Applying as a Low-Cost Method for Reduction of Pesticide Migration from Graveyards

1. Introduction

Pesticides are toxic chemicals for fighting against various diseases and pests. These compounds are carcinogenic, teratogenic, embryotoxic, and mutagenic. Expired or not used, they become very dangerous wastes, that when improperly stored, penetrate in uncontrolled way to the natural environment making the threat for all living forms (Ignatowicz 2007, Zbytniewski, Buszewski 2002). Therefore, the Sophia Declaration was created to underline the negative influences of persistent organic pollutants, useless plant protection means, and other substances unsafe for human, environment, animals, and natural resources conditions such as ground waters or soil, and to emphasize the economic results related. The Declaration stressed the accelerating activities to remove the above mentioned pollutants and appealed to governments and local organizations to consider removal of useless dangerous substances as a priority. It also turn to European Union and other sponsors to support domestic initiatives that introduce strategies of removal the persistent organic pollutants, useless plant protection means, and other dangerous substances.

According to assessment made by Ministry of Environment Protection, the total weight of pesticide wastes in Poland can reach even up to 60 thousand tons. Therefore, there is a need to search for methods to reduce pesticide migration to the environment and incorporate new concepts. Studies on the application of sorption processes utilizing low-cost natural and waste materials as the shield for penetration of pesticides and metals (as pesticides contamination) into the environment should be carried on to reduce contaminants migration into the environment.

Phytoremediation by plants could be an additional element to limit the contaminants migration. The success of phytoremediation depends mainly on the properly selected plant species (Hendersona *et al.* 2006, Ignatowicz 2009a, Susarla *et al.* 2002). Desirable features making possible to apply a plant for remediation are: fast growth, producing large amounts of biomass in short time, developed root system, higher tolerance to pollution, great ability to accumulate toxins in above-ground parts, resistance to diseases, pests, and weather conditions. All above requirements are met by energetic plants, including *Salix viminalis*. This species does not require special soil conditions, thus its cultivation may be performed on chemically contaminated areas where production of consumption plants is not allowed.

The study was performed to check the possibility to reduce the migration of deposited pesticide wastes by applying low-cost waste sorption substances that would make a barrier protecting against pesticide penetration to the hydrosphere. It would protect ground and surface waters that are often the source of drinking water for people and animals. Present study was aimed at evaluating the usefulness of *Salix viminalis* to phytoremediation of sorption subsoil (consisting of the soil and compost) contaminated with pesticides. In future, it would allow for applying the sorption screen around pesticide graveyard, which reduces pesticide migration into the environment, and grown energetic plants – through phytoremediation – would prolong the sorbent vitality and remove pesticides accumulated in above ground parts by means of combustion.

2. Experimental conditions

2.1. Sorbates and sorbents

On a basis of literature and own studies data, chloroorganic pesticides that most often occurred near the graveyards at the highest concentrations were selected as representative sorbats (Ignatowicz 2009b). Technical grade DDT of 99,8±0,1% purity obtained from Institute of Industrial Organic Chemistry, Warsaw, Poland was used as an adsorbate. A sample solution of pesticide has been prepared by dissolving 1 g of DDT in 10 ml of methanol and then diluted to 1 L with deionised water.

Compost achieved directly from dairy treatment plant in Sokółka was used as natural sorbent. The Sokółka compost is produced as a by-product at the sewage treatment plant in Sokółka and is made of sewage sludge after mechanical-biological purification plant of municipal and dairy sewage. It is an example of treatment plant where biological section is based on SBR type sequential reactors. The plant's capacity is 6000 m^3/d, and the amount of produced sludge about 330 ton d.m./year. The sewage treatment plant in Sokółka is an uncommon object within Podlasie region where the sludge management problem was comprehensively solved. The sludge composting is conducted at the plant. The process is based on the following technology: dehydrated sludge is delivered by a conveyor to a box where it is mixed with carbon carriers and sawdust.

Such prepared mixture serves to make composting prisms. Those prisms are raised in special halls. When the prisms are raised, the grates are put into them to remove gases that are formed during the composting. After completing the first composting phase, prisms are covered with a foil and remained for three weeks, when intensive processes of sludge fermentation occur and the temperature is increased up to 60°C. Then, a ventilator is plugged to the grates to create aerobic environment within the prism (aeration time – about 14-20 days). Produced compost is maintained in prisms (for about 2.5 months). The characteristics of the compost are given in Table 1.

Table 1

The characteristic of compost

Non-metals (mg/kg_{dm})						
Ca	Mg	Total N	$N\text{-}NH_4^+$	Total P	C	K
5.61	0.46	1.39	0.009	1.47	0.45	5.61
Metals (mg/kg_{dm})						
Pb	Cu	Cd	Cr	Ni	Zn	Hg
7.0	22.7	0.63	9.9	5.8	210	2.5
Other (%)						
pH	Hydration		Dry mass		Organic matter	
6.7	67.5		32.5		67.5	

2.2. Sorption procedure

Studies under static conditions were performed in accordance to methodology applied in Belgium, Germany, France, Italy, England, USA, and Poland. They were aimed at plotting the adsorption isotherms due to which it is possible to compare the sorption capacities of different adsorbats on different adsorbents (Hamadi *et al.* 2004, He *et al.* 2006, Mashayekhi *et al.* 2006, Tsui, Roy 2007). Selected adsorbent, previously degassed, washed with distilled water and dried, was ground in spherical mortar and dried in electric drier at 150°C for 3 hours till constant weight. Such prepared sorbent served for weighing following samples: 0.001, 0.002; 0.005; 0.01; 0.025 g per 100 ml solution. Representative samples of adsorbent were added into the conical flasks with glass stopper and containing working solution of the pesticide (10 mg L^{-1}). Flasks were shaken in electric oven at constant oscillation amplitude (9) for 24 hours, and then remained for 48 hrs to reach a complete adsorption balance. After that, samples were subjected to double filtration on soft filter paper. Then, contaminants content in a filtrate was determined using MS/GC method. Statistic calculations were performed using Statistica software.

2.3. Adsorption isotherms

The sorption data were subjected to four commonly used isotherms models, namely Langmuir (1918), Freundlich (1894) and BET (1938), to evaluate the maximum saturation capacity of adsorbent (Atkins 2006).

The first mathematical fit to an isotherm was published by Freundlich and is a purely empirical formula for microporous and heterogeneous adsorbates:

$$A=x/m=kc^{1/n}$$

where: x is the quantity adsorbed, m is the mass of the adsorbent (A ($mg \cdot g^{-1}$) is the amount of pesticide adsorbed on the adsorbent surface at equilibrium), c ($mg \cdot L^{-1}$) the pesticide concentration in aqueous solutions at equilibrium, k ($mg \cdot g^{-1}$) is the maximum multilayer adsorption capacity and $1/n$ is a characteristic constant which measures the adsorption intensity. (k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature). As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

Langmuir isotherm is a semi-empirical isotherm derived from a proposed kinetic mechanism. Langmuir isotherm is a model for monolayer localized physical adsorption on homogeneous surface; may be extended with heterogeneity effects, lateral interactions and multilayer effects. It is based on four assumptions:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent,
- Adsorbed molecules do not interact,
- All adsorption occurs through the same mechanism,
- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir equation may be written as:

$$A=a_m\, Kc \,/\, 1+Kc$$

where: A ($mg \cdot g^{-1}$) is the amount of pesticide adsorbed on the adsorbent surface at equilibrium, c ($mg \cdot L^{-1}$) the pesticide concentration in aqueous solutions at equilibrium, a_m ($mg \cdot g^{-1}$) is the maximum monolayer adsorption capacity, K ($L\ mg^{-1}$) is the constant related to the free energy of adsorption.

Often molecules do form multilayer, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid. In 1938 Stephan Brunauer, Paul Emmett, and Edward Teller developed a model isotherm that takes that possibility into account. The Langmuir isotherm is usually better for chemisorption and the BET isotherm works better for physisorption for non-microporous surfaces.

The Langmuir equation may be written as:

$$A=ac / (1+c)(1+Kc)$$

where: A ($mg \cdot g^{-1}$) is the amount of pesticide adsorbed on the adsorbent surface at equilibrium, c ($mg \cdot L^{-1}$) the pesticide concentration in aqueous solutions at equilibrium, a ($mg \cdot g^{-1}$) is the maximum multilayer adsorption capacity, K ($L\ mg^{-1}$) is the constant related to the free energy of adsorption.

2.4. Phytoremediation procedure

Investigations upon phytoremediation of sorption material were conducted under pot experiment conditions. The experimental design included 4 objects: control pot and 3 other pots containing soil amended with pesticides. The initial studies confirmed the usefulness of soil mixture collected from pesticide graveyards and composting sewage sludge to make a sorption shield around that site. *Salix viminalis* was grown in 4 pots of 0,3 m^2 area and 90 L capacity filled with above mixtures. The vegetation period has lasted since spring 2008 till late autumn 2009. After acclimatization, mixtures of chemically pure chlorooorganic pesticide DDT were continuously added (which imitated surface supply) onto 3 experimental plots. During the whole experimental period, 5 mg of each active substance per pot was administered. After harvest, samples of soil, above and under ground parts of plants were collected.

2.5. Analytical procedure

Pesticide concentrations were determined in collected samples using gas chromatography. Metals concentrations were determined in mineralizates obtained according to EPA 3015 procedure using microwave digester Mars 5, by means of ICP-AES technique, except of mercury determined by CV-AAS technique.

3. Modelling of sorption isotherms

Achieved study results are presented in Table 2 and Figure 1-4. Characteristics of applied adsorbents (Table 1) indicate that both meet requirements of compost for natural applications. Following curves were achieved A_F = 1439,84 c ^{2,03} for compost at correlation coefficient of R=0.929 (Fig. 1); A_L = 852,96 c/1+8,88 c at correlation coefficient of R=0.803 (Fig. 2); and A_{BET} = 2,694 c/(1+c)(1+893,22 c) at correlation coefficient of R=0.915 (Fig. 3).

Constants *k* and *1/n* were estimated by means of the least squares by Gauss-Newton method applying Statistica software, and then the errors for these constants were evaluated (Fig. 3). Isotherms were calculated applying Statistica software by means of the least squares by Gauss-Newton method and achieved constants *a* and *k* are presented in Figure 1-4. Figures present adsorption isotherms for studied pesticides on applied low-cost natural adsorbents as a function of adsorbate amount adsorbed by adsorbent weight unit (*x/m*) vs. adsorbate's balance concentration (c_0).

Table 2

Mean concentration of pesticides in soil and *Salix viminalis*

Pesticides (mg kg_{dm}^{-1})	Limit detection	Control test			Test 1-3		
		Soil	*Salix viminalis*		Soil	*Salix viminalis*	
			stem	leaves		stem	leaves
DDT	0.005	0.1950	0.009	0.004	0.3241	0.006	0.004

The correlation coefficients (R) were employed to ascertain the fit of all isotherms with the experimental data. The coefficients R values were found higher for the Freundlich (0.929) and BET (0.915) models than for the Langmuir (0.803) model. This indicates that the BET and Freundlich isotherms are clearly the best fitting isotherm model for experimental datas. According to the two used models, important gaps in the adsorption capacities of the low-cost adsorbents have been noted.

4. Sorption isotherms

The nature of the studied pesticides (a chlorinated and hydrophobic molecule) suggests that its adsorption is of the hydrophobic type directly bound to the specific surface of the adsorbent particles. The isotherms study was performed according to the protocol described in the experimental chapter. The obtained results lead, firstly, to plot *a*, the amount of pesticide adsorbed on the adsorbent surface at equilibrium ($mg \cdot g^{-1}$) against c_e, the pesticide concentration in the aqueous solution at equilibrium in order to classify the isotherms according to the classification of Giles *et al.*, 1960 (Atkins 2006). This one includes four main groups: L, H, S and C. The experimental adsorption isotherms of pesticides in aqueous solutions on the studied materials are presented in Fig. 1-4. The same group of isotherms according to Giles' classification (S) was achieved for all pesticides.

According to Hamdaoui and Nafrechoux (2007) primarily the pesticide molecules bind to the adsorbent through only one grouping and the adsorption becomes progressively easier as the absorbed quantity increases. Thus, the first fixed molecules facilitate the adsorption of the following molecules because of the lateral attraction.

Next, the shape of these isotherms indicates that the chloroorganic pesticide are adsorbed as a monolayer and that there is no strong competition between the pesticide molecules and water to occupy the adsorption surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface.

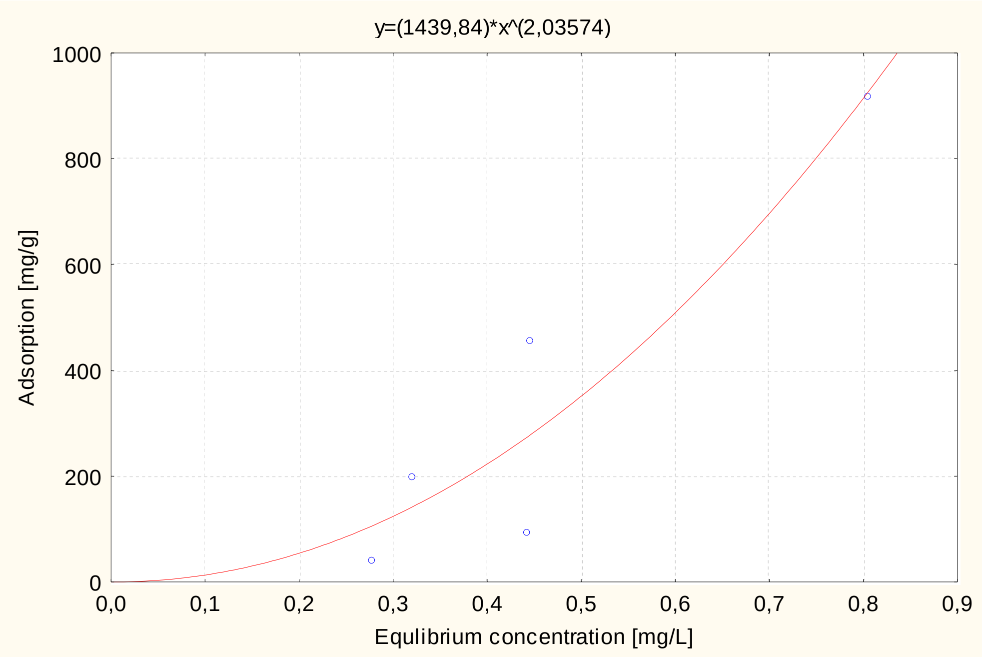

Fig. 1. Freundlich's isotherm of sorption DDT on compost

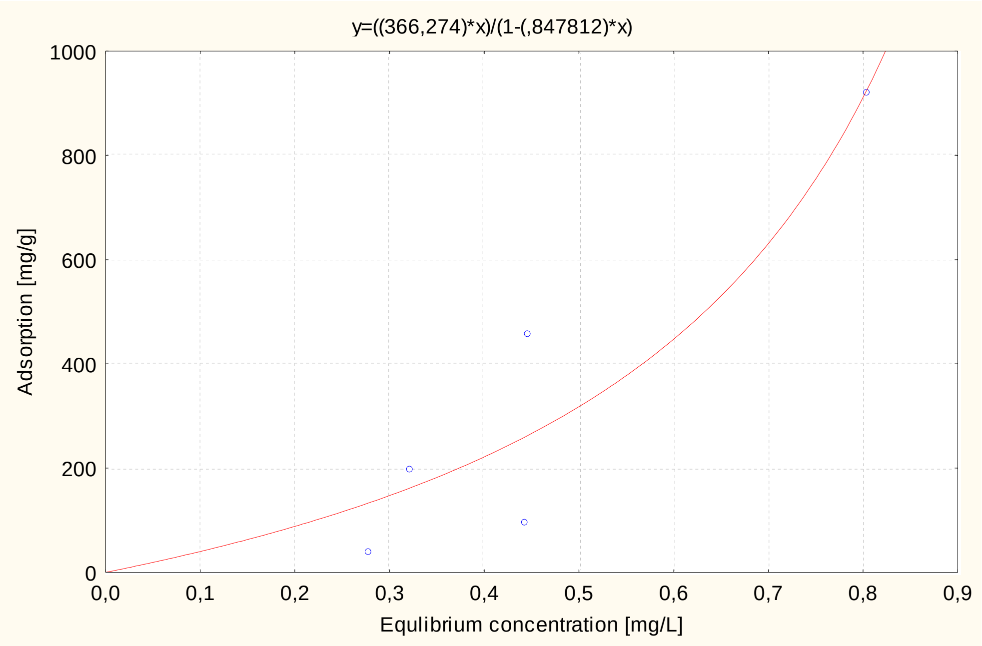

Fig. 2. Langmuir's isotherm of sorption DDT on compost

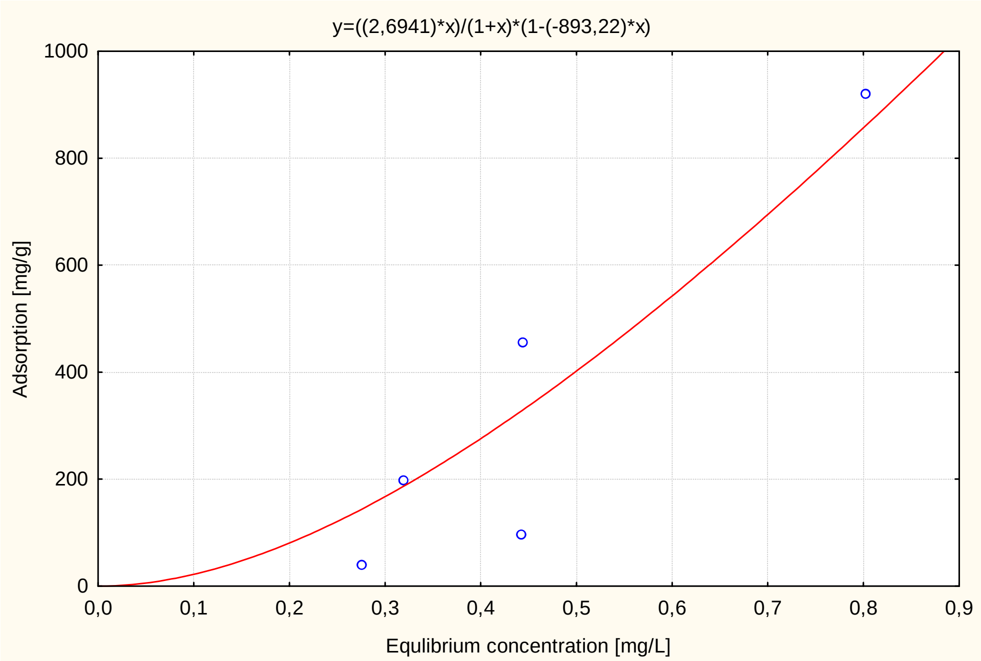

Fig. 3. BET's isotherm of sorption DDT on compost

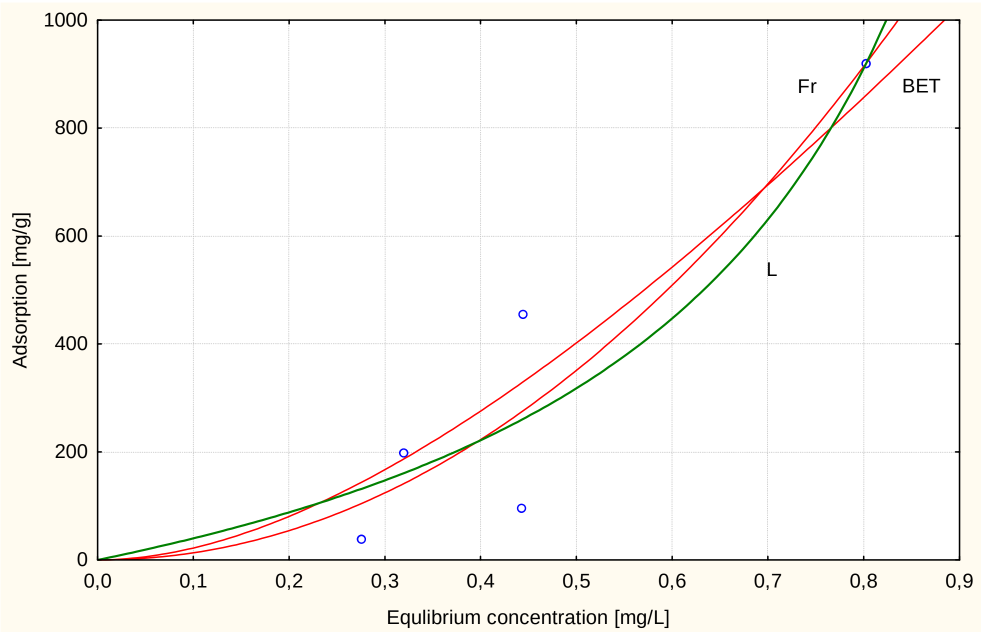

Fig. 4. Isotherm of sorption DDT on compost

This type of isotherm is relative to microporous adsorbents with a diameter lower than 25 Å, the adsorbent being saturated at the moment of the monolayer replenishment (Atkins 2006, Ignatowicz 2009b). There would be weak interactions therefore on these adsorbent surfaces because the number of layers cannot increase freely.

Knowledge on *1/n* parameter value in Freundlich's formula allows for assessing the adsorption intensity of a given substance from water phase on adsorbent; value of *k* constant determines the sorption capacity of a adsorbent at balance concentration in a solution. (Fig. 1) Higher *k* value corresponds to higher sorption capacity. In own studies, higher value of *k* coefficient was achieved for compost, which proves its usefulness in application as sorption screen around the pesticide graveyard. Constants *1/n* in Freundlich's formula are directional coefficients of isotherms equal to the tangent of line inclination angle in logarithmic coordinates. Therefore, the higher *1/n* value, the more intensive adsorption process.

5. Phytoremediation study

Plants *Salix viminalis* set in the first experimental year (set as several-year-old seedlings from a plantation) revealed high yields of above ground parts. Opportunity to get high yields allows for proposing *Salix viminalis* as one of the species useful for chemically degraded areas reclamation, particularly phytoremediation of pesticides from the sorption barrier. Own studies were also confirmed by Borkowska and Wardzińska (2003) and Ignatowicz (2009a), who observed more abundant yields of *Salix viminalis* on subsoil amended with compost than on mineral soil. It referred both to plant height and yield biomass. Besides high yield-forming potential, *Salix viminalis* also shows a great ability to intake pesticides from the subsoil. Much higher levels of absorbed pesticides (Table 2) were recorded in soil mixed with composting dairy sludge (0,3241 mg kg DM) than in native soil (0.1950 mg kg DM). Similar dependence was observed in samples of *Salix viminalis* above-ground parts. The leaves of plant cultivated on sorption subsoil accumulated more pesticides. Higher toxins concentrations were detected in stems (DDT 0.006-0.009 mg kg DM) than in leaves (0.004 mg kg DM), regardless the subsoil on which *Salix viminalis* was cultivated. The results support data of Garcinuno *et al.* 2003 and Macek *et al.* 2007 and allow to conclude that *Salix viminalis* can be used for phytoremediation of soils contaminated with pesticides, and particularly to prolong vitality of sorption barrier around a pesticide burial area. More abundant yields of *Salix viminalis* on the subsoil amended with compost than mineral soil allows to predic large amounts of a biomass for energetic purposes, thus removing accumulated pesticides by means of combustion.

Conclusions

The present study indicates the suitability of the low-cost adsorbent – compost – for removal of graveyard's chloroorganic pesticides from aqueous solutions. The adsorption process is described using Freundlich's, Langmuir's, and BET's formulae. The BET and Freundlich models fit better the experimental data. According to the two used models, important gaps in the adsorption capacities of the low-cost adsorbents have been noted.

The same group of isotherms according to Giles' classification (S) was achieved for DDT pesticide. In the first case, the pesticide molecules bind to the adsorbent through only one grouping and the adsorption becomes progressively easier as the absorbed quantity increases. Thus, the first fixed molecules facilitate the adsorption of the following molecules because of the lateral attraction. In the second case, the shape of these isotherms indicates that the chloroorganic pesticide are adsorbed as a monolayer and that there is no strong competition between the pesticide molecules and water to occupy the adsorption surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface. This type of isotherm is relative to microporous adsorbents with a diameter lower than 25 Å, the adsorbent being saturated at the moment of the monolayer replenishment.

The results allow for concluding that *Salix viminalis* can be used for phytoremediation of soils contaminated with pesticides, and particularly to prolong vitality of sorption barrier around a pesticide burial area. More abundant yields of *Salix viminalis* on the subsoil amended with compost than mineral soil allows for predicting large amounts of a biomass for energetic purposes, thus removing accumulated pesticides by means of combustion.

Acknowledgments

Financial support for this research was provided by Ministry of Science and Higher Education within the project N N304 274840.

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