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SORPTION PROCESS FOR MIGRATION REDUCTION OF PESTICIDES FROM GRAVEYARDS

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Absteact: The paper deals with the study upon the possibility to reduce migration of deposited pesticide wastes by using natural and waste sorption agents that would make a screen against plant protection means penetration into the hydrosphere. Sewage sludge from dairy treatment plant "Mlekovita" in Wysokie Mazowieckie as well as the same sludge with sawdust composted under natural conditions in Rudka Forestry Inspectorate was applied as natural sorption agents. Freundlich's and Langmuir's isotherms revealed that raw (no composting) sewage sludge showed better sorption features towards chloroorganic pesticides.

Keywords: sorption, pesticide, graveyard, burial ground, compost, sewage sludge

INTRODUCTION

Pesticides, as toxic compounds, are cancerogenic, teratogenic, embryotoxic and mutagenic. They are detected in all environmental elements: atmosphere, hydrosphere, geosphere, flora, fauna, and of course, man.(Ignatowicz, 2007, Biziuk, 2001). Outdated or not used pesticides become very dangerous wastes, that when inappropriately stored, penetrate into the natural environment making a threat for all life forms (Ignatowicz, 2007, Biziuk, 2001). The past left tens of thousands of tons of accumulated pesticide wastes that have been storing continuously since 50's. Those reserves grew, among others in 70's when, due to ecological and toxicological reasons, many of these means were withdrawn from the market and agricultural application. Also wrong management, distribution and uncontrolled import of plant protection means have contributed. Part of means was remained at the stores, another part was placed in graveyards building of which was started in 70's in a form of wells of 3-4 meter deep made of concrete circles of 1-3 meter diameter or built as brick constructions that were buried with 0.5 m thickness soil layer after filling (Biziuk, 2001, Stobiecki, 1999). In accordance to estimations by Ministry of Natural Environment Protection, a total weight of pesticide wastes in Poland may reach even to 60 000 tons. About ten thousand tons of active substance, including highly toxic DDT, was stored in about 350 graveyards in Poland. The largest amounts of wastes are accumulated in former Szczecin, Koszalin, Bydgoszcz, and Toruń regions. Up-to-date supervisions of technical condition of graveyards revealed that the worst situation was found in eastern Poland. In total, 42 tons of wastes, including 6 tons of empty wrappings were collected under the ground (Biziuk, 2001, Stobiecki, 1999, Wołkowicz at al., 2003).

Previous designing procedures did not take into account the long-term effects of the graveyard exploitation. Neither hydrological conditions, land characteristics, nor environmental conditions were taken into account, and no geological investigations were performed at localizing these objects, which resulted in their building on geological forms with great permeability and sometimes even on water-carrying layers. Supervision made by Sanitary and Epidemiological

Station revealed that 1/3 of graveyards did not meet localization conditions. They were closer than 300 m from water intake points, water reservoirs and agricultural areas. At least 75 graveyards were situated near rivers and lakes, 100 were near drinking water intakes and about 140 of them near residential areas; one graveyard was found in Silesian Culture and Recreation Park in Chorzów. However, stores within former PGR's (National Agricultural Farms) are the largest threat. There are usually ground caves with no protection, control and supervision. Technical status of those stores is catastrophic. They are the source of toxins and poisons emitted into the natural environment: soil, water, and air. Ground and surface waters, namely underground water reservoirs, near graveyards are contaminated (Wołkowicz at al., 2003, Ignatowicz, 2007) Thus, chemicals penetrate into the water-carrying layers making the hazard for human's health and even life.

Among 16 pesticide stores in Podlasie region, 7 of them are localized within Upper Narew river area, and the remaining at the direct neighborhood of other surface flows. Chambers of majority of graveyards are leaky, which is proved by soil and water analyses due to supervisions (Wołkowicz at al., 2003, Ignatowicz, 2007). There is also possibility to worsen the construction condition along with the occurrence of corroding the concrete bunkers and wells, the outdated pesticides are deposited, and in consequence, a toxic leakage. The leakage can be transported by underground water and then in a form of so-called underground inflow, it is caught by a network of surface waters. Accumulation of outdated pesticides, even after removal, will be a potential source of a threat and natural environment pollution for many years. Accumulation of toxic substances at one place along with confirmed pesticide emission into the underground water make a serious hazard for people. A graveyard contains a variety of substances that reacting to one another can produce often more toxic and mutagenic compounds than the substrates. Although local penetration of poisons into the water or ground may have no direct and significant effects on inhabitants, short filtration way (often through light, permeable and with low sorption capacity soils) makes a great threat for quality of surface water that transports toxins to a considerable distance. Mean flow rate of underground water near the graveyards in Podlasie region is about 80-100m/year, which means that in the case of any constructional damage, a constant supply of pollution into the open waters will be happening for many years. Therefore, there is a necessity to search for the solutions to reduce the pesticide migration in an environment as well as to introduce new concepts. Thus, it seems to be purposeful to undertake studies upon application of sorption process using selected adsorbents as a screen for pesticides in order to reduce their migration from other graveyards, stores and contaminated soils and concrete. (Mashayekhi at al., 2006, Li at al., 2005, Nemeth-Konda at al., 2002, Long at al., 2006,Allen at al.,2004) The present research was aimed at searching for a possibility to reduce the migration of deposited pesticide wastes by applying natural and waste sorption substances that would make a barrier for plant protection means against penetration to the hydrosphere. It would protect ground and surface waters that are often the source of drinking water for people and animals.

MATERIAL AND METHODS

On a basis of literature data and own studies, chloroorganic pesticides that most often occurred near the graveyards at the highest concentrations were selected as representative sorbats. Individual pure active substances (HCH, DDE, and aldrin) were applied. Sewage sludge achieved directly from dairy treatment plant "Mlekovita" in Wysokie Mazowieckie (Dąbrowski, 2006) as well as the same sludge with sawdust addition composted under natural conditions in Rudka Forest Inspectorate was used as natural adsorbents. (Boruszko, 2005) „Mlekovita" is the largest dairy plant in Podlasie region, and one of the largest in Poland. Individual biological sewage treatment station generates almost 1 100 tons of dry sludge that can be re-used. The characteristics of the sludge and compost are given in Table 1. The used waste products comply with the requirements of the ordinance of the

Minister of the Environment concerning agricultural usage of municipal sewage sludge (Dz.U. z 2002 r., nr 134, poz. 1140).

Table 1. The characteristic of sewage sludge and compost.

Sorbent	Properties						
	Manurial [g/kg dm]						
	Ca	Mg	Nog	$N\text{-}NH_4^+$	Pog	C	K
sludge	21.9	13.1	39.2		31.4		
compost	20.2	4.20	8.1	0.20	6.1	265.8	2.2
	Metal [mg/kg dm]						
	Pb	Cu	Cd	Cr	Ni	Zn	Hg
sludge	3.3	24.3	0.15	10.9	3.8	137	0.12
compost	5.4	25.1	0.30	4.3	3.5	123	0.20
permisssible standard	500	800	10	500	100	2500	5
	Other [%]						
	pH	Hydration		Dry mass		Organic matter	
sludge		-		-		66.5	
compost	5.88	73.7		26.3		70.3	

Studies under static conditions were performed in accordance to American methodology by Chemviron Carbon applied in Belgium, Germany, France, Italy, England, USA, and Poland (Laboratory...,1991, Mashayekhi at al., 2006, Li at al., 2005, Wibowo at al., 2007, Kumar at al., 2003, Rodriquez-Cruz at al., 2005, Long at al., 2006, Qin at al., 2007, Nemeth-Konda at al., 2002).

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. 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 (4 mg/dm^3). Flasks were shaken in mechanical shaker (358 S type) at constant oscillation amplitude (9) for 24 hours, and then remained for 24 hrs to reach a complete adsorption balance. After that, samples were subjected to double filtration on soft filter paper. The first and last portions of the filtrate were neglected. Then, pollution concentration in a filtrate according to obligatory methods was determined using gas chromatograph GC/MS/MS 4000 combined with mass spectrometer as well as gas chromatograph AGILENT6890.

Freundlich's ($A=kc^{1/n}$) and Langmuir's ($A=a_m kc/1+kc$) isotherms (Atkins, 2001, Paderewski, 1999, Anielak, 2000, Jankowska at al., 1991, Spadatto and Hornsby, 2003) were plotted on a base of achieved results applying Statistica and Sorp-Lab (Piekarski, 2007) software in order to analyze the processes.

RESULTS AND DISCUSSION

Achieved study results are presented in Figures 1-3 and Table 2. Characteristics of applied adsorbents (Table 1) indicate that both meet requirements of sewage sludge for natural applications. The adsorption process is described using Freundlich's and Langmuir's formulae.(Atkins, 2001, Paderewski, 1999, Anielak, 2000, Jankowska at al., 1991, Spadatto and Hornsby, 2003) Following curves were achieved: A = 630.594 c $^{0.387}$ and A=39936 c/1+157c) for dairy wastewater treatment plant at correlation coefficient of R=0.725 and A = 250.384 c $^{0.166}$ and A=66300c/1+446c for compost at correlation coefficient of R=0.743. Adsorption isotherms allow for concluding that adsorption of chloroorganic pesticides occurred better for the whole range of balance concentrations for dairy wastewater treatment plant with no composting.

Constants k and $1/n$ were estimated by means of the least squares method applying Statistica software, and then the errors for these constants were evaluated. Values of k and $1/n$ parameters as well as correlation coefficients R for particular adsorbates are presented in Table 2. Langmuir's isotherms were calculated applying Sorp-Lab software and achieved constants a_m and k are presented in Table 2.

Table 2. The coefficients of the Freundlich and Langmuir adsorption isotherms.

Isoterm	Freundlich $A=kc^{1/n}$			Langmuir $A=a_mkc/1+kc$	
	k	1/n	R	a_mk	k
sludge	630.594	0.387	0.725	39936	157
compost	250.384	0.166	0.743	66300	446

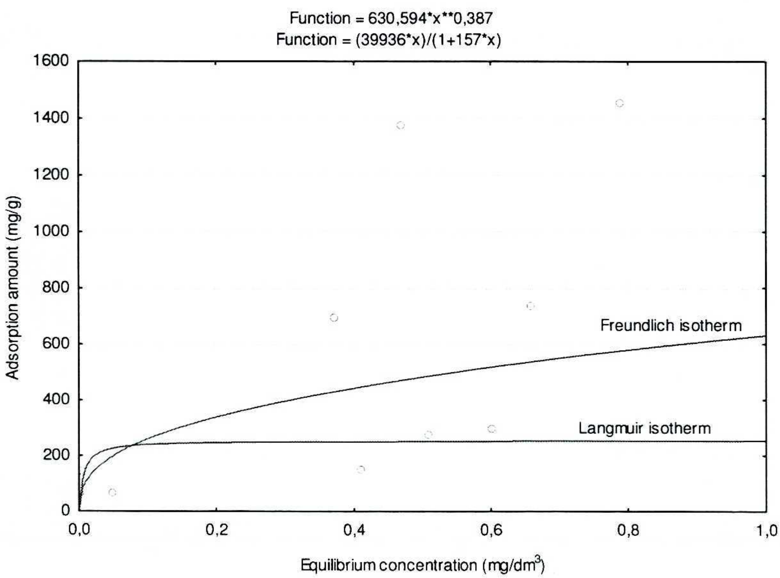

Fig. 1. The Freundlich and Langmuir adsorption isotherms of pesticide on sewage sludge.

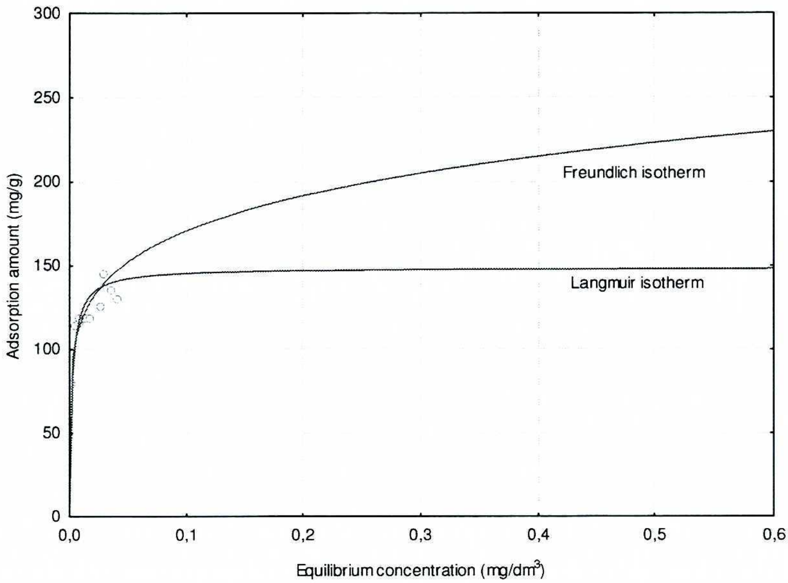

Fig. 2. The Freundlich and Langmuir adsorption isotherms of pesticide on compost

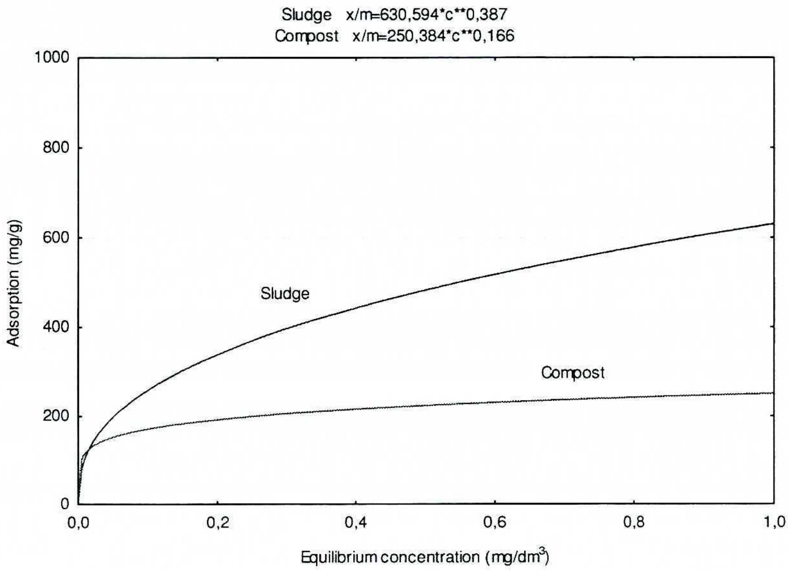

Fig. 3. The comparison of the Freundlich isotherms of pesticide on chosen natural sorbents.

Figures 1-3 present adsorption isotherms for studied pesticides on applied natural adsorbents as a function of adsorbate amount adsorbed by adsorbent weight unit (*x/m*) vs. adsorbate's balance

(equilibrium) concentration (c_0). The same group of isotherms according to Giles' classification (L) was achieved for both dairy wastewater treatment plant and compost.(Atkins, 2001, Paderewski, 1999, Jankowska, 1991, Rodriquez-Cruz at al., 2005) It includes isotherms for systems in which solvent is not strongly adsorbed and is not competitive for dissolved substance being adsorbed. (Ochsner at al., 2006) Isotherm's shape also proves the flat arrangement of adsorbate's molecule at adsorbent's active centers. The shape corresponding to Langmuir's isotherm is characterized by monotonic approach to limit adsorption that is most probably responsible for complete monomolecular layer covering all adsorbate's surface. (Ignatowicz and Skoczko, 2002, Yuh-Shan, 2006) Figure 3 apparently shows that, in the case of compost, the limit adsorption is reached much faster and at lower balance concentrations not exceeding 220 mg/g level. For dairy wastewater treatment plant, Freundlich's isotherm does not approach monotonically to limit adsorption within the same balance concentrations range, and it can be predicted as over 600 mg/g.
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. Higher *k* value corresponds to higher sorption capacity. In own studies, higher value of *k* coefficient was achieved for dairy wastewater treatment plant, 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. Also 1/n coefficient for the sludge is two times higher, which proves higher intensity of chloroorganic pesticides retain.

CONCLUSIONS

1. Sewage sludge proved to be the best natural sorbent for the process for migration reduction of chloroorganic pesticides from tombs.
2. It is indispensable to analyze the Freundlich adsorption isotherm coefficients to access the optimum amount of the sorbent for pesticide detoxication.

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