

Chloroorganic Pesticide Adsorption from Water Solution Using Sewage Sludge Vermicompost as a Natural Sorbent

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ABSTRACT

Dozens of thousands of tons of pesticide waste have been stored since 1950s. The corrosion of concrete bunkers and wells where the expired pesticides are deposited causes the risk of toxic leakage due to deteriorating conditions of these constructions. Such hazardous spill might be transported by underground waters in the form of so-called underground inflow and subsequently might reach a network of surface waters. Evaluating the adsorption potential of natural sorbent for pesticide was the main goal of this research. The adsorption balance was examined in order to analyze the influence of the adsorption mechanism of HCH molecules on vermicompost. The adsorption of HCH isotherms by vermicompost at constant temperature was tested experimentally. The Freundlich, Langmuir and BET's adsorption isotherm models describe the experimental data within the acceptable error ranges. The Freundlich model proved to be more suitable for the experimental data. The form of isotherms indicates that HCH is adsorbed as a monolayer; therefore no obstacles occur in order for water and pesticide molecules to cover the adsorption surface.

Keywords: sorption, vermicompost, isotherm, pesticide

INTRODUCTION

Pesticides are toxic chemicals used to eradicate numerous pests and diseases. These compounds might be carcinogenic, teratogenic, embryotoxic, and mutagenic. Improperly stored, unused or expired pesticides become dangerous waste, which infiltrates into the natural environment in an uncontrolled way, thus posing a threat to all living organisms. Dozens of thousands of tons of pesticide waste have been stored since 1950s (Ignatowicz, 2011, 2017). The corrosion of concrete bunkers and wells where the expired pesticides are deposited causes the risk of toxic leakage due to deteriorating conditions of these constructions (Ignatowicz, 2011). Such hazardous spill might be transported by underground waters in the form of so-called underground inflow and subsequently might reach a network of surface waters (Ignatowicz, 2017). Evaluating the adsorption potential of natural sorbent for pesticide was the main goal of this research. The

adsorption balance was examined in order to analyze the influence of the adsorption mechanism of HCH molecules on vermicompost.

SORPTION ISOTHERMS

Among the several existing isotherms, the sorption data were subjected to five commonly used isotherms models, namely (Table 1) Langmuir (1918), Freundlich (1894), BET (1938), to evaluate the maximum saturation capacity of adsorbent (Ochsner et al., 2006; Atkins, 2006).

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

$$q_e = K_F c^{1/n} \quad (1)$$

where: q_e (mg/g) is the amount of HCH adsorbed on the adsorbent surface at equilibrium, c (mg/L) the HCH concentration in aqueous solutions at equilibrium,

K_F – constant – is the maximum multilayer adsorption capacity and $1/n$ is a characteristic constant which measures the adsorption intensity (K_F 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 the proposed kinetic mechanism. Langmuir isotherm constitutes a model for monolayer localized physical adsorption on a homogeneous surface; it 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:

$$q_e = q_m \frac{k c}{1+k c} \tag{2}$$

where: q_e (mg/g) is the amount of HCH adsorbed on the adsorbent surface at equilibrium, c (mg/L) the HCH concentration in aqueous solutions at equilibrium, q_m (mg/g) is the maximum monolayer adsorption capacity, k is the constant related to the free energy of adsorption.

Molecules often 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 BET equation may be written as:

$$\Theta = \frac{1}{1-c} \left(\frac{Kc}{1+(k-1)c} \right) \tag{3}$$

where: Θ (q_e/q_m) is the fractional coverage, c (mg/L) the HCH concentration in aqueous solutions at equilibrium, k is the constant related to the free energy of adsorption.

METHODS

Sorbate

On the basis of the literature data and own studies, chloroorganic pesticides that most often occurred in the drinking water near the graveyards

Table 1. The sorption isotherms

Isotherm	Type of relation of physicochemical quantities	Formula	Linear formula	Formula constant	Method of estimation
Monolayer					
Freundlich	Adsorption on heterogeneous surface with monolayer effect; micro-porous solids	$q_e = K_F c_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e$	$A = kc^{1/n}$ n, k	Gauss-Newton
Langmuir	Adsorption on homogeneous surface with monolayer effect (lateral interactions and multilayer effect may be easily incorporated)	$q_e = \frac{q b c}{1+b c}$	$q_e = \frac{1}{b} \frac{q}{c} + q$	$A = ac/(1+kc)$ a, k	Gauss-Newton
Multilayer					
BET	Adsorption on homogeneous surface with multilayer effect	$\Theta = \frac{1}{1-c} \left(\frac{Kc}{1+(k-1)c} \right)$	$\frac{c}{q_e(1-c)} = \frac{1}{qm k} + \frac{k-1}{qm k} c$	$A = ac/(1+c)(1+kc)$ a, k	Gauss-Newton

at the highest concentrations were selected as representative sorbate (Ignatowicz, 2009; 2011). Individual pure active substances HCH were applied. Technical grade HCH of $99.8 \pm 0.2\%$ purity obtained from Institute of Industrial Organic Chemistry Analytical Department in Poland was used as a 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 twice distilled deionised water. The prepared solutions were applied in the concentrations of 10 mg pesticide per litre.

Sorbent

The vermicompost made from municipal sewage sludge after aerobic stabilization was applied as a sorbent. The characteristics of the compost are given in Table 2. The used waste products comply with the requirements of the Regulation of the Minister of the Environment concerning agricultural usage of municipal sewage sludge.

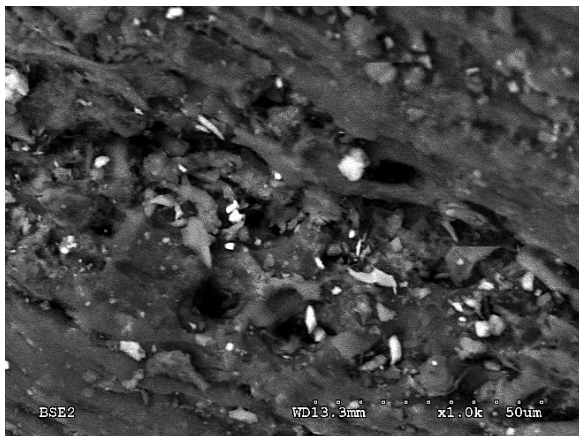


Figure 1. Scanning electron microscope (SEM) photos of vermicompost.

Table 2. The characteristics of vermicompost

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	1231	1.2
Permissible standard						
500	800	10	500	100	2500	5
Other (%)						
pH	Hydration	Dry mass		Organic matter		
5.88	46.0	54.0		54.0		

Sorption procedure

The studies were performed under static conditions in accordance with the methodology applied in Belgium, Germany, France, Italy, England, the USA, Poland and other countries (Ignatowicz, 2011, 2017; Hamadi et al., 2004; Hamdaoui et al., 2007; Kumar et al., 2003; Witbowo et al., 2007; Yuh-Shan, 2006; Sahaa et al., 2008; El-Sharkawy et al., 2006).

Sorbent after prior degassing, cleansing with distilled water and drying, was crushed with a mortar and dried using an electric drier at the temperature of 150°C for 3 hours until it became solid mass. From such material test portions were prepared with the mass of 0.001–0.025 g for 100 ml of solution. Representative sorbent samples were added to the conical flasks containing pesticide solution with the concentration of 10 mg/L.

The flasks were shaken on a vortex mixer with constant vibration amplitude for 24 hours, then they were left for 24 hours in order to obtain full sorption balance. After that time, the samples underwent double filtration using soft tissue drains. The first and last portions of the filtrate were discarded. Then, the pollutant concentration in the filtrate was measured, according to the accepted method. The sorption process analysis was conducted on the basis of the obtained results (using Statistica software). The Freundlich, Langmuir, BET, Temkin and Jovanovic isotherms were estimated as non-linear models with the least squares method with the use of Gauss-Newton algorithm.

Analytical procedure

The HCH concentrations were determined in the collected samples in accordance with the obligatory methodology using an AGILENT6890 gas chromatograph 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 µm 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 (Balinova, 1996; Głowacki, 2014; Hussen et al., 2007; Kogut et al., 2014).

RESULTS AND DISCUSSION

The achieved study results are presented in Figure 3. The characteristics of the applied adsorbent (Table 1) indicate that the requirements of compost for natural applications are met. The parameters calculated according to the isotherm models under study are listed in Table 3. The adsorption process is described using Freundlich's, Langmuir's, Tiemkin, Jovanovic and BET's formulae:

$$\text{Freundlich } A=kc^{1/n} \quad (4)$$

$$\text{Langmuir } A=a_m kc/1+kc \quad (5)$$

$$\text{BET } A=ac/(1+c)(1+kc) \quad (6)$$

The following curves were achieved $A_F = 422.3 c^{0.35}$ for compost at coefficient of correlation of $R=0.91$; $A_L = 3175.6 c/1-1077.4 c$ at the coefficient of correlation equal $R=0.75$; and $A_{BET} = 5321.2 c/(1+c)(1-4.89c)$ at the coefficient of correlation $R=0.76$.

The isotherms were calculated applying the Statistica software by means of the least squares by Gauss-Newton method; the achieved constants a and k are presented in Figure 3. The figure presents the adsorption isotherms for the studied HCH pesticide on vermicompost as a function of adsorbate amount adsorbed by adsorbent weight unit (x/m) vs. concentration of the HCH at the equilibrium (c_0).

The correlation coefficients (R) were employed to ascertain the fit of all isotherms with the experimental data. From Table 3, the values of R coefficients were found higher for the Freundlich model than for the Langmuir and BET models. This indicates that the Freundlich isotherms are clearly the best fitting isotherm model for the experimental data. (Neethu et al., 2017; Ignatowicz, 2017).

The nature of the studied HCH pesticide (a chlorinated and hydrophobic molecule) suggests that its adsorption is of the hydrophobic type directly bound to the specific surface of the adsorbent particles (Hamadi et al., 2004). 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 HCH adsorbed on the vermicompost surface at equilibrium (mg/g) against c_e , the HCH concentration in the aqueous solution at equilibrium in order to classify the isotherms according to

Table 3. The coefficients of the adsorption isotherms (level of confidence 95%, $\alpha=0.05$)

Izoterm	a	b	R
Freundlich	422.3	0.35	0.91
Langmuir	3175.6	-1077.4	0.75
BET	5321.2	-4.89	0.76

the classification of Giles et al., 1960 (Hamdaoui et al., 2007). This one includes four main groups: L, H, S and C. The experimental adsorption isotherms of HCH in aqueous solutions on the studied carbon are presented in Figure 3. The isotherm according to Giles' classification (L) was achieved for HCH. (Neethu et al., 2017; Moawed et al., 2017; Chin-Pampillo, 2016) The L shape of the adsorption isotherms means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface (molecules adsorbed flat on the surface). Figure 3 shows that the value of experimental maximum adsorption capacity (q_m experimental) for the chloroorganic compound HCH on vermicompost is about 225 mg/g.

According to Hamdaoui and Nafrechoux, the HCH molecules bind to the adsorbent only through 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. The shape of these isotherms indicates that the HCH is 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,

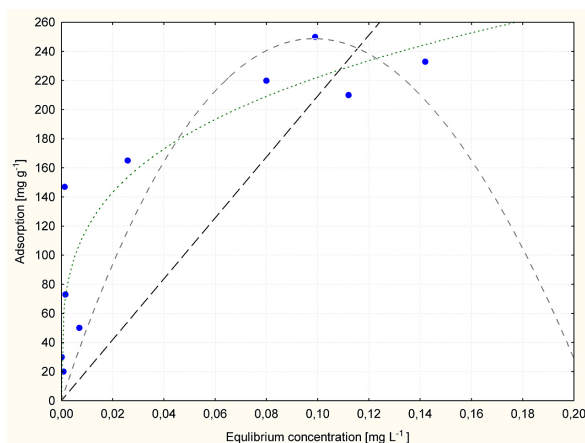


Figure 2. The comparison of model's isotherms of pesticide on compost

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 (Ignatowicz, 2011, 2017; Hamdaoui, 2007). Therefore, there would be weak interactions on these adsorbent surfaces because the number of layers cannot increase freely.

The equilibrium data were further analyzed using the Freundlich equation using the same set experimental data, by plotting $\ln q_e$ versus C_e . The calculated Freundlich isotherm constants and the corresponding coefficient of correlation values were shown in Table 3. The coefficients of correlation are high ($R \geq 0.921$) showing a good linearity. The magnitude of the exponent n ($n=1.36$) gives an indication on the favorability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics.

The knowledge on the $1/n$ parameter value in Freundlich's formula allows for assessing the adsorption intensity of a given substance from water phase on adsorbent; value of KF constant determines the sorption capacity of an adsorbent at balance concentration in a solution. Higher KF value corresponds to higher sorption capacity. In the author's own studies, higher value of KF coefficient was achieved for vermicompost, which proves its usefulness in application as sorption HCH. Constants $1/n$ in Freundlich's formula constitute directional coefficients of isotherms equal to the tangent of line inclination angle in logarithmic coordinates. Therefore, the higher the $1/n$ value, the more intensive the adsorption process.

CONCLUSIONS

The present study indicates the suitability of the vermicompost for removal of graveyard chloroorganic pesticide HCH from aqueous solutions. The adsorption process is described using Freundlich, Langmuir, and BET formulae. The Freundlich model was better as far as fitting the experimental data is concerned.

The group of isotherms according to Giles' classification (L) was achieved for chloroorganic pesticide. The HCH molecules bind to the adsorbent through only one grouping and the adsorption becomes progressively easier as the adsorbed

quantity increases. Thus, the first fixed molecules facilitate the adsorption of the following molecules because of the lateral attraction. The shape of these isotherms indicates that the chloroorganic pesticide HCH is 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.

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