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Hexachlorocyclohexane (HCH) isomers adsorption from water solution using natural sorbent

Katarzyna Ignatowicz

Department of Technology in Engineering and Environmental Protection, Białystok University of Technology, ul. Wiejska 45a, 15-351 Białystok, Poland, email: k.ignatowicz@pb.edu.pl

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ABSTRACT

Dozens of thousands of tons of pesticide waste have been stored since 1950's. Corrosion of concrete bunkers and wells where the outdated pesticides are deposited causes the risk of toxic leakage due to deteriorating conditions of these constructions.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. Adsorption balance was examined in order to analyze the influence of the adsorption mechanism of isomers HCH molecules on vermicompost. The adsorption of isomers α-HCH, β-HCH and γ-HCH (lindane) isotherms by vermicompost at constant temperature was experimentally tested. The Freundlich, Langmuir, Temkin, Jovanovic and BET's adsorption isotherm models describe experimental data within the acceptable error ranges. The Freundlich, Jovanovic and Temkin models proved to be more suitable for the experimental data. The isotherms' form indicates that isomers HCH is adsorbed as a monolayer, therefore no obstacles occur in order for water and pesticide molecules to cover the adsorption surface.

Keywords: Sorption; Pesticide; Isotherm

1. 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 penetrates to 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 1950's [1–6]. Corrosion of concrete bunkers and wells where the outdated pesticides are deposited causes the risk of toxic leakage due to deteriorating conditions of these constructions [4,5–8]. 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 [3,5]. Evaluating the adsorption potential of natural sorbent for pesticide was the main goal of this research. Adsorption balance was examined in order to analyze the influence of the adsorption mechanism of isomers α-HCH, β-HCH and γ-HCH (lindane) molecules on vermicompost [1,4,5–9].

2. Sorption isotherms

In order to evaluate the maximum volume of absorbent saturation and to determine the sorption mechanism, six commonly used isotherm models were used, which describe experimental data (Table 1), isotherm Langmuir (1918), Freundlich (1894), BET (1938), Jovanovic (1969) and Temkin (1963) [10–13].

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Table 1
Characteristic of sorption isotherms [8,11–14]

Isotherm	Type of relation of physicochemical quantities	Formula	Linear formula	Formula constant	Method of estimation
Monolayer					
Freundlich	Adsorption on heterogeneous surface with monolayer effect; microporous 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)	$q_e = \frac{qbc}{1+bc}$	$q_e = \frac{1}{-b}\frac{q}{c} + q$	$A = ac/1 + kc$ a, k	Gauss–Newton
Temkin	Adsorption on heterogeneous surface with monolayer effect	$\Theta = \frac{RT}{\Delta Q} \ln k\, c_e$ $q_e = q_m + K\, lgc$	$\Theta = \frac{RT}{\Delta Q} \ln k + \frac{RT}{\Delta Q} \ln c_e$	$A = a + k\, lgc$ a, k	Gauss–Newton
Jovanovic	Adsorption of organic substance from dilute solutions on heterogeneous surface with monolayer effect (vertical interactions and multilayer effect may be easily incorporated)	$\Theta = 1 - \exp(-kc)$		$A = a(1 - \exp(-kc)$ a, k	Gauss–Newton
Multilayer					
BET	Adsorption on homogeneous surface with multilayer effect	$\Theta = \frac{1}{1-c}\left(\frac{Kc}{1+(k-1)c}\right)$	$\frac{c}{q_e(1-c)} = \frac{1}{q_m k} + \frac{k-1}{q_m k} c$	$A = ac/(1 + c)(1 + kc)$ a, k	Gauss–Newton

2.1. Freundlich model

Freundlich isotherm is an experimental equation describing adsorption on heterogenic surfaces (energetically heterogeneous) and microporous adsorbents:

$$q_e = K_F c^{1/n} \tag{1}$$

where q_e (mg/g) – real adsorption, K_F (mg/g) – constant, expressing maximum adsorption on the sorbent's surface and l/n is a characteristic constant connected with sorption process intensity. Constants n and K_F are determined by experiment in given temperature.

2.2. Langmuir model

Langmuir isotherm is basic adsorption isotherm. According to Langmuir isotherm, the adsorbate might produce on the surface of the adsorbent a so-called monolayer of particles interacting with adsorption spots ("vertical" interaction), but not interacting (or slightly interacting) among themselves ("horizontal" interaction). The adsorbate particles present in the liquid phase hit the surface – the probability of their adsorption increases with available free surface. The adsorbed particles are characterized by certain desorption probability. Both types of probabilities depend on temperature and the amount of adsorption energy. Together with pressure, the frequency of particles hitting the surface grows, and together with the number of adsorbed particles, the available surface decreases. The equation assumes that it is impossible to form a multilayer, adsorption energy is constant (energetically uniform, thus heterogeneous surface), side interactions are disregarded. Langmuir isotherm equation is presented as:

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

where q_e (mg/g) – real adsorption in the state of sorptic balance, c (mg/L) – concentration of pesticide in the solution in the state of balance, q_m (mg/g) maximum adsorption on the sorbent's surface, k constant connected with adsorption energy.

2.3. Jovanovic model

Jovanovic model preserves the assumptions contained in the Langmuir model, while enabling additional vertical interactions which result in multilayer sorption effect. Jovanovic equation might function as local isotherm equation, in general, integral equation describing adsorption on heterogeneous surface. Jovanovic isotherm can be presented as:

$$q_e = q_m (1 - \exp(-kc)) \quad (3)$$

where q (mg/g) is the amount of adsorbent adsorbed on the surface of adsorbent in balance, c (mg/L) is the concentration of adsorbent in water solution in balance, q_e (mg/g) is the maximum volume of multilayer adsorption, k constant connected with adsorption energy.

2.4. Temkin model

The model is an experimental, two-parameter equation of adsorption isotherm on a heterogeneous solid. The isotherm is connected with constant, endless (unlimited by minimal or maximal energy) decomposition of adsorption spots energy. Temkin isotherm equation [3] assumes that the adsorption heat of all the particles in a layer decreases in a linear way due to the interaction between the adsorbent and the adsorbate, while adsorption is characterized by equal distribution of bond energy. Temkin model can be presented as follows:

$$\Theta = (RT/\Delta Q) \ln kc \quad (4)$$

where $\Theta = q/q_m$ – surface covering (q – adsorption size, q_m – adsorption size in monolayer), R is universal gas constant (kJ/mol K), T temperature (K), $\Delta Q = (-\Delta H)$ change in adsorption energy (kJ/mol), k Temkin balance constant.

2.5. BET model

Particles often form a multilayer network; thus, the Langmuir model loses its validity. In 1938 Stephan Brunauer, Paul Emmett and Edward Teller developed the model, taking into consideration additional interaction between particles. Langmuir isotherm has a better application for chemisorption, whereas BET isotherm for physiosorption on a non-microporous surface. Langmuir isotherm can be presented as:

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

$$A = ac/(1 + c)(1 + kc) \quad (5)$$

where A (mg/g) is the amount of pesticides adsorbed on the adsorbent's surface in balance, c (mg/L) is the pesticide concentrations in water solutions in balance, a (mg/g) is the maximum volume of multilayer adsorption, k is the constant connected with adsorption energy.

3. Methods

3.1. Sorbate

On the basis of literature data and own studies, chloro-organic pesticides that most often occur in drinking water near graveyards at the highest concentration were selected as representative sorbate [1–5]. Individual pure active substance isomers α-HCH, β-HCH and γ-HCH (lindane) were applied. Technical grade γ-HCH of 99.8% ± 0.2% purity, α-HCH of 99.8% ± 0.3% purity and β-HCH of 99.8% ± 0.2% 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 deionized water. The concentrations of prepared solutions were applied: 10 mg pesticide per litre.

3.2. Sorbent

As sorbent, the vermicompost made from municipal sewage sludge after aerobic stabilization was applied. The characteristics of the compost are given in Table 2 and 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.

3.3. Sorption procedure

Studies under static conditions were performed in accordance to methodology applied in Belgium, Germany, France, Italy, England, the USA, Poland and other [1–9,12–18]. Sorbent after prior degassing, cleansing with distilled water and drying was crushed with a mortar and dried using an electric drier

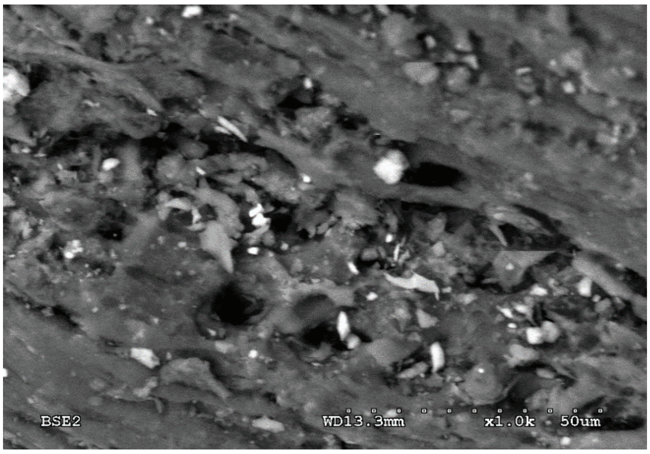

Fig. 2. Scanning electron microscope (SEM) photos of vermicompost.

in the temperature of 150°C for 3 h until it became solid mass. 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. The first and last portions of the filtrate were discarded. Then, pollutant concentration in the filtrate was denoted, according to the accepted method. Sorption process analysis was conducted on the basis of the obtained results (using STATISTICA software). Freundlich, Langmuir, BET, Temkin and Jovanovic isotherms were estimated as non-linear models with the method of the smallest squares with the use of Gauss–Newton algorithm.

3.4. Analytical procedure

α-HCH, β-HCH and γ-HCH 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 [19–22].

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 (RSD) 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%.

Table 2
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	

4. Results and discussion

The obtained research results are presented in Fig. 3 and Table 3. The sorption process was also described with Freundlich, Langmuir, BET, Temkin and Jovanovic equations:

$$\text{Freundlich } A = kc^{1/n} \tag{6}$$

$$\text{Langmuir } A = a_m kc/1 + kc \tag{7}$$

$$\text{BET } A = ac/(1 + c)(1 + kc) \tag{8}$$

$$\text{Temkin } A = a + k\,lgc \tag{9}$$

$$\text{Jovanovic } A = a(1 - \exp(-kc)) \tag{10}$$

Following curves were achieved $A_F = 420.3c^{0.3}$ for compost at correlation coefficient of $R = 0.91$; $A_L = 3{,}150.6\ c/1 - 1057.4c$ at correlation coefficient of $R = 0.55$ and $A_{BET} = 5{,}300.2c/(1 + c)(1 - 4.8c)$ at correlation coefficient of $R = 0.76$ and $A_T = 286.0 + 74.6\ lgc$ at $R = 0.88$, and $A_J = 230.1\ (1 - \exp(-64c))$ at $R = 0.82$.

The constants in mathematical models were determined with the smallest squares method with the use of statistical package STATISTICA; afterwards, the error range within

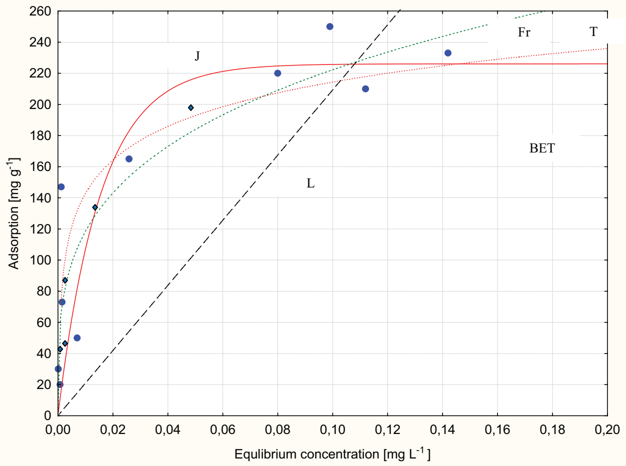

Fig. 3. Comparison of model's isotherms of pesticide (isomers HCH) on vermicompost: Fr – Freundlich, L – Langmuir, T – Temkin, J – Jovanovich, BET – BET.

Table 3
Coefficients of the adsorption isotherms (level of confidence 95%, α = 0.05)

Isotherm	*a*	*b*	*R*
Freundlich	420.3	0.3	0.91
Langmuir	3,150.6	–1,057.4	0.55
Temkin	286.0	74.6	0.88
BET	5,300.2	–4.8	0.76
Jovanovic	230.1	64.0	0.82

these constants was established. The values of constant parameters, as well as correlation coefficient R of individual adsorbents are presented in Table 3. The calculated correlation coefficients have values from 0.55 to 0.91, so matching the applied models to sorption process description is varied. Isomers HCH sorption process on vermicompost is best described by Freundlich, Temkin and Jovanovic isotherm (R = 0.82 – 0.91). It points to a conclusion that vermicompost is characterized by heterogeneous surface and during sorption there are reactions occurring not only in the monolayer [1,2,13,23,24].

According to Shattar et al. [25], the equilibrium data were simulated by the nonlinear Langmuir, Freundlich, Temkin and Redlich–Peterson isotherm models. The adsorption behavior was well interpreted by the Langmuir isotherm model, with a monolayer adsorption capacity for ametryn of 207.71 mg/g. According to Choumane and Benguella [26], the adsorption isotherm data follows the Langmuir equation in which the parameters were calculated. According to Mohammad et al. [8], the experimental isotherms data were analyzed using the Freundlich, Temkin, Dubinin–Radushkevich isotherms equations. The best experimental data were obtained for low-cost adsorbents by the Freundlich isotherm model with high correlation coefficients (R = 0.97).

Fig. 3 shows adsorption isotherms of the examined pesticides on the applied sorbent as function of adsorbed by mass unit sorbent (compost) adsorbate (HCH) (x/m) from equilibrium concentration of adsorbate in water solution (c_0). A group of isotherms according to Giles classification: L was obtained [12,13]. The L shape of the adsorption isotherms indicates that no strong competition occurs between 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). From Fig. 3, the values of experimental maximum adsorption capacity (q_m experimental) for the chloro-organic compound HCH on vermicompost is about 240 mg/g. According to Shattar et al. [25], the adsorption behavior was well interpreted by the Langmuir isotherm model, with a monolayer adsorption capacity for ametryn of 207.71 mg/g.

According to Hamdaoui and Nafrechoux [13] the HCH 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. The shape of these isotherms indicates that the isomers α-HCH, β-HCH and γ-HCH (lindane) 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 [1,2,4,13]. There would be weak interactions therefore on these adsorbent surfaces because the number of layers cannot increase freely.

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 420.3 was obtained, which confirms vermicompost's usefulness in applying it as sorption screen for removing chloro-organic 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 [13,15,27,28].

The parameters of Temkin model as well as the correlation coefficients are given in Table 3. The higher values of the coefficient of correlation show a good linearity whatever the maximum adsorption capacity used for the calculation of surface coverage. The variation of adsorption energy, $\Delta Q = (-\Delta H)$, is positive for the examined isomers α-HCH, β-HCH and γ-HCH (lindane), which indicates that the adsorption reaction is exothermic. In order to seek a regularity for the observed changes between the variations of adsorption energy of the tested chloro-organic compounds, it seems that the chloro-group has a negative increment (exothermic effect) [28].

5. Conclusions

On the basis of the conducted experiment, it was concluded that:

1. Vermicompost can be used for HCH pesticide sorption from water solutions.
2. HCH sorption process on vermicompost is best described by Freundlich (R = 0.91) isotherm, which proves the sorbent heterogeneous surface. Reactions occur in monolayer during sorption.
3. On the basis of sorption equations, isotherm group L was obtained according to Giles classification.

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References

[1] K. Ignatowicz, Selection of sorbent for removing pesticides during water treatment, J. Hazard. Mater., 169 (2009) 953–957.

[2] K. Ignatowicz, Metals content chosen for environmental component monitoring in graveyards, Fresenius Environ. Bull., 20 (2011) 270–273.

[3] K. Ignatowicz, Sorption process for migration reduction of pesticides from graveyards, Arch. Environ. Protect., 34 (2008) 143–149.

[4] K. Ignatowicz, Pesticide waste burials in the area of Podlaskie Province, Rocz. Ochr. Śr., 10 (2008) 545–555.

[5] M. Włodarczyk-Makuła, Influence of selected organic micropollutants on organisms, Civil Environ. Eng. Rep., 24 (2017) 83–97.

[6] K. Kusmierek, M. Sankowska, A. Swiatkowski, Kinetic and equilibrium studies of simultaneous adsorption of monochlorophenols and chlorophenoxy herbicides on activated carbon, Desal. Wat. Treat., 52 (2014) 178–183.

[7] A.M. Donia, A.A. Atia, R.A. Hussien, R.T. Rashad, Comparative study on the adsorption of malathion pesticide by different adsorbents from aqueous solution, Desal. Wat. Treat., 47 (2012) 300–309.

[8] S.G. Mohammad, S.M. Ahmed, A.F.M. Badawi, A comparative adsorption study with different agricultural waste adsorbents for removal of oxamyl pesticide, Desal. Wat. Treat., 55 (2015) 2109–2120.

[9] K. Ignatowicz, Use of natural waste materials as sorbents for limiting the migration of pesticides from graveyards, Chem. Rev., 87 (2008) 464–467.

[10] T.E. Ochsner, B.M. Stephens, W.C. Koskinen, R.S. Kookana, Sorption of a hydrophilic pesticide, Soil Sci. Soc. Am., 70 (2006) 1991–1997.

[11] P.W. Atkins, Physical Chemistry, 8th ed., Oxford University Press, 2006.

[12] N.K. Hamadi, S. Swaminathan, X.D. Chen, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater., B112 (2004) 133–141.

[13] O. Hamdaoui, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon - Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater., 147 (2007) 381–394.

[14] A. Kumar, S. Kumar, S. Kumar, Adsorption of resorcinol and catechol on granular activated carbon: equilibrium and kinetics, Carbon, 41 (2003) 3015–3025.

[15] N. Witbowo, L. Setyadhi, D. Witbowo, J. Setiawan, S. Ismadji, Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: influence of surface chemistry on adsorption, J. Hazard. Mater., 146 (2007) 237–242.

[16] Y.-S. Ho, Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods, Pol. J. Environ. Stud., 15 (2006) 81–86.

[17] B.B. Sahaa, A. Chakraborty, S. Koyama, S. Yoon, I. Mochida, M. Kumja, C. Yap, K. Choon Ng, Isotherms and thermodynamics for the adsorption of n-butane on pitch based activated carbon, Int. J. Heat Mass Transfer, 51 (2008) 1582–1589.

[18] I.I. El-Sharkawy, B.B. Saha, S. Koyama, K. Choon Ng, A study on the kinetics of ethanol-activated carbon fiber: theory and experiments, Int. J. Heat Mass Transfer, 49 (2006) 3104–3110.

[19] A. Balinova, Strategies for chromatographic analysis of pesticide residues in water, J. Chromatogr. A, 754 (1996) 125–135.

[20] A. Hussen, R. Westbom, N. Megersa, L. Mathiasson, E. Bjorklund, Selective pressurized liquid extraction for multi-residue analysis of organochlorine pesticides in soil, J. Chromatogr. A, 1152 (2007) 247–251.

[21] K. Ignatowicz, Occurrence study of agro-chemical pollutants in waters of Suprasl catchment, Arch. Environ. Protect., 35 (2009) 69–77.

[22] P. Kogut, J. Piekarski, K. Ignatowicz, Start-up of biogas plant with inoculating sludge application, Rocz. Ochr. Śr., 16 (2014) 534–545.

[23] K. Ignatowicz, J. Piekarski, I. Skoczko, J. Piekutin, Analysis of simplified equations of adsorption dynamics of HCH, Desal. Wat. Treat., 57 (2016) 1420–1428.

[24] N. Narayanan, S. Gupta, V.T. Gajbhiye, K.M. Manjaiah, Optimization of isotherm models for pesticide sorption on biopolymer-nanoclay composite by error analysis, Chemosphere, 173 (2017) 502–511.

[25] S.F.A. Shattar, N.A. Zakaria, K.Y. Foo, Enhancement of hazardous pesticide uptake, ametryn using an environmentally friendly clay-based adsorbent, Desal. Wat. Treat., 79 (2017) 188–195.

[26] F.Z. Choumane, B. Benguella, Removal of acetamiprid from aqueous solutions with low-cost sorbents, Desal. Wat. Treat., 57 (2016) 419–430.

[27] E.A. Moawed, A.M. Radwan, Application of acid modified polyurethane foam surface for detection and removing of organochlorine pesticides from wastewater, J. Chromatogr. B, 15 (2017) 1044–1045.

[28] J.S. Chin-Pampillo, M. Masís-Mora, K. Ruiz-Hidalgo, E. Carazo-Rojas, C.E. Rodríguez-Rodríguez, Removal of carbofuran is not affected by co-application of chlorpyrifos in a coconut fiber/compost based biomixture after aging or pre-exposure, J. Environ. Sci., 46 (2016) 182–189.