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Adsorption of Lambda Cyhalothrin on to Athi River Sediments: Apparent Thermodynamic Properties

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Abstract

Lambda-Cyhalothrin is extensively used in agriculture, horticulture, and public health management in Kenya. The pesticide is effective against many vegetable pests, rice and other disease agents. The adsorption of L-Cyhalothrin onto sediments of Athi River was studied using UV-visible and the results were analyzed by fitting data into isotherm models including Freundlich and Dubinin-Radushvich plot to understand the environmental impacts of this pesticide. The models presented different numerical values but the results demonstrated similar characteristics. The study was aimed at determination of adsorption characteristics of L-Cyhalothrin on sediments from Athi River. Different masses of sediments were spiked with different concentrations of L-Cyhalothrin. The mixtures were shaken at varied times to reach equilibrium. The amounts of pesticide adsorbed were determined by analyzing the difference between the UV-visible Spectrophotometer data and the initial concentrations. Line Plots were used to determine other thermodynamic variables. Various isotherm models were used to explain the adsorption characteristics of the Lambda-Cyhalothrin. It stands out that Dubinin-Radushvich (D-R) with average R2: 0.935, 0.938 and 0.898 fitted best in this experiment while Freudlich R2: 0.783, 0.899 and 0.812 for all sediment samples, Upstream, Midstream, and Downstream, respectively. The spontaneity of the adsorption process was also realized in ΔG (Gibb's free energy) values as predicted by Freundlich. In both models, Midstream ΔG was negative (-) showing complete spontaneous characteristics. Also in Upstream, ΔG was negative (-) for Freundlich whereas Downstream ΔG was positive (+). Generally, adsorption capacity of Athi river sediments was low due to low mineral contents and total organic Carbon including other physicochemical properties specifically, textures, Nitrogen content including its temperature and moisture contents.

Keywords: Lambda-cyhalothrin; Thermodynamic variables; Dubinin-Radushvich isotherm; Athi River

Introduction

The use of pesticides including insecticides, herbicides, fungicides, rodenticides, and acaricides can be dated before the 16th century when chemicals such as arsenic sulphide, Paris green (Copper acetoarsenite) were used to control Malaria transmissions. Though the use of synthetic organic pesticides began around 1940 Lambda-Cyhalothrin is an artificial insecticide that characterizes the biochemical effects of natural pyrethrin pesticide It is the active ingredient in many insecticides such as Karate, Warrior, and Icon that are commonly applied to control insects and pests in public health emergency, agricultural/horticultural farming and in homes [1]. It is effective against many crop and disease vector insects and ticks. The use of Pesticides including Lambda-Cyhalothrin in livestock and crop farming have led to increased food security and livelihood in many developing countries though uncontrolled excessive use is hazardous to human life as well to the environment. Lambda-Cyhalothrin and other pesticides rapidly disappear upon application in the environment [2] Studies have proven that approximately 2-5% of applied pesticides go to targeted organisms and subsequently the rest end up in the environment [3]. Pesticide substrates in the environment undergo several chemical processes including oxidation, absorption, degradation, halogenations, transfer and other microbial actions [4] Transfer of pesticide residues away from the targeted sites through volatilization, spray drift, agricultural runoff, leaching, or crop removal is a major determining factor in assessing the overall environmental impacts of pesticides [5]. Acute (short-term) human exposure can lead to skin irritation, burn or allergic reaction [6]. It is very toxic particularly to various species of fish and other aquatic organisms.

Materials and Methods

The following instruments, materials and reagents were used: UV-Visible spectrophotometer (UV-1700 Schamadzul), Mini Orbital Shaker, Analytical balance (Fischer scientific A-160), Lambda-Cyhalothrin (karate 25 g/kg pure), Glass bottles, Distilled water, Stop watch, Acetone (90% pure) and River sediment from Athi River.

Procedures

The samples were dried for a week and pulverized to maintaining its originality. The Calcium, Potassium and sodium contents were analyzed using Flame Photometer, whereas other elements including Phosphorus, Magnesium and Manganese were determined calorimetrically, [7] The available total organic carbon content was analyzed by oxidative spectrophotometer, [8] The total N was determined thru distillation followed by Titration, [9]. The PH was also determined simply by a pH meter and other trace metals (Fe, Zn and Cu) using an Atomic Absorption Spectrophotometer (AAS), [10]. The cation ion exchange capacity of the metallic elements at neutral pH was determined by Titration after distillation [11] To conduct the adsorption study, 2, 4, 6, 8, 10, 20, 40, 60, 80, and 100 g/L were prepared and adsorption values determined at the UV-vis between 200 to 900 nm. The existence of the adsorption/desorption equilibrium of 2.0 g, 1.0 g, 0.5 g, 0.2 g and 0.1 g of the soil samples were investigated. The dried sediments were placed in glass bottles and shaken with the pesticide for an hour. The aqueous parts were poured and filtered with a Whitman filter paper to obtain a clear concentrated L-Cyhalothrin solution. The absorbance of Ce and Qe was obtained at the UV-Visible spectrophotometer at 218 nm. ΔG, n and K were found using 0.5 g of each sample mixed with deionized water. The samples were spiked with 50, 40, 30, 20, and 10 ppm of L-Cyhalothrin and shaken for 15 min, 30 min, 45 min and 60 min using

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an orbital shaker. Similarly, concentration study of L-Cyhalothrin was carried out using UV visible Spectrophotometer.

Results and Discussion

The soils properties have significant impacts on its adsorption capacity. The profile of the soils according to Table 1 on Athi River soil showed that the organic carbon content is low for all three sampling sites, (0.54, 0.91 and 0.75 respectively). This means the adsorption capacity of these samples is generally low thus not proportionately. Another factor that influences the adsorption is the physical dipole-dipole attraction (Van der Waals force) that improves the adsorption capacity for the soil. Below in Table 1 are the sediment profiles of the Athi River.

Concentration study

The prepared standard solution of Lambda-Cyhalothrin behaved well at λ max 218 nm at UV-Visible spectra as shown below in Figure 1. The plot of absorbance against concentration at 218 nm shaped a straight line. This means Beer's Law is obeyed

$$A=\varepsilon CL \quad (1)$$

In the above equation, A is the absorbance, L is the path length of the light and C is concentration. The symbol ἑ, is the molar absorption coefficient for the chemical species of interest.

Adsorption isotherm

The process of adsorption is defined as the summative accumulation of a chemical species at the interface of an aqueous solution and a solid phase [12] The chemical species is called adsorbate and the surface at which it accumulates is called adsorbent. The adsorption kinetics of Lambda-Cyhalothrin onto Athi River sediments was carried out by preparing 10 ml of Lambda-Cyhalothrin in various concentrations (10 ppm- 50 ppm) and shaken at varying times (15 minutes, 30 minutes, 45 minutes and 60 minutes) on an orbital shaker. The mixture was filtered and the concentrated residual solution was analyzed using UV-spectrophotometer (SHEMAZU 1700). The amount of the pesticide adsorbed (mg/g) was determined using the Vanderburgh and Van Griekenm's formula [13]

$$Q=v(c_i-c_f)/w \quad (2)$$

Where Q is the amount of solute adsorbed, V is the volume of the absorbate, C_i and C_f are the initial and final concentrations, respectively. W is the weight in gram of the adsorbent and data fitted into freudlich and Dubinin-Radushkevich isotherm models.

Field	Upstream (A)	Midstream (B)	Downstream (C)
Sediment depth	2-5 cm	2-5 cm	2-5 cm
Parameters	Value	Value	Value
Total Nitrogen %	0.08	0.11	0.10
Total Org. Carbon %	0.54	0.91	0.75
Phosphorus ppm	8.00	11..00	40.00
Potassium me %	0.82	1.06	0.60
Calcium me%	23.90	30.20	5.10
Magnesium me%	3.28	3.36	1.76
Manganese me%	2.12	2.68	0.61
Copper ppm	1.56	1.55	1.71
Iron ppm	191.00	174.00	39.30
Zinc ppm	5.00	5.94	2.04
Sodium me%	1.00	1.29	0.50
Elect. Cond. Ms/cm	0.93	0.86	N/A

Table 1: Sediment profile of Athi River.

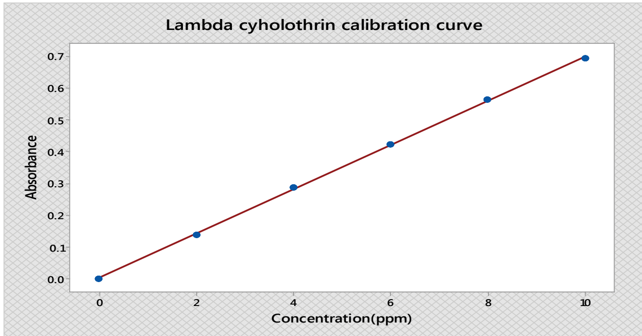

Figure 1: Plot of Concentration from 0-12 ppm of Lambda-Cyhalothrin.

Freundlich isotherm model

The same data obtained from the statistics of the research were exposed to Freundlich isotherm which gave positive (+) ΔG values for sample C (Downstream) and negative (-) ΔG for samples A and B (Up and Mid Streams, respectively). This means that samples A and B underwent spontaneous adsorption using Freudlich isotherm while sample C was nonspontaneous. Thus, the Freundlich Isotherm is characteristic of heterogeneous surface, (Freundlich, 1906). It can be expressed as:

$$q_e=k_f c^{1/n} e \quad (3)$$

From equation 1.2, qe (mg/g) is amount of pesticide adsorbed and Ce (mg/L) is the equilibrium concentration and n is a constant that measures the adsorption of non-linearity between the solute concentration in the solution and the adsorption. n is characteristic of the quasi-Gaussian heterogeneity related to the adsorption surface. Kf (L/g) is the Freundlich isotherm constant. The linearized equation for Freundlich isotherm is expressed as follows:

$$\ln q_e=\ln k^f+1/\ln c_e \quad (4)$$

From this expression, plots of lnqe versus ln C_e as presented in this linear form of Freundlich Isotherm have slopes at 1/n and intercepts at lnKF. Figures 2-4 below were generated using the data highlighted in Table 2 above. The data fitted strongly in the adsorption of Lambda-Cyhalothrin unto Athi River sediments of the three (3) sampling areas. This can be validated from the regression (r^2) values ranging from 0.742 to 0.992 and the linearity of the plot in Figures 2-4.

Dubinin-Radushkevich (d-r) isotherm model

This model was used to show the apparent adsorption energy heterogeneity at sites of adsorption. This model has fitted well with high solute activities including intermediate concentration range data. This approach was originally applied to differentiate between the physical and chemical adsorptions of metal ions with it main free energy (E) per molecule [14] The equation and its linear forms are expressed below:

$$\ln q_e=\ln q_d-B_D E^2 \quad (5)$$

$$E=RT \ln [1+1/c_e] \quad (6)$$

From the above expressions, q_D is adsorption strength of soil/ sediment (mg/g), B_D is Dubinin-Radushkevich constant (mol^2/KJ^2), qe is amount of adsorbate at equilibrium (mg/g), and E is Polanyi potential (Dubinin isotherm constant). T is the absolute temperature (k), R is the universal gas constant (j/molk) and Ce is the adsorbate equilibrium concentration (mg/L). One unique characteristic of this model is that it is temperature dependent. This allows for all suitable data to lie in the same curve called characteristic curve when adsorption data at separate

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Time (minute)	Sample	LnK^F	KF	R^2	ΔG	
15	A	0.8957	1.883	6.5732	75.4	-4,665.27
	B	1.002	1.691	5.4249	82.9	-1,921.94
	C	2.136	-0.322	0.7247	78.1	797.78
30	A	0.9518	1.834	6.2589	86.1	-4,543.88
	B	1.841	0.5828	1.7915	99.2	-1,444.56
	C	1.966	-0.2400	0.7867	90.4	594.62
45	A	0.8852	1.852	6.3726	75	-4,588.48
	B	1.174	1.549	4.7066	84.4	-3,837.67
	C	3.228	-2.2880	0.1015	74.2	5,668.69
60	A	1.053	1.635	5.1295	76.6	-4,050.85
	B	1.249	1.484	4.41055	93.3	-3,676.74
	C	2.930	-2.151	0.1164	82	5,329.27

Table 2: Freundlich adsorption data.

Time (minute)	Sample	Ln qD	BD	qD	R^2	E (KJ/mol)
15	A	3.854	-0.000002	47.1814	91.8	-353,553.39
	B	3.844	-0.000002	46.7120	93.8	-353,553.39
	C	4.421	-0.000006	83.1794	86.4	-117,851.13
30	A	3.795	-0.000001	44.4782	98	-707,106.78
	B	3.839	-0.000002	46.4790	89.6	-353,553.39
	C	4.203	-0.000005	66.8867	96.9	-141,421.36
45	A	3.841	-0.000002	46.5720	91.5	-353,553.39
	B	3.995	-0.000002	54.3258	94.1	-353,553.39
	C	5.139	-0.000010	170.5451	85.7	-70,710.68
60	A	3.952	-0.000002	52.0393	92.6	-353,553.39
	B	3.888	-0.000002	48.8132	97.5	-353,553.39
	C	4.754	-0.000010	116.0475	90.2	-70,710.68

Table 3: Dubinin-Radushkevick isotherm Data.

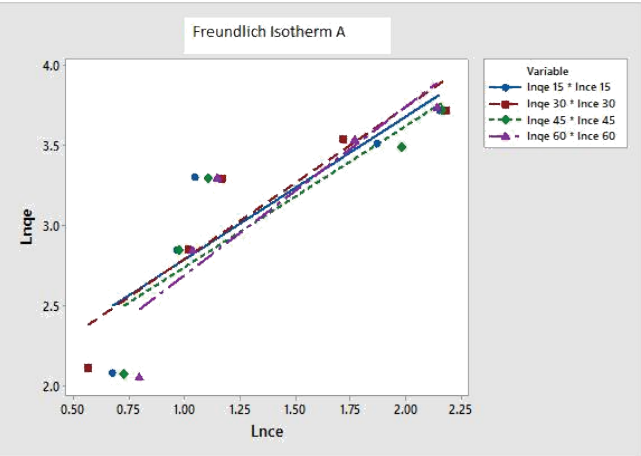

Figure 2: Freundlich Isotherm for Sample.

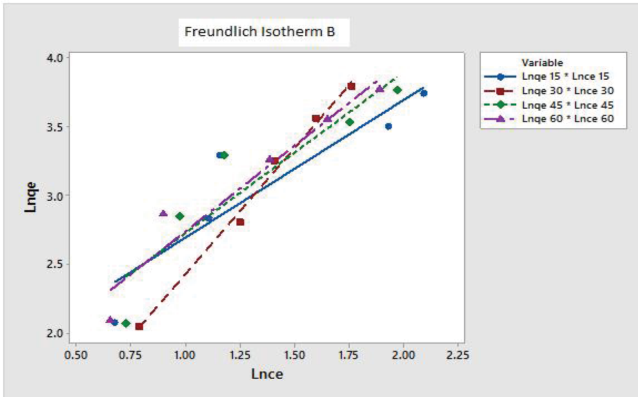

Figure 3: Freundlich Isotherm for Sample B.

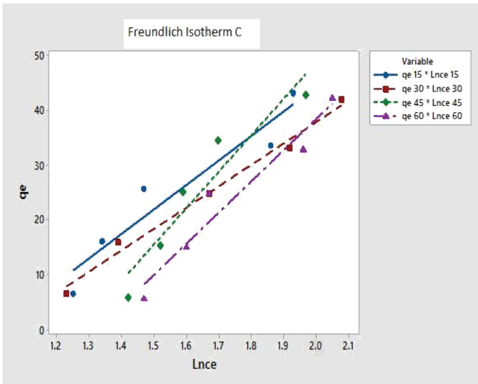

Figure 4: Freundlich Isotherm for Sample C.

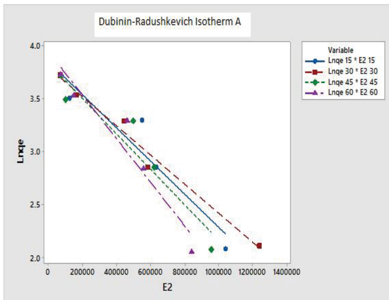

Figure 5: D-R Isotherm for Sample A.

temperatures are plotted as function of the amount adsorbed (lnqe) against the energy (E). Table 3 below gives the summary parameters use in D-R data to generate the graphs in Figures 5-7. From Table 3 above, the potential energy (E) can be calculated from the value of B_D using the formula: $lnqe=lnq_D-B_DE^2$. For example, in 15 minutes of shaking time, lnqe 15=3.844 -0.000002 E^2, r^2=0.938. Lnq_D=3.844, B_D=0.000002 $q_D=e^{3.844}$ and E=-353,553.39 kj/mol. Generally, when the adsorption energy value falls below 8 Kj/mol, the adsorption process is said to be characterized by physiosorption, i.e., physical binding of the pesticide to the surface of the soil/sediment. If the value is higher than 8 kj/mol but less than 20 kj/mol, it is said to be characterized by ion exchange and similarly, its values beginning from 20 kj/mol and above are said to be characterized by particle diffusion [15-18]. From Table 3, E (Kj/mol) values are lesser than 8 kj/mol, which deduces that the adsorption process of Lamda-Cyhalothrin was predominantly a physiosorption process. From Figure 5 the data fitted well in Dubinin-Radushkevich isotherm at the various shaking times (15 minutes, 30 minutes, 45 minutes and 60 minutes), for samples A and B whereas sample C has some deviations, though the regression (r^2) values range from 0.857-0.980.

Conclusion

Adsorption of Lambda-Cyhalothrin decreases with increase in mass of loam sediment. The longer the contact time the higher the adsorption. Increase in concentration results in decreased proportion of adsorption. This is because at high initial concentration, the number of moles of Lambda-Cyhalothrin available to the surface area is high,

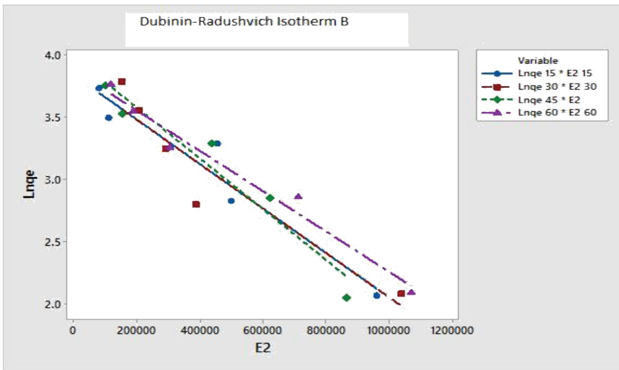

Figure 6: D-R Isotherm for Sample B. .

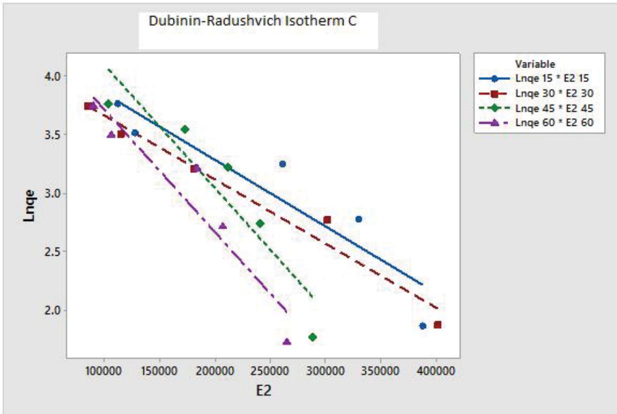

Figure 7: D-R Isotherm for Sample C. .

so functional adsorption becomes dependent on initial concentration. Adsorption of lambda cyhalothrin followed Fredlich-peterson isotherm model with regression values ranging from 0.954 to 0.992. As shaking time increased from 15 minutes to 60 minutes, the value of n increased from 0.1998 to 0.2914. The value of ΔG (Gibb's free energy) was 11.7946 ± 0.3 Kjol/mol which indicated that adsorption of Lambda-Cyhalothrin by Athi River sediments was spontaneous, indicating high affinity to the sediments.

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