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Removal of Lambda-Cyhalothrin from Aqueous Solution Using Algae – Kinetic, Isotherm and Thermodynamic Studies

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ABSTRACT

The present study aims to determine the ability of algae in sequestering Lambda-cyhalothrin (L-C) from aqueous solution. A series of experiments were carried out in batch mode to find equilibrium data for sorption of Lambda-cyhalothrin (L-C), FTIR analysis was utilized to investigate the impacts of functional groups of algae in the biosorption process. Pseudo second-order kinetics model (R^2 = 0.991) well describe the kinetics of adsorption of L-C onto algae sites while the adsorption mechanisms was controlled by external mass transfer as well as intraparticle diffusion. Langmuir isotherm model better fit the experimental data than Freundlich isotherm model. The higher adsorption capacity was found to be 6.954 mg/g. Thermodynamic parameters indicating that sorption of L-C onto algae was endothermic in nature. Only 40% reduction in the sequestration efficiency was noticed after five sequential regeneration cycles. The maximum sorption efficiency was found to be (95.6%) under the best conditions adsorbent dosage = 1 g/100ml, pH = 7, initial L-C concentration = 10 mg/l with a contact time of 60 minutes at 25 °C. This work demonstrated that algae are a promising adsorbent for L-C removal from aqueous solution.

Keywords: adsorption, algae, kinetics, lambda-cyhalothrin, regeneration**.**

INTRODUCTION

Agrochemicals are widely utilized in the agriculture sector to control pests and boost crop output. Nevertheless, the widespread and unregulated usage of these substances worldwide possess harm to the environment and organisms, as well as humans (Mahmoud et al., 2021). The harmful effects of pesticide usage differ significantly depending on the inherent properties of their active constituents such as persistence, toxicity, etc. as well as usage patterns like application time and technique, applied amounts, soil and crop type, etc. Lambda-cyhalothrin (L-C) pesticide is a manufactured pyrethroid pesticide that is the same to pyrethrin insecticide chemicals which found naturally in chrysanthemum blooms. Lambda-cyhalothrin is an improved isomeric type of cyhalothrin's two biologically present diastereoisomeric sets of isomersis that is used for plant protection (Registration, n.d.). Lambdacyhalothrin is poisonous when consumed, breathed, or applied to the skin that can cause headache, dizziness, nausea, skin tingling, and other clinical symptoms. Contact with extremely high levels can cause loss of consciousness, convulsions, and, in rare cases, death (Insecticide et al., 2011). The elimination of pesticides from wastewater is an important concern therefore several methods have been investigated in several research such as adsorption (Mohammed and Ali, 2023). Adsorption has been found to be one of the most successful and economical techniques for removing pesticides from wastewater due to its high effectiveness, ease of operation, and simple recovery of the adsorbents (Al-Ghouti and Da'ana, 2020). The biosorption process which utilized natural wastes or agricultural is a potential approach and is suggested as a perfect process to eliminate hazardous wastes (Mohammed et al., 2019). The dead biomasses were used as adsorbent for many hazardous wastes. The usage of these dead biomasses in bio sorption has many advantages like they are easy to regenerate after sequential cycles and they can be used at room temperature (Dzizi et al., 2022; Sulaymon et al., 2013).

Algae is an effective biosorbent that can be used to eliminate pollutants from wastewater due to their functional groups (sulfate, amino, carboxyl, and hydroxyl) which can be found on the cell surface and it can be played an important role in biosorption method (Najim and Mohammed, 2018). Recently, algae have been studied to remove contaminants such as: dyes (Khan et al., 2024), heavy metals (Dzizi et al., 2022; Mohammed and Najim, 2020), phenol (Alobaidi and Alwared, 2023) Insecticides (Reyad et al., 2022). This study aims to use algae as biosorbents to remove Lambda-Cyhalothrin pesticide from wastewater. Batch studies were performed to study the effect of different significant factors such as temperature, pH, adsorbent dosage, contact time, and initial concentration of Lambda-Cyhalothrin. The isothermal, kinetics and thermodynamic of adsorption have been studied in order to obtain knowledge into the mechanism of adsorption processes, knowing about the sorption process's mechanism onto sorbents, and determining the feasibility and spontaneity of these processes.

EXPERIMENTAL WORK

Adsorbate and adsorbent

Lambda-Cyhalothrin (L-C) ($C_{25}H_{19}ClF_3NO_3$) pesticide was utilized as an adsorbate. An appropriate dilution of a stock solution (1000 mg/l)was made. T80 Double Beam Ultraviolet visible spectroscopy (pg Instruments, UK) was used to measure the concentration of Lambda-Cyhalothrin at a wavelength of 250 nm. Figure 1 depicts the structure of Lambda-Cyhalothrin An amount of algae was gathered from a Tigris river in Baghdad, Iraq and examined in laboratories of the Iraqi Ministry of Sciences and Technology/Water Treatment Directory for their classifications. The weight percentage of these gathered algae: 80% Chrysophyta, 14% Chlorophyte, and 6% Cyanophyta. The collected algae was then washed many times with tap and deionized water to remove impurities, sticking dirt, bird feathers, worms, and salts before being dried under the sun for three days and then dried in an oven at 60 °C for three hours to verify that the sample was thoroughly dried. The dried algae is crushed to powder (Figure 2) to get particles with diameters ranging from 63 μm–74 μm (Isam et al., 2023).

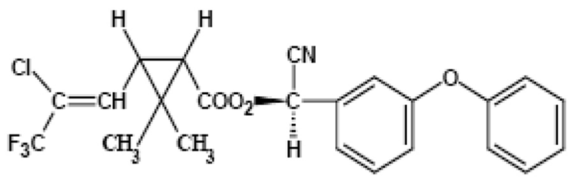

Figure 1. Chemical structure of Lambda-Cyhalothrin

Adsorption experiments in batch system

The experiments of batch adsorption were performed to evaluate the effects of parameters (temperature, pH, adsorbent dosage, and L-C initial concentration). Equation 1 and Equation 2 were employed to compute the amount of LC adsorbed q_e (mg/g) and the percentage of removal effectiveness, respectively (Mohammed et al., 2015, 2022).

$$q_e = \frac{C_i - C_e}{W} v \quad (1)$$

$$Re(\%) = \frac{C_i - C_e}{C_i} 100 \quad (2)$$

where: q_e (mg/g) is the quantity of L-C pesticide adsorbed at equilibrium, C_i (mg/l) is the initial concentrations of LC in solution, C_e (mg/l) equilibrium concentrations of L-C, W(g) is the algae mass, and V(L) is the initial volume of L-C.

Thermodynamic, isotherm and kinetic study

Equation 3, 4 and 5 have been used to determine the thermodynamic parameters for L-C adsorption on algae ΔH°, ΔG°, and ΔS° at temperatures (293K, 298K, 303K, 308K and 313K)

$$\Delta G = -RTln\, k_d \quad (3)$$

$$lnk_d = \frac{\Delta s}{R} - \frac{\Delta H}{RT} \quad (4)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (5)$$

where: K_d is the thermodynamic equilibrium constant (q_e/C_e), R is the universal gas constant (8.314 J/mol.K), T is the temperature of solution, $\Delta H°$(kJ/mol) is the enthalpy change, $\Delta G°$(kJ/mol) is the standard free energy and $\Delta S°$(J/mol.K) is the standard entropy change (Mohammed and Alnasrawi, 2024).

Figure 2. Algae before and after drying and grinding

The adsorption isotherm was used to illustrate the adsorption capacity at different solution concentrations, which helps to understand the interaction between adsorbent and adsorbate. To fit the findings from the experiment with Langmuir and Freundlich isotherm models (Equation 6 and 7) were utilized, respectively (Mohammed and Kareem, 2019; Smječanin et al., 2022).

$$\frac{1}{q_e} = \frac{1}{K_L * q_m} \times \frac{1}{C_e} + \frac{1}{q_m} \quad (6)$$

$$ln\, q_e = ln\, K_F + \frac{1}{n}\, ln\, C_e \quad (7)$$

where: n is the adsorption intensity, q_m (mg/g) is the Langmuir maximum adsorption capacity, K_L is Langmuir constant, and K_F is Freundlich constant.

The kinetic parameters were analyzed utilizing pseudo-first-order model, pseudo-second-order model and intra particle Diffusion model, as described by Equation 7, Equation 8, and Equation 9 respectively (Elkhattabi et al., 2018; Mohammed and Ali, 2023).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$\frac{t}{qt} = \left(\frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}\right) \quad (9)$$

$$q_t = k_{diff}.t^{0.5} + c \quad (10)$$

where: q_t (mg/g) is the quantity of L-C removed from an aqueous solution at time t, k_1 (min^{-1}) is the constant of pseudo-first order model, k_2 (g/(mg.min)) is the constant of pseudo-second order and k_d (g/(mg.min$^{0.5}$)) represent the rate constants for intra-particle diffusion kinetic model. The intercept values, t and C, correspond to the thickness of the boundary layer (Olal, 2016).

RESULTS AND DISCUSSION

FTIR analysis

The natural adsorbent's surface and functional groups were identified using a The Fourier transform infrared spectroscopy (Shimadzu, Japan). FTIR analysis was conducted before and after the Lambda-cyhalothrin adsorption process. The findings are shown in Figures 3a and 3b. The adsorbent's spectrum shows the presence of particular functional groups present in algae (such as hydrocarbon, hydroxyl, alkynes, and alkenes) which promote the presence of fucoidan, polyalginate, and fatty acid groups in algae (Alobaidi and Alwared, 2023).

Figure 3a depicts the peaks of algae before L-C adsorption: 3410.15 cm^{-1} could be recognized to the hydroxyl group (Habib et al., 2020), 2916.37cm^{-1} and 2860.43 cm^{-1} to the carbonyl group, 1647.21 cm^{-1} to the amide group (Ali and Mohammed, 2023), 1417.68 cm^{-1} to the alkanes group, 1151.5 cm^{-1} to the carboxyl group (Isam et al., 2023), and 628.79 cm^{-1} could be recognized to the aromatic group (Permatasari et al., 2021). Figure 3b shows the FTIR spectra of algae after adsorption. The O-H peak of algae altered from 3410.15 to 3415.93 cm^{-1}, demonstrating that algae O-H surface and L-C probably contributed in the adsorption process. L-C biosorption resulted in new peaks in the 1651–1521 cm^{-1} range.

Effect of various parameters

The impact of pH on the biosorption of Lambda-Cyhalothrin was investigated under constant parameters 50 mg/l initial L-C concentration, 1

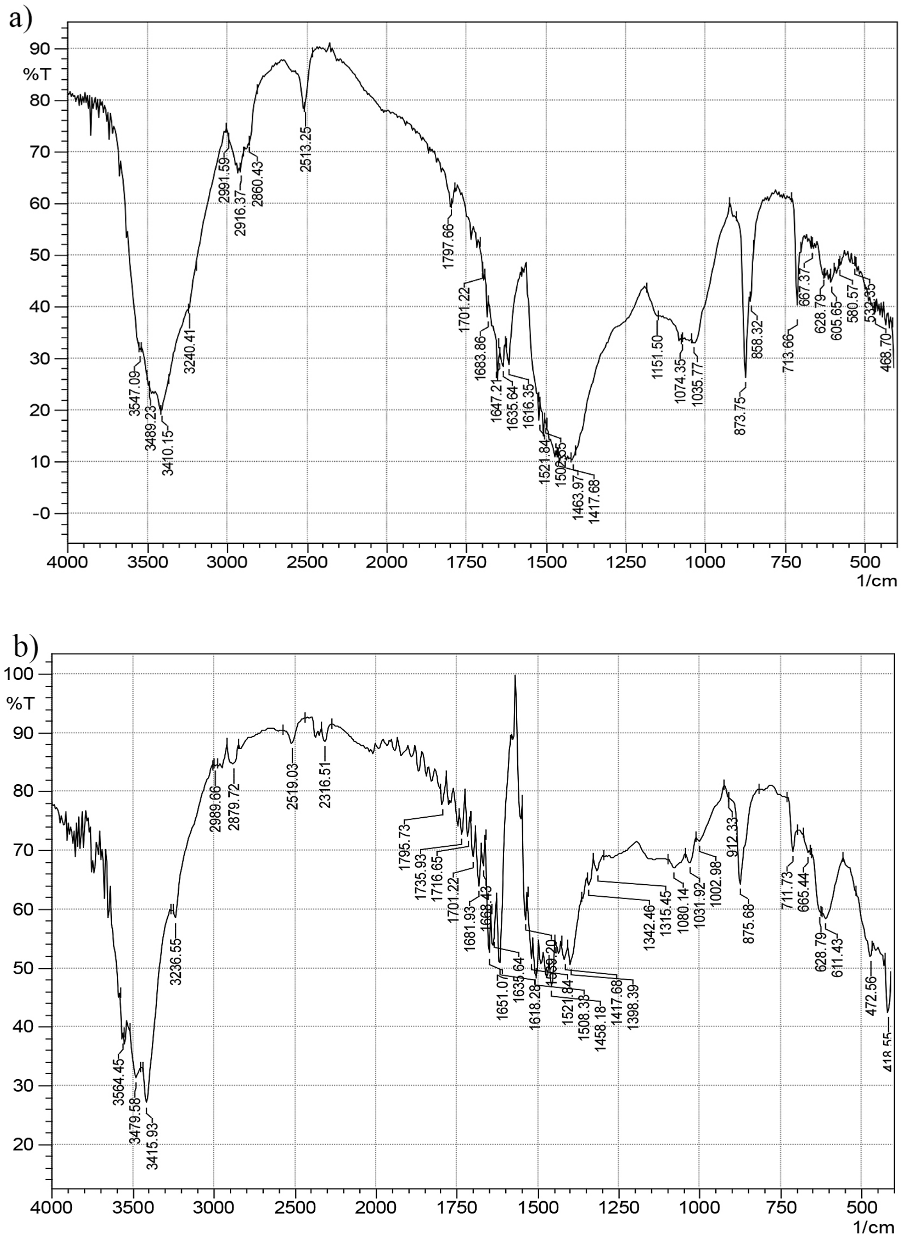

Figure 3. FTIR spectra analysis of algae (a) before L-C biosorption and (b) after L-C biosorption

g/100 ml adsorbent dose, 250 rpm, and 298k using different pH values ranging from 3 to 8 at 60 min contact time. The pH was adjusted with 0.01 M HCl or NaOH. The influence of pH on L-C removal has been studied using the zero charge point (pH_{pzc}) of algae. The pH where the the surface of adsorbent has a net zero charge is known as pH_{pzc} (Hassan and Samaka, 2022). Based on Figure 4a, the Point zero charge (pH_{pzc}) of algae was found to be 5.4. At pH > pH_{pzc}, the biosorption of cationic pesticide onto biosorbent is favorable because of the presence of active functional groups (Mokhtar et al., 2017). L-C removal efficiency enhances as the initial pH increases from 3 to 8, with a maximum removal efficiency of 87.523% achieved at pH 7 as shown in Figure 4b.

This biosorption algae has been attributed mostly to the characteristics of its cell wall, however electrostatic attraction will additionally have an important role. Fewer anionic adsorption sites on the algae were formed at low pH levels, and adsorption was unfavorable, perhaps due to extra H^+ which competing with pesticide molecules for sorption sites on the algae. All algal cells on the surface are susceptible to pesticide molecule binding. No substantial changes were found above pH 7, since when pH is high, the surface of adsorbent particle may be negatively charged, resulting in the increase of cationic pesticides via electrostatic forces of attraction (Pratiwi et al., 2019).

The impact of adsorbent dosage (0.4–2 g/100ml) on the efficiency of adsorption was investigated and the results are shown in Figure 4c. The biomass dose is an important metric used to assess the amount of biosorbent for a certain initially concentration; it is one of the most significant variables that influenced the biosorption process,. It is obvious from Figure 4c that pesticide removal effectiveness increases from 54.15 to 87.52% when algal mass increases from 0.4 to 1 g/100 ml, at higher adsorbent dosages, which constitute an excess and waste of adsorbent, L-C removal was not significantly increased, and it remained approximately the same. Based on these results, 1 g/100ml was chosen as the optimal dosage of algae.

Figure 4d shows the impact of contact time on adsorption at 1 g/100ml of algae for 50 mg/l of initial pesticides concentration at 25 °C. This Figure shows that the adsorption process was rapid for the first 30 minutes, but afterward biosorption slowed. This phenomenon is owing to the availability of accessible biosorption sites at the earlier contact

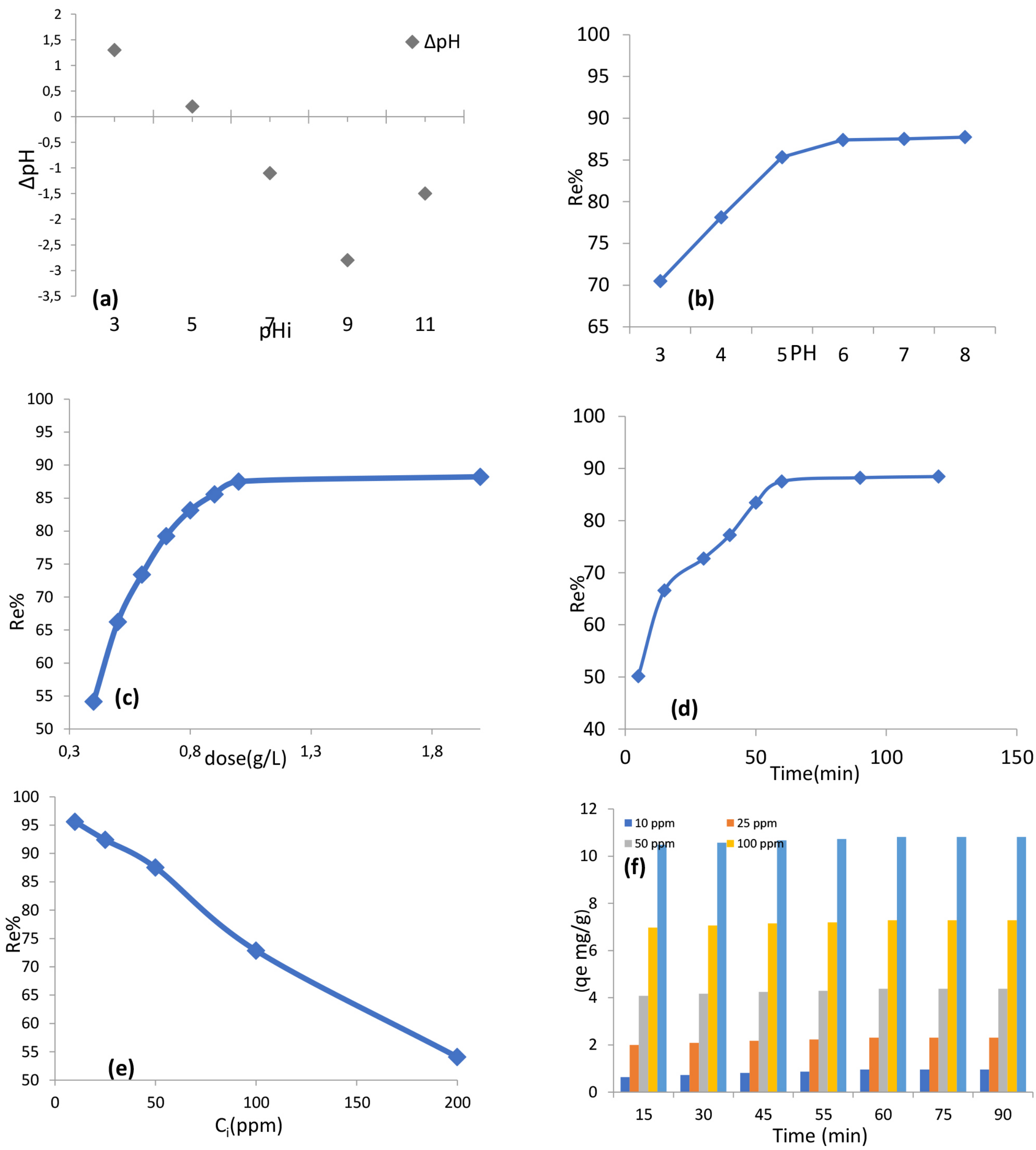

Figure 4. Parameters effects on L-C adsorption; (a) pH_{pzh}; (b) pH; (c) algae dose; (d) contact time; (e) L-C initial concentration and (f) adsorption uptake

time; nevertheless, these available biosorption sites diminish over time due to repulsive interactions that arise between the L-C molecules and the algal surfaces (Abdulkareem and Alwared, 2019; Utomo et al., 2016). As a result, 60 minutes were determined to be the optimal time period for the further experiments in this study.

Biosorption effectiveness as a function of initial concentration for Lambda-Cyhalothrin (L-C) ranging from (10–200 mg/l) was investigated at adsorbent dosage of(1 g/100ml), pH of solutions was 7 and shaker speed was 200 rpm for 60 min. contact time at 25 °C, the results are illustrated in Figure 4e. It is noticeable that with increasing L-C initial concentration, the biosorption capacity likewise increased, whereas L-C removal efficiency decreased. The interaction of L-C with unoccupied active biosorbent enhances the biosorption process as the L-C concentration increases. The L-C removal percentage would decrease at higher concentrations because the solution would have fewer sites available than the initial pesticide molecules (Khan et al., 2024; Nait-merzoug et al., 2021). The high concentration of pesticide ions acts as a driving force, overcoming the barrier of the mass transfer layer between the algae and pesticides in the solution (Mousavi et al., 2019).The equilibrium uptake capacity (q_e) increased form 0.956mg/g to 10.816mg/g when the initial concentration of L-C increased from 10ppm to 200 ppm as shown in Figure 4f

The effect of temprature and thermodynamic study

Temperature generally impacts algae's biosorption ability (Lin et al., 2020; Mullai et al., 2022). Figure 5 indicates that at temperatures of 20 °C -40 °C, the adsorption effectiveness of algae increased from 85.39% to 91.34%, indicating that increasing the adsorption process's temperature increases algal adsorption capacity by increasing contaminant mobility in aqueous solution, which promotes adsorption site accessibility. The thermodynamic parameters are listed in Table 1. ΔS° positive results indicate greater randomness during L-C adsorption by algae. The positive ΔH° value indicates that the interaction of L-C with algae was endothermic in nature.

Sorption isotherm study

The resulting isotherm study data were fitted into the Langmuir and Freundlich models, as

Table 1. Thermodynamic parameters for L-C adsorption on algae

Temperature (k)	Δ*G*° (kJ/mol)	Δ*H*° (kJ/mol)	Δ*S*° (J/ mol K)
293	1.308285	17.47437	55.38953
298	0.879154		
303	0.706532		
308	0.387129		
313	0.174349		

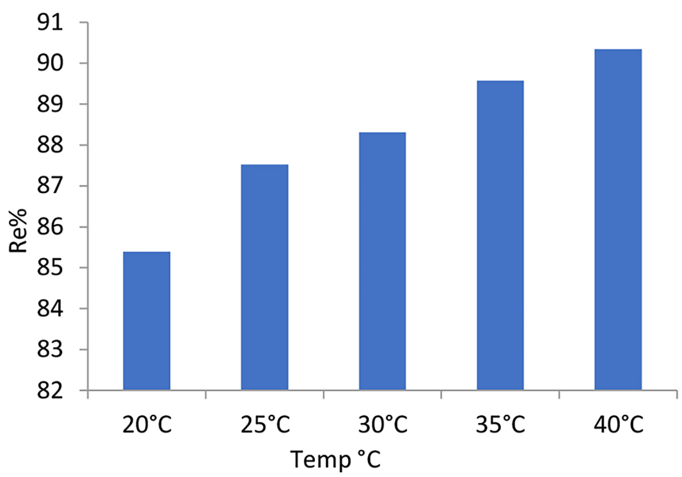

Figure 5. Temperature effects (W = 1 g/l00ml; C_i = 50 mg/l; PH = 7; rpm = 200)

illustrated in Figures 6a, 6b and the resulting values are tabulated in Table 2. The finding from the models were compared, and the two models represent the data very well, as indicated by the highest values of $R^2 > 0.97$. The Langmuir model isotherm better represent L-C adsorption onto algae ($R^2 = 0.9836$) than the Freundlich model, which indicated mono-layered adsorption phenomena with a maximum adsorption capacity of 6.95410 mg/g. The "1/n" ratio, which represents the intensity of adsorption, was (0.4502) and the 1/n value ≤ 1 indicates that L-C adsorption occurred rapidly and favorably. The separation factor (R_L) used to quantify adsorption favorability was < 1, suggesting that algae adsorption was favorable for all tested experiments (Birungi and Chirwa, 2015).

Table 2. Isotherm parameters for L-C adsorption on algae

Model	Parameters	Values
Langmuir	qmax(mg/g)	6.95410
	KL	0.35506
	RL	0.05332
	R^2	0.9836
Freundlich	KF	1.60657
	1/n	0.4502
	R^2	0.9792

Kinetic study

The kinetics of biosorption is essential for studying on the elimination of pollutants from wastewater due to its valuable insights into the sorption reaction mechanism and the reaction pathways. thus, the kinetics of L-C adsorption onto algae have been studied using pseudo first order, pseudo second order and intra-particle diffusion kinetics model, with experimental data at various time in Equations 8, 9 and 10, respectively.

Based on the kinetic model data in Figures 7a, 7b, 7c and Table 3 for L-C adsorption, it is possible to conclude that the pseudo-second order kinetic model ($R^2 > 0.9467$) better fitted the kinetics of L-C adsorption than the pseudo-first order ($R^2 > 0.7109$), also the predicted values of the pseudo second order model qe matched the experiment data better than paeudo first order model. Thus, the adsorption of L-C onto algae biomass was induced by chemical adsorption, which comprises both chemical interaction and electrostatic attraction between the adsorbate and the adsorbent. Figure 7c shows that the relation between q_t and $t^{0.5}$ is linear, and the linear figure is formed of two phases; the first portion is sharper and dictated by the sorption of the outer surface, whilst the second may be progressively changed. Additionally, it can be shown that the linear plot of each biosorbent did not pass through the origin, implying that intraparticle diffusion was not the rate-limiting step (Deng et al., 2010; Permatasari et al., 2021).

REGENERATION

Adsorbent regeneration is essential in industrial practice for contaminant removal from wastewater, both economically and environmentally. To

Table 3. Kinetics parameters for L-C adsorption onto algae

Model		Pseudo 1st order			Pseudo 2nd order		
C_0	$q_{e\,exp}$. (mg/g)	k_1 (min^{-1})	q_{ecal}. (mg/g)	R^2	k_2 (g mg^{-1}min^{-1})	$q_{ecal.}$ (mg/g)	R^2
10	0.956	-0.00159	1.609462	0.8684	0.120966	1.039825	0.9856
25	2.31025	-0.00261	6.603501	0.7824	0.088368	2.414876	0.9919
50	4.376	-0.00181	4.863703	0.8535	0.034676	4.708098	0.991
100	7.286	-0.00187	10.17364	0.7377	0.018522	7.722008	0.9792
200	10.816	-0.00197	18.92531	0.7109	0.006448	12.16545	0.9467
Model		Intra-particle diffusion					
		Portion 1			Portion 2		
C_0	$q_{e\,exp}$. (mg/g)	k_{diff}(mg g^{-1} min-$^{0.5}$)	C (mg/g)	R^2	k_{diff}(mg g^{-1} min$^{-0.5}$)	C (mg/g)	R^2
10	0.956	0.1226	0.0807	0.9155	0.0604	0.4566	0.8269
25	2.31025	0.1463	1.0835	0.957	0.1123	1.3813	0.8313
50	4.376	0.6	o.395	0.9458	0.1333	3.2833	0.7185
100	7.286	0.4533	2.9176	0.9748	0.6089	2.2382	0.8467
200	10.816	0.9904	1.628	0.9548	1.1574	1.2309	0.8405

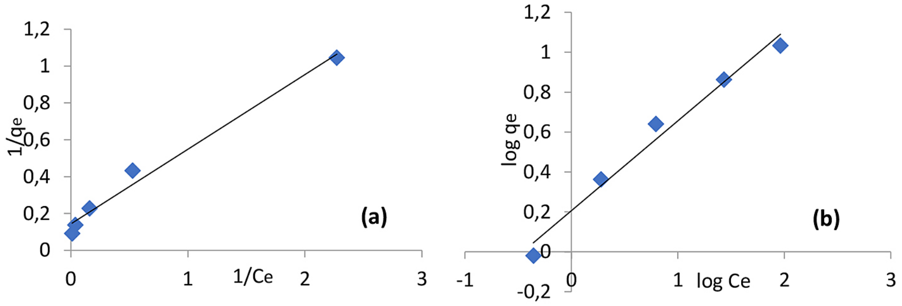

Figure 6. Adsorption of L-C onto algael (a) Langmuir Isotherm, (b) Freundlich Isotherm

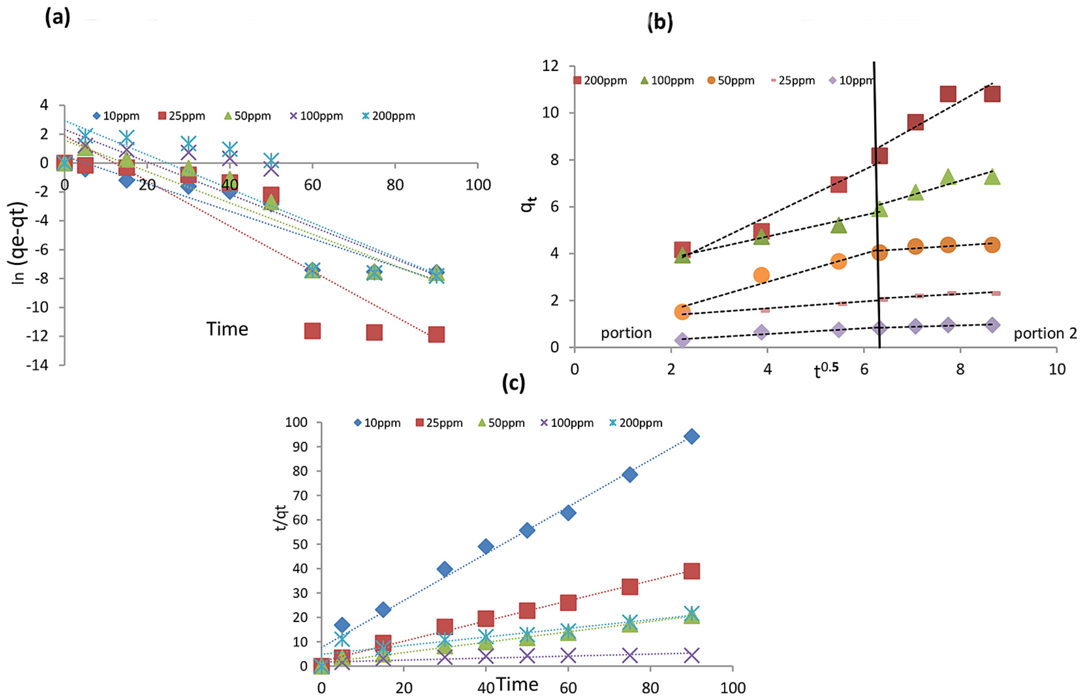

Figure 7. Kinetics models of biosorption (a) pseudo 1st order and (b) pseudo 2nd order and (c) intra-particle diffusion mode

test the feasibility of removing and recovering L-C from algal biomass, many cycles of biosorption-desorption were carried out using 0.1 M HNO_3 as an eluent agent, which was subsequently reused in sequential cycles. The regeneration process is based on the desorption of L-C from exhausted sorbent. The regeneration method involved extracting the algal biomass from the aqueous solution by filtering, washing it many times with purified water, and drying it in an oven at 60 °C until totally dry. Furthermore, the experiment was conducted under the following conditions: Contact time = 60 min, pH = 7, agitation speed = 200 rpm, adsorbent dosage = 1 g/100ml, temperature= 25 °C and C_o= 50mg/l, the process repeated for five cycles, and the biosorption effectiveness was 87.52%, 85.31%, 73.14%, 59.68%, and 40.03% for the first to fifth cycles. Figure 8 shows that the biosorption effectiveness steadily decreased, with the lowest efficiency occurring after the fourth regeneration. Algae that used in regeneration treatments can suffer structural damage owing to the diffusion of trace pollutants into pores However; the biosorbent used in this study demonstrated sufficient recyclability, indicating that it might be a potential option for serving as an effective and sustainable adsorbent for L-C biosorption.

CONCLUSION

The present study indicated Algal biomass effectively removal of Lambda-cyhalothrin (L-C) from synthesis wastewater. The FT-IR analysis revealed that the algal biomass had significant

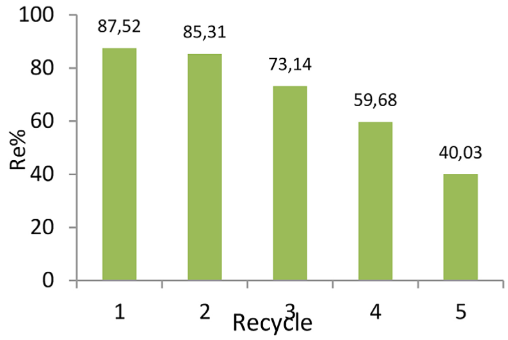

Figure 8. Five cycle of adsorption- desorption for L-C (W = 1 g/l00ML; T = 25 °C; C_i = 50 mg/l; pH = 8; rpm = 200, time = 60 min.)

biosorption abilities due to its active groups. The efficiency for the adsorption of L-C on algae was 95.6% under the following conditions: adsorbent dosage = 1 g/100 ml, pH = 7, initial L-C concentration = 10 mg/l with a contact time of 60 min. at 25 °C. The thermodynamic experiments showed that the biosorption of L-C onto algae was endothermic. The Langmuir model can better describe isothermal data than the Freundlich isotherm model, which suggests a monolayer adsorption phenomena. Thermodynamic studies revealed that L-C adsorption onto algae was endothermic in nature, while the kinetic research effectively fit by pseudo second order with very high R^2, indicating chemisorption adsorption method. These findings indicate that the utilized algae was an effective for the removal of L-C. Additionally, it can be easy to regenerate using 0.1M HNO_3 and can be utilized for several cycles.

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