Kinetic and equilibrium modeling of pesticides adsorption using Oil Shale Ash

Z. AL-QODAH[1*], A. T. SHAWAQFEH[2], W. K. LAFI[1#], A. M. KHALIL[1$]
Department of Chemical Engineering
1: Al-Balqaa Applied University
Amman, Marka, 11134, P. O. Box 340558
2: Mutah University
Karak, 61710, P. O. Box 34
JORDAN

Abstract: - Adsorption characteristics of the pesticides Deltamethrin were studied using Shale oil ash as an adsorbent. Langmiur and Frendlich models fit the adsorption data with $R^2 > 0.97$ in all cases. The highest adsorption capacities for Deltamethrin were 11.4 mg/g. When the initial concentration was 15 mg/l the Q_{max} values obtained with SOA of 202.25 μm average diameter, a temperature of 25 ^{o}C, 400 rpm mixing speed, pH = 3 were 11.4 and 8.6 mg/g, respectively. The desorption experiments using acetate buffer showed a maximum recovery of 74% for Deltamethrin and 45% for Lambda-Cyhalothrin.

Key-words:- Adsorption, Pesticides, Oil shale ash Adsorption isotherms, Adsorption capacity, Langmiur isotherm, Frendlich isotherm.

* Author to whom all correspondence should be addressed.

1 Introduction

Pesticides are among the major organic compounds encountered in wastewater effluents of pesticide industry and domestic activities [1]. They are very dangerous and harmful to the living systems because they are toxic and carcinogenic in nature even at low concentration [2]. For these reasons, environmental regulations in many countries have become strict for drinking water and wastewater treatment in the last few years, especially regarding pesticides [3].

Unfortunately, the removal of pesticides from wastewater is an extremely complex problem due to the wide range of pesticides chemical structures and properties [4]. Nevertheless, adsorption processes using suitable adsorbent have shown high removal efficiency and many advantages [5,6]. However, the high cost of activated carbon production had led to interest in utilizing low cost raw materials as adsorbents for pollutants including pesticides. These include: Fly ash [5], snail pedal mucus [7], clay minerals and soil [8,9] and others. Recently, it was shown that shale oil ash is a promising and efficient adsorbent for organic pollutants such as reactive dyes [10]. The chemical composition of SOA indicates that chemical composition of SOA consists of a wide variety of acidic, basic and amphoteric oxides. For this reason, the intent of this contribution was to study the adsorptive capabilities of SOA to pesticides found in waste water of VABCO Industrial (Dhlail, Jordan).
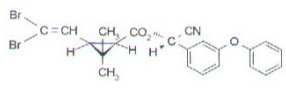
2 Experimental
2.1 Adsorbent preparation

Samples of shale oil stones were crushed and then burned using electrical furnace at 800 ^{o}C for 2 hour. The residual ash was cooled, then milled and sieved into several fractions. 20 g of the fraction of 150-250 μm diameter was Mixed with 100 ml 0.2M HCl and warmed to 50 ^{o}C with continuous stirring for 25 minutes in order to activate the surface of the particles by dissolving some soluble portion of the ash. The ash then was filtered and washed with distilled water and finally dried to be analyzed.

2.2 Pesticides

The pesticide used in this study is Deltamethrin. The chemical structure of this pesticide is shown in Table 1.

Table 1. Chemical Structure of Deltamethrin.

Pesticide	Deltamethrin
Chemical Structure	
Chemical formula	$C_{22}H_{19}Br_2NO_3$
Molecular mass (g/mol)	505.2

The choice of was mortified by two reasons. First, its concentration in the water effluents of the factory is relatively high. Secondly, it is halogenated compounds and their treatment by other methods such as photo-oxidation seems to be relatively difficult. A 1000 mg/l stock solution was prepared by dissolving 1 g of each pesticide in 200 ml of distilled water in a stirred beaker. After the complete dissolution the volume of the solution was completed to 1 liter by the addition of the distilled water. The weak solutions used in the further experiments were prepared by diluting samples of this stock solution.

2.3 Adsorption Isotherms

Adsorption isotherm experiments were performed by adding 0.1 g of the SOA to 100 ml of the pesticides solution in a glass bottle with screw cap. The initial concentrations of each pesticide were: 2.5, 5, 10, 15, 20 and 25 ppm. The mixtures were placed in an orbital shaker bath (GallenKamp, UK) at 200 rpm for 72 h. The solutions were then centrifuged and the filtrate was analyzed. This procedure was repeated at three different temperatures of, 30, 40 and 45 oC, using SOA of 250-355 µm diameters.

2.4 The kinetic study

The kinetic study experiments were performed by batch technique using a series of Erlenmeyer flasks of 1L volume equipped with a mixer. The working volume was 0.7 L and the adsorbent mass was 0.7 g in all the experiments. The effect of initial concentration on the pesticides equilibrium concentrations in the solution was studied. Samples of the solution were withdrawn to be analyzed. Each experiment continued until equilibrium conditions were reached when no further decrease in the ion concentration was observed.

2.5 Measurements

The pesticide concentration was measured using the TOC Analyzer (Shimadzu® Total Carbon Analyzer) by combustion method through measuring the CO2 product in the effluent gases. was used. The instrument was calibrated according to the standard procedure and solution provided by the manufacturer. The syringe was cleaned thoroughly prior to each sampling-injection step. Measurements were repeated three times on average for each sample to ensure accuracy.

3 Equilibrium and kinetic models
3.1 Adsorption isotherms

Two of the most common sorption models were used to fit the experimental data. The Langmiur model which can be written as:

$$Q_e = Q_{max} b C_e / (1+bC_e) \qquad (1)$$

where Q_{max} is the maximum metal uptake under the given conditions, b is a constant related to the affinity between the adsorbent and the adsorbate.

The second model is Frendlich model which can be written as:

$$Qe = k C_e^{(1/n)} \qquad (2)$$

where k and n are Frendlich constants, which are correlated to the maximum adsorption capacity and adsorption intensity, respectively, [11].

3.3 Kinetic models

Two kinetic models are used to fit the experimental data. The first model is the pseudo-first-order kinetic model which is expressed by the following equation [12]:

$$dQ/dt = k_1(Q_e – Q_t) \qquad (3)$$

where Q_e and Q_t are the specific quantity of pesticide adsorbed with the ash (mg/g) at equilibrium and at any time, t, respectively. k_1 is the equilibrium rate constant (min^{-1}). Integrating equation 9 between the two boundary conditions where t varies from 0 to t and Q_t varies from 0 to Q_t gives:

$$\log Q_t / (Q_e - Q_t) = 0.4342 \, k_1 t \qquad (4)$$

The value of the model parameters k_1 can be determined by plotting $\log (Q_e - Q_t)$ versus t to produce a straight line of slope 0.4342 k_1 and intercept $\log Q_e$.

The second kinetic model is the pseudo-second-order kinetic model which is expressed by the following equation (13):

$$dQ/dt = k_2(Q_e - Q_t)^2 \qquad (5)$$

where k_2 is the equilibrium rate constant of the pseudo-second-order kinetic model (min^{-1}). Integrating equation 12 between the two boundary conditions where t varies from 0 to t and Q_t varies from 0 to Q_t gives:

$$1 / (Q_e - Q_t) = 1/ Q_t + k_2 t \qquad (6)$$

Equation 13 can be linearized to take the form:

$$1 / Q_t = 1/(k_2 Q_e)^2 + t/ Q_e \qquad (7)$$

The value k_2 can be determined by plotting t/Q_e versus t to obtain a straight line of slope $1/Q_e$ and intercept of $1/(k_2 Q_e^2)$.

4 Results and Discussion

4.1 Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Fig. 1 shows plots for the adsorption of Deltamethrin on SOA at different concentrations and three temperatures.
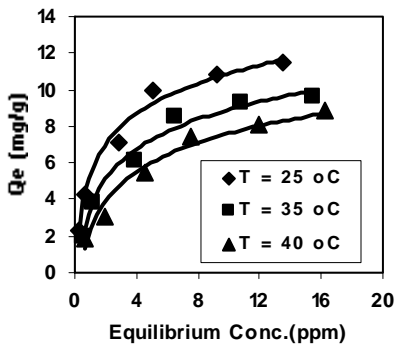

Fig. 1: Adsorption isotherms for Deltamethrin, pH = 7.3, rpm = 200 and time 72 h.

It is evident from Fig. 1 that the loading capacity of the SOA decreases as the temperature increases. For example, if the initial concentration of the solution is 10 mg/l the loading capacity for Deltamethrin are 7.1, 6.15 and 5.5 mg/g for temperatures of 25, 35 and 40 ^{0}C, respectively.

Langmiur and Freundlich models were tested to fit the isotherm data for the adsorption of Deltamethrin on SOA. Figure 2 shows the conformation of the experimental data into Langmiur isotherm model indicating the homogenous nature of the ash. In addition this

result demonstrates the formation a monolayer of Deltamethrin on the outer surface of the ash.
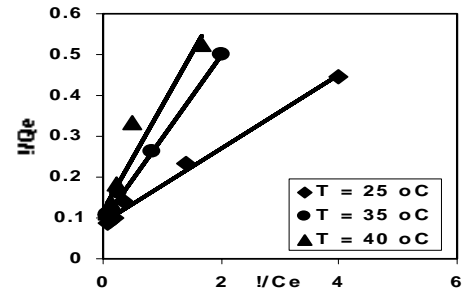

Fig. 2: Langmiur plot for Deltamethrin.

On the other hand, Fig. 3 shows that the adsorption of Deltamethrin on shale oil ash follows also Freundlich isotherm model.
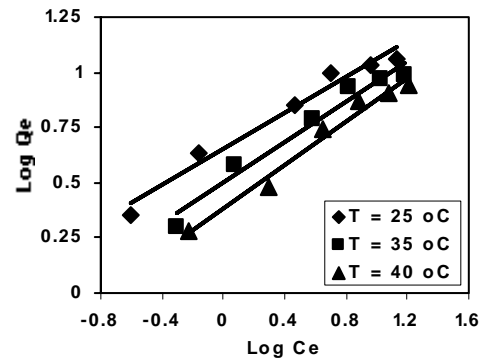

Fig. 3: Freundlich plot for Deltamethrin.

The values of the two model parameters are given in Table 2. The highest loading capacity was 10.96 mg/g at 25 ^{o}C. It can be seen that n values are $1<n<3$, which suggests the adsorption of Deltamethrin on the ash is favorable. In addition, the values of R^2 are > 0.93, indicating that the data fit well to the two models.

Table 2. Langmiur and Frendlich constants for Deltamethrin at different temperatures

Model,	Parameter	Temperature ^{o}C		
		25	35	40
Langmiur	$Q_{max,}$ (mg/g)	10.9	10.6	8.25
	b (l/mol) $x10^{-6}$	2.01	0.90	0.94
	R^2	0.99	0.99	0.93
Freundlich	k	4.48	3.14	2.4
	n	2.44	2.16	2.01
	R^2	0.97	0.96	0.98

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4.2 Effect of pesticides concentration and contact time on adsorption

The effect of initial concentration of Deltamethrin on the rate of adsorption by SOA is shown in Fig. 4.
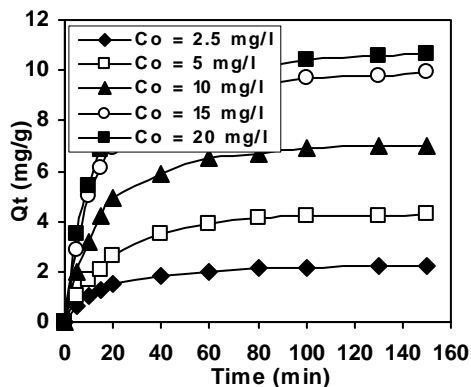

Fig. 4: Effect of initial concentration on the adsorption rate of Deltamethrin onto SOA. 1g/700 ml solution, pH = 7.3, T = 25 ^{o}C, rpm = 400 rpm, d_p = 202.25 μm.

It is evident from Fig. 4 that the quantity of pesticides adsorbed increases with time for all initial concentration. For example, as C_o of Deltamethrin increases from 2.5 to 20 mg/l the loading capacity of SOA Q_t increases from 1.85 to 9 mg/g in the first 40 min of start up. However, the uptake rate of the pesticide drastically decreases with time until it approaches a pseudo steady state after 60 minutes. This behavior indicates negligible further removal of the pesticide and referred to the continuous decrease in the concentration driving force. This is a surface phenomenon behavior and it is attributed to the hydrophobic nature of the pesticides used (12). Due to this effect, the adsorption sites of SOA are filled up with the pesticide molecules in a very short time.

Fig. 5 and Fig. 6 show the pseudo-first-order and the pseudo-second-order kinetics for adsorption of direct blue dye on shale oil ash. The kinetic parameters of these two models are given in Table 3. As it can be seen in Table 3, the calculated values of Q_e in the case of the second order kinetic model are closer to the experimental values compared to those calculated by the first-order-kinetic model. For example when C_o = 20 mg/l, the experimental Q_e was 10.8 mg/g and those calculated by the first and second order kinetic models are 7.1 and 10.43 mg/g, respectively. At lower C_o, 5 mg/l for instance, the

experimental values was 4.3 mg/g whereas those for the two models were 3.4 and 4.6 mg/g, respectively. These facts suggest that the pseudo second order adsorption mechanism is predominant and the overall adsorption process is controlled by the chemisorption process [12].
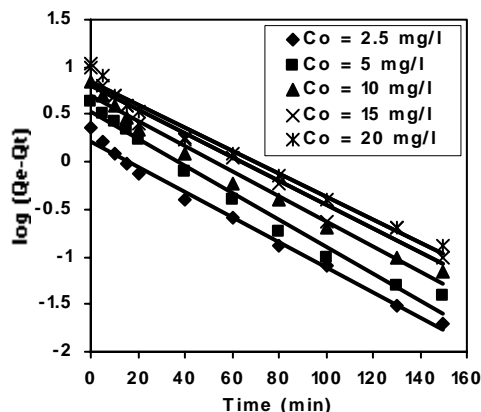

Fig. 5. Pseudo-first-order kinetics for adsorption of Deltamethrin on shale oil ash
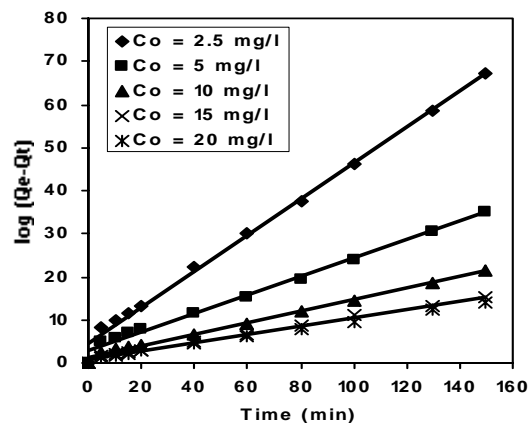

Fig. 6. Pseudo-second-order kinetics for adsorption of Deltamethrin on shale oil ash
Table 3. Kinetic parameters of the adsorption of Deltamethrin with the ash.

C_o (mg/	Q_e exp	Pseudo first Order kinetics			Pseudo second Order kinetics		
		Q_e cal	k_1 x 10	R^2	Q_e cal.	k_2	R^2
2.5	2.25	1.8	31	0.97	2.39	0.8	0.99
5	4.3	3.4	32	0.98	4.6	0.13	0.99
10	7.1	5.1	32	0.98	7.5	0.023	0.98
15	10	6.4	29	0.97	9.5	0.01	0.98
20	10.8	7.1	28	0.98	10.43	0.008	0.99

5. Conclusions

The adsorption of Deltamethrin pesticide was carried out using shale oil ash adsorbent. The adsorption isotherm data fit both Langmiur and

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Freundlich isotherm models. On the other hand the kinetic parameters estimated from the pseudo first and second order kinetics show that the kinetic data fit to the pseudo-second-order kinetics rather than the first order model. These results indicate that the adsorption of Deltamethrin with the ash is controlled by the chemisorption process.

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