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## Adsorption Isotherm of an Insecticide Methomyl onto Natural Clay

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### Abstract

Adsorption isotherm of an insecticide methomyl onto natural clay has been investigated. The experimental data were fitted to isotherm models, Langmuir, Freundlich and Redlich Peterson. The Langmuir model fit the experimental data significantly better than Freundlich and Redlich Peterson models. A dimensionless separation factor,  $R_s$ , was used to judge the favorable adsorption. A chart based on material balance using single batch adsorber was constructed for different percentage of methomyl removal using the Langmuir model where the mass of natural clay required to treat a specified volume of solution is calculated. The effect of temperature showed the exothermic nature of the process. The enthalpy change,  $\Delta H$ , of adsorption has been evaluated and it has a value of (-17.54 kJ/mol).

**Keywords** *methomyl, Natural clay, Adsorption isotherm, Isotherm models.*

### الملخص العربي

يهدف هذا البحث الى دراسة امكانية استخدام الطفلة الطبيعية كمادة رخيصة الثمن ومتوفرة وذلك لامتناز المبيد الحشري الميثوميل من المحاليل المائية. تم دراسة تأثير كل من قطر حبيبات الطفلة وكذلك درجة حرارة المحلول علي سعة الامتناز وقد اوضحت النتائج الأولية أن عملية الاتزان بين الطفلة والمبيد تستغرق أقل من ثلاث ساعات. وقد استخدمت النماذج الرياضية: لانجمير، فرويندليك، وريدليك بيترسون في تحليل النتائج المعملية. وتم مقارنة النتائج العملية مع النتائج النظرية المستنتجة من النماذج الرياضية المختلفة ووجد انها تتوافق بشكل جيد مع نموذج لانجمير أكثر من النماذج الأخرى ومن ثم استخدم هذا النموذج لحساب كتلة الطفلة اللازمة لمعالجة كميات مختلفة من المحلول عند نسب ازالة متعددة. ومن دراسة

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تأثير درجة الحرارة وجد أن عملية الامتزاز هي عملية طاردة للحرارة وتم حساب التغير في المحتوى الحرارى وكان مقداره - ( .17.54 kJ/mol )

## 1. Introduction

Water is a basic need of life and is used in many ways to cater to the needs of daily life, so the control of water pollution is one of today's major scientific activities. Indiscriminate use of pesticides leads to the contamination of soils, surface and ground waters. Numerous cases of pesticide residue have been reported in the literature (Kiriakopoulos et al. 2005). Pesticides, which indeed seem indispensable for the nutrition of mankind, take a special place among the environmentally problematic substances. Small quantities of pesticides may enter the water environment through drift, leaching and run-off from nearby applications. Also, pesticides can enter water through spills, leaks and back-siphoning from nearby mixing, loading, storage, equipment cleanup sites and improper disposal of pesticides and containers. Pesticides may cause injury by containing the no target organism directly or may leave a residue that causes later injuries. Natural water, viz. lakes, rivers, streams and oceans have been reported to be contaminated with residue of various pesticides (Rao 1996; Hatfield et al. 1996). The ground water contamination due to pesticides has also been reported (Alam 1996). The contamination of water of ponds, rivers and ground water sources with various insecticides and herbicides is posing a direct threat to human health. The insecticide methomyl is widely used which controls ticks and spiders. It is used for foliar treatment of vegetable, fruit and field crops, cotton, commercial ornamentals, and in an around poultry houses and dairies (Gosselin et al. 1984).

Most of the past work has focused on the removal of pesticides from water by the more traditional and more expensive methods such as cation exchange (Weber et al. 1968), and dialysis (Devitt and Wiesner 1998). Advanced oxidation processes using hydrogen peroxides are, often ineffective because carbonate and bicarbonate ions, which are abundant in all natural water, react as strong free radical scavengers. Pesticides are not completely degraded into inorganic compounds such as CO<sub>2</sub> by ozonation (Bonne et al. 2000). These findings suggest that the breakdown products of pesticides remain in water after treatment, need complementary operations and are not economical. The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems (Khlifi et al. 2010). Filtration through membranes needs another method such as oxidation reaction catalyzed by enzyme to transform the pesticide into an insoluble product, so that this method is highly expensive (Boussahel et al. 2000). Compared with the above methods, adsorption of different pesticides onto activated carbon and clay minerals has demonstrated efficiency and economic



## 2.2. Equilibrium Experiments

The equilibrium adsorption experiments have been undertaken to assess the efficiency of natural clay to remove insecticide methomyl from aqueous solutions and also finding isotherm constants. Preliminary experiments showed that such equilibrium was established within 2.5 h, however all equilibrium experiments were allowed to run for 3 h to ensure uniformity where shaking speed was set at 120 strokes per min. The experiments were conducted for three particle size ranges, 355-500, 500-630 and 630-800  $\mu\text{m}$ , and three different temperatures, 25, 40 and 60  $^{\circ}\text{C}$ , by shaking a 0.5g of natural clay with 50 ml of methomyl solution at different initial concentrations for an equilibrium time, 3 h. After shaking, the supernatant solution was separated from adsorbent by centrifugation at 400 rpm for 15 min. The remaining concentrations of methomyl solution were determined. All the adsorption experiments were carried out in duplicate and the average is taken. These data were used to calculate the adsorption capacity,  $q_e$ , of adsorbent. The adsorption capacities,  $q_e$ , of each adsorbent were determined by:

$$q_e = V(C_0 - C_e)/m \quad (1)$$

Where  $q_e$  is the solid phase methomyl concentration (mg/g),  $C_0$  is the initial methomyl concentration in the liquid phase (mg/l),  $C_e$  is the liquid phase concentration at equilibrium (mg/l),  $V$  is the volume of methomyl solution (l) and  $m$  is the mass of adsorbent used (g). Finally, the adsorption capacity was plotted against the equilibrium concentration,  $C_e$ .

## 3. Results and Discussion

### 3.1. Characterization of Natural Clay

The porosity characteristics as well as the chemical composition of adsorbent, play an important role in adsorption processes. The porosity ( $\epsilon_p$ ), the mean pore radius ( $r_{\text{max}}$ ), the solid-phase density ( $\rho_s$ ) and the particle density were determined using mercury Porosimetry and specific gravity measurements. The values obtained for natural clay were  $\epsilon_p=0.41$ ,  $r_{\text{max}}=22.32 \text{ \AA}$ ,  $\rho_s=1.98 \text{ g/cm}^3$ , and  $\rho_p=1.17 \text{ g/cm}^3$ . The specific surface area of the natural clay was also determined using BET method (Brunauer et al. 1932), with a value of  $66.53 \text{ m}^2/\text{g}$ .

The chemical composition of natural clay used was found to be as, silica (56.72%), L.O.I.(13.08%) and alumina (19.92%) are the major constituents of the natural clay while other metal oxides are present in traces or small amounts (4.89%  $\text{Fe}_2\text{O}_3$ , 0.36%  $\text{CaO}$ , 0.11%  $\text{MgO}$ , 3.00%  $\text{Ti O}$ , 1.08%  $\text{Cl}$ ). The mineralogical analysis of the natural

clay under test revealed that it consists approximately of 58% kaolinite and 42% montmorillonite.

### 3.2. Equilibrium Time

Preliminary tests were undertaken to assess the contact time necessary for methomyl-clay system to come to equilibrium, and for experimental purposes, each system was given a contact time in excess of this period, so that this information may be used to predict experimental conditions required to perform adsorption isotherms. A series of contact experiments were undertaken at varying initial methomyl concentrations, 19.99 and 43.71 mg/l. After 120 min methomyl removal was 32.9% and 27.6% when using initial concentrations 19.99 and 43.71 mg/l respectively.

Fig. 2 shows that the amount of methomyl adsorbed from aqueous solutions increased with time, where equilibrium being achieved within 2.5 h at  $25 \pm 1$  °C. The plot of adsorption versus time depicted in the figure is smooth and continuous, indicating monolayer coverage of adsorbate on the surface of the adsorbent (McKay et al. 1987).

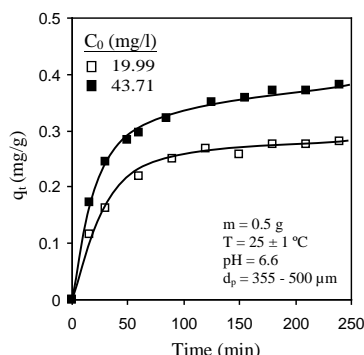


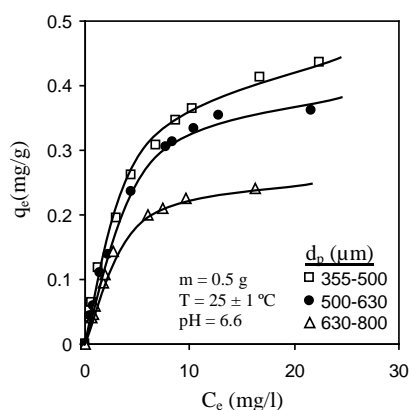
Fig. 2. Equilibrium time for adsorption of methomyl onto natural clay.

### 3.3. Adsorption Isotherm

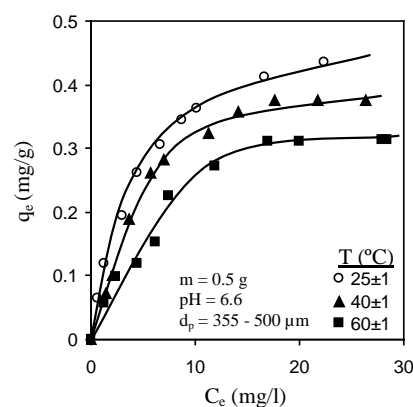
The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm. The adsorption isotherm is fundamental in describing the interactive behavior between solute and adsorbent, and is important for the design of adsorption system. Figs. 3 and 4 show the adsorption isotherms of methomyl onto natural clay for different particle size ranges and temperature respectively. As it is clear from Figs. 3 and 4, the shape of the isotherm indicated L-behavior according to Giles classification (Giles et al. 1960). Effect of particle size on adsorption isotherm represented in Fig. 3 shows adsorption capacity increases with decreasing particle size rang this may be attributed to the large surface area when small

particle size are used. This is in agreement with the statement that if the mechanism of uptake is simply one of adsorption on a specific external site, then the rate should vary reciprocally with the first power of the diameter, whereas in intraparticle diffusion the rate should vary with the reciprocal of the square of the diameter (Singh and Rawat 1994).

Fig. 4 represents the adsorption isotherm of methomyl onto natural clay at different temperatures (25, 40 and 60°C) when the particle size is constant (355-500  $\mu\text{m}$ ). It is evident that the adsorption of methomyl decreases with an increase in temperature indicating that the process is exothermic. The decrease in the amount of methomyl adsorbed with rise of temperature may be due to the enhanced escaping tendency of methomyl molecules from the surface of adsorbent (desorption). On the other hand, may be explained on the basis of solubility and chemical potential relationship. In the present case the solubility of methomyl increases with temperature and chemical potential will also increase, i.e., both the normal temperature effects act in the same direction and thus the decrease in the amount of uptake is expected, which is borne out by the present results.



**Fig. 3.** Adsorption isotherms for methomyl onto natural clay for different particle size ranges.



**Fig. 4.** Adsorption isotherms for methomyl onto natural clay for different temperatures.

### 3.4. Analysis of Adsorption Isotherm Data

Analysis of such isotherm data is important in order to develop a model which both accurately represents the experimental adsorption results and could be used for design purposes. Several isotherm models are available for this analysis. In this study three of

these have been selected to simulate the experimental data, i.e. Langmuir, Freundlich and Redlich-Peterson isotherms.

### 3.4.1. Langmuir Isotherm

The first isotherm tested was that of Langmuir which may be represented by the expression:

$$q_e = (K_L \cdot C_e) / (1 + a_L \cdot C_e) \quad (2)$$

The linear form convenient for determining the constants,  $K_L$  and  $a_L$  is:

$$C_e / q_e = (1/K_L) + (a_L / K_L) C_e \quad (3)$$

Fig. 5 shows the Langmuir plot at different particle size ranges. Linear plots suggest the applicability of the Langmuir isotherm for the present system. Values of  $K_L$  and  $a_L$  have been calculated at different system variables and are tabulated in Table 1. The values of the constant,  $K_L/a_L$ , correspond to the maximum adsorption capacity ( $q_{max}$ ) of clay for methomyl.

The Langmuir constant,  $K_L$ , can be used to determine the enthalpy change ( $\Delta H$ ) during the adsorption process using the Clausius-Clapeyron Equation (McKay et al. 1987):

$$K_L = A_c \cdot \exp(-\Delta H/RT) \quad (4)$$

Hence a plot of  $\log K_L$  versus  $1/T$  as shown in Fig. 6 produces a straight line with the gradient  $(-\Delta H/ 2.303R)$  from which ( $\Delta H$ ) may be calculated using the least-squares method and correspond to (-17.54 kJ/mol) which conform the exothermic nature of the process.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter,  $\check{R}$ , which is defined by the following relationship:

$$\hat{R} = 1 / (1 + a_L \cdot C_0) \quad (5)$$

The equilibrium parameter indicates the shape of isotherm as follows: unfavorable for  $\check{R} > 1$ , linear for  $\check{R} = 1$ , favorable for  $0 < \check{R} < 1$  and irreversible for  $\check{R} = 0$ . The values of  $\check{R}$  have been calculated and are tabulated in Table 1. One example is depicted in Fig. 7, which is a plot of the dimensionless solid-phase concentration,  $Q_e$ , against the

dimensionless liquid-phase concentration,  $X_e$  at different particle size ranges. The general relationship for the equilibrium parameter ( $\hat{R}$ ) is:

$$\hat{R} = X_e (1 - Q_e) / Q_e (1 - X_e) \tag{6}$$

Where

$$X_e = C_e / C_{ref} \quad , \quad Q_e = q_e / q_{ref} \tag{7}$$

For a single solute adsorption system,  $C_{ref}$ , is usually the highest liquid-phase concentration encountered and  $q_{ref}$  is the equilibrium solid-phase concentration co-existing with  $C_{ref}$ .

Substituting Equations (6) & (7) into (5) and simplifying, Equation (5) becomes:

$$\hat{R} = 1 / (1 + a_L \cdot C_{ref}) \tag{8}$$

Since  $C_{ref}$  is the highest liquid-phase concentration encountered (i.e.  $C_{ref} = C_0$ ), it follows that Equations (8) and (5) are identical. The degree of "favorability" is generally related to the reversibility of the system thereby giving a qualitative assessment of the methomyl-natural clay interactions. Indeed, the degree of reversibility of the system is,  $0 < \hat{R} < 1$ , which represents the reversible isotherm case in the favorable range.

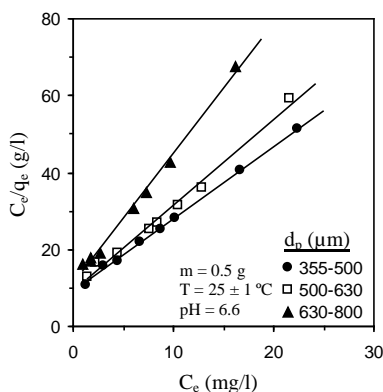


Fig. 5. Langmuir plots for different particle size ranges.

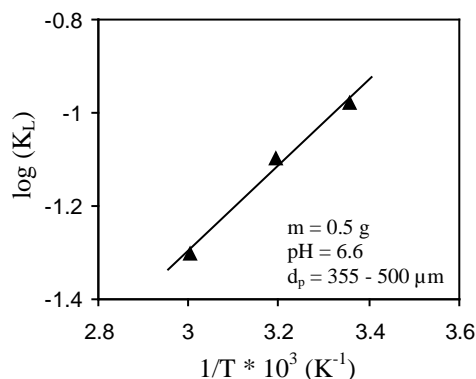


Fig. 6. Plot of log  $K_L$  against  $1/T$  for adsorption of methomyl onto natural clay.

3.4.2.

Freundlich Isotherm



The equilibrium data for the adsorption of methomyl onto natural clay at different variables have also been analyzed using the Freundlich isotherm as given by Eq. (9).

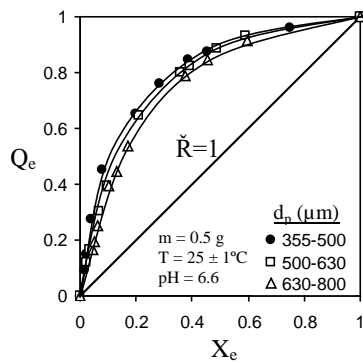
$$q_e = K_F \cdot C_e^{1/n} \quad (9)$$

The Freundlich equation predicts that the methomyl concentrations on the adsorbent will increase so long as there is an increase in the methomyl concentration in the aqueous solution (Chan et al. 2008). To determine exponent,  $n$ , and the constant,  $K_F$ , the equation linearized as follows:

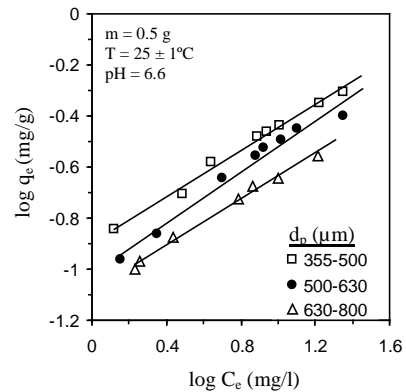
$$\log q_e = \log K_F + (1/n) \log C_e \quad (10)$$

Fig. 8 shows the Freundlich plot of the methomyl-clay system at different particle size ranges on the basis of Equation (10). The Freundlich parameters,  $K_F$  and  $n$  have been calculated using the least-squares method applied to the straight lines and are listed in Table 1.

The magnitude of exponent,  $n$ , gives an indication of the favorability and capacity of the adsorbent-adsorbate system, values of  $n > 1$  represent favorable adsorption (Treybal 1985). In this work the values of  $n$  are greater than one ( $n > 1$ ) which indicates that the methomyl shows favorable adsorption by natural clay.



**Fig. 7.** Equilibrium parameter plots for the adsorption of methomyl onto natural clay at different particle size ranges.



**Fig. 8.** Freundlich plots for different particle size ranges.

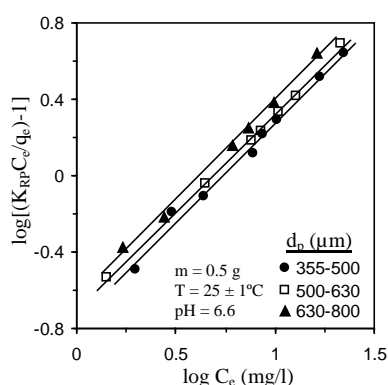
### 3.4.3. Redlich-Peterson Isotherm

The Redlich-Peterson isotherm is represented by the Eq. (11):

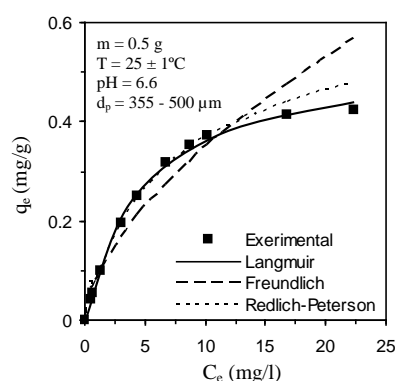
$$q_e = (K_{RP} \cdot C_e) / (1 + a_{RP} \cdot C_e^\beta) \quad (11)$$

For  $\beta=1$ , Eq. (11) converts to the Langmuir isotherm; and for  $1 < (a_{RP} \cdot C_e^\beta)$  it is identical with the Freundlich isotherm. The parameters of Equation (11) were determined by minimizing the distance between the experimental data points and the theoretical model predictions using an iterative computer program for data fitting. Table 1 shows the Redlich-Peterson parameters for methomyl-clay system at different particle size ranges. Fig. 9 shows plots of Redlich-Peterson model in linear form:

$$\log \{ [K_{RP} \cdot C_e / q_e] - 1 \} = \log a_{RP} + \beta \log C_e \quad (12)$$



**Fig. 9.** Redlich-Peterson plots for different particle size ranges.



**Fig. 10.** Comparison between experimental and theoretical isotherms for the adsorption of methomyl onto natural clay.

### 3.5. Simulation Results and Correlations

Using the appropriate constants of the Langmuir, Freundlich, and Redlich-Peterson models, the theoretical isotherm curves were predicted using known values of  $C_e$ . Fig. 10 shows a comparison of the experimental points with the Langmuir, Freundlich, and Redlich-Peterson models, in order to establish which model yields the "best fit". It is clear from the results of this study that the Langmuir model fits the experimental adsorption data significantly better than the Freundlich, and Redlich-Peterson models. This conclusion was supported by comparing correlation coefficients generated by

linear plots performed on the Langmuir, Freundlich and Redlich-Peterson model data, Table 1. These coefficients are a measure of the conformity of the data to a linear trend, a value of one would indicate a perfect fit. The correlation coefficients obtained from the Langmuir plots were higher overall (i.e. closer to 1) than those obtained for other models. The results obtained showed that the Langmuir model could be applied to the adsorption of methomyl onto natural clay over the entire solute concentration range studied in experimental studies.

**Table 1.** Langmuir, Freundlich and Redlich-Peterson isotherm parameters for adsorption of methomyl onto natural clay at different system variables.

	Langmuir isotherm				Freundlich isotherm			Redlich-Peterson isotherm				
	$K_L$ (l/g)	$a_L$ (l/mg)	$q_{max.}$ (mg/g)	$R$ (-)	C.F	$K_F$ (l/g)	$n$ (-)	C.F	$K_{RP}$ (l/g)	$a_{RP}$ (l/mg) <sup>1/β</sup>	$β$ (-)	C.F
<b><math>d_p(\mu m)</math></b>												
355-500	0.105	0.195	0.539	0.114	0.99	0.085	1.634	0.94	0.105	0.220	0.93	0.88
500-630	0.100	0.218	0.459	0.103	0.99	0.077	1.638	0.95	0.100	0.321	0.81	0.96
630-800	0.080	0.260	0.308	0.088	0.98	0.062	1.712	0.92	0.080	0.340	0.82	0.90
<b><math>T(^{\circ}C)</math></b>												
25	0.105	0.195	0.539	0.114	0.99	0.085	1.634	0.94	0.105	0.221	0.93	0.88
40	0.079	0.164	0.486	0.132	0.98	0.078	1.775	0.89	0.079	0.280	0.77	0.88
60	0.050	0.119	0.421	0.174	0.97	0.570	1.788	0.94	0.050	0.124	0.99	0.95

*C.F.: Correlation Factor*

### 3.6. Designing Batch Adsorber from Isotherm Data

Adsorption isotherm studies can also be used to predict the design of single stage batch adsorber system (McKay et al. 1985; Alkan et al. 2008). The schematic diagram for a single-stage adsorption process is shown in Fig. 11. The effluent solution to be treated has a volume  $V$  (l) and the pollutant concentration is reduced from  $C_0$  to  $C_e$  (mg/l) in the adsorption process. The amount of adsorbent added is  $m$  (g) of adsorbate-free solid and the adsorbate loading changes from  $q_0 = 0$  to  $q_e$  (mg/g). Clay was applied in removing insecticide methomyl with a vision of reducing the cost of the adsorption process and as a step to reduce environmental problems.

The mass balance that equates the adsorbate, methomyl, removed from the liquid to that picked up by the adsorbent is:

$$V(C_0 - C_e) = m(q_e - q_0) = mq_e \quad (13)$$

The Langmuir isotherm data may now be applied to Equation (13) since the Langmuir isotherm gave the best fit to experimental data.

$$\frac{m}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{[K_L C_e / (1 + a_L C_e)]} \quad (14)$$

Fig. 12 shows a series of plots derived from Equation (14) for the adsorption of methomyl onto natural clay and depicts the amount of effluent which can be treated to remove the methomyl content by 20, 30, 40, 50 and 60% using various masses of the adsorbent.

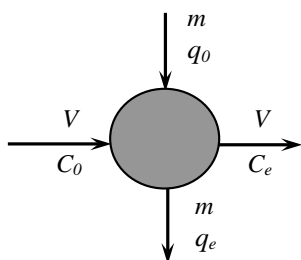


Fig. 11. Single stage batch adsorber

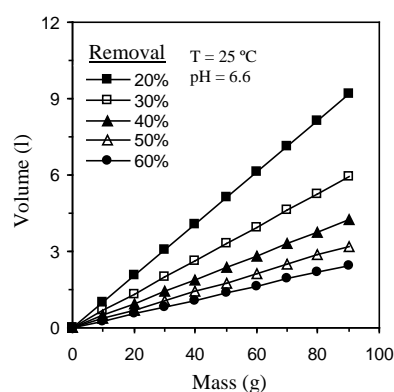


Fig. 12. Volume of effluent treated versus mass of natural clay (355 - 500  $\mu\text{m}$ ) for different percentage methomyl removal

#### 4. Conclusions

It was found that natural clay reached equilibrium with methomyl solution in time less than three hours. The results indicated that percentage of insecticide removal ranged from 27.6 to 32.9 for initial concentration varied from 43.71 to 19.99 mg/l. The adsorption isotherms have been plotted to obtain the Langmuir, Freundlich and Redlich-Peterson constants at different system variables. It is clear from the results of this study that the Langmuir model fits the experimental adsorption data significantly better than the Freundlich, and Redlich-Peterson models. Equilibrium parameter,  $\bar{R}$  was used to assess the nature of the equilibrium, the results indicated that methomyl-natural clay system exhibit "favorable" adsorption (i.e.  $0 < \bar{R} < 1$ ). The negative value of  $\Delta H$  (-17.54 kJ/mol) showed that the adsorption has an exothermic nature.

## Nomenclature

$A_c$	Clausius-Clapeyron constant (-)
$a_L$	Langmuir constant (l/mg)
$a_{RP}$	Redlich-Peterson constant [(l/mg) <sup>1-β</sup> ]
$C_0$	initial liquid-phase concentration (mg/l)
$C_e$	equilibrium liquid-phase concentration (mg/l)
$C_{ref}$	reference liquid-phase concentration (mg/l)
$d_p$	adsorbent particle size range (μm)
$K_F$	Freundlich constant (l/g)
$K_L$	Langmuir constant (l/g)
$K_{RP}$	Redlich-Peterson constant (l/g)
$m$	adsorbent mass (g)
$n$	Freundlich exponent (-)
$Q_e$	dimensionless solid-phase concentration at equilibrium
$q_e$	equilibrium solid-phase concentration (mg/g)
$q_{ref}$	reference solid-phase concentration at onset of monolayer coverage (mg/g)
$R$	universal gas constant (J/mol.K)
$T$	temperature (°C or K)
$V$	effluent volume (l)
$X_e$	dimensionless liquid-phase concentration at equilibrium
$\Delta H$	enthalpy change (kJ/mol)
$\tilde{R}$	dimensionless equilibrium parameter, defined by Equation (5)
$\beta$	Redlich-Peterson exponent (-)

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