Removal of an insecticide (methomyl) from aqueous solutions using natural clay

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Abstract Adsorption of an insecticide (methomyl) onto natural clay have been investigated as a possible alternative method for its removal from aqueous solutions. The study was aimed to use low cost material as a step towards cleaner environment. The influence of system variables, such as particle size (d_p) and temperature on the adsorption capacity have been studied. It was found that natural clay reached equilibrium with methomyl solution in time less than 3 h. The experimental data were fitted to equilibrium isotherm models, Langmuir, Freundlich and Redlich–Peterson. A dimensionless separation factor, $\widehat{R}$, was used to judge the favorable adsorption. 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 effect of temperature showed the exothermic nature of the process. The enthalpy change (ΔH) of adsorption has been evaluated and it has a value of, −17.54 kJ/mol. The Langmuir model fit the experimental data significantly better than Freundlich and Redlich–Peterson models. A chart based on material balance using single batch adsorber was constructed for different percentage of methomyl removal using the Langmuir isotherm where the mass of natural clay required to treat a specified volume of solution is calculated.

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 activity. 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 [1]. 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, inrinsates and containers. Pesticides may cause injury by containing the nontarget 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

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Nomenclature

A_c	Clausius–Clapeyron constant (–)
a_L	Langmuir constant (l/mg)
a_{RP}	Redlich–Peterson constant $((l/mg)^{1-\beta})$
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
ΔH	enthalpy change (kJ/mol)
$\widehat{R}$	dimensionless equilibrium parameter, defined by Eq. (5)
β	Redlich–Peterson exponent (–)

with residue of various pesticides [2,3]. The ground water contamination due to pesticides has also been reported [4]. 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 [5].

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 [6], and dialysis [7]. 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_2 by ozonation [8]. 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 [9]. 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 [10]. Compared with the above methods, adsorption of different pesticides onto activated carbon and clay minerals has demonstrated efficiency and economic feasibility and gained high favorability for removing pesticides that are chemically and biologically stable [11].

Adsorption on solid surfaces is important from both scientific aspects and industrial (environmental) applications. For preliminary design of adsorption technologies, the adsorption equilibrium capacity of an adsorbent for special adsorbate has to be estimated. As in any separation process, adsorption efficiency is a complex attribute dependent on the kinetic and equilibrium properties of the adsorbate/adsorbent system.

The present work has focused on the evaluation of natural clay as low-cost adsorbent to remove the methomyl from aqueous solutions. The adsorption equilibrium of methomyl onto natural clay at different system variables was determined. The isotherm data were analyzed using three models, viz. the

Langmuir, Freundlich and Redlich–Peterson and the unknown parameters in the proposed model were evaluated under different system variables.
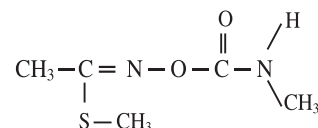
2. Experimental

2.1. Materials

The adsorbate used in this study was the an insecticide, methomyl, (S-Methyl-N[(methylcarbbamoyl)oxy]-thioacetimidate). The chemical structure of methomyl is shown in scheme 1.

The adsorbate (methomyl) used in this study was supplied by Egyptian Company for commerce and agriculture, Egypt. The concentrations of methomyl solutions were measured by a UV-Spectrophotometer (Shimadzu, Inc. Kyoto Japan model U.V-1601). All measurements were made at the wavelength corresponding to maximum absorbance, λ_{max}, which is 233 nm for methomyl.

The natural clay used in the present study was collected from Wadi El-Mohasham Shale, El-Sheikh Fadl Village, El-Minia Governorate, Egypt. Natural clay was crushed and sieved through different standard sieves into various particle size ranges. The clay particle size fractions obtained were heated at 550 °C for 2 h to eliminate organic and carbonaceous materials. The dried material was ground to pass through screens and stored in sealed containers.

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

Scheme 1   Chemical structure of methomyl.

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 μm, and three different temperatures, 25, 40 and 60 °C, by shaking a 0.5 g 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:

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

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 (ε_p), the mean pore radius (r_{max}), the solid-phase density (ρ_s) and the particle density were determined using a mercury porosimeter and specific gravity measurements. The values obtained for natural clay were ε_p = 0.41, r_{max} = 22.32 , ρ_s = 1.98 g/cm^3, and ρ_p = 1.17 g/cm^3. The specific surface area of the natural clay was also determined using the nitrogen BET surface area method, with a value of obtained was 66.53 ∩ 10^4 cm^2/g.

The chemical composition of natural clay used was found to be as, silica (56.72%) 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% Fe_2O_3, 0.36% CaO, 0.11% MgO, 3.00% TiO,...). The mineralogical analysis of the natural clay under test revealed that it consists approximately of 58% kaolinite, 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. 1 shows that the amount of methomyl adsorbed from aqueous solutions increased with time, where equilibrium being achieved within 2.5 h at 25 1 °C. The plot of adsorption versus time depicted in the figure is smooth and continuous,
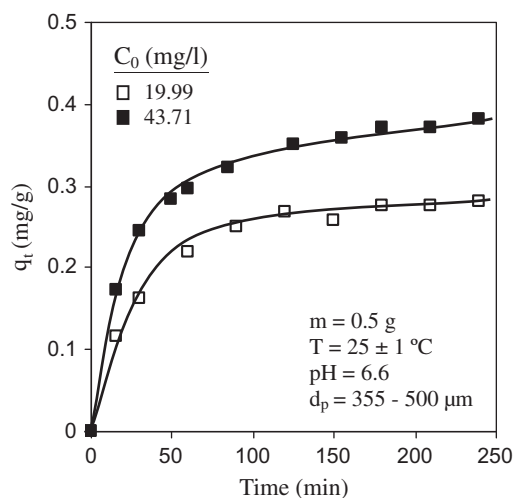

Figure 1 Equilibrium time for adsorption of methomyl onto natural clay.

indicating mono layer coverage of adsorbate on the surface of the adsorbent [12].

3.3. Equilibrium adsorption

The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm. The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solute and adsorbent, and is important for the design of adsorption system. Figs. 2 and 3 show the adsorption isotherms of methomyl onto natural clay for different particle size ranges and temperature respectively. As it is clear from Figs. 2 and 3, the shape of the isotherm indicated L-behavior according to Giles classification [13]. Effect of particle size on adsorption isotherm represented in Fig. 2 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
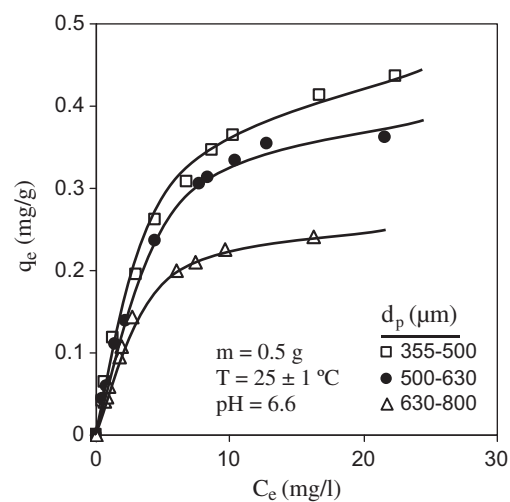

Figure 2 Adsorption isotherms for methomyl onto natural clay for different particle size ranges.
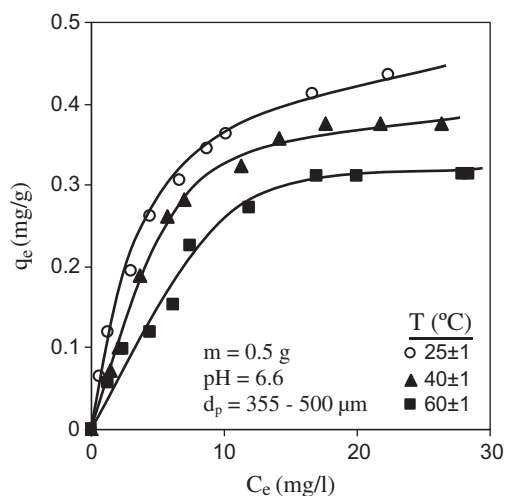
Figure 3 Adsorption isotherms for methomyl onto natural clay for different temperatures.

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 [14].

Fig. 3 represents the adsorption isotherm of methomyl on natural clay at different temperatures (25, 40 and 60 °C) when the particle size is constant, 355–500 μm. 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.

3.4. Equilibrium isotherm modeling

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. the Langmuir, Freundlich and Redlich–Peterson isotherms.

3.4.1. Langmuir isotherm

The Langmuir adsorption isotherm has found successful application for many sorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogenous sites within the adsorbent. It is then assumed that once a methomyl molecule occupies a site, no further adsorption can take place at that site. Moreover, the

model is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer (as $C_t \rightarrow \infty$) capacity can be represented by the expression:

$$q_e = (K_L \cdot C_e)/(1 + a_L \cdot C_e) \tag{2}$$

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

$$C_e/q_e = (1/K_L) + (a_L/K_L)C_e \tag{3}$$

Fig. 4 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 (ΔH) during the adsorption process using the Clausius–Clapeyron equation [12]:

$$K_L = A_c \cdot \exp(-\Delta H/RT) \tag{4}$$

Hence a plot of log K_L versus $1/T$ as shown in Fig. 5 produces a straight line with the gradient ($-\Delta H/2.303R$) from which (ΔH) 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, $\widehat{R}$, which is defined by the following relationship:

$$\widehat{R} = 1/(1 + a_L \cdot C_0) \tag{5}$$

The equilibrium parameter indicates the shape of isotherm as follows: unfavorable for $\widehat{R} > 1$, linear for $\widehat{R} = 1$, favorable for $0 < \widehat{R} < 1$ and irreversible for $\widehat{R} = 0$. The values of $\widehat{R}$ have been calculated and are tabulated in Table 1. One example is depicted in Fig. 6, which is a plot of the dimensionless solid-phase concentration, Q_e, against the dimensionless liquid-
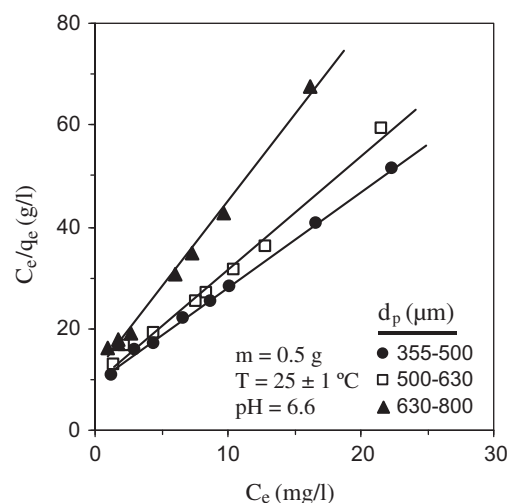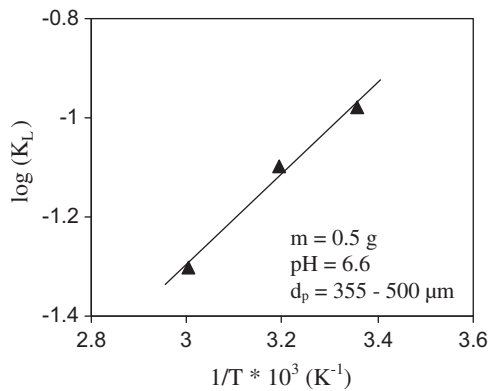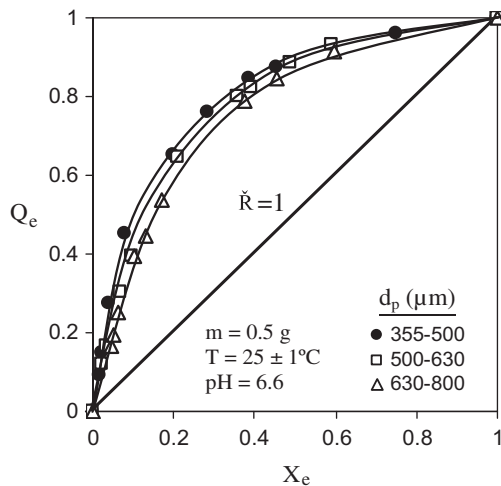

Figure 4 Langmuir plots for different particle size ranges.

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 model			
	K_L (l/g)	a_L (l/mg)	q_{max} (mg/g)	$\widehat{R}$ (–)	C.F	K_F (l/g)	n (–)	C.F	K_{RP} (l/g)	a_{RP} (l/mg)$^{1/\beta}$	β (–)	C.F
d_p (µm)												
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
T (°C)												
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.

Figure 5 Plot of log KL against $1/T$ for adsorption of methomyl onto natural clay.

Figure 6 Equilibrium parameter plots for the adsorption of methomyl onto natural clay at different particle size ranges.

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

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

where

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

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 Eqs. (6) and (7) into (5) and simplifying, Eq. (5) becomes:

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

Since C_{ref} is the highest liquid-phase concentration encountered (i.e. $C_{ref} = C_0$), it follows that Eqs. (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, $0 < \widehat{R} < 1$, which represents the reversible isotherm case in the favorable range.

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. The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written:

$$q_e = K_F \cdot C_e^{1/n} \tag{9}$$

The amount of adsorbed material is the summation of adsorption on all sites. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of monolayer. 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 [15]. To determine exponent, n, and the constant, K_F, the equation linearized as follow:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{10}$$

Fig. 7 shows the Freundlich plot of the methomyl-clay system at different particle size ranges on the basis of Eq. (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.

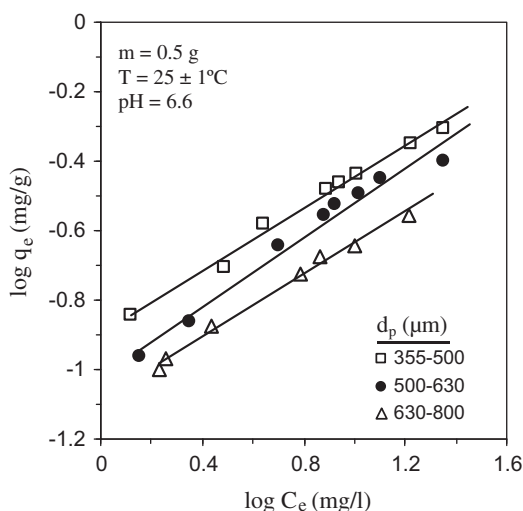The magnitude of exponent, n, gives an indication of the favorability and capacity of the adsorbent-adsorbate system,

Figure 7 Ferundlich plots for different particle size ranges.
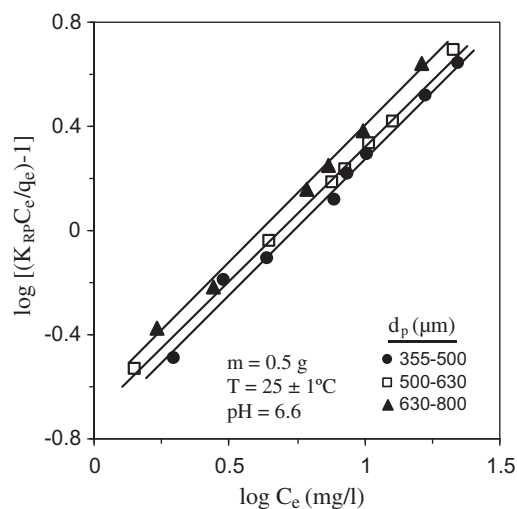

Figure 8 Redlich–Peterson plots for different particle size.

values of $n > 1$ represent favorable adsorption [16]. In this work the values of n are greater than one ($n > 1$) which indicates that the methomyl shows favorable adsorption by natural clay.

3.4.3. Redlich-Petersom isotherm

The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equations and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. The Redlich–Peterson isotherm is represented by the Eq. (11):

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

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 Eq. (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. 8 shows plots of Redlich–Peterson model in linear form, Eq. (12).

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

3.5. Comparison of isotherms

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. 9 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
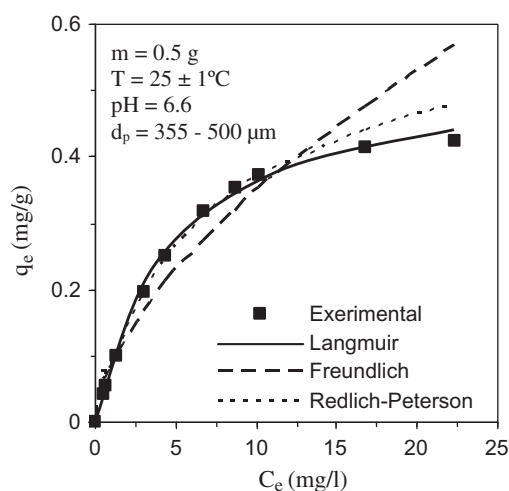

Figure 9 Comparison between experimental and theoretical isotherms for the adsorption of methomyl onto natural clay.

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.

3.6. Single-stage batch adsorber

Adsorption isotherm studies can also be used to predict the design of single stage batch adsorber system [17,18]. The schematic diagram for a single-stage adsorption process is shown in Fig. 10. 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 adsobate 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
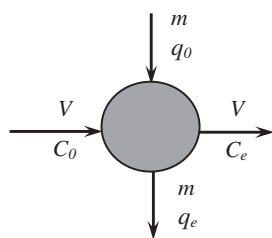
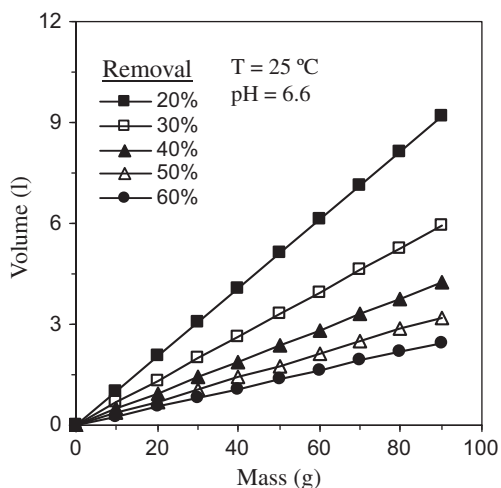**Figure 10** A single-stage batch adsorber.

Figure 11 Volume of effluent treated versus mass of natural clay (355–500 μm) for different percentage mothomyl removal.

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,

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

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

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

Fig. 11 shows a series of plots derived from Eq. (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.

4. Conclusions

The adsorption isotherm of methomyl onto natural clay from aqueous solutions has been studied at different systems variables. The removal of methomyl increases with the lapse of time and attains equilibrium in 150 min. The removal efficiency of methomyl ranged between 32.9% and 27.6% for initial methomyl concentrations 19.99 and 43.71 mg/l

respectively. The adsorption isotherms corresponding to the natural clay may be classified as type-L (Giles classification). A limited adsorption capacity was observed for methomyl onto natural clay especially at high temperature and large particle size. The adsorption isotherms have been plotted to obtain the Langmuir, Freundlich and Redlich–Peterson constants at different system variables. Theoretical isotherms were compared with experimental adsorption data and the general results of this study reveal that the Langmuir model can be used to describe the system adequately, as β in Redlich–Peterson model is very close to unity beside high correlation coefficient for Langmuir linear fitting. Equilibrium parameter, $\hat{R}$ was used to assess the nature of the equilibrium the results indicated that methomyl-natural clay system exhibit "favorable" adsorption (i.e. $0 < \hat{R} < 1$). The negative value of ΔH (−17.54 kJ/mol) showed that the adsorption has an exothermic nature.

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