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Adsorption Equilibria of an Insecticide Diazinon onto Natural Clay

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Abstract

Adsorption isotherm has been investigated for the adsorption of diazinon onto natural clay. The influence of particle size range of natural clay on the adsorption capacity has been studied with three different ranges. The results showed that the adsorption capacity of the natural clay increased from 4.9 mg/g (65.5% removal) to 6.1 mg/g (81.0% removal) for decreasing the particle diameter from 500-710 μm to 250-355 μm . The experimental results have been fitted with the Langmuir, Freundlich and Redlich-Peterson models. It is clear from the results that the Freundlich model fits the experimental data significantly better than the Langmuir and Redlich-Peterson models.

الملخص العربي

تعتبر مشكلة تلوث المياه بالمبيدات من أهم المشكلات التي شغلت منظمة الصحة العالمية وكذا العلماء لما لهذه المشكلة من أضرار على صحة الإنسان والحيوان والكائنات البحرية. وتهدف هذه الدراسة إلى إمكانية استخدام الطفلة الطبيعية في إزالة المبيدات وبخاصة المبيد الحشري (diazinon) من المحاليل المائية وتعتبر الطفلة الطبيعية مادة مازة رخيصة جدا ومتوفرة بكثرة. ولقد أجريت تجربة لدراسة تأثير الحبيبات (ثلاث مستويات) على سعة المادة المازة. وأوضحت النتائج أن زيادة سعة الاتزان على الطفلة من 5.5 % إلى 1 % إزالة عندما نقص حجم الحبيبات من 700- 00 إلى 355- 50 ميكرومتر. وقد تم تحليل النتائج المعملية لعملية الاتزان بواسطة لنماذج الرياضية المعروفة (لانجمير، فرويندليك، بيترسون). وقد تبين من الدراسة أن النتائج المعملية تتوافق الى حد كبير مع نموذج فرويندليك ومنه أمكن الحصول على

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الثابت الخاصة به لاستخدامها في تحديد حركية الامتزاز. وقد خلصت الدراسة الى أنه يمكن استخدام الطفلة طبيعية كمادة مازة رخيصة ومتوفرة محليا لإزالة المبيد الحشري (liazinon) من المحاليل المائية بحجم حبيبات من 250 - 355 ميكرومتر.

Keywords *Natural clay, diazinon, Adsorption isotherm, Adsorption isotherm models.*

1. Introduction

Water is a basic need of life and is used in many ways to cater the needs of daily life, so the control of water pollution is one of today's major of scientific activity. Indiscriminate use of pesticides leads to the contamination of soils, surface and ground waters. Numerous cases of pesticide residues have been reported in the literature (Halder et al. 1989). Pesticides, which indeed seem indispensable for the nutrition of mankind, take a special place among the environmentally problematic substances. Small quantities of the 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 and equipment cleanup sites and improper disposal of pesticides, reinstates and containers. Pesticides may cause injury to non-target organisms 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 ponds, rivers and ground water sources with various pesticides and herbicides is posing a direct threat to human health.

Most of the previous works have 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 (Greenberg et al. 2002) using hydrogen peroxides often ineffective because carbonate and bicarbonate ions, which are abundant in all natural water, react as strong free radical scavengers, also using chlorine dioxide, several degradation products of environmental toxic impact are produced. Pesticides are not completely degraded into inorganic compounds such as CO₂ by ozonation (Bonne et al. 2000), these findings suggested that the breakdown products of pesticides remain in water after treatment and require complementary operations and are not economical. Beside oxygen also nitrates present in natural water is a very effective scavenger for reducing and oxidizing species formed by ionizing γ -irradiation (Nathalie et al. 1999). The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems (Kauffmann et al. 2000). 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 cost (Boussahel et al. 2000).

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 (Mangat and Elefsiniotis 1999).

The basic object of the present paper was to determine the effectiveness of natural clay in the purification of solutions containing an insecticide diazinon. The scope of the investigation includes characterization of natural clay and batch studies to evaluate the adsorption capacity. The work is directed primarily towards studying the adsorption isotherm as well as the effect of particle size of natural clay on the adsorption capacity. The isotherm data have been analyzed using three models, viz. the Langmuir, Freundlich and Redlich-Peterson. A comparison of the experimental adsorption data with theoretical isotherms were studied in order to develop a model which both accurately represents the experimental adsorption results and could be used for design purposes.

2. Experimental

The adsorbate used in this study was the insecticide diazinon. The chemical structure of diazinon is shown in Fig. 1.

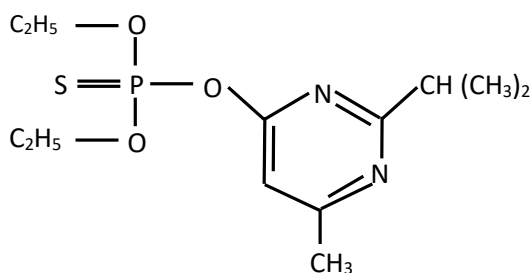


Fig. 1. Chemical structure of diazinon.

The adsorbate diazinon used in this study was supplied by Egyptian Company for Chemical and Pharmaceuticals (ADWA), Tenth of Ramadan city, Egypt. Diazinon was prepared as stock solution of concentration 40 mg.dm^{-3} and was subsequently diluted to required concentrations using distilled water. The concentration of diazinon in aqueous solutions was determined using a Spectrophotometer (Buck Scientific, Inc. model 390). All measurements were made at the wavelength corresponding to

maximum absorbance, λ_{\max} , which is 248 nm for diazinon. Dilutions of concentrated samples were undertaken when the absorbance exceeded 0.6 to give accurate results.

The natural clay used in the present study was crushed and sieved through different standard sieves into various particle size ranges. The clay particle size fractions obtained were vigorously stirred in 6 Vol. % H_2O_2 solution (5 ml.g⁻¹ sample), and then in (2 N) CH_3COOH solution (5 ml/g sample) at 90°C to eliminate organic and carbonaceous materials, respectively (El-Geundi et al. 1995). The sample was then filtered, washed thoroughly with distilled water and finally dried at 105°C. The dried material was ground to pass through screens and stored in sealed containers to use. The chemical composition of natural clay used was found to be as; silica (54.15%) and alumina (20.33%) are the major constituents of the natural clay while other metal oxides are presenting traces or small amounts. The silica: alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) for natural clay used was quite low (2.66) and this is an important parameter which governs the uptake of adsorbates. The mineralogical analysis of the natural clay under test revealed that it consists approximately of 51% Kaolinite, 46% montmorillonite, and 3% illite.

Adsorption isotherms were determined by the bottle-point method (El-Geundi 1990 & 1991). The adsorption capacity of the natural clay for diazinon were determined by contacting a constant mass of (0.1 g) clay with a fixed volume (50 ml) of diazinon solution, the latter having a range of concentrations (5-40 ppm). The clay / diazinon solution were placed in sealed glass bottles in a Griffin constant temperature shaker bath at constant agitation.

3. Results and Discussion

3.1 Characterization of 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 ($\bar{r}_{p_{\max}}$), and the solid-phase density (ρ_s) of the natural clay were determined using a mercury Porosimetry and specific gravity bottle respectively and the values obtained were $\epsilon_p=0.37$, $\bar{r}_{p_{\max}} = 32 \text{ \AA}$, and $\rho_s=2.35 \text{ g.cm}^{-3}$.

From mercury Porosimetry the following values were obtained for the dry natural clay:

$$\begin{aligned} V_p &= 0.083 \text{ cm}^3.\text{g}^{-1} \\ V_{\text{macro}} &= 0.069 \text{ cm}^3.\text{g}^{-1} \\ V_{\text{meso}} &= 0.014 \text{ cm}^3.\text{g}^{-1} \end{aligned}$$

$$\begin{aligned}
 V_{\text{micro}} &= V_p - (V_{\text{macro}} + V_{\text{meso}}) \\
 &= 0.083 - (0.069 + 0.014) = \text{zero}
 \end{aligned}$$

The natural clay can thus be regarded as a macro porous material. The specific surface area of the natural clay was determined using BET method (Brunauer et al. 1932) and the value obtained was $112 \times 10^4 \text{ cm}^2/\text{g}$.

3.2. Effect of Contact Time

Preliminary tests were undertaken to assess the contact time necessary for the system to come to equilibrium, and for experimental purposes, the system was given a contact time in excess of this period (Fig. 2). So that this information may be used to predict experimental conditions required to perform adsorption isotherms.

It is evident from Fig. 2 that the removal of diazinon increases with time and attains equilibrium in 100 minutes for all initial concentrations of diazinon solution under present investigation. The average removal at saturation was found to be 82.0%, 61.8% and 51.5% for 20, 30 and 40 mg.dm^{-3} initial concentrations of diazinon solution respectively at temperature of $25 \pm 2^\circ\text{C}$ (Fig. 3). It is further noted from Figs. 2 and 3 that the removal of adsorbate species is rapid in the initial stages of contact time and gradually decreases with lapse of time until saturation. The removal curves are single smooth and continuous indicating the formation of monolayer coverage on the surface of adsorbent (Singh et al. 1992).

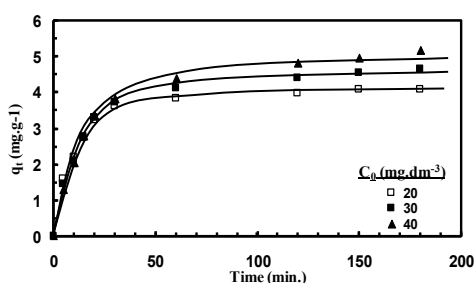


Fig. 2. Equilibrium time for the adsorption of diazinon onto natural clay.

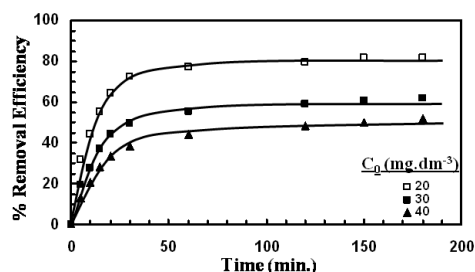


Fig. 3. Effect of initial concentration on the removal of diazinon by adsorption onto natural clay.

3.3. Adsorption Isotherm

The purpose of investigating adsorption isotherm is, firstly, to measure the adsorption capacity of the adsorbent particle concerned and secondly, to ascertain the liquid-solid equilibrium distribution of the solute concerned. The distribution of diazinon

between the adsorbent and the liquid phase, when the system is in a state of equilibrium, is important to establish the capacity of the adsorbent for diazinon. Preliminary experiments showed that such equilibrium was established within 100 minutes; however, all equilibrium experiments were allowed to run for 180 minutes.

Fig. 4 depicts the adsorption isotherms measured at different particle size ranges, 250-355, 355-500 and 500-710 μm , and demonstrates the marked effect of the particle size of natural clay on the adsorption of diazinon. According to the classification of (Giles et al. 1974a, b), the adsorption isotherm obtained may be classified as L-type. In this case, adsorption is very efficient at low concentration, but it becomes increasingly difficult, as the concentration increases, for a solute molecule to find a vacant adsorption site. The results show that the adsorption capacity of the natural clay increased from 4.9 mg/g (65.5%) to 6.1 mg/g (81.0%) for decreasing the particle diameter from 500-710 μm to 250-355 μm .

The higher efficiency in removing diazinon observed in the case of smaller-sized fraction of natural clay may be caused by the larger surface area as shown in Fig. 5. 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).

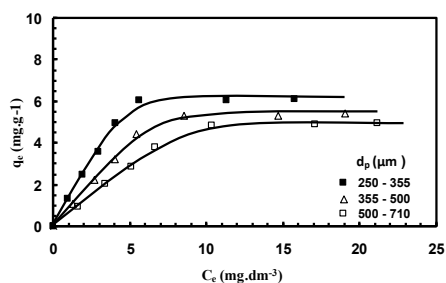


Fig. 4. Adsorption isotherms for diazinon onto natural clay at different particle size ranges.

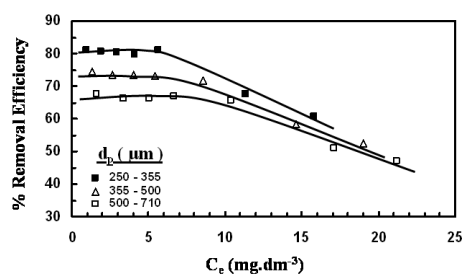


Fig. 5. Percent removal of diazinon by natural clay at different particle size ranges.

3.4. Analysis of 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 (Ruthven 1984; Subramanyam and Das 2012). 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 first isotherm tested was that of the Langmuir isotherm (Langmuir 1916) which may be represented by the equation:

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

This may be converted into a linear form convenient for plotting and determining the constants, K_L and a_L :

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

The plot of C_e/q_e against C_e at different particle size ranges is shown in Fig. 6 and is seen to be linear over a certain concentration range. Linear plots of C_e/q_e against C_e at different particle size ranges suggest the applicability of the Langmuir isotherm for the present system, and demonstrate monolayer coverage of the adsorbate at the outer surface of the adsorbent (Panday et al. 1986).

Values of K_L and a_L at different particle size ranges have been calculated using the least-squares method 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 a particular diazinon. Referring to Table 1, it can be seen that there is a gradual variation in the maximum adsorption capacity (q_{\max}) with particle size range.

Table 1. Estimated parameters of the Langmuir model

d_p (μm)	K_L (dm^3/g)	a_L (dm^3/mg)	q_{\max} (mg/g)	\bar{R} (-)	Correlation Coefficient
250-355	2.34	0.30	7.80	0.156	0.96
355-500	1.42	0.19	7.47	0.193	0.95
500-710	0.87	0.12	7.25	0.257	0.93

The influence of whether the adsorption is favorable or unfavorable on the isotherm shape has been considered by Weber and Chakravorti (1974). The isotherm shape can be classified by the dimensionless equilibrium parameter, \bar{R} , given in Eq. 3:

$$\bar{R} = 1 / (1 + a_L \cdot C_0) \quad (3)$$

The equilibrium parameter indicates the shape of the isotherm as follows:

Values of \bar{R}	Types of isotherm
$\bar{R} > 1$	Unfavorable
$\bar{R} = 1$	Linear
$0 < \bar{R} < 1$	Favorable
$\bar{R} = 0$	Irreversible

Values of \bar{R} for diazinon-clay system have been calculated and are tabulated in Table 1. The values of \bar{R} 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 (\bar{R}) for any isotherm is:

$$\bar{R} = X_e (1 - Q_e) / Q_e (1 - X_e) \quad (4)$$

Where,

$$X_e = C_e / C_{\text{ref}}, \text{ and } Q_e = q_e / q_{\text{ref}}$$

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 Eq. 4 into Eq. 3 and simplifying, Eq. 3 becomes:

$$\bar{R} = 1 / (1 + a_L \cdot C_{\text{ref}}) \quad (5)$$

Since C_{ref} is the highest liquid-phase concentration encountered (i.e. $C_{\text{ref}} = C_0$), it follows that Eqs. 3 and 5 are identical. The degree of "favorability" is generally related to the reversibility of the system thereby giving a qualitative assessment of the diazinon-natural clay interactions. Indeed, the degree of reversibility of the clay-diazinon system is, $0 < \bar{R} < 1$, which represents the reversible isotherm case in the favorable range.

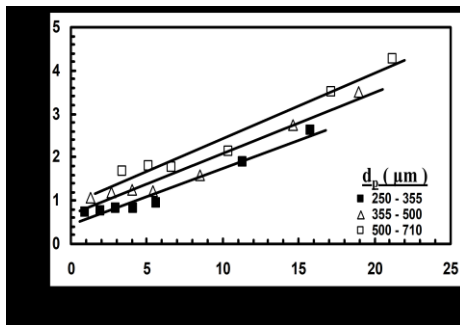


Fig. 6. Langmuir plot for the adsorption of diazinon at different particle size ranges.

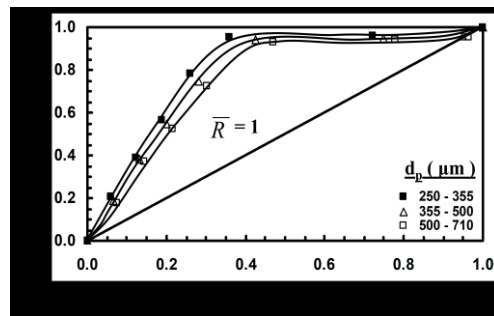


Fig. 7. Equilibrium parameter plot for the adsorption of diazinon at different particle size ranges.

3.4.2. Freundlich Isotherm

3.4.2. Freundlich Isotherm

The experimental equilibrium data for the adsorption of diazinon onto natural clay at different particle size ranges have also been analyzed using the Freundlich isotherm (Freundlich 1906) as given by Eq. 6.

$$q_e = K_F \cdot C_e^{1/n} \quad (6)$$

The equation may be linearized via a logarithmic plot which enables the exponent, n , and the constant, K_F , to be determined from Eq. 7.

$$\log q_e = \log K_F + (1/n) \log C_e \quad (7)$$

Inspection of the results derived from the Freundlich analysis and depicted by Eq. 7 shows that a plot of $\log q_e$ versus $\log C_e$ exhibits some curvature. Indeed, the results can be better represented by more than one straight line (Fritz et al. 1981). A general equation for the entire concentration range may be expressed as:

$$q_e = K_{F,i} \cdot C_e^{1/n_i} \quad (8)$$

Fig. 8 shows the effect of the particle size ranges on the Freundlich isotherm for diazinon on the basis of Eq. 8. The Freundlich parameters, K_F and n have been calculated using the least-squares method applied to the straight lines shown in Fig. 8 and are listed in Table 2 together with the appropriate concentration ranges (C.R.) and the correlation coefficients obtained.

Table 2. Estimated parameters of the Freundlich model

d_p (μm)	First section of plot				Second section of plot			
	K_F (dm^3/g)	n (-)	C.R. (mg/dm^3)	Correlation Coefficient	K_F (dm^3/g)	n (-)	C.R. (mg/dm^3)	Correlation Coefficient
250-355	1.37	1.11	0.6-5.0	0.99	4.52	8.62	5 - 20	0.90
355-500	0.88	1.05	0.8-7.0	0.99	3.68	7.14	7 - 25	0.90
500-710	0.58	1.01	2.0-9.0	0.99	2.64	4.60	9 - 25	0.95

Two important conclusions can be derived from the data presented in Table 2. First, the fact that the Freundlich model successfully describes the adsorption isotherm of the diazinon over a wide concentration range suggests that the adsorption sites were not saturated at any of the concentration considered in this study. Second, contrary to

a frequent assumption, the measured adsorption isotherms for the diazinon considered were non-linear. 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 according to Treybal (1985). In this work the values of n are greater than one ($n > 1$) for both sections of plot which indicates that the diazinon shows favorable adsorption by natural clay.

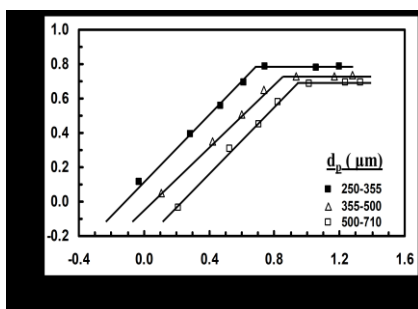


Fig. 8. Freundlich plot for the adsorption of diazinon at different particle size ranges.

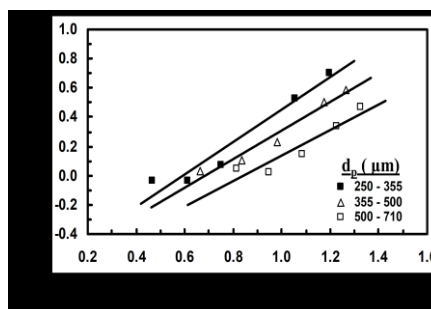


Fig. 9. Redlich-Peterson plot for the adsorption of diazinon at different particle size ranges.

3.4.3. Redlich-Peterson Isotherm

Another isotherm which incorporates intermediate terms between the Langmuir and Freundlich equations describes the isotherm better than the classical isotherm models because of its mathematical flexibility (Subramanyam and Das 2009). The Redlich-Peterson isotherm has been used in this work and is represented by the Eq. 9:

$$q_e = (K_{RP} \cdot C_e) / (1 + a_{RP} \cdot C_e^\beta) \quad (9)$$

For $\beta=1$, Eq.9 converts to the Langmuir isotherm; and for $1 < (a_{RP} \cdot C_e^\beta)$ it is identical with the Freundlich isotherm. The linear form is shown in Eq. 10 from which the constants, K_{RP} , a_{RP} and β , which characterize the isotherm, can be determined:

$$\log \{ [K_{RP} \cdot C_e / q_e] - 1 \} = \log a_{RP} + \beta \log C_e \quad (10)$$

The plot of $\log \{ [K_{RP} \cdot C_e / q_e] - 1 \}$ against $\log C_e$ is shown in Fig. 9 and is seen to be linear over a certain concentration range. The Redlich-Peterson parameters at different particle size ranges have been calculated using an iterative computer program for data fitting and minimizing the correlation coefficient, and are tabulated in Table 3.

Table 3. Estimated parameters of the Redlich-Peterson model

d_p (μm)	K_{RP} (dm^3/g)	a_{RP} (dm^3/g) $^{1/\beta}$	β (-)	Correlation Coefficient
250-355	2.65	0.49	0.90	0.88
355-500	1.69	0.35	0.90	0.85
500-710	1.08	0.23	0.90	0.75

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 . Figs. 10, 11 and 12 show 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 Freundlich model fits the experimental adsorption data significantly better than the Langmuir, and Redlich-Peterson models.

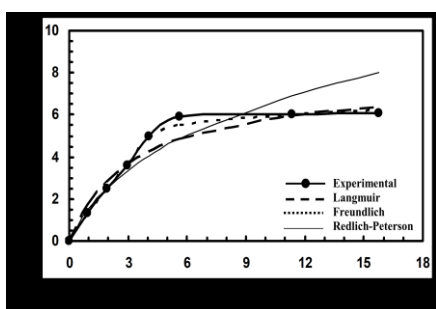


Fig. 10. Comparison of theoretical isotherm plots with experimental data for the adsorption of diazinon at $d_p = 250\text{-}355 \mu\text{m}$.

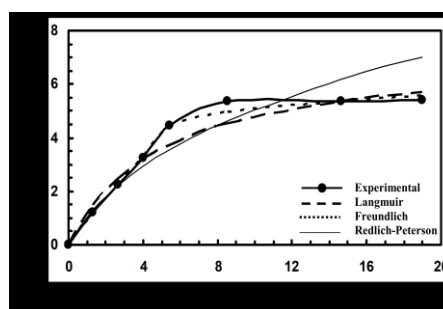


Fig. 11. Comparison of theoretical isotherm plots with experimental data for the adsorption of diazinon at $d_p = 355\text{-}500 \mu\text{m}$.

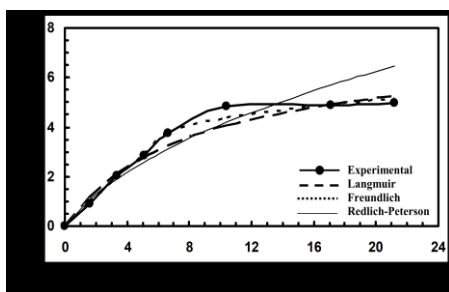


Fig. 12. Comparison of theoretical isotherm plots with experimental data for the adsorption of diazinon at $d_p = 500\text{-}710 \mu\text{m}$.

The results obtained showed that the Freundlich model could be applied to the adsorption of diazinon onto natural clay over the entire solute concentration range adopted in experimental studies (Figs. 10, 11 and 12). On the other hand, the Freundlich model better fitted the experimental data since the correlation coefficients obtained from the Freundlich plots were higher overall (i.e. closer to 1) than those obtained from the Langmuir and Redlich-Peterson plots. These coefficients are a measure of the conformity of the data to a linear trend, a value of one would indicate a perfect fit.

4. Conclusion

The experimental results from laboratory-scale studies indicate that natural clay has the ability to adsorb considerable quantities of diazinon. The results showed that the adsorption capacity of the natural clay increased from 4.9 mg/g (65.5% removal) to 6.1 mg/g (81.0% removal) for decreasing the particle diameter from 500-710 μm to 250-355 μm . Decrease particle size of natural clay gave a good improvement in diazinon removal. Equilibrium isotherms have been determined and the data obtained correlated using equations based on the Langmuir, Freundlich and Redlich-Peterson models. Theoretical isotherms were compared with experimental data and the general results of this study reveal that the Freundlich isotherm better fitted the experimental adsorption data since the correlation coefficients obtained from the Freundlich plots were higher overall than those obtained from the other models. Equilibrium parameter (\bar{R}) was used to assess the nature of the equilibrium for diazinon and the results indicated that diazinon-natural clay system exhibit "favorable" adsorption.

Nomenclature

a_L	parameter of Langmuir isotherm (dm^3/mg)
a_{RP}	parameter of Redlich-Peterson isotherm $[(\text{dm}^3/\text{mg})^{1-\beta}]$
C_0	initial liquid-phase concentration (mg/dm^3)
C_e	equilibrium liquid-phase concentration (mg/dm^3)
C_{ref}	reference liquid-phase concentration (mg/dm^3)
d_p	adsorbent particle size range (μm)
K_F	parameter of Freundlich isotherm (dm^3/g)
K_L	parameter of Langmuir isotherm (dm^3/g)
K_{RP}	parameter of Redlich-Peterson isotherm (dm^3/g)
n	Freundlich exponent (dimensionless)
Q_e	dimensionless solid-phase concentration at equilibrium
q_e	equilibrium solid-phase concentration (mg/g)
q_{max}	maximum adsorption capacity of clay for a particle diazinon (mg/g)
q_{ref}	reference solid-phase concentration at onset of monolayer coverage (mg/g)

\bar{R}	dimensionless equilibrium parameter, defined by equation (5)
$\bar{r}_{p\max}$	mean pore radius ($^{\circ}\text{A}$)
V_p	pore volume of adsorbent particle (cm^3g^{-1})
X_e	dimensionless liquid-phase concentration at equilibrium.

Greek symbols

β	Redlich-Peterson exponent (dimensionless)
ε_p	Porosity of particles (-)
ρ_s	Solid phase density (g.cm^{-3})
λ_{\max}	Wave length corresponding to maximum absorbance (nm)

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