Adsorption Equilibrium of a Herbicide (Pendimethalin) onto Natural Clay

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ABSTRACT: The equilibrium adsorption of a herbicide (pendimethalin) onto natural clay from aqueous solutions was studied experimentally using different system variables. The influence of such variables, such as particle size (dp), pH and temperature, on the adsorption capacity was studied. Equilibrium modelling was carried out using the Langmuir, Freundlich and Redlich–Peterson models with the corresponding constants being calculated for the different system variables. The results indicate that the maximum adsorption capacity (q_{max}) at an acidic pH value (3.44) was approximately double that observed at an alkaline pH value (9.62). It was also found that the effect of particle size was significant and that the temperature plays an interesting role in the adsorption process. The enthalpy change (∆H) for adsorption was evaluated as −29.36 kJ/mol. It is clear from the results of this study that the Freundlich model fitted the experimental adsorption data significantly better than the Langmuir or the Redlich–Peterson models.

INTRODUCTION

The quality of drinking water has become a major issue for public and political debate in recent years. One area that has received close attention is that of pesticides. This term includes insecticides, wood preservatives and herbicides, and covers many substances widely used by agriculture, industry and local authorities, and even domestically. Small quantities of the pesticides may enter the water environment through run-off to rivers or infiltration to groundwater aquifers.

After a review of the literature, the authors have concluded that a number of advanced treatment options exist. Adsorption of different herbicides onto activated carbon and clay minerals has been demonstrated as being both efficient and economically feasible. This method is gaining favour rapidly for removing pesticides that are chemically and biologically stable (Mangat and Elefsoiniotis 1999).

The technique of adsorption has been found to be useful for controlling the extent of water pollution due to dyes, metallic species, surfactants and organic pollutants (El-Geundi 1997). The major advantages of an adsorption system for water pollution control are less investment in terms of the initial cost and land, simple design and easy operation. It also has the advantage that its removal efficiency towards organic waste constituents is superior to that of conventional biological treatment processes.

Most commercial adsorption systems employ activated carbon as the adsorbent, but carbon is relatively expensive and there is a continual search for cheaper alternatives. Initial findings have indicated that natural clay has a high adsorptive capacity for dyes (El-Geundi 1996, 1997) and is

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relatively cheap. A vast amount of natural clay is available in Egypt, but the use of local natural clay as an adsorbent for herbicides has received only limited study. However, experimental results from laboratory-scale studies have indicated that natural clay has the ability to adsorb considerable quantities of a herbicide (pendimethalin) (Abd El-Ghany 2003).

The major purpose of the present work was to determine the adsorption equilibrium of pendimethalin onto natural clay as well as the effect of particle size ($d_p$), pH and temperature on the adsorption process. The resulting isotherm data have been analyzed using three models, viz. the Langmuir, Freundlich and Redlich–Peterson. The parameters from these three models characterizing the corresponding adsorption isotherms have been calculated for the different system variables. Such a comparison between the experimental adsorption data and the theoretical isotherms has been made in order to develop a model which represents the experimental adsorption results accurately and can be used for design purposes.

EXPERIMENTAL

The adsorbate used in this study was the herbicide, pendimethalin. This is a selective herbicide which is adsorbed by roots and leaves, and allows the control of most annual grasses and certain broad-leaved weeds in cotton, soybean and other crops. The chemical structure of pendimethalin is shown in Figure 1. Pendimethalin was supplied by the Egyptian Company for Chemical and Pharmaceuticals (ADWIA), Tenth of Ramadan City, Egypt and its concentration in aqueous solutions was determined using a Buck Scientific spectrophotometer, model 390. All measurements were made at a wavelength of 454 nm corresponding to the maximum absorbance, $\lambda_{max}$, for pendimethalin. To obtain accurate results, dilution of concentrated samples was undertaken when the absorbance exceeded 0.6.

The natural clay used in the present study was collected from Wadi El-Mohasham shale, El-Sheikh Fadl Village, El-Minia Governorate, Egypt. This was crushed and sieved through different standard sieves to obtain a range of particle sizes. The clay particle size fractions thus obtained were stirred vigorously at 90°C in 6 vol% H$_2$O$_2$ solution (5 ml/g sample size) and then in 2 N CH$_3$COOH solution (5 ml/g sample size) to eliminate organic and carbonaceous materials, respectively (El-Geundi et al. 1995). The resulting 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 prior to use.

Adsorption isotherms were determined by the bottle-point method (El-Geundi 1990). The adsorption capacity of the natural clay towards pendimethalin was determined by contacting a constant mass (0.1 g) of clay with a fixed volume (50 ml) of pendimethalin solution whose initial concentration was in the range 10–130 ppm. The natural clay/pendimethalin solution suspensions

![Figure 1. Chemical structure of pendimethalin.](image-url)
were placed in sealed glass bottles in a constant temperature shaker bath and shaken at a constant rate. The pH of each sample was adjusted to the desired pH value in the range 3.4–9.6 using aqueous 0.5 M solutions of either NaOH or HCl. Prior to adding the adsorbent, the bottles containing the pendimethalin solutions were raised to the desired temperature (30°C or 40°C).

RESULTS AND DISCUSSION

Characterization of natural clay

The porosity as well as the chemical composition of the adsorbent plays an important role in adsorption processes. In the present studies, the porosity ($\varepsilon_p$), the mean pore radius ($r_p$), and the solid-phase density ($\rho_s$) of the natural clay were determined using mercury porosimetry and specific gravity measurements. The values thus obtained were $\varepsilon_p = 0.37$, $r_p = 32$ Å and $\rho_s = 2.35$ g/cm$^3$, respectively.

The following values were also obtained from mercury porosimetry for the dry natural clay: $V_p = 0.083$ cm$^3$/g; $V_{macro} = 0.069$ cm$^3$/g; $V_{meso} = 0.014$ cm$^3$/g; $V_{micro} = V_p - (V_{macro} + V_{meso}) = 0.083 - (0.069 + 0.014) = 0$. The natural clay can thus be regarded as a macroporous material.

The specific surface area of the natural clay was determined using the nitrogen BET surface area method, with a value of 112 $\times 10^4$ ± 2 cm$^2$/g being obtained.

The chemical composition of the natural clay used was found to be silica (54.15%) and alumina (20.33%) as the major constituents with other metal oxides being present in trace or small amounts (Fe$_2$O$_3$, 6.86%; CaO, 2.6%; MgO, 2.26%; Na$_2$O, 2.16%; K$_2$O, 1.36%). The silica/alumina (SiO$_2$/Al$_2$O$_3$) ratio for the natural clay used was quite low (2.66), this being an important parameter which governs the uptake of pesticides.

Mineralogical analysis of the natural clay under test revealed that it consisted approximately of 51% kaolinite, 46% montmorillonite and 3% illite.

Adsorption isotherms

The purpose of investigating adsorption isotherms is, firstly, to measure the adsorption capacity of the adsorbent particles concerned and, secondly, to ascertain the liquid–solid equilibrium distribution of the solute concerned. Determining the distribution of pendimethalin between the natural clay and the liquid phase when the system is in a state of equilibrium is important in establishing the capacity of the clay for pendimethalin. Preliminary experiments showed that such an equilibrium was established within 120 min; however, all equilibrium experiments were allowed to run for 180 min.

Plotting the amount of pendimethalin adsorbed at equilibrium, $q_e$, against its initial concentration in the aqueous phase, $C_e$, gave a characteristic S-shaped curve as shown in Figures 2–4. From the shapes of the initial portions of the curves, the isotherms corresponding to the pendimethalin may be classified as type-S (Giles classification) suggesting a low affinity of the pendimethalin molecules for the active sites on the natural clay surface together with strong competition from the solvent molecules for the available adsorption sites (Giles et al. 1960).

Analysis of isotherm data

To develop a model which both accurately represents the experimental adsorption behaviour and can be used for design purposes, it is important to analyze the adsorption isotherm data obtained.
Several isotherm models are available for such an analysis. Three of these have been selected to simulate the experimental data in the present study, i.e. the Langmuir, Freundlich and Redlich–Peterson isotherms.

(a) Langmuir isotherm
The first isotherm tested was that of Langmuir which may be represented by the equation:

\[ q_e = \frac{K_L C_e}{1 + a_L C_e} \]  

(1)
This may be converted into a linear form which is convenient for plotting and determining the constants \( K_L \) and \( a_L \):

\[
\frac{C_e}{q_e} = \left(\frac{1}{K_L}\right) + \left(\frac{a_L}{K_L}\right)C_e
\]

(2)

The plots of \( \frac{C_e}{q_e} \) versus \( C_e \) for different particle size ranges, pH values and temperature ranges are shown in Figures 5–7, respectively, and are seen to be linear over a certain concentration range. Linear plots of \( C_e/q_e \) against \( C_e \) for different system variables suggest the applicability of the...
Langmuir isotherm to the present system and demonstrate monolayer coverage of the adsorbate on the outer surface of the adsorbent (Panday et al. 1984).

The values of $K_L$ and $a_L$ have been calculated for the different system variables studied 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 the clay for pendimethalin. The data listed in Table 1 indicate a gradual variation in the maximum adsorption capacity ($q_{max}$) with particle size range.

The value of the maximum adsorption capacity at acidic pH (3.44) is approximately double that for alkaline pH (9.62). Temperature also plays an interesting role in the adsorption. Increasing the...
temperature from 20°C to 40°C led to a decrease in the maximum adsorption capacity from 31.05 mg/g to 14.13 mg/g. This demonstrates the exothermic nature of the process.

The Langmuir constant, \( K_L \), can be used to determine the enthalpy change (\( \Delta H \)) during the adsorption process via the Clausius–Clapeyron equation:

\[
\ln K_L = -\frac{\Delta H}{2.303RT} + \text{constant}
\]

In the present work, the equation was used in the linear form:

\[
\log K_L = \log \Lambda_e - \frac{\Delta H}{2.303RT}
\]

As shown in Figure 8, a plot of \( \log K_L \) versus \( 1/T \) was linear with a gradient of \( -\Delta H/2.303RT \) from which \( \Delta H \) could be calculated as 29.36 kJ/mol using the least-squares method, thereby confirming the exothermic nature of the process.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, \( R \) (Weber and Chakravorti 1974), which is defined by the relationship:

\[
R = \frac{1}{1 + a_L C_a}
\]

The equilibrium parameter indicates the shape of the isotherm as listed below:

| Values of \( R \) | Types of isotherm |
|-------------------|-------------------|
| \( R > 1 \)       | Unfavourable       |
| \( R = 1 \)       | Linear             |
| \( 0 < R < 1 \)   | Favourable         |
| \( R = 0 \)       | Irreversible       |

Values of \( R \) for the natural clay/pendimethalin system have been calculated and are tabulated in Table 1. One example allowing an estimation of the \( R \) value is depicted in Figure 9, which
shows plots of the dimensionless solid-phase concentration, $Q_e$, against the dimensionless liquid-phase concentration, $X_e$, for different particle size ranges. The general relationship for the equilibrium parameter ($\Gamma$) for any isotherm is:

$$R = X_e(1 - Q_e)/Q_e(1 - X_e)$$  \hspace{1cm} (6)

where

$$X_e = C_e/C_{eq}$$  \hspace{1cm} (7)

and

$$Q_e = q_e/q_{eq}$$  \hspace{1cm} (8)

Figure 8. Clausius–Clapeyron plot of $\log K_L$ versus $1/T$ for the adsorption of pendimethalin onto natural clay.

Figure 9. Equilibrium parameter plots for the adsorption of pendimethalin at different particle size ranges. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C; pH = 8.19. The data points refer to the following particle size ranges: □, 80–125 µm; ■, 250–355 µm; ▲, 500–710 µm.
For a single-solute adsorption system, $C_{\text{ref}}$ is usually the highest liquid-phase concentration encountered and $q_{\text{ref}}$ is the equilibrium solid-phase concentration co-existing with $C_{\text{ref}}$. Substituting equations (6), (7) and (8) into (5) and simplifying gives:

$$R = \frac{1}{1 + n C_{\text{ref}}}$$  \hspace{1cm} (9)

Since $C_{\text{ref}}$ is the highest liquid-phase concentration encountered (i.e. $C_{\text{ref}} = C_0$), it follows that equations (9) and (5) are identical. The degree of “favourability” is generally related to the reversibility of the system, thereby giving a qualitative assessment of the natural clay–pendimethalin interactions. Indeed, the degree of reversibility of the natural clay/pendimethalin system is $0 < R < 1$, which represents the reversible isotherm case in the favourable range.

(b) Freundlich isotherm

The experimental equilibrium data for the adsorption of pendimethalin onto natural clay at different variables have also been analyzed using the Freundlich isotherm as:

$$q_e = K_F C_e^1/n$$  \hspace{1cm} (10)

The equation may be linearized via a logarithmic plot which enables the exponent, $n$, and the constant, $K_F$, to be determined via equation (11):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (11)

Inspection of results derived from a Freundlich analysis based on equation (11) shows that a plot of $\log q_e$ versus $\log C_e$ generally 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:

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} (12)

Figures 10–12 show the effect of the particle size range, pH value and temperature, respectively, on the Freundlich isotherm for pendimethalin on the basis of equation (12). The Freundlich parameters, $K_F$ and $n$, have been calculated using the least-squares method and are listed in Table 2 together with the appropriate concentration ranges and the correlation coefficients obtained.

Two important conclusions can be derived from the data presented in Table 2. Firstly, the fact that the Freundlich model successfully described the adsorption isotherm of the pendimethalin over a wide concentration range suggests that the adsorption sites were not saturated at any of the concentrations considered. Secondly, contrary to a frequent assumption, the measured adsorption isotherms for pendimethalin were all non-linear.

The magnitude of the exponent, $n$, gives an indication of the favourability and capacity of the adsorbent–adsorbate system. Values of $n > 1$ represent favourable adsorption according to Treybal (1985). In this work, the values of $n$ were less than unity ($n < 1$) for low concentrations of pendimethalin (first section of plot) and greater than unity ($n > 1$) for high concentrations of pendimethalin (second section of plot). This indicates that natural clay exhibits favourable adsorption towards pendimethalin at high concentrations of the latter.

(c) Redlich–Peterson isotherm

Another isotherm model which is intermediate between those described by the Langmuir and Freundlich equations often describes the isotherm better than the latter equations because of its
FIGURE 10. Freundlich plots for the adsorption of pendimethalin at different particle size ranges. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C. The data points refer to the following particle size ranges: ▲, 40–125 µm; ■, 250–355 µm; ●, 500–710 µm.

FIGURE 11. Freundlich plots for the adsorption of pendimethalin at different pH values. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C. The data points refer to the following pH values: ▲, 3.44; ■, 8.19; ●, 9.62.

This mathematical flexibility is due to the Redlich-Peterson isotherm which has been employed in this work in terms of the equation:

\[ q_e = \left( K_{RP} C_e \right)^{1/\beta} \]

When \( \beta = 1 \), equation (13) converts to the Langmuir isotherm; when \( 1 < \beta \), it is identical with the Freundlich isotherm. The linear form is shown in equation (14) which allows the constants \( K_{RP}, a_{RP} \) and \( \beta \) which characterize the isotherm, to be obtained:

\[ \log \left( \left( K_{RP} C_e \right) q_e \right) - 1 = \log a_{RP} + \beta \log C_e \]
Plots of versus log $C_e$ are shown in Figures 13–15 and are seen to be linear over a particular concentration range. The Redlich–Peterson parameters at different particle size ranges, pH values and temperature ranges have been calculated using an iterative computer program for data-fitting and minimizing the correlation coefficient. These are listed in Table 3.

![Figure 12. Freundlich plots for the adsorption of pendimethalin at different temperatures. Experimental conditions: wt. of adsorbent employed = 0.1 g; pH = 8.19; $d_p$ = 500–710 µm. The data points refer to the following temperatures: 20 ± 1°C; 30 ± 1°C; 40 ± 1°C.](image)

**TABLE 2. Estimated Freundlich Model Parameters for Different System Variables**

| First section of plot | Second section of plot |
|-----------------------|-----------------------|
| $K_F$ (dm³/g) | $n$ (-) | C.R. | Correlation coefficient | $K_F$ (dm³/g) | $n$ (-) | C.R. | Correlation coefficient |
| Particle size, $d_p$ (µm) | | | | | | | |
| 80–125 | 0.08 | 0.62 | 12–30 | 0.97 | 13.44 | 9.52 | 30–75 | 0.97 |
| 250–355 | 0.10 | 0.74 | 17–45 | 0.89 | 10.88 | 7.82 | 45–83 | 0.96 |
| 500–710 | 0.01 | 0.41 | 21–48 | 0.81 | 12.94 | 13.90 | 48–95 | 0.95 |
| pH | | | | | | | |
| 3.44 | 0.15 | 0.68 | 12–40 | 0.97 | 11.46 | 4.19 | 40–70 | 0.88 |
| 6.19 | 0.08 | 0.62 | 12–30 | 0.97 | 13.44 | 9.52 | 30–75 | 0.97 |
| 9.62 | 4.12 × 10⁻¹⁰ | 0.16 | 62–92 | 0.97 | 4.93 | 5.66 | 92–133 | 0.96 |
| Temperature (°C) | | | | | | | |
| 20 ± 1 | 0.01 | 0.44 | 12–35 | 0.99 | 8.08 | 4.78 | 35–97 | 0.89 |
| 30 ± 1 | 0.01 | 0.41 | 21–48 | 0.81 | 12.94 | 13.90 | 48–95 | 0.94 |
| 40 ± 1 | 9.28 × 10⁻⁹ | 0.20 | 42–70 | 0.97 | 12.16 | 34.30 | 70–106 | 0.88 |

*C.R. = concentration range.

Plots of $\log\left(\left[\frac{K_F}{C_e}\right] q_e - 1\right)$ versus log $C_e$ are shown in Figures 13–15 and are seen to be linear over a particular concentration range. The Redlich-Peterson parameters at different particle size ranges, pH values and temperature ranges have been calculated using an iterative computer program for data-fitting and minimizing the correlation coefficient. These are listed in Table 3.
Simulated results and correlations

Using the appropriate constants for the Langmuir, Freundlich and Redlich–Peterson models, it is possible to predict the theoretical isotherm curves using known values of $C_e$. Figures 16–18 provide 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 depicted in the figures that the Freundlich model fitted the experimental adsorption data significantly better than the Langmuir and Redlich–Peterson models.

Figure 13. Redlich–Peterson plots for the adsorption of pendimethalin at different particle size ranges. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C. The data points refer to the following particle size ranges: △, 80–125 μm; ■, 250–355 μm; ▲, 500–710 μm.

Figure 14. Redlich–Peterson plots for the adsorption of pendimethalin at different pH values. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C. The data points refer to the following pH values: △, 3.44; ■, 8.19; ▲, 9.62.

Simulated results and correlations

Using the appropriate constants for the Langmuir, Freundlich and Redlich–Peterson models, it is possible to predict the theoretical isotherm curves using known values of $C_e$. Figures 16–18 provide 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 depicted in the figures that the Freundlich model fitted the experimental adsorption data significantly better than the Langmuir and Redlich–Peterson models.
The results obtained showed that the Freundlich model could be applied to the adsorption of pendimethalin onto natural clay over the entire solute concentration range adopted in the experimental studies (Figures 16–18). This model provided the best fit to the experimental data since the average percentage deviation for the Freundlich model was lower than those for the other models tested as shown by the data recorded in Table 4. This conclusion is supported by a comparison of the correlation coefficients generated by linear plots obtained from an application of the Redlich–Peterson model. The correlation coefficients for the Redlich–Peterson model parameters are provided in Table 3 for different system variables.

### Table 3. Estimated Redlich–Peterson Model Parameters for Different System Variables

| Variable            | \(K_{ RP} \) (dm³/g) | \(a_0 \) (dm³/g)⁻¹ | \(\beta\) | Correlation coefficient |
|---------------------|-----------------------|---------------------|----------|------------------------|
| Particle size, \(d_p\) (µm) |                       |                     |          |                        |
| 80–125              | 1.20                  | 0.28                | 0.52     | 0.55                   |
| 250–355             | 0.80                  | 0.32                | 0.42     | 0.48                   |
| 500–710             | 0.75                  | 0.41                | 0.39     | 0.54                   |
| pH                  |                       |                     |          |                        |
| 7.44                | 1.90                  | 0.26                | 0.56     | 0.54                   |
| 8.19                | 1.20                  | 0.28                | 0.52     | 0.48                   |
| 9.62                | 0.30                  | 0.24                | 0.46     | 0.44                   |
| Temperature (°C)    |                       |                     |          |                        |
| 20 ± 1              | 1.25                  | 0.42                | 0.49     | 0.66                   |
| 30 ± 1              | 0.75                  | 0.41                | 0.39     | 0.54                   |
| 40 ± 1              | 0.60                  | 0.22                | 0.58     | 0.60                   |
Langmuir, Freundlich and Redlich–Peterson models to the experimental data. These coefficients are a measure of the conformity of the data to a linear trend, with a value of unity indicating a perfect fit. The data listed in Table 5 indicate that overall the correlation coefficients obtained from the Freundlich plots were higher (i.e. closer to unity) than those obtained from the Langmuir and Redlich–Peterson plots.

Figure 16. Comparison of experimental data with theoretical isotherms for the adsorption of pendimethalin at $d_p = 80–125 \mu m$. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C. The various lines and data points refer to the following isotherm models: —, experimental; ..., Freundlich; —, Langmuir; ..., Redlich–Peterson.

Figure 17. Comparison of experimental data with theoretical isotherms for the adsorption of pendimethalin at pH = 3.44. Experimental conditions: wt. of adsorbent employed = 0.1 g; temperature = 30 ± 1°C. The various lines and data points refer to the following isotherm models: —, experimental; ..., Freundlich; —, Langmuir; ..., Redlich–Peterson.
The adsorption of pendimethalin onto natural clay from aqueous solutions has been studied using different system variables. High adsorption capacities were obtained at low temperature (20°C), small particle size (80–125 µm) and acidic pH (3.44). The data from the corresponding adsorption

![Figure 18. Comparison of experimental data with theoretical isotherms for the adsorption of pendimethalin at 20 ± 1°C. Experimental conditions: wt. of adsorbent employed = 0.1 g; pH = 8.19. The various lines and data points refer to the following isotherm models: — , experimental; — , Freundlich; — , Langmuir; — , Redlich–Peterson.](image)

**TABLE 4. Comparison of Average Percentage Deviations of Isotherm Models**

| Particle size, $d_p$ (µm) | Freundlich | Langmuir | Redlich–Peterson |
|---------------------------|------------|----------|-----------------|
| 80–125                    | 0.07       | 1.58     | 0.80            |
| 250–355                   | 0.02       | 1.68     | 0.55            |
| 500–710                   | 1.19       | 4.71     | 1.48            |
| pH                        |            |          |                 |
| 3.44                      | 0.07       | 1.11     | 0.54            |
| 8.19                      | 0.07       | 1.58     | 0.80            |
| 9.62                      | 0.50       | 0.85     | 0.40            |
| Temperature (°C)          |            |          |                 |
| 20 ± 1                    | -0.01      | 2.67     | 1.26            |
| 30 ± 1                    | 1.19       | 4.71     | 1.48            |
| 40 ± 1                    | 0.42       | 1.14     | 0.52            |

*Average percentage deviation = \( \frac{100}{N} \sum \left( \frac{q_c - q_{cal}}{q_{cal}} \right) \)

**CONCLUSIONS**

The adsorption of pendimethalin onto natural clay from aqueous solutions has been studied using different system variables. High adsorption capacities were obtained at low temperature (20°C), small particle size (80–125 µm) and acidic pH (3.44). The data from the corresponding adsorption
isotherms were fitted by the Langmuir, Freundlich and Redlich–Peterson adsorption models and the corresponding constants obtained for the different system variables studied. A comparison of the theoretical isotherms with the experimental adsorption data revealed that the Freundlich isotherm gave a better fit since the average percentage deviation for this model was lower than those for the other models studied. This conclusion was supported by comparing the correlation coefficients generated by linear plots obtained from the Langmuir, Freundlich and Redlich–Peterson model data. The correlation coefficients obtained from the Freundlich plots were higher overall than those obtained from the Langmuir and Redlich–Peterson plots. The equilibrium parameter (\( R \)) was used to assess the nature of the equilibrium for pendimethalin. The results obtained indicated that the natural clay/pendimethalin system exhibited “favourable” adsorption (i.e., \( 0 < R < 1 \)).

NOMENCLATURE

| NOMENCLATURE | SYMBOL | DESCRIPTION |
|--------------|--------|-------------|
| Clausius–Clapeyron constant (\(^\circ\)C) | \( A_c \) | |
| parameter of Langmuir isotherm (dm\(^3\)/mg) | \( a_L \) | |
| parameter of Redlich–Peterson isotherm ([dm\(^3\)/mg]) \(^1/\beta\) | \( a_{RP} \) | |
| initial liquid-phase concentration (mg/dm\(^3\)) | \( C_0 \) | |
| equilibrium liquid-phase concentration (mg/dm\(^3\)) | \( C_e \) | |
| reference liquid-phase concentration (mg/dm\(^3\)) | \( C_{ref} \) | |
| adsorbent particle size (\( \mu \)m) | \( d_p \) | |
| parameter of Freundlich isotherm (dm\(^3\)/g) | \( K_F \) | |
| parameter of Langmuir isotherm (dm\(^3\)/g) | \( K_L \) | |
| parameter of Redlich–Peterson isotherm (dm\(^3\)/g) | \( K_{RP} \) | |
| Freundlich exponent (dimensionless) | \( n \) | |

| TABLE 5. Comparison of Correlation Coefficients for Isotherm Models |
|-------------------------|---------|---------|---------|
|                         | First section of plot | Second section of plot |
| Particle size, \( d_p \) (\( \mu \)m) | | |
| 80–125                  | 0.97    | 0.97    | 0.75    | 0.55 |
| 250–355                 | 0.89    | 0.96    | 0.71    | 0.48 |
| 500–710                 | 0.81    | 0.94    | 0.56    | 0.54 |
| pH                      | |       |         |
| 3.44                    | 0.97    | 0.88    | 0.76    | 0.54 |
| 8.19                    | 0.97    | 0.97    | 0.75    | 0.48 |
| 9.62                    | 0.97    | 0.96    | 0.59    | 0.44 |
| Temperature (\(^\circ\)C) | |       |         |
| 20 ± 1                  | 0.99    | 0.89    | 0.70    | 0.66 |
| 30 ± 1                  | 0.81    | 0.94    | 0.56    | 0.54 |
| 40 ± 1                  | 0.97    | 0.88    | 0.58    | 0.60 |
$Q_e$ solid-phase concentration at equilibrium (dimensionless)
$q_e$ equilibrium solid-phase concentration (mg/g)
$q_{r,0}$ reference solid-phase concentration at onset of monolayer coverage (mg/g)
$R$ universal gas constant $[(\text{atm dm}^3)/(\text{mol K})]$
$\beta$ Redlich–Peterson exponent (dimensionless)

Greek symbols

$\beta$ Redlich–Peterson exponent (dimensionless)

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