Abstract: The movement of pesticides in the soil has a significant effect, causing the failure of pest control, and environmental contamination. The results of this study were to investigate the environmental behaviour of glyphosate in the soil column. The data’s kinetic reaction was confirmed that glyphosate is subjected to Pseudo-first order rather than Pseudo-second order with the rate constant 0.042 h⁻¹. This indicated that decreasing glyphosate concentrations can occur and gradually decline with time. The data also pointed out that glyphosate was more fitted to Freundlich compared to the Langmuir model. It scored 3.083 to 1.814, indicating the behaviour of glyphosate occurred in the various surfaces. The contribution coefficient of glyphosate between the soil and its solution Kd valued 0.33 mL. g⁻¹, explaining that the herbicide is less mobile and tends to adsorb on soil particles. Overall data demonstrated that the kinetics of glyphosate under this current condition tends to be immobile.

Keywords: Adsorption, Equilibrium, Glyphosate, Soil, Soil column.

Introduction

Glyphosate, or N-(phosphonomethyl) glycine, is a nonselective, broad-spectrum herbicide, and its applied post-emergence weed control. It has been used to control several weeds since 1970 (Baylis, 2000). There is a growing concern resulting from the heavy use of glyphosate in agro ecosystems. This resulted in many ecological impacts to various organisms in soil (Hagner et al., 2019).

Excessive use of glyphosate causes it to bond to the soil. This is because glyphosate's phosphonic acid moiety interacts with polyvalent cations adsorbed on clay and, more broadly, soil organic matter to bind to soil (De Jonge et al., 2001). This process is called “the adsorption”, which is considered the most important for ionic and nonionic natural pesticides. A molecule is transported from a fluid bulk to a solid surface in this surface process. This process can be caused by physical forces or chemical connections (Ahmad et al., 2001). However, a number of studies on the kinetic adsorption of pollutants in soil has been carried out to evaluate its risk. But little data was published about the fate behaviour of glyphosate using soil column. For example, a study by Torodovic (2009) demonstrated that the behaviour of glyphosate relies on various factors, such as ecological impacts, properties of herbicide itself, fate of soil microorganisms, and parameters of the soil. Whereas, Mamy & Barriuso (2005) confirmed the adsorption of glyphosate in the soil is subject to phosphate content, soil copper, amorphous iron, and the structure of glyphosate ionisable based on soil pH. While
Laitinen (2009) explained that the residues of glyphosate remain in the water as a result of its adsorbed to soil. Also it formed like non-extractable residues, accelerant the biodegradation or may the leaching. Another study performed by Veiga et al. (2001) pointed out that glyphosate atoms in soil can be attached to the oxydic division or electrostatically absorbed by clay minerals and natural matter via hydrogen bridges.

The equilibrium approach was used to analyse the glyphosate data by (Khenifi et al., 2010). They discovered that using linear regression to compute the Langmuir, Freundlich, and adsorption equilibrium is more accurate. An equilibrium classic method is widely used to assess adsorption of pollutants in the ecosystem. Although, the most common methods for estimating the adsorption of contaminants in the soil column is a significant process that is mostly used due to their precise and easy to apply. In this field, Magga et al. (2008) used the soil column to determine the biodegradation, sorption, and transport of three different pesticides in groundwater. As a result of the widespread usage of glyphosate in Iraqi soils, the current study was utilised to analyse and anticipate the glyphosate kinetic, behaviour, and fate in order to determine the pesticide's ability to pollute agricultural soils and groundwater.

Materials & Methods

Soil properties and sorption study of glyphosate by soil column

The experiment is completely dependent on the method mentioned by Nur et al. (2014), which was modified by Al-Fartoosy (2020) to study the movement of pesticides in the soil. It was carried out utilising a soil column and a batch equilibrium approach. To ensure that all microorganisms were killed, the soil was autoclaved three times at 121°C for 15 minutes each time. A 10 cm plastic column with 4.5 diameters and a filter paper in the bottom was filled with 80 g of dry soil. In order to allow the soil to reach maximum capacity (saturating=1.6 mmol. g⁻¹), 50 mL of 0.01 M CaCl₂ was added and held for 24 hours to achieve equilibrium. The plastic soil columns were placed in the incubator shaker’s holder and tied down with tissue for 24 hours at 30°C and 120 RPM. To quantify glyphosate residues, 20 mL of 10 mg L⁻¹ glyphosate was run through the column once it had reached equilibrium using GC-FID. Three elution samples were collected through the column after 0, 2, 4, 6, 8, and 10 hours. The physiochemical properties of studied soil are shown in table (1).

Table (1): The physiochemical characteristics of soil.

| Texture | Sand% | pH | Moisture content | Organic matter% | CEC (meq 100g⁻¹) |
|---------|-------|----|------------------|-----------------|-----------------|
| Silt%   | 41    |    |                  |                 |                 |
| Clay%   | 13    | 6.7| 5.14             | 1.2             | 6.63            |

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The model of reaction

The pseudo-first-order (PFO) and second-order (PSO) reaction models were applied, which are mentioned in (Nur et al., 2014).

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \] ................................. (1).

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{k_2 q_e^2} \] ................................. (2).

Where \( k_1 \) = the rate constant of glyphosate equilibrium for adsorption per hour for the Pseudo-first order kinetic model (PFO), \( k_2 \) = the rate constant of glyphosate equilibrium for adsorption per hour for the Pseudo-second order kinetic model (PSO). \( q_e \) = glyphosate initial concentration in soil (mg L\(^{-1}\)), \( q_t \) = glyphosate adsorbed on soil (mg L\(^{-1}\)) at different time (t).

Thomas model

The Thomas equation was applied (Carvalho et al., 2007) using the following equation for a nonlinear model (Eq. 3).

\[ \frac{C_0}{C_t} = \frac{1}{1 + \left( \frac{q_0}{C_t} \right) (q_m - C_v)} \] ................................. (3).

but to generate a linear model, a natural logarithm of \([C_0/C_t]-1\) can be taken versus time.

Where: \( K_{Th} \) = Thomas rate constant (mL min\(^{-1}\) mg\(^{-1}\)), \( q_0 \) = equilibrium glyphosate adsorbed per g of soil (mg g\(^{-1}\)), \( C_0 \) = initial glyphosate concentration (mg L\(^{-1}\)), \( C_t \) = glyphosate concentration at time t (mg L\(^{-1}\)), \( M \) = mass of soil (g), \( Q \) = filtration velocity mL.min\(^{-1}\) and \( t \) = time (min), and \( V \) = the flow rate (mL min\(^{-1}\)).

The distribution coefficient

It can be determined by applying the following equation (Gupta and Gajbhiye, 2002).

\[ kd = \frac{c_e}{c_o} \] ................................. (4).

Where the Kd is the partition coefficient of glyphosate sorption constant, \( q_e \) = the glyphosate concentrations in the soil (mg g\(^{-1}\)), and \( C_e \) is the concentrations of glyphosate (mg L\(^{-1}\)) during the equilibrium.

\[ C_s = \frac{[C_i - C_e V_{eq}]}{m} \] ................................. (5).

\( C_i \) = the concentration of glyphosate used mg. L\(^{-1}\) or mL.g\(^{-1}\), \( C_e \) = previously described, \( V_{aq} \) is volume analysed (mL) and \( m \) = the mass of soil used (g).

Langmuir and Freundlich models

In order to determine Langmuir and Freundlich isotherm models for the adsorption of glyphosate in the soil column, those parameters were applied using two different equation models. The value of KL obtained by applying the linear form of the Langmuir through the plotting of the Ce/Cs versus Ce will generate a straight line.

Langmuir model has been performed by following the equation (Djozan et al., 2009).

\[ q_e = \frac{(abc_e)}{(1+bc_e)} \] ................................. (6).

Where, \( q_e \): Glyphosate concentration adsorbed per unit mass of soil, KL: Langmuir isotherm constant, \( C_e \) is Glyphosate concentration at equilibrium, aL: Langmuir isotherm constant.

On the other hand, the data of glyphosate adsorption were assessed according to the
Freundlich model by using the equation (7) (Ho et al., 2002).

\[ q_e = a_F C_e^{b_F} \] .......................... (7).

Where, \( q_e \): Glyphosate concentration adsorbed per unit mass of soil, \( b_F \), \( a_F \) are Freundlich isotherm constants, and \( C_e \text{ mol L}^{-1} \) is the equilibrium Glyphosate concentration in the solution. The plotting of \( \ln (q_e) \) versus \( \ln (C_e) \) will provide the linear form of the Freundlich constant model.

**Analysis of glyphosate**

The analysis protocol of glyphosate was followed the same protocol that used in the Al-Farttoosy (2020) with some modification. The process has been performed at the Ministry of Science and Technology, samples were analysed using a Gas Chromatography–Flame Ionisation Detector (GC-FID) (Thermo Scientific Trace 1300 GC) with the following column type and temperature: 30m 0.25mm Chrompack capillary column CP-Sil 24CB.

The following were the conditions of the operational conditions: column temperature was programmed at 10°C/min from 170 to 270°C; injection and detection temperatures were both 280°C; and nitrogen flow rate was 10 ml.min\(^{-1}\). Glyphosate peak heights were measured. Three replicates are represented in each outcome.

**Statistical analysis**

All data were calculated as mean standard deviation (SD), Linear Model, and kinetics models were used to assess data using various models (the pseudo-first, the pseudo-second-order kinetic models, Langmuir, Freundlich models, and Thomas model). GraphPad Prism 8.0.1 (244), (2D graphing and statistics software), Inc. San Diego, CA 92108, was used to conduct this study.

**Fig. (1): The kinetic reaction models of Glyphosate in soil column: A- PFO adsorption, B-PSO adsorption.**

**The reaction models**

Glyphosate concentrations have been determined to understand their kinetic reaction in the soil column. The assessment was applied using two different models, including pseudo-first and pseudo-second reaction models. Based on the received data, glyphosate concentration suffers from the adsorbed compound. This kinetic was
subjected to the PFO, and the rate constant reaction was 0.042 h\(^{-1}\) with the \(R^2\) 0.99. In case of the assessment of the PSO, the rate constant model was 0.005, and the value of \(R^2\) was 0.98 h\(^{-1}\) (fig. 1). This confirmed that glyphosate concentrations in the soil undergo the PFO. Both the pseudo-first order and pseudo-second order is commonly used to indicate that adsorption kinetics, according to (Revellame et al., 2020). However, when it comes to the adsorption of dyes and other chemicals from aqueous solutions onto cellulose-based materials, the PSO is more appropriate, according to the literature. In the line with this result, our findings showed that monitoring glyphosate behaviour in the soil, the glyphosate undergoes to the PFO rather than the PSO.

The importance of these models is to assist the monitor and follow up the behaviour of glyphosate in the soil, which strongly provide an indicator about the fate of this herbicide.

**Thomas model**

The Thomas model is one of the most well-known models for determining the ability of pollutants to penetrate the soil column. The current finding revealed that glyphosate travelled down the soil column and that predicting the Thomas model is simple. The rate constant of the Thomas model was investigated in this study. The linear relationship between the natural logarithm of the first concentration divided on the concentration over time yielded the \(K_{Th} \) 0.05 mL min\(^{-1}\) gm\(^{-1}\) (fig 2). This means glyphosate suffers slow movement. However, this model is considered a crucial model for understanding the adsorption normal description (Han et al., 2008).

As a result of the acquired data, the Thomas model was found to be suitable for glyphosate adsorption under the experimental conditions, as evidenced by the high coefficient of R-squared.

The importance of executing the Thomas model stems from the anticipation of adsorption on the one hand, as well as the potential application of this technology in other domains such as water purification and treatment on the other (Tovar-Gómez et al., 2013). As a result, this method may be used to forecast breakthrough curves and explain the dynamic adsorption of various contaminants in a fixed-bed column system (Amiri et al., 2019). Finally, this strategy demonstrated the method’s ability to predict glyphosate dynamic adsorption.

**Fig. (2): A linear line of glyphosate based on Thomas model**

The distribution or partition coefficient

Another variable parameter can be used to monitor and predict the behaviour of pollutants in the environment. This parameter is called The distribution or partition coefficient, Kd (OECD, 2000). The Kd is 0.33 mL. g\(^{-1}\). This indicated that glyphosate has less ability to distribute between those two partitions, where it might be adsorbed on the soil particle, leading to less availability in the medium. In contrast, Prata et al. (2003) explained that the development of inner sphere complexes with metals of soil oxides, which are connected to the soil phosphate...
adsorption ability, results in glyphosate sorption by soils. Eventually, glyphosate can be strongly adsorbed on the soil.

**Langmuir and Freundlich isotherms models**

The results of fig. (3A and 3B) illustrated that glyphosate undergoes two different models, the Freundlich and Langmuir. It can be seen that glyphosate concentrations in the soil column more fit to the Freundlich than Langmuir model based on the regression equation and the correlation coefficient $R^2$. The values of Freundlich ranged from 0.3.083 to 1.814 with the $R^2$ 0.98. In contrast, Langmuir valued between 0.8610 to 1.834 $\mu g m.L^{-1}$ and the $R^2$ was 0.93. The Langmuir model can point to the linkage between adsorbent active sites and the types of adsorbed and at the end, Langmuir can be used for a monolayer, which is found on the uniform surface. Whereas Freundlich model can be performed on mono- and multilayers. In addition to homo- and heterogeneous Surfaces (Ali et al., 2016).

Consequently, it is clearly shown that the surface of studying soil contains various surfaces. For this reason, glyphosate undergoes the Freundlich than the Langmuir model.

![Fig. (3): Adsorption model of glyphosate in the soil column: A- Freundlich model, B- Langmuir model.](image)

**Conclusions**

During this investigation, the aim was to assess glyphosate behaviour in the soil using the soil column method. The most obvious finding to emerge from this study is that glyphosate is not mobile due to its adsorption on the soil particles. The Kinetic behaviour of glyphosate subjected into the Pseudo-First Order. While the distribution coefficient of glyphosate indicates that glyphosate adsorbed on the soil particle. Also, the findings pointed out that glyphosate is fitted to the Freundlich model compared to the Langmuir model.

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**Conflicts of interest**

The authors declare that they have no conflict of interests.

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**Contributions of Authors**

A. H. A.: Idea, setting up the experiments, working up, Modeling calculations, collecting
the studied soil.

J. N. A.: Writing up the paper, checking the whole paper up in terms of scientific discussion, and its conclusions, Read and revise the manuscript, collecting the references relevant to the paper.

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مقارنة المعاملات المختلفة لمعرفة السلوك الحركي للغلافوسيت في عموذ التربة

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المستخلص: يمتلك امتصاص المبيدات في التربة تأثيراً معنويّاً يؤدي إلى فشل المكافحة وتلوث التربة. كشفت نتائج هذه الدراسة عن السلوك البيئي للغلافوسيت في عمود التربة. أكد التفاعل الحركي للبيانات أن الغلافوسيت خضع لتفاعل من الدرجة الأولى الكاذبة بدلاً من الدرجة الثانية الكاذبة وأن معدل ثابت التفاعل 0.043 ساعة١ً مثيرة إلى ان تناقص تركيز الغلافوسيت تدريجي مع مرور الوقت. كما أشارت البيانات إلى ان الغلافوسيت أيضًا أكثر ملاءمة لنموذج فرندش مقارنة بنموذج لانجمور، إذا سجل Kd 3.083 إلى 1.814 ربما يشير إلى حدوث سلوك الغلافوسيت على الأسطح المختلفة. بلغت قيمة معامل توزيع الغلافوسيت 0.33 مل جم١ً مما يوضح أن مبيد الأعشاب أقل قدرة على الحركة وميل إلى الامتصاص على جزيئات التربة. أظهرت البيانات الإجمالية أن حركة الغلافوسيت في ظل هذه الحالة الحالية تميل إلى أن تكون غير متحركة.

الكلمات الرئيسية: الامتصاص، التوزيع، غلافوسيت، التربة، عمود التربة.