The kinetic behaviour of Difenoconazole fungicide in the Clay loam soil using High-Performance Liquid Chromatography

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Abstract

Pesticide contamination has become a central issue across the worldwide because of the overuse and misuse of pesticides in agricultural fields. The present study was conducted to explore the kinetic behaviour of Difenoconazole in the clay loam soil. This investigation has been performed using High-Performance Liquid Chromatography (HPLC). The results demonstrated that Difenoconazole is subjected to the first order model, registering 0.01 Mg kg^{-1} as a rate-breaking dawn constant K, compared to the second order that has recorded 0.015 mg kg/mins. In contrast, the distribution coefficient of Difenoconazole reached 1.53 mL g^{-1}. This indicates that Difenoconazole has a high ability to move between the soil and its aqueous. Interestingly, According to the model study, has been observed that Difenoconazole followed the Langmuir model instead of the Freundlich model. The aL/KL value was 0.166 and the bF value was 0.159. This indicates that Difenoconazole moves on the non-regulator surface. Based on the Langmuir model, it takes 55.9 minutes for the first reaction order and 642 minutes for the second reaction order to degrade 50% of the initial concentration.

Keywords: Difenoconazole, Distribution Coefficient, First-order kinetic, Freundlich Isotherm, Langmuir Isotherm.

Introduction

Difenoconazole 250 EC) DFZ) (1-[2-[4-(4-chlorophenoxy)-2-chlorophenyl]-4-methyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (Fig. 1), is a systemic fungicide that has preventive and curative action against various diseases in different crops. It belongs to the group of demethylation inhibitors (DMI) that interfere with the biosynthesis of ergosterol, a compent of the fungal cell membrane. Difenoconazole 250 EC can control diseases such as venturia, powdery mildew, early blight, *Alternaria* spp, and *Rhizoctonia* sp. It is available in different formulations and trade names, such as Divecor , Dividend, Score, Skel, and others. Difenoconazole has high chemical stability, as well as high light chemical stability, low biodegradability and a high potential for easy movement in the environment (1). These properties make it stable and stable in the soil and the environment (2). Adsorption is the process of binding a substance to the surface of another substance. Adsorption of difenoconazole in soils is influenced by various factors, such as soil properties, environmental conditions, and the presence of other chemicals. difenoconazole has a high octanol-water partition coefficient, which means it is more likely to adsorb to organic matter in soil than to dissolve in water (3). Difenoconazole adsorption in soil is negatively correlated with soil pH, which means it adsorbs more strongly in acidic soils than in alkaline soils (4). Difenoconazole adsorption in soil is enhanced by the presence of adjuvants, which are substances that improve the performance of pesticides. Adjuvants can increase the contact area and reduce the surface tension between Difenoconazole and soil particles (3).

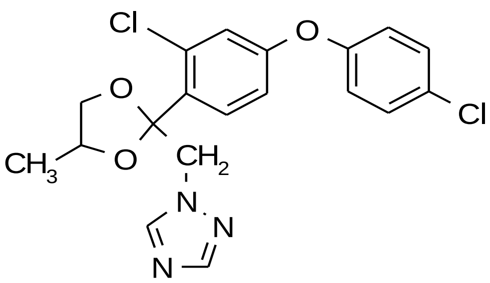

Fig. 1. Difenoconazole chemical structure.

Difenoconazole adsorption in soil can affect its degradation and mobility. Adsorbed Difenoconazole is more resistant to microbial degradation and less prone to leaching than dissolved Difenoconazole (5). Agricultural wastewater was tested from a rice field in Malaysia and the concentration of the fungicide Difenoconazole was (300µg/L^{-1}) (6). In addition, a study found that high concentrations of the fungicide had a toxic effect on surface water. which negatively affects aquatic life (7). It has been revealed that high concentrations of the fungicide Difenoconazole on wheat plants can cause yellowing and drying of the tips of the leaves. This can hinder plant growth and result in a decrease in leaf area. The symptoms on plant become more severe with an increase in the concentration of the fungicide (5). The objective of the recent study is to evaluate the fate and chemical behaviour of Difenoconazole in the soil using different mathematic models.

Materials and Methods

Chemicals

The manufacturer of Score 25% is Syngenta CO. Ltd. The active ingredient is Difenoconazole, and it is available as an emulsifiable concentrate fungicide.

Difenoconazole Batch adsorption assays

An experiment has been conductes to observe the impact of Difenoconazole fungicide on the environment. The investigation complied with the established methodology (8 and 9). Three 250 mL flasks containing 100 g of dirt each were filled with 50 mL of Difenoconazole in order to evaluate the adsorption kinetics reaction. As a control, distilled water was applied to three more flasks. To bring the flasks into equilibrium, they were all shaken for a whole day at 150 rpm in an incubator. One millilitre of supernatant was added to one millilitre of Eppendorf the day after the equilibrium was attained, and the centrifuges were run for thirty minutes at 3500 rpm. After that, the aliquot was passed through the 022 filter. The HPLC has been used to calculate Difenoconazole residues.

Sample extraction

Each sample is put into a graduated cylinder containing 100 millilitres. 200 millilitres of ethyl acetate is then added to the cylinder and well stirred for three minutes. The mixture is then filtered through a dry cotton pad. After transferring the filtrates into a separatory funnel, 40 ml of a 20% sodium chloride solution was added. Three extractions were then conducted using 50 ml of redistilled methylene chloride. The anhydrous sodium sulphate and cotton were used to filter the organic phase. Using a rotary evaporator, the filtrates were concentrated nearly to dryness at 40 °C (10).

HPLC analysis

An HPLC model, SYKAMN (Germany), was utilized to detect the presence of Difenoconazole. The mobile phase consisted of an isocratic flow of 60% Acetonitrile and 40% Water, with a flow rate of 1.0 mL/min. The column used was C18-ODS (25 cm*4.6 mm), and the detector was UV-Vis with a wavelength of 254 nm (10).

Statistical-Calculations Evaluation

The data was analysed using several models, including linear and kinetic models. According to (11) the distribution coefficient Kd, Langmuir, Freundlich, and first and second-order kinetic models were computed. GraphPad Prism 8.0.1 (244), a 2D graphing and statistics tool created by Inc., situated in San Diego, California 92108, was used to conduct the study.

Results and Discussion

Kinetic reaction of Difenoconazole

Difencanazole's chemical kinetics were assessed utilising first- and second-order kinetic reactions. Straight lines appear in all plots of the logarithm of the normalised concentration as a function of reaction time (Figure 2), suggesting that the reaction is approaching a first-order reaction. The rate constant per minute was 0.017 mg L^{-1} demonstrating the clay loam soil's comparatively sluggish Difenoconazole breakdown. This is because of the soil properties (Table 1). It refers to a high amount of organic carbon, which contributes to the persistence of Difenoconazole in the soil.

(12) pointed out that the first-order kinetics best described the dissipation behaviour of Difenoconazole with a rate dissipation constant reached 0.017 mg L^{-1}/minutes. This kinetic reaction was compared to the Second-order. But it scored a dissipation rate of 0.0015 mg L^{-1}/minutes. According to (13), the fate of the pesticide glyphosate follows the FOR at a rate constant of 0.042 $hour^{-1}$. According to Hameed and Al-Farttoosy's study (9) carbendazim likewise exhibits FOR behaviour, with a rate constant of 4 × 10-4 minute $^{-1}$. Issa (14) conducted that the FOR was applied to three distinct insecticides: Indoxacarb, Imidacloprid, and lambda-cyhalothrin. The rates per $minute^{-1}$ were 0.01, 0.07 and 0.04 constants. When it comes to the biological activity of pesticides, this test is very important. Because certain insecticides progressively lose their effectiveness while others continue to work.

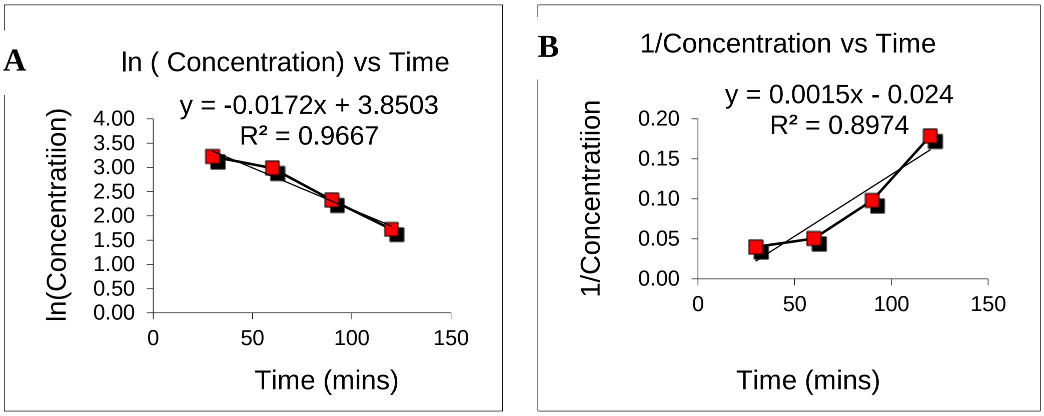

Fig 2. Beltanol reaction of A) The first order and B) The second order.

Table 1. The soil properties.

Type	EC ms/cm	pH (IU)	Total phosphorus (mg/l)	Total nitrogen (mg/l)	Total organic carbon (%)
The studied soil	10.8	7.95	0.064	5.6	3.29

Adsorption isotherm models

Figure (3) revealed the adsorption isotherm of Difenoconazole in the clay loam soil. By comparing the linear regression coefficient that is tabled in (Tales 2 and 3), the result showed that the Difenoconazole fungicide underwent the Langmuir model rather than the Freundlich model. According to Langmuir, the surface coverage is directly proportional to the rate of desorption from the surface, and the adsorption and desorption rates are equal at equilibrium (15).

When the Difenoconazole is subjected to the Langmuir model, indicating that the movement of the pesticide occurred in a mono-layer in the soil. The highest adsorption was estimated. This result is consistent with the results of several studies, including the study of (14) demonstrated that the Indoxacarb 0.013 L g^{-1} and Imidacloprid 0.249 L g^{-1} subjected to the Langmuir model (KL). In this study also Chlorantraniliprole 2.82 and Lambda-cyhalothrin 2.75 quite fitted the Freundlich model. It's important to note that this study differs from those conducted by (13). The latter found that glyphosate follows the Freundlich model. Studying both models is crucial to understanding how Difenoconazole naturally moves in soil particles and its ability to reach groundwater.

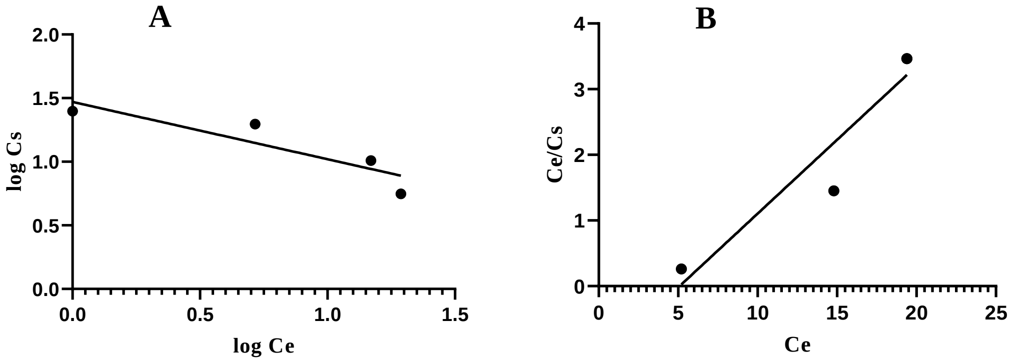

Fig 3. The sorption behaviour kinetic: A) Freundlich model, B) Langmuir model.

Table 2. Isotherm constant of Difenoconazole adsorption based on the Langmuir model using linear regression.

Ce	Ce/cs	Slope	1/KL	R^2	Equation
5.08	1.114	0.224	0.814	0.904	Y= 0.2247x-1.143

Table 3. Isotherm constant of Difenoconazole adsorption based on the Freundlich model using linear regression.

Ln (Ce)	Ln (qe)	Slope	Ln (aF)	R^2	Equation
3.266	1.47	0.45	0.1499	0.7997	Y=-0.4501X+1.479

On the other hand, the half-life (Time required to degrade 50% of initial concentration) of Difenoconazole is shown in Table (4). The table showed that Difenoconazole needs full dissipation is 55.98 days and 642 days based on the first and second-order reaction kinetic respectively.

The results of Table (4) showed that the Difenoconazole has a long persistence time and requires a long time to degrade and disappear, and this is the reason why is Mycoremediation.

Table 4. The Difenoconazole rate constant and half-lives.

Parameter	First-order	Second-order
half-lives (min^{-1})	55.98	642
R^2	0.966	0.897

Difenoconazole Distribution Coefficient

The distribution coefficient of the pesticide between soil particles and its solution is an important tool that gives an indication of its availability. A high coefficient of Kd affects the ability of the pesticide to distribute between the soil and its solution. Based on our result, the Kd of Difenoconazole Coefficient scored 1.53 mL g^{-1}. In this regard, (16) confirmed that the diethyl methyl phosphonate (Sarin's simulant) underwent The Langmuir model KL 0.14 L g^{-1} of DEMP data was a better fit than the Freundlich model in the soil column. The significance of these two models belongs to the determination of the potential of chemicals for soil mobility is determined by the Freundlich and Langmuir models.

Conclusion

This study aims to provide better understanding of the behaviour of Difenoconazole fungicide after it reaches the soil. The investigation revealed that Difenoconazole undergoes a First-order reaction rather than a Second-order reaction. Additionally, it follows the Langmuir model instead of the Freundlich model. Further, the results confirmed that Difenoconazole can be distributed between the soil and its solution. Kinetic analysis also indicated that Difenoconazole takes a long time to break down based on the First-order reaction, and even longer in the case of the Second-order reaction.

Conflict of interest

The authors declare no conflict of interest.

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