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Adsorption-Desorption, And Kinetic Study Of Diazinon By Batch Equilibrium

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Abstract

Adsorption of organic compounds in the soil is a crucial process in terms of pesticide effectiveness. Adsorption of pesticides can lead to decreasing of its toxic effect against various pests, and finally fail the pests targeted control. This study was performed to assess the diazinon adsorption-desorption kinetic behaviour in the soil. The results revealed that diazinon is subjected to soil sorption. The kinetic reaction of diazinon underwent the pseudo-second order reaction, achieving a rate constant from 0.00056 to 0.003565 hour^{-1}. This reaction revealed that diazinon behaviour is influenced by two factors in the soil. The equilibrium of diazinon was achieved after 2-6 hours in soil, providing an important sight on diazinon behaviour. Where the diazinon concentrations decreased gradually to reach 5.95 mg mL^{-1}. The adsorption isotherm showed that diazinon is a best fit to the Langmuir model, which ranged from 0.798 to 1.062 µg mL^{-1} rather than the Freundlich model that was between 2.102 to 2.687. These findings of this study have a number of important implications for the future, not only water-soil pollution, but also pests control.

Keywords: Pseudo-First order; Pseudo-Second order, Freundlich model Langmuir model,

1. Introduction

Diazinon (o,o-diethyl-o-[2-isopropyl-6-methyl-4-pyrimi-dinyl] phosphorothioate) is an organophosphorus insecticide compounds that control various insects in vegetables, ornamentals, crops, and fruits. This substance is featured with non-systemic and non-selectivity action in pest control whereas in foliage or soil. It was first performed in 1956 in the United State (Wang & Liu, 2016). The effect of diazinon is limited to inhibiting the enzyme acetylcholinesterase (AchE) (Haider & Rauf, 2014), and it also causes many serious diseases (Harchegani et al., 2018)**.** Consequently, the using of diazinon has been restricted by the United States Environmental Protection Agency (US EPA) since 2003, to minimise its health harm (Banks et al., 2005). The use of diazinon resulted in water and soil contamination. Therefore, it's crucial to monitor its mobility and potentially groundwater pollution. Many parameters can be used to monitor the pollutant concentrations in the environment. For example, the adsorption assessment is an essential process to provide adequate information about the organic pesticides. This process relies on pH, surface area, ionic strength, and cation exchange capacity (Kodešová et al., 2011). Pesticide adsorption undergoing two different operations. Firstly, the sorption sites are saturated by the adsorbate transport in the soil. Secondly, the activation energy of sportive bonds is related to the mechanism of sorption on the site (Subramaniam et al., 2005). Owing to the excessive use of diazinon in different agricultural soils, the current study is aimed to investigate the diazinon batch equilibrium in soil to understand its behaviour in the clay territory using multiple models like pseudo-first order reaction PFO, pseudo-second order reaction PSO, Freundlich and Langmuir models.

2. Material and Methods

To study the adsorption kinetic of diazinon, 3 flasks of 250 mL containing 100 mg soil were treated with 50 mL of 1 mL L^{-1} (0.1 mL 100 g^{-1}) diazinon EC. While 3 another flasks were treated by distilled water as a control treatment. All flasks were incubated in a shaking incubator at 150 rpm for 24 hours to achieve the equilibrium. After, one day of the equilibrium, 1 mL of supernatant was transferred into 1 mL eppendoff. The centrifuges were performed at 3500 rpm for 30 minutes. Then the aliquot was filtered using 022µ filter. After that, the filtered aliquot was injected 1 µl in the gas chromatography – flame Inoisation detector (GC-FID).

In order to study diazinon desorption, the rest solution was discarded from the flasks and placed the same amount of distilled water and left for 24 h. After one day of the soil equilibrium, 1 mL of each flask was withdrawn and centrifuged at 3500 rpm for 30 minutes. The concentrations of diazinon were determined by injection 1 µl in GC-FID.

To study the effect of temperature on diazinon adsorption isotherms, investigating three various temperatures (25, 35, 45) °C were selected. The same method was used to examine the sorption isotherm. The physicochemical properties of soil were characterised as mentioned in Table 1. Diazinon residues were analysed using GC-FID according to the method mentioned in (Mosaddegh et al., 2014).

Table (1): The Physiochemical Characteristics of Soil

texture			pH	Moisture content	Organic matter%	CEC (meq 100g^{-1})
Sand%	Silt%	Clay%				
41	13	46	6.7	5.14	1.2	6.63

3. Results and Discussion

3.1. Kinetic Reaction Models Isotherm

The kinetic study of diazinon in the soil was compared using two types of kinetic models (Simonin, 2016), the pseudo first order (PFO) equation [1].

$$Ln\,(qe - qt) = lnqe - k1t \quad \text{....1)}.$$

And the pseudo second order (PSO) by following the equation [2] (Simonin, 2016).

$$\frac{t}{q(t)} = \frac{t}{qe} + \frac{1}{K_2 q_e^2} \quad \text{....2)}.$$

Where k1= the rate constant of diazinon equilibrium for adsorption per hour for the PFO, k2 = the rate constant of diazinon equilibrium for adsorption per hour for the PSO. qe = diazinon initial concentration in soil (mg L^{-1}), qt= diazinon adsorbed on soil (mg L^{-1}) at different time (t).

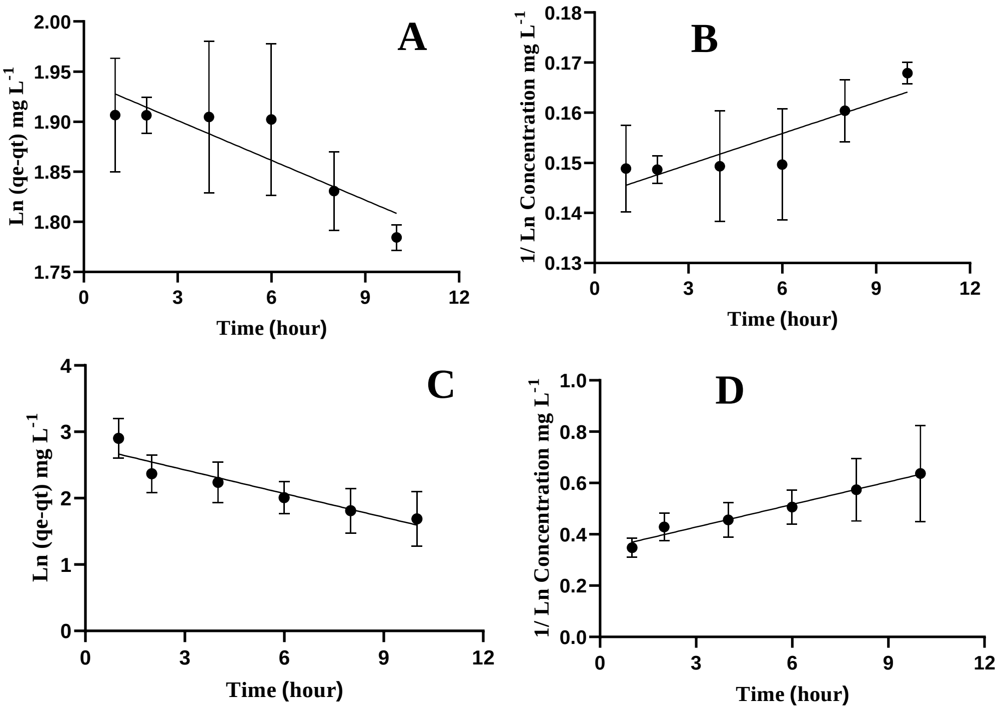

Figure (1): Two kinetic reaction models of diazinon in soil: A) PFO sorption, B) PSO sorption, C) PFO desorption, and D) PSO desorption.

The data of diazinon was described using two different models, the first and second order. From this profile, the data does not show that diazinon underwent the PFO based on the value of R^2, which was 0.77. The PFO was calculated using the equation (1), where the rate of reaction in the vicinity of (0.02307-0.003417) $hour^{-1}$. These data were extracted from the relationship between the (qe-qt) against time (Fig 1A). Meanwhile the results revealed that diazinon underwent the second order reaction. The rate of reaction ranged between (0.00056-0.003565) $hour^{-1}$ and the value of R^2 was 0.78. Where this result was calculated using the equation (2), the rate constant of adsorption diazinon was measured from the relationship between 1/concentrations versus time (Fig 2B). Although the kinetic evaluation of diazinon appeared in the straight lines, both in the PFO and PSO, it can be concluded that diazinon subjected to PSO more fitting rather than the PFO with respect to its studied concentrations. According to Lafi and Al-Qodah (2006), explaining the kinetic behaviour of removing pesticides from hydrous media.

In contrast, the reaction of diazinon desorption in soil are shown in (Fig 1C and 1D). These results obtained from the simple linear regression analysis of desorption of diazinon concentrations in soil. A simple linear regression analysis shows that the concentrations of diazinon undergoes the PSO. The rate of diazinon reached between (0.02255 to 0.3617) h^{-1}, and the R^2 value was 0.97. On the other hand, the PFO ranged between (0.3765 – 0.03765) h^{-1}, while the R^2 was 0.94.

According to the rate of adsorption and desorption reaction, it can be seen that diazinon tends to desorption more than adsorption. As the rate of reactions are various. In the case of adsorption there was less than desorption for both PFO and PSO. This suggests that diazinon might be influenced by various factors in soil, leading to it being available and potentially causing water-soil pollution. This result with a line of Copaja & Gatica-Jeria (2021) found that diazinon does not tend to adsorption unless the soil contains more than 2% organic matter because diazinon is a hydrophobic compound.

3.2. Equilibrium Isotherm of Diazinon

The results obtained from the diazinon kinetic analysis in soil are set out in Figure (2). From this figure, it can be seen that the time required to achieve the completely equilibrium of diazinon in the soil. Interestingly, diazinon has reached to the equilibrium time at 2, 4, and 6 hours.

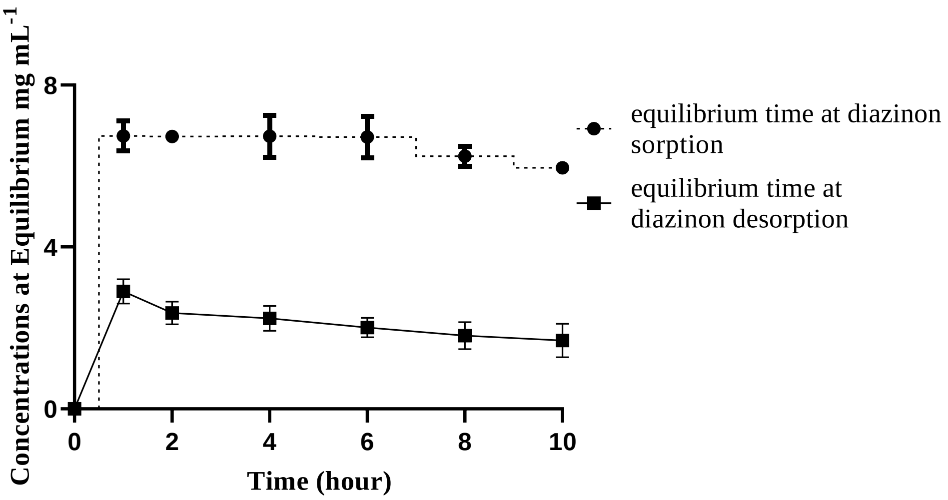

Figure (2): Diazinon concentrations at equilibrium time.

However, in terms of desorption isotherm, diazinon concentrations have been balanced in the soil after 2 hours and consistently continually. Those results also confirmed that diazinon suffered desorption compared to the adsorption in the soil, leading to soil-water contamination when it applied to control pests that attack some economy plants in the agricultural fields.

3.3. The Freundlich and Langmuir exemplary

The Freundlich model can be applied to characterise the sorption procedure of chemicals on active sites or heterogeneous surfaces (Uduakobong A. Edet and Augustine O. Ifelebuegu 2020). While the Langmuir equation is a model that can be used to describe the adsorption of a molecule on a monolayer of non-reaction particles (Be'nard & Chahine, 2008). Therefore, in order to assess behaviour of diazinon in soil, Freundlich and Langmuir models were used using two different linear equations. the linear equation of Freundlich was carried out by implementation Eq. (3) (Edet & Ifelebuegu, 2020).

$\log q_e = \text{loq } K_F + 1/n \log C_e$…………………………………………………………………..3).

where K_F = adsorption capacity L/mg, and 1/n= adsorption intensity

However, the Langmuir equation was calculated by applying Eq. (4) (Ayawei et al., 2017).

$C_e/q_e = 1/q_m K_e + C_e/q_m$ ……………………………………………………………....4).

Where Ce= Diazinon concentrations at equilibrium (mg g^{-1}), KL= Langmuir constant (mg g^{-1}).

The results of the linear regression 95% confidence intervals of diazinon data can be compared in Figure (3). These data were evaluated using the Graph Pad Prism 8.0.1 (244). It can be seen from the data that diazinon achieved best-fit values with Langmuir model based on the correlation coefficients (R^2), which was 0.989 (S.E. 0.04737). Whereas it was 0.987 (S.E. 0.1296) in the case of Freundlich model. On the other hands, the Langmuir constant and Freundlich value were ranged between (0.798-1.062 µg mL^{-1}) and also (2.102-2.687) respectively.

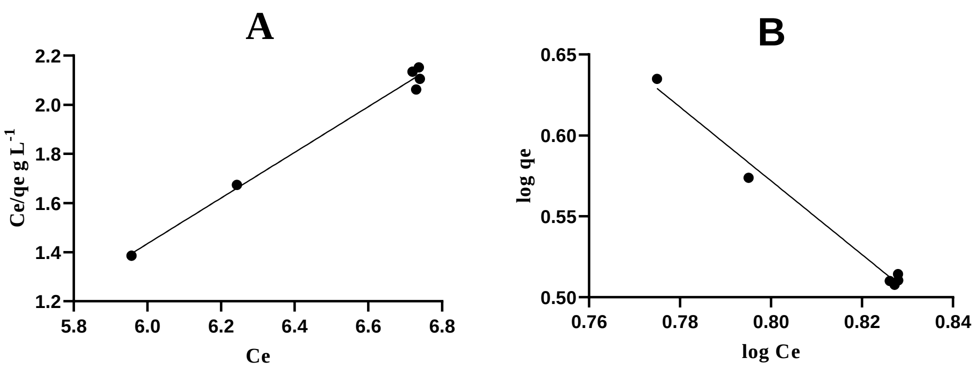

Figure (3): The adsorption of diazinon model A) Langmuir model B) Freundlich model.

3.4. Equilibrium constant

An important parameter for diazinon was studied in the soil. It is the thermodynamic. This parameter was calculated by applying the thermodynamic equilibrium constant, K_0 in the following equation [5] (Kumar et al., 2013). The equilibrium constant of diazinon in the soil ranged between (0.4284-0.5637), (0.3348-0.4228), and (0.03916-0.4213) at 293.15, 303.15, and 313.15 kelvin. The equilibrium constant K_0 were measured by applying:-

$\ln K_0 = \ln Cs/Ce$…………………………………………………………………….(5

The K_0 was extracted from the plotting ln Cs/Ce against Cs.

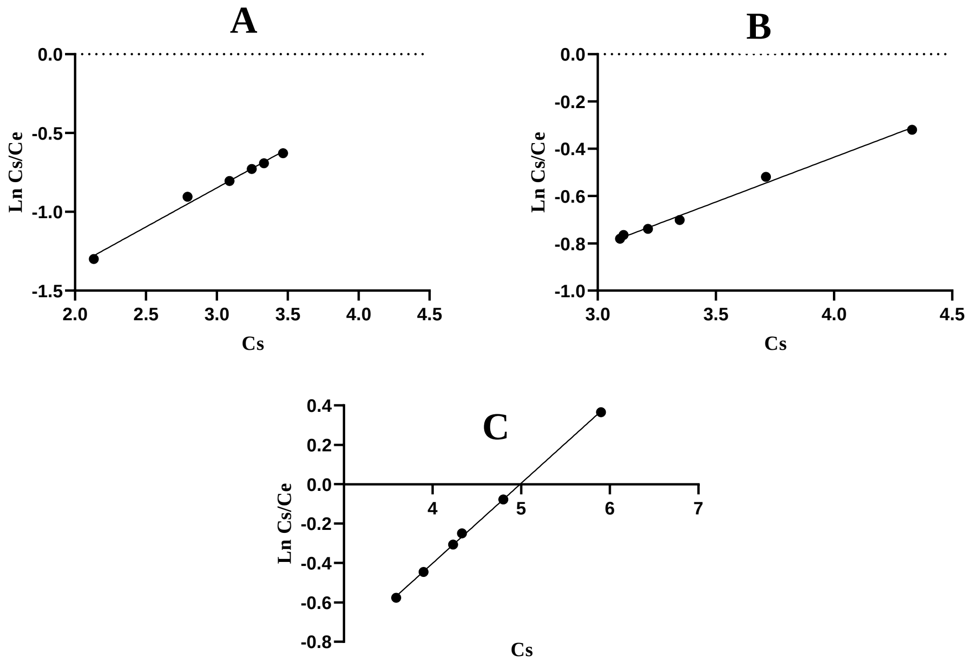

Figure (4): Equilibrium constant of diazinon extracted by plots of ln (Cs/Ce) as a function of Cs at different temperatures. A) at 293.15, B) at 303.15, and C) at 313.15 kelvin) in the studied soil.

4. Conclusion

Taken together, these results provide quite information on diazinon behaviour in soil. Firstly, diazinon is subjected to the PSO rather than PFO. An equilibrium time of diazinon can be achieved at 2-4 hrs. Furthermore, diazinon underwent the Langmuir model rather than the Freundlich model; there is a potential absorption of diazinon. These sorption values confirmed that diazinon was relatively non-mobile in the studied soil, and then this characteristic makes diazinon unavailable to pest control, particularly in dried or semi soil.

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