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Abstract

Adsorption has evolved into a more intriguing criterion for assessing pesticide behaviour in soil. Our findings highlighted the environmental behaviour of the fungicide carbendazim. The findings showed that after one hour of application, carbendazim tends to be equilibrium, in particular two, and three hours, their concentrations were measured 70.5 parts per million. Additionally, the outcomes demonstrated that carbendazim is undergoing a pseudo-first order reaction with a reaction rate of 4×10^{-4} minute ⁻¹. The examination of carbendazim utilising the Langmuir and Freundlich model revealed that carbendazim experiences the Langmuir model ranged between (0.02163 to 0.02305) KL L g⁻¹ compared to the Freundlich model that registered (0.5162 to 0.4661). The results also revealed that carbendazim released into soil after 5 hours of application.

Keywords: Kinetic reaction, Langmuir, Freundlich, Distribution coefficient, Carbendazim, Equilibrium method.

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Introduction

Carbendazim is a member of the class of benzimidazole that is 2-aminobenzimidazole in which the primary amino group is substituted by methoxycarbonyl group, а а systemic benzimidazole fungicide, is applied regularly to control plant diseases, particularly soil borne disease over the course of a growing season (YU et al., 2009). As a result of the extensive use of carbendazim in ecosystems has grown to be a serious problem. It can be considered a significant pollutant that can be found in food, soil, and water where it causes immediate and delayed harmful effects on people, invertebrates, aquatic life, and soil microorganisms (Singh et al., 2016). Pesticides are exposed to various mechanisms when they reached the soil. One of the most significant operation is called the "sorption".

Sorption is a crucial step in determining how organisms will ultimately be transported, persistent, bioactive, and exposed to harm from pesticides in the environment. The structural and chemical properties of the pesticides that regulate several crucial physicochemical parameters for the environment, such as volatility, water solubility, and octanol-water partition coefficient, are connected to the extent of sorption (Gagn *et al.*, 2011). One of the main areas of current research is the studying of the environmental behaviour of pesticides in the soils. Therefore, it is considered the usual practice to examine the pesticides' soil adsorption properties as a metric for assessing the likelihood that pesticides would pollute groundwater (Yu et al., 2020). Based on the literature, numerous researchers from all over the world have studied carbendazim. It is considered an ecotoxic contaminant typically discovered in water reservoirs (Alvarado-Gutiérrez et al., 2020). Therefore, many studied have been applied using the batch equilibrium technique to monitor the movement of pesticides in the soil or water. For an example, Vagi *et al.*, (2010) measured the Freundlich and Langmuir constants to characterise the adsorption of organo phosphorus two pesticides. In China, Ming et al. (2021) investigated the impact of yellow soil thickness on the ability of carbendazim and imidacloprid to bind to surfaces. They discovered that whereas imidacloprid adsorption reduced, carbendazim adsorption rose with the addition of 3 g of yellow soil.

Different parts of Basrah are contaminated with carbendazim, according to Raheem (2012). For instance, the results showed that the carbendazim residues ranged between 0-3.05 g/g at Abu Al-Kaseeb, Al-Hartha, Al-Zubair, and



Shatt Al-Arab stations, with the highest value of 3.05 g/g being recorded there and the lowest value being at Al-Zubair. The studying of pesticides behaviour kinetic has been performed by the equilibrium method (Al-malike, et al., 2015a; Al-malike, et al., 2015b), which is considered the common protocol can be applied to monitor the pesticides movement.

Owing to there are few studies to understand carbendazim adsorption and its behaviour in the soil of Iraq, the key objective of this investigation is to determine the carbendazim kinetic and its behaviour under Basra's soil conditions.

Materials and Method

Chemical compound and Soil treatment

Carbendazim 50%EC (Figure 1) was used in this study. The protocol described in the study has been followed (Al-farttoosy, 2021). The procedure includes: three 250 mL flasks holding 100 g of soil each was treated with 50 mL of 1 mL L⁻¹ carbendazim to evaluate the adsorption kinetics of the drug. As a control, distilled water was used to treat 3 more flasks. To reach equilibrium, all flasks were shaken at 150 rpm for 24 hours in an incubator. 1 mL of supernatant was added to 1 mL of eppendoff after the equilibrium had been in place for one day. The centrifuges were run for 30 minutes at 3500 rpm. The aliquot was then put through a 022 filter. Then, using spectrophotometry at 280 nm, the filtered aliquot was utilized to calculate the amounts of carbendazim.



Figure (1): The chemical Structure of Carbendazim.

Results and Discussion

Carbendazim Equilibrium Isotherm

Fig. 1 depicts the decrease in carbendazim concentrations during the course of the experiment. Additionally, it demonstrated that the carbendazim concentrations were in equilibrium status after the first two hours of treatment, specifically after (2, and 3) hours, while after 5 hours, the concentrations then gradually started to decrease.

In the line with this result, (Al-farttoosy, 2021) found the diazinon pesticide reached to the equilibrium status after (2 -6) hours. Thus, the Fig (2) confirmed also that carbendazim not available after one hour of application. Their residues tend to be steady and slowly decreasing.

However, the concentration of carbendazim is not considerably lower despite the decline. As a result, it is clear that carbendazim tends to be immobile initially before becoming slightly mobile but with minimal consequence. Either there were no vacancy sites on the soil, or carbendazim, which caused the loss of carbendazim's ability to move in the soil.



Figure (2): Carbendazim concentrations at equilibrium time.

Kinetic reaction

According to Simon's (2016) descriptions of the pseudo-first and pseudo-second orders using equations (1 and 2, respectively), the kinetic reaction of carbendazim in the soil was assessed.

Ln
$$(qe - qt) = lnqe - k1t$$
1), and
 $\frac{t}{q(t)} = \frac{t}{qe} + \frac{1}{k_2 q_e^2}$ 2).

Where k1= the rate constant of carbendazim equilibrium adsorption per hour. The PFO, k2 = the rate constant of carbendazim equilibrium adsorption per hour. The PSO. qe= carbendazim initial concentration in soil (mg L⁻¹), qt= carbendazim adsorbed on soil (mg L⁻¹) at different time (t). This plot was extracted by the plotting Ln (qe-qt) versus the time. The rate of carbendazim reaction resulted from the slop of



the linear relationship. Because of the R² results, which was 0.68 rather than 0.67, carbendazim is put through a pseudo-first order reaction. In this area, Al-Farttoosy and AlSadoon (2022) obtained that glyphosate undergoes the pseudofirst order. They linked the glyphosate kinetic reaction by a time.

(Bouya *et al.*, 2014) reported that Carbendazim's electrochemical oxidation on a boron-doped diamond anode was subjected to the pseudo-first order. While Panda et al (2018) evaluated the biodegradation of carbendazim by using zero, first and second order. They found that carbendazim more fitting into the second order reaction with R^2 0.90 compared to the rest of the kinetic reactions.



Figure (3): Carbendazim kinetic reaction order at A) Pseudo-First order and B) Pseudo-Second Order.

Furthermore, two alternative models have been used to evaluate carbendazim. They are Freundlich and Langmuir models. The linear relationships between carbendazim concentrations and the soil vacancies were shown by the plots in (Figs. 3A and 3B). Consequently, carbendazim is subjected to the Langmuir model as opposed to the Freundlich models.

The linear equation of Freundlich was carried out by implementation Eq. (3) (Edet and Ifelebuegu, 2020).

 $\log qe = \log K_F + 1/n \log C_e \dots 3).$

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

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

Where Ce= carbendazim concentrations at equilibrium (mg g⁻¹), KL= Langmuir constant (mg g⁻¹).



Figure (4): Carbendazim adsorption models A) Langmuir model B) Freundlich model.

Contrary to expectations, this study did not agree with the study that carried out by Matser and Leistra (2000) confirmed that carbendazim undergoes the Freundlich model. Han *et al.*, (2019) found that carbendazim more fitted to the Freundlich model in the soil. They also revealed that adsorption of carbendazim depends on the cation exchange capacity (CEC) and soil organic matter content (OMC).

Furthermore, Al-Farttoosy and AlSadoon (2022) reported that the changes of glyphosate concentration in the soil resulted in that the herbicide fits to the Freundlich model. But according to the correlation coefficient R², which was 0.9997 our results confirmed that carbendazim undergoes the Langmuir model (0.02163 to 0.02305) L g⁻¹, compared to the Freundlich model ranged between 0.5162 to 0.4661) and the R² was 0.9992. This means that carbendazim can be sorpted on the monomolecular layer of surface soil.

While the distribution coefficient of carbendazim K_d has scored 1.752 mL g⁻¹. As This parameter calculates how much chemical is absorbed into the soil for every unit of water, also to characterise the studied soil. On the other hand, Freundlich solid-water distribution coefficients are another name for it (Kf) (OECD, 2000).

Kumar *et al.*, (2020) revealed the importance of the Kd value for each studied soil. Moreover, they concluded it is during the evaluating radionuclide transport modelling and risk analysis near nuclear sites, Kd values are to be estimated for site-specific conditions.

Carbendazim desorption

Carbendazim desorption was calculated by following the equation (5)

 $\frac{\text{MDesorption} =}{\frac{\text{amount of adsorbed pesticide}}{\text{total amount of adsorbed pesticide}} \times 100 \dots 5).$



Hence, the Fig (5) showed that the "desorption" process, which is the opposite of adsorption, can also take place. Through this procedure, carbendazim has begun to dissolve and being available to leach through the soil profile. The findings also demonstrated that carbendazim start to be desorption after 300 minutes, with more than 50% of the entire carbendazim concentration being released to the soil.

Matser and Leistra (2000) confirmed that carbendazim can release into the soil and be more bioavailability. This means carbendazim can move down and be the first source of ground water pollution.

Berglöf *et al.*, (2002) found that carbendazim sorption increased when organic carbon (OC) and clay contents rose using the batch equilibration technique. Also, they studied the effect of pH on carbendazim sorption. They confirmed that the sandy ST soil sorption of carbendazim (OC 0.3 percent; clay content 26.3 percent) increased as the pH dropped, but the CT soil sorption of carbendazim reduced as the pH dropped.



Figure (5): Carbendazim desorption in the studied soil.

Conclusion

According to laboratory adsorption tests, carbendazim reaches equilibrium within an hour of application. Additionally, the carbendazim was subjected into pseudo-first order. The findings demonstrated that carbendazim can disperse in both soil and water. Furthermore, carbendazim better matched the Langmuir model. Finally, a process known as desorption allows carbendazim to release into the soil solution after 5 hours of the equilibrium.

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