

Environmental behavior assessment Thiophanate methyl in the soil using different mathematical models

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Abstract

One of the most common fungicides, Thiophanate-methyl (TM), has been extensively used to prevent fusarium wilt disease. Understanding the kinetic behavior of the TM-fungicide in the greenhouse soil was aimed at the current research. The findings demonstrated that TM-fungicide goes through the pseudo-first-order model (PFO), which results in a rate constant $K = 0.421 \text{ minutes}^{-1}$. As a result, TM-fungicide needs $16.46 \text{ minutes}^{-1}$ to degrade 50% of the initial concentration. The power function for TM-fungicide ranged from -1.826 to $0.0360 \text{ minutes}^{-1}$, and the distribution coefficient was 6.5 mL g^{-1} . Regarding the adsorption of Langmuir and Freundlich, TM-fungicide is more fitting to the Freundlich with the $aF = 25.73$ and the $bF = 0.078$ compared to the Langmuir model. The TM-fungicide starts to release to the soil after 4-5 hours, achieving extensive, effective control of the soil pests, Moreover, TM-fungicide is highly mobile in the soil based on the current conditions.

Keywords: Adsorption, kinetic, Fate study, Greenhouse soil, Mathematics models, Thiophanate-methyl.



Introduction

Pesticides have become more significant tools in the agricultural production. Although they have negative effects on the soil, air, and water, but Fruit production would decrease by 78%, vegetable production by 54%, and cereal production by 32% without the usage of pesticides. Hence, pesticides are essential for decreasing illnesses and raising crop yields all around the world .(24)

The increasing use of these agrochemicals in crop farms, orchards, fields, and forests has resulted in the poisoning of surface and groundwater, which has become a severe environmental issue in recent years. Surface runoff, leaching, wind erosion, deposition aerial applications, industrial discharges, and several other sources all contribute to this contamination. Hence, a solid sorption understanding is essential for predicting the mobility of pesticides in soils and aquifers. For example, 50% of pesticide leachate is found in England and Wales due to its polarity and mobility(11)

Yousef et al., (25) reported that the process of adsorption involves the attraction of a solute (adsorbate) to a solid surface (adsorbent), and must take into account the rate of adsorption, which varies depending on the adsorbents chemical and physical.

Thiophanate-methyl, which belongs to the benzimidazole group and is one of the most commonly used fungicides, is dimethyl 4,4,0-(o-phenylene) bis (3-thioallophanate) (Fig. 1). TM is a systemic fungicide used to manage a

wide range of fungal diseases in a variety of crops, including cereals, fruits, and vegetables, including mould, spot, mildew, scorch, rot, and blight. Additionally, it is used as a seed pre-planting treatment, a fungicide for treating timber, and post-harvest food storage (20 and 23). As the amount of TM utilized increased, its genotoxic impact on lizards was evaluated using the micronucleus test, chromosome aberration analysis, and single-cell gel electrophoresis assay.

In addition, the study of Briggs et al (7) revealed that the residues of TM were over 7% in the runoff water after one day of application in July, and were found from the preventative treatment to be 2% in August .

Another evaluation study by Da Silva et al.(12) showed that pregnant rats exposed to the TM during the organogenesis period in rats decreased maternal liver weight, focal necrosis and micro vesicular steatosis, inflammatory infiltrate, and hepatocytes with a psychotic nucleus, in addition to increasing the incidence of skeletal anomalies .

Consequently, this implies the behavior, kinetic, and fate study is not only a crucial process but also a necessary operation to understand the TM fate under the Basra soil. Therefore, in this study, we seek to conduct a broad and comprehensive evaluation using environmental, mathematical modeling of the TM in order to understand its environmental behavior to reduce its toxic effect that resulted from water and soil contamination or translocate to the

tomato fruits during the Fusarium wilt control.

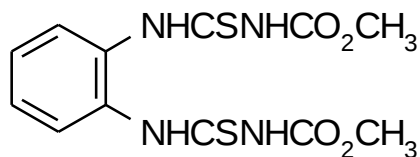


Figure 1: Chemical structure of Thiophanate-methyl (TM).

Materials and Methods

Thiophanate-methyl fungicide's effects on the environment have been researched. The established study protocol has been followed by Al-Farttoosy(3) and Hameed and Al-Farttoosy(14). Three 250 mL flasks containing 100 g each of soil were each filled with 50 mL of TM to measure the adsorption kinetics reaction. As a control, distilled water was applied to three more flasks. To balance the flasks, they were all shaken at 150 rpm for 24 hours in an incubator. One mL of supernatant was added to one mL of Eppendorf one day after the equilibrium was attained. Running the centrifuges for 30 minutes at 3500 rpm. The aliquot was then subjected to the 022 filters. Spectrophotometry was then used to determine the amounts of TM from the filtered aliquot at 269 nm.

Calculations and Statistical Analysis

The linear model and kinetics models were applied to analyze the data using various models. The mean, standard deviation (SD) of all the data was determined (the pseudo-first, the pseudo-second-order kinetic models, Langmuir, Freundlich models, and Thomas model) and calculated as mentioned in Al-Farttoosy (3). The sorption of TM from the soil is described using the power function equation. It can be calculated using the Equation $\ln(C_t) = \ln C_0 - k \ln t$ (22). Where C_t = TM amount that was released at time t . by plotting $\ln C_t$ against $\ln t$, a straight line was generated with a slope K and intercept is $\ln C_0$. GraphPad Prism 8.0.1 (244), a 2D graphing and statistics program

created by Inc. in San Diego, California 92108, was used to conduct the study.

Results and Discussion

Equilibrium isotherm of thiophanate-methyl

During the 300 minutes of the experiment, the quantities of TM decreased, as seen in (Fig. 1). Additionally, it is shown that within the first three hours of treatment, the

concentrations of TM were in an equilibrium state. The quantities of TM were at their lowest and were also stable after the two-hour experiment. In agreement with this finding, Hameed and Al-Farttoosy (14) observed that carbendazim concentrations were in an equilibrium state for the first two hours of treatment before gradually starting to decline. On the other hand, another study has found that the diazinon pesticide reached an equilibrium between (2-6) hours after application.(3)

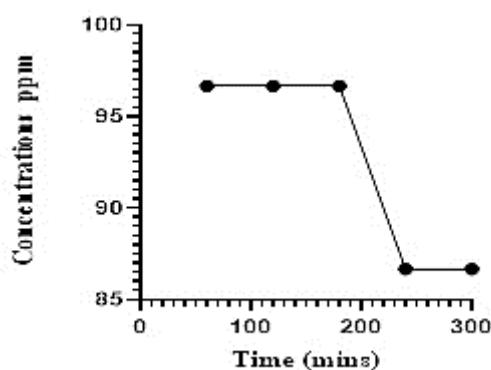


Figure (1): concentrations of Thiophanate-methyl at equilibrium time.

Evaluation of adsorption pseudo-first/second order kinetic

The importance of the model is to analyze the potential for TM-fungicide kinetic in the soil. Fig (2) shows the adsorption kinetic of TM fungicide in the soil. According to the correlation coefficient R^2 , the results indicate that TM fungicide undergoes the pseudo-first-order rather than the pseudo-second-order. This confirmed that the TM fungicide concentrations decreased

gradually over time. The course of this experiment was performed for 300 minutes. In previous studies, it was detected that most pesticides are subjected to the PFO. For example, Hameed and Al-Farttoosy (14) mentioned that the pseudo-first order reaction is considered the common kinetic behavior in the Carbendazim. On the contrary glyphosate followed pseudo-first-ordered the pseudo-second order model as shown by the studying of Chen et al, (9).

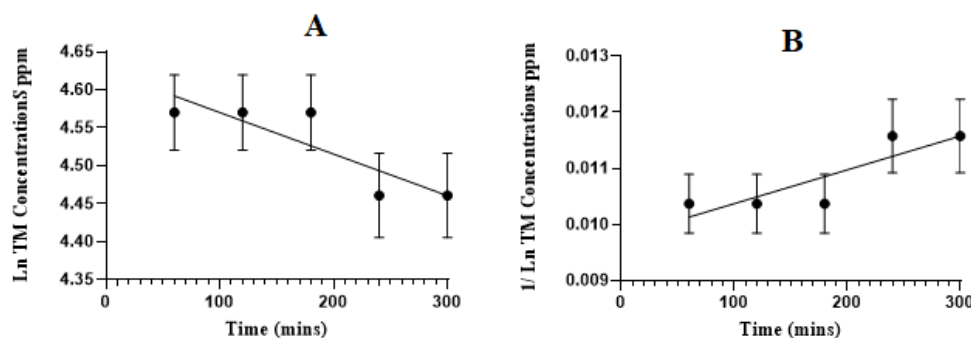


Figure (2): kinetic reaction order of Thiophanate-methyl at A) Pseudo-First order and B) Pseudo-Second Order.

Furthermore, Al-Farttoosy and AlSadoon (4) reported that glyphosate undergoes the PFO. While other investigations which were carried out by Al-Farttoosy (20) found that diethyl methyl phosphonate (DEMP) behaves according to kinetic reaction study to the PFO. Another study performed by Al-Farttoosy (3) revealed that diazinon insecticide was subjected to the PSO reaction compared to the PFO. Similarly to this work, Charious et al (8) clarified that the rate constant of first-order irreversible reaction resulted from the adsorbed pesticide to the soil. Moreover, to attain effective concentrations in the rhizosphere, chemical pesticides must be

used in large doses, but this leads to the build-up of dangerous residues. In addition, enhancing pesticide effectiveness is necessary to prevent environmental damage. In this field, the rate constant reaction of TM fungicide was 0.042 min⁻¹. This outcome means that the TM is hard to dissipate. In a sense, it needs time to dissipate and disappear from the Soil. In contrast, biologically this fungicide has long been effective against the soil fungi. The importance of this study of behavior kineticity is to understand the fate of chemical compounds in the soil, including the leachate, groundwater, and contaminants, and forecasting.

Table 1: The rate of TM-fungicide degradation and half-lives.

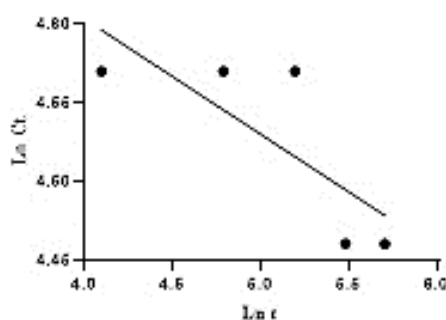
Fungicide name	Degradation rate $K \text{ min}^{-1}$		Half-lives $DT_{50} \text{ min}^{-1}$	
	PFO	PSO	PFO	PSO
Thiophanate-methyl	0.0421	0.000006	16.46	115500

Distribution coefficient K_d and Power Function Understanding the mobility of chemicals in the ecosystem and how they are distributed among soil, sediment, and water compartments require knowledge of the K_d coefficient, which is a key parameter (19). Thiophanate-methyl sorption was stated by a linear connection of the distribution coefficient because of how frequently used and straightforward this is. It is assumed that the soil matrix holds quantities of thiophanate-methyl.

Thiophanate-kd methyl's value was 6.5 mL g⁻¹, indicating that it is well distributed throughout the soil and that it is adsorbed there. It also indicated that it

can migrate to reach the water. Sulfamethoxazole (SMX), which varied between (1.13-2.41) L Kg⁻¹ in the soil, as compared to the high values of K_d in sulfadiazine (SDZ), which ranged from 1.54 to 3.41 L Kg⁻¹. This is showing that compared to SMX, SDZ had a greater affinity for soil adsorption.(15)

Fig (3) revealed the power function of the TM residue concentration during the time. The sorption of thiophanate-methyl from the soil is described by the power function equation mentioned in (Calculations and Statistical Analysis). The value of the TM-sorption power function ranged from (- 1.826- 0.03607) min⁻¹ (SE=0.60).

**Figure (3): Power function of TM fungicide behavior in the soil.**

Langmuir and Freundlich Model

The results of Fig (4) show the two different line models, Langmuir and Freundlich. Based on Table (2) and Table (3), TM-fungicide is subjected to the Freundlich kinetic. In the Freundlich

adsorption model, the adsorbate (Singh, 2016) forms a monomolecular layer on the surface of the adsorbent. Therefore, in our study TM-fungicide represents the adsorbate material (Fig 4-B).

Pyraoxystrobin fungicide is demonstrated in this field by Liu et al (17). They discovered that the Freundlich model is followed by this fungicide. This is true because the amount of organic matter is the only variable that affects the adsorption. This result indicates that TM-fungicide was highly adsorbed on the soil, perhaps as a

result of the large number of vacant sites in the territories. The study of Boyed et al (6) reported that the findings show that soils with high clay and organic matter contents generally have the highest Freundlich model values. This is because soil's ability to absorb organic contaminants is a function of the amount of organic carbon in the soil.

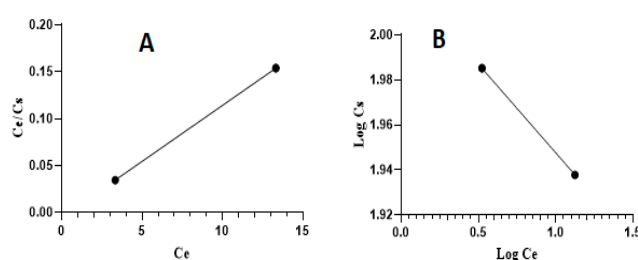


Figure 4: The adsorption kinetic: A: Langmuir model, B: Freundlich model.

Whereas the Langmuir model means the equilibrium between an adsorbate and an adsorbent system, is restricted to one molecular layer at or before a relative pressure of unity is reached, is described by the Langmuir adsorption isotherm. It is normally useful for characterizing the chemisorption process when ionic or covalent chemical interactions are established between the adsorbent and the adsorbate. Langmuir makes the

assumption that the adsorption and desorption rates are equal at equilibrium and that the fractional surface coverage is directly proportional to the rate of desorption from the surface (18). In 16 vineyard soils, Andrades et al (5) studied the fungicide metalaxyl's adsorption and mobility. This study supported the metalaxyl's Freundlich model's adsorption in the presence of the organic soil materials.

Table 2: Data of TM-fungicide isotherm constant of Freundlich model for the adsorption by linear regression.

Freundlich model			
Fungicide	Freundlich aF (Freundlich isotherm)	Freundlich bF (Freundlich constant)	R ²
Thiophanate-methyl	25.73	0.07877	1

Table 3: Data of TM-fungicide isotherm constant of Langmuir model for the adsorption by linear regression.

Fungicide	Langmuir model		R ²
	Langmuir KL L g ⁻¹	Langmuir aL L mmol ⁻¹	
Thiophanate-methyl	0.01194	83.78	0.9997

Desorption of Thiophanate-Methyl

Pesticide mobility in the soil and access to groundwater, as well as their impact on plants and various soil microbes, are all crucial factors for the sorption-desorption process (16). For this reason, the desorption process was investigated of TM-fungicide due to its application to the soil against various pests. According to the current result. The previous study data of Ahmed et al (1) revealed that TM-fungicide is strongly adsorbed in the soil and cannot be desorbed irreversibly.

But the current study illustrates that the TM-fungicide starts to release constantly to the soil after 4 and 5 hours by 11.53% respectively as shown in (Fig 5). This implies the effectiveness of the fungicide against the Fusarium fungus after 5 hours of application. Before this time, a TM-fungicide was adsorbed by different soil forces or might be vacancy the soil sites .

Since TM-fungicide has a cationic nature due to its belonging to the benzimidazole group, it tends to be highly adsorption in the soil compared to its desorption (13).

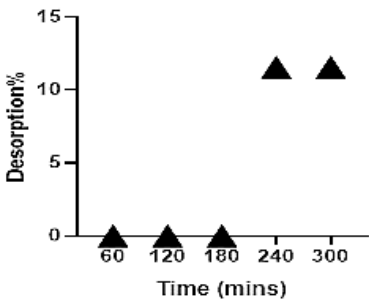


Figure 5: Desorption of Thiophanate-methyl fungicide in the studied Soil.

Conclusion

During this investigation, the aim was to assess Thiophanate-methyl behavior in the soil. This study has identified TM-fungicide equilibrium in the soil after the application. This equilibrium was started and was adsorbed to the soil after 1-3 hours. In addition, the TM is subjected to the pseudo-first-order (PFO) rather than

the pseudo-second-order (PSO). In terms of the TM-fungicide distribution coefficient, it was more mobile. The outcomes also confirmed that the TM-fungicide undergoes the Freundlich model compared to the Langmuir model. Regarding the TM-fungicide desorption, it is released to the soil after 4-5 hours. Eventually, the TM fungicide was implicated to cause soil contamination.

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Conflict of interest

The authors have no conflict of interest.

References

- 1- **Ahmad, K. S.; N. Rashid; M. F. Nazar and Tazaiyen, S. 2013.** Adsorption and desorption characteristic of Benzimidazole based fungicide Carbendazim in Pakistani Soils. Journal of the Chemical Society of Pakistan, (34). <https://link.gale.com/apps/doc/A335710185/AONE?u=anon~11fa4dd1&sid=googleScholar&xid=0efcb8a7>
- 2- **Al-Farttoosy, A.2020.** Microbial-based ioremediation of an exemplar Organophosphorus Chemical Warfare Agent. The University of Sheffield. England. The UK. pp. 190.
- 3- **Al-Farttoosy, A. H.2021.** ‘Adsorption-desorption, and Kinetic Study of Diazinon by Batch Equilibrium.’, Nat. Volatiles & Essent. Oils, 8(6):4933-4939.
- 4- **Al-Farttoosy, A. H and J. N. Al Sadoon.2022.** Comparison of different coefficients to know the Kinetic behavior of Glyphosate in soil column. Basrah Journal of Agricultural Sciences, 35(2):110–118.<https://doi.org/10.37077/25200860.2022.35.2.08>.
- 5- **Andrades, M. S.; M. J. Sa´nchez-Martin and Sa´nchez-Camazano, M.2001.** Significance of soil properties in the adsorption and mobility of the fungicide Metalaxyl in Vineyard Soils. J. Agric. Food Chem., 49:2363-2369.
- 6- **Boyed, S. A.; M. M. Mortland and; C.T Chiou.1988.** Sorption characteristics of organic compounds on hexadecyl trimethylammonium-smectites. J. Soil Sci. Soc. Am., 52:652-65.
- 7- **Briggs, J.; T. Whitwell; R. T. Fernandez and Riley. M. B.2002.** Effect of integrated pest management strategies on chlorothalonil, metalaxyl, and thiophanate-methyl runoff at a container nursery. Journal of the American Society for Horticultural Science, 127(6):1018-1024.
- 8- **Chariou, P. L.; A.B. Dogan; A.G. Welsh; G.M. Saidel; H. Baskaran and Steinm. N. F.2019.** Soil mobility of synthetic and virus-based model nanopesticides. Nat Nanotechnol. 14(7):712–718. <https://doi.org/10.1038/s41565-019-0453-7>
- 9- **Chen, F. X.; Zhou, C.R.; Li, G. P and Peng, F. F.2016.** Thermodynamics and kinetics of glyphosate adsorption on resin D301. Arabian Journal of Chemistry, 9:1665–1669. <https://doi.org/10.1016/j.arabjc.2012.04.014>.
- 10- **Clausen, L.; I. Fabricius and Madsen, L.2001.** Adsorption of pesticides onto Quartz, Calcite, Kaolinite, and a-Alumina, J. Environ. Qual., 30:233-240.
- 11- **Cosgrove, S.; J. Bruce and Peter, J.2019.** Pesticide removal from drinking water sources by adsorption: a review,



- Environmental Technology Reviews, (8)1:1-24 .
<https://doi.org/https://10.1080/21622515.2019.15935>.
- 12- **Da Silva, J. N.; R. Nayra; A. Monteiro; A. Patricia; A. Antunes and Favareto, A. A.2020.** Maternal and developmental toxicity after exposure to formulation of chlorothalonil and thiophanate-methyl during organogenesis in rats, An. Acad. Bras. Cienc.,92(4):1026.
<https://doi.org/10.1590/0001-3765202020191026>
 - 13- **Flores, F. M.; T. Undabeytia; M. Jaworski; E. Morillo and Torres Sánchez, R. M.2020.** Organomontmorillonites as adsorbent materials for thiophanate-methyl removal: Adsorption-desorption studies and technological applications. Journal of Environmental Chemical Engineering, 8(4):103806.
<https://doi.org/https://doi.org/10.1016/j.jece.2020.103806>.
 - 14- **Hameed, S. N and A. H. Al-Farttoosy.2022.** Carbendazim kinetic, and its adsorption in the soil. 20(7):2969–2973.
 - 15- **Hu, S.; Y. Zhang; G. Shen; H. Zhang; Z. Yuan and Zhang, W. 2019.** ‘Adsorption/desorption behavior and mechanisms of sulfadiazine and sulfamethoxazole in agricultural soil systems’, Soil and Tillage Research, 186:233–241. DOI: [10.1016/j.still.2018.10.026](https://doi.org/10.1016/j.still.2018.10.026)
 - 16- **Konda, N. L.; G. Füleky; G. Morovjan and Csokan, P.2002.** Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. Chemosphere, 48(5):545–552.
[https://doi.org/https://doi.org/10.1016/S0045-6535\(02\)00106-6](https://doi.org/https://doi.org/10.1016/S0045-6535(02)00106-6).
 - 17- **Liu, X.; H. Wu; T. Hu; X. Chen and Ding, X.2018.** Adsorption and leaching of novel fungicide pyraoxystrobin on soils by ¹⁴C tracing method. Environ Monit. Assess 190190(2):1-10.
<https://doi.org/10.1007/s10661-017-6458-5>.
 - 18- **Luo, X and F. Deng.2019.** Nanomaterials for the removal of pollutants and resource reutilization. A volume in Micro and Nano Technologies. Elsevier.
<https://doi.org/10.1016/C2017-0-01288-0>.
 - 19- **OECD.2000.** Adsorption/desorption using a batch equilibrium method. OECD Guideline for the testing of chemicals 106. Organization for Economic Cooperation and Development. Paris. France. pp. 1-45.
 - 20- **Petkar, A.; D. B. Langston; J. W. Buck; K. L. Stevenson and Ji, P. 2017.** Sensitivity of *Fusarium oxysporum* f. sp. *niveum* to prothioconazole and thiophanate-methyl and gene mutation conferring resistance to thiophanate-methyl. Plant Disease, 101(2):366–371.
<https://doi.org/10.1094/PDIS-09-16-1236-RE>
 - 21- **Rebich, R.A.; R. H. Coupe and Thurman, E. M.2004.** Herbicide concentrations in the Mississippi River Basin - the importance of



- chloroacetanilide herbicide degradates, *Science of the Total Environment*, 321(1-3):189-199. <https://doi.org/10.1016/j.scitotenv.2003.09.006>.
- 22- **Simonin, J. P.** 2016. On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Chemical Engineering Journal*, 300:254–263. <https://doi.org/10.1016/j.cej.2016.04.079>.
- 23- **Tomlin, C.** 2003. *The Pesticide Manual*, 13th ed. British Crop Protection Council. UK .
- 24- **Tudi, M.; H. D. Ruan; L. Wang; J. Lyu; R. Sadler; D. Connell and Chu, C.** 2021. Agriculture development, pesticide application and its impact on the environment. *Environmental Research and Public Health*, 18(1112): 1–23.
- 25- **Yousef, R.; H. Qiblawey and El-Naas M. H.** 2020. Adsorption as a process for produced water treatment: A review. *Processes*, 8(12):1–22. <https://doi.org/10.3390/pr8121657>.

