Available online at http://bjas.bajas.edu.iq
https://doi.org/10.37077/25200860.2022.35.2.08
College of Agriculture, University of Basrah

Basrah Journal of Agricultural Sciences

ISSN 1814 – 5868 **Basrah J. Agric. Sci., 35(2): 110-118, 2022** **E-ISSN: 2520-0860**

Comparison of Different Coefficients to Know the Kinetic Behaviour of Glyphosate in Soil Column

Alaa H. Al-Farttoosy[1,*] & Jenan N. Al Sadoon[2]
[1]Department of Plant Protection, College of Agriculture, University of Basrah, Iraq
[2]Pharmaceutical Chemistry, College of Pharmacy, University of Basrah, Iraq

***Correspondence author email**: alaa.hassan@uobasrah.edu.iq

Received 18th March 2022; Accepted 25th June 2022; Available online 6th September 2022

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 organi sms 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-Farttoosy (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 $CaCl_2$ 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			pH	Moisture content	Organic matter%	CEC (meq $100g^{-1}$)
	Sand%	41				
	Silt%	13				
	Clay%	46	6.7	5.14	1.2	6.63

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).

$$Ln\,(qe - qt) = \ln qe - k1t \quad \ldots\ldots (1).$$

$$\frac{t}{q_t} = \frac{t}{qe} + \frac{1}{k_2 qe^2} \quad \ldots\ldots (2).$$

Where k1= the rate constant of glyphosate equilibrium for adsorption per hour for the Pseudo-first order kinetic model (PFO), k2 = the rate constant of glyphosate equilibrium for adsorption per hour for the Pseudo-second order kinetic model (PSO). qe = glyphosate initial concentration in soil (mg L^{-1}), qt= 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).

$$\frac{C0}{Ct} = \frac{1}{1+e(\frac{Kth}{Q})\ (q_m m - ^{Ci\,Vef})} \quad \ldots\ldots (3).$$

but to generate a linear model, a natural logarithm of [(C0/Ct)-1] can be taken versus time.

Where: - K_{Th} = Thomas rate constant (mL min^{-1} mg^{-1}), q0 = equilibrium glyphosate

adsorbed per g of soil ($mg.g^{-1}$), C0 = initial glyphosate concentration ($mg.L^{-1}$), Ct= 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).

$$kd = \frac{C_s}{C_e} \quad \ldots\ldots (4).$$

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

$$Cs = \frac{[(C_i - C_e)V_{eq}]}{m} \quad \ldots\ldots (5).$$

Ci = the concentration of glyphosate used mg. L^{-1} or $mL.g^{-1}$, Ce = previously described, Vaq 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).

$$qe = \frac{(abC_e)}{(1+bC_e)} \quad \ldots\ldots (6).$$

Where, qe: Glyphosate concentration adsorbed per unit mass of soil, KL: Langmuir isotherm constant, Ce 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).

$$qe = aFC_e^{bF} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

Where, qe: Glyphosate concentration adsorbed per unit mass of soil, bF, aF are Freundlich isotherm constants, and Ce mol L^{-1} is the equilibrium Glyphosate concentration in the solution. The plotting of Ln (qe) versus Ln (Ce) 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.

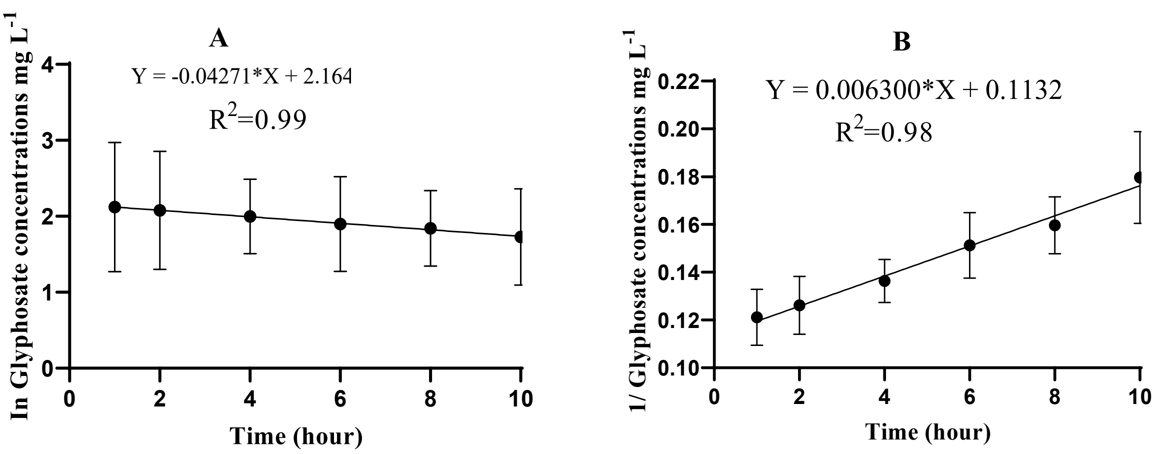


Fig. (1): The kinetic reaction models of Glyphosate in soil column: A- PFO adsorption, B-PSO adsorption.

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.

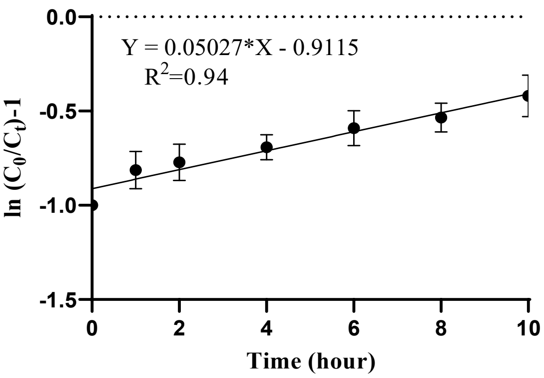
Thomas model

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 $\mu gm.L^{-1}$ 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.

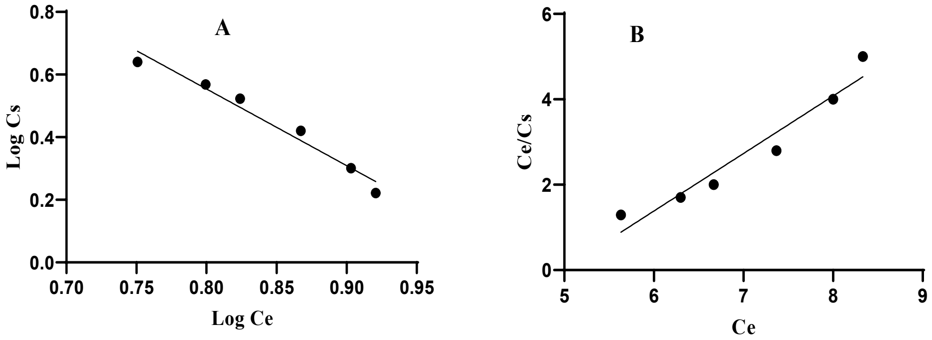


Fig. (3): Adsorption model of glyphosate in the soil column: A- Freundlich model, B- Langmuir model.

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.

Acknowledgements

The authors would like to thank James P. Bezzina, Ph. D. student at the University of Sheffield, UK for his help in calculations of kinetic data.

Conflicts of interest

The authors declare that they have no conflict of interests.

ORCID:

A. Al-Farttoosy: https://orcid.org/0000-0002-2222-4561

J. AlSadoon: https://orcid.org/0000-0001-6929-3954

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.

References

Ahmad R., Kookana R. S., Alston A. M., & Bromilow, R. H. (2001) Differences in sorption behaviour of carbaryl and phosalone in soils from Australia, Pakistan, and the United Kingdom. *Soil Research, 39*, 893-908. https://doi.org/10.1071/SR00021

Al-Farttoosy, A. (2020). *Microbial-based Bioremediation of an Exemplar Organophosphorus Chemical Warfare Agent.* Ph. D. Thesis, the University of Sheffield-UK July.190pp. http://etheses.whiterose.ac.uk/27389/

Ali, I., ALOthman, Z. A., & Al-Warthan, A. (2016). Sorption, kinetics and thermodynamics studies of atrazine herbicide removal from water using iron nano-composite material. *International Journal of Environmental Science and Technology, 13,* 733–742. https://doi.org/10.1007/s13762-015-0919-6

Amiri, M. J., Khozaei, M., & Gil, A. (2019) ‘Modification of the Thomas model for predicting unsymmetrical breakthrough curves using an adaptive neural-based fuzzy inference system. *Journal of Water and Health*, *17*(1), 25-36. https://doi.org/10.2166/wh.2019.210

Baylis, A. D. (2000). Why glyphosate is a global herbicide: strengths, weaknesses and prospects. *Pest Management Science*, *56*(4), 299-308. https://doi.org/10.1002/(SICI)1526-4998(200004)56:4<299::AID-PS144>3.0.CO;2-K

Carvalho, M.F., Duque, A.F., Gonçalves, C., & Castro, P.L.M. (2007) ‘Adsorption of fluorobenzene onto granular activated carbon: isotherm and bioavailability studies. *Bioresource Technology*, *98*(18), 3424-3430. https://doi.org/10.1016/j.biortech.2006.11.001

De Jonge, H.; de Jonge, L. W., Jacobsen, O. H., Yamaguchi, T., & Moldrup, P. (2001). Glyphosate sorption in soil of different ph and phosphorus content. *Soil Science, 166*(4), 230-238. https://journals.lww.com/soilsci/Fulltext/2001/04000/GLYPHOSATE_SORPTION_IN_SOILS_OF_DIFFERENT_pH_AND.2.aspx.

Djozan, D., Mahkam, M., & Ebrahimi, B. (2009). Preparation and binding study of solid-phase microextraction fiber on the basis of ametryn-imprinted polymer. Application to the selective extraction of persistent triazine herbicides in tap water, rice, maize and onion. *Journal of Chromatography A*, *1216*(12), 2211-2219. https://doi.org/10.1016/j.chroma.2008.12.101

Gupta, S. & Gajbhiye, V. T. (2002) Adsorption–desorption, persistence, and leaching behavior of dithiopyr in an alluvial soil of India, *Journal of Environmental Science and Health, Part B*, 37(6), 573-586. https://doi.org/10.1081/PFC-120015440

Hagner, M., Mikola, J., Saloniemi, I., Saikkonen, K., & Helander, M. (2019). Effects of a glyphosate-based herbicide on soil animal trophic groups and associated ecosystem functioning in a northern agricultural field. *Scientific Reports*, *9*(1), 1-13. https://doi.org/10.1038/s41598-019-44988-5

Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y., & Zou, L. (2008) Use of rice husk for the adsorption of congo red from aqueous solution in column mode. *Bioresource Technology, 99*(8), 2938-2946. https://doi.org/10.1016/j.biortech.2007.06.027

Ho, Y. S., Porter, J. F., & McKay, G. (2002) ‘Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water, Air, and Soil Pollution, 141*(1–4), 1-33. https://doi.org/10.1023/A:1021304828010

Khenifi, A., Derriche, Z., Mousty, C., Prévot, V., & Forano, C. (2010) Adsorption of glyphosate and glufosinate by Ni2AlNO3 layered double hydroxide. *Applied Clay Science*, *47*(3), 362-371. https://doi.org/10.1016/j.clay.2009.11.055

Laitinen, P. (2009). *Fate of the organophosphate herbicide glyphosate in arable soils and its relationship to soil phosphorus status.* the Faculty of Natural and Environmental Sciences of the University of Kuopio, MTT Agrifood Research Finland, Plant Production, FI-31600 Jokioinen, Finland. 138pp.

Magga, Z., Tzovolou, D. N., Theodoropoulou, M.

A., Dalkarani, T., Pikios, K., & Tsakiroglou, C. D. (2008). Soil column experiments used as a means to assess transport, sorption, and biodegradation of pesticides in groundwater. *Journal of Environmental Science and Health, Part B*, *43*(8), 732-741. https://doi.org/10.1080/03601230802388868

Mamy, L., & Barriuso, E. (2005). Glyphosate adsorption in soils compared to herbicides replaced with the introduction of glyphosate resistant crops. *Chemosphere*, *61*(6), 844-855. https://doi.org/10.1016/j.chemosphere.2005.04.051

Nur, T., Loganathan, P., Nguyen, T. C., Vigneswaran, S., Singh, G., & Kandasamy, J. (2014). Batch and column adsorption and desorption of fluoride using hydrous ferric oxide: Solution chemistry and modeling, *Chemical Engineering Journal*, *247*, 93-102. https://doi.org/10.1016/j.cej.2014.03.009

OECD (2000). OECD 106 Adsorption - Desorption Using a Batch Equilibrium Method, OECD Guideline for the Testing of Chemicals, (January), 1-44.

Prata, F., Cardinali, V. C. B., Lavorenti, A., Tomisielo, L., & Regitano, J. B.. (2003). Glyphosate sorption and desorption in soils with distinct phosphorus levels, *Scientia Agricola*, *60*(1), 175-180. https://doi.org/10.1590/S0103-90162003000100026

Revellame, E. D, Fortela, D. L., Sharp, W., Hernandez, R., & Zappi, M. E. (2020) Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review. *Cleaner Engineering and Technology*, *100032*. https://doi.org/10.1016/j.clet.2020.100032

Torodovic, G. R. (2009). Behavior of organic pollutants in the soil environment. special focus on Glyphosate and AMPA. EQA-*International Journal of Environmental Quality, 2*(2)*,* 59-72. https://doi.org/10.6092/issn.2281-4485/3821

Tovar-Gómez, R., Moreno-Virgen, M. R., Dena-Aguilar, J. A., Hernández-Montoya, V., Bonilla-Petriciolet, A., & Montes-Morán, M. A. (2013) Modeling of fixed-bed adsorption of fluoride on bone char using a hybrid neural network approach. *Chemical Engineering Journal, 228*, 1098-1109. https://doi.org/10.1016/j.cej.2013.05.080

Veiga, F., Zapata, J. M., Marcos, M. L. F., & Alvarez, E. (2001). Dynamics of glyphosate and aminomethylphosphonic acid in a forest soil in Galicia, North-West Spain. *Science of the Total Environment, 271,* 135-144. http://doi.org/10.1016/S0048-9697(00)00839-1

مقارنة المعاملات المختلفة لمعرفة السلوك الحركي للغلايفوسيت في عمود التربة

علاء حسن الفرطوسي[1] وجنان نعمة السعدون[2]

[1]قسم وقاية النبات، كلية الزراعة، جامعة البصرة

[2]فرع الكيمياء الصيدلانية، كلية الصيدلة، جامعة البصرة

المستخلص: يمتلك امتصاص المبيدات في التربية تأثيرا معنوياً يؤدي الى فشل المكافحة وتلوث التربة. كشفت نتائج هذه الدراسة عن السلوك البيئي للغلايفوسيت في عمود التربة. أكد التفاعل الحركي للبيانات ان الغلايفوسيت خضع للتفاعل من الدرجة الاولى الكاذبة بدلا من الدرجة الثانية الكاذبة وان معدل ثابت التفاعل 0.043 ساعة$^{-1}$ مشيرا الى ان تناقص تراكيز الغلايفوسيت تدريجي مع مرور الوقت. كما اشارت البيانات الى ان الغلايفوسيت ايضا أكثر ملائمة لنموذج فرندلش مقارنة بنموذج لانجمور، اذا سجل 3.083 الى 1.814 مما يشير الى حدوث سلوك الغلايفوسيت على الاسطح المختلفة. بلغت قيمة معامل توزيع الغلايفوسيت Kd 0.33 مل جم^{1} ، موضحًا أن مبيد الأعشاب أقل قدرة على الحركة ويميل إلى الامتصاص على جزيئات التربة. أظهرت البيانات الإجمالية أن حركية الغلايفوسيت في ظل هذه الحالة الحالية تميل إلى أن تكون غير متحركة.

الكلمات الرئيسية: الامتزاز، التوازن، غليفوسات، التربة، عمود التربة.