International Research Journal of Pure & Applied Chemistry

21(24): 35-41, 2020; Article no.IRJPAC.64392
ISSN: 2231-3443, NLM ID: 101647669

A Review on Adsorption and Desorption of Different Pesticides in Various Soil

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Authors' contributions

This work was carried out in collaboration among all authors. Authors DDL collected and compiled the review research articles and relevant scientific literature. Authors SS and VBP wrote the first draft of the manuscript. Authors KGP and TRA helped in proof reading of the draft of the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2020/v21i2430332
Editor(s):
(1) Prof. Mohamed Fadel, National Research Center, Egypt.
(2) Dr. Richard Sawadogo, Research Institute for Health Sciences Ouagadougou, Burkina Faso.
Reviewers:
(1) Tamara Lazarevic-Pasti Vinca, Belgrade University, Serbia.
(2) Mahmood A. Albo Hay Allah, Iraq.
Complete Peer review History: http://www.sdiarticle4.com/review-history/64392

Mini-review Article

Received 25 October 2020
Accepted 31 December 2020
Published 31 December 2020

ABSTRACT

Pesticides are important to the success of agriculture as well as an inevitable factor to maintain good public health. Over the years, the consumption of pesticides has increased manifold, particularly during the past two decades. However, this increase has caused great concern over the presence of residues or leftover pesticides in the environment. The understanding of adsorption and desorption behavior of different pesticides is an important phenomenon to describe the fate of

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pesticide in soil and other environmental compartment like water and sediment. The soil is considered as ultimate sink of pesticide as these were reached to soil directly or indirectly from the point/non-point sources. Adsorption–desorption processes are necessary in understanding pesticides retention behavior and its potential mobility within the soil. The behavior of pesticides in the soil depends on factors such as the physico-chemical properties of pesticides, the active surface of mineral, organic components and the amount of the pesticide applied. Henceforth, adsorption and desorption of soil applied pesticides needed to deal with greater sincerity. This review primarily ascertains dominant properties of pesticides including surface area, pH, surface functional groups, carbon content and aromatic structure and evaluate the adsorption and desorption of pesticide in agricultural soils. In addition, a vision for future research prospects has been anticipated by considering the pesticide bioavailability as residues in soil, influence of soil organic matter, clay content, pH and soil temperature on pesticide removal, pesticide properties and its behavior in soils.

Keywords: Pesticides; adsorption; desorption; soil characters; organic matter.

1. INTRODUCTION

In modern agriculture, the employment of pesticides is inevitable because they're required to manage weeds, insects and other pests which gradually deteriorate the soil quality. Accumulation of pesticide residues exceeding the self-purification capacity of the soil, which resulted in serious soil pollution and deteriorated soil quality, has been the results of extensive and inefficient use of pesticides over the last several decades. The potential impacts of pesticides on the environment and public health needs extensive attention Cheng et al. [1]. The behavior of pesticides within the soil depends on factors such as the physico-chemical characteristics of the pesticide, the active surface of the soil mineral and organic components, and therefore the amount of the pesticide applied Govi et al. [2]. Investigation of phenomena of pesticides sorption in soils is more importance from environmental point of view. Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface. This can occur because of physical forces or by chemical bonds. Usually, it is reversiblethe reverse process is called desorption.it is often difficult to find out the difference between adsorption and desorption and that is why term sorption used.Pesticide sorption affects other processes like transport, degradation, volatilization and bioaccumulation, which influence the ultimate fate of those compounds within the soil environment Gao et al [3]. Moreover, soils are a heterogeneous mixture of components, inwhich include organic and inorganic compoundscomposition and surface activity. They'll bind pesticides and reduce the bioavailability Torrents and Jayasundera [4]. Adsorption-desorption isotherms are usually explained by linear models or Freundlich models.The Freundlich equation or Freundlich adsorption isotherm,an adsorptionisotherm, is an empirical relationship between the quantity of a gas adsorbed into a solid surface and the gas pressure. It isIt has been shown that sorption-desorption capacity of pesticides in soils depend on the soil physical, chemical and biological properties and properties of pesticide [5-7]. Thus, knowledge of the pesticide adsorption–desorption characteristics of soil is important for predicting their mobility and fate in soil environments. Moreover, to know whether bioremediation may be a feasible option or not for the clean-up of contaminated soil. However, only some studies are being conducted on desorption characteristics of pesticides from various soils though they're of fundamental importance to quantify the transport of pesticides and the selection of proper remediation technique. The importance of organic matter, particle size, similarly as pH of the soil for sorption has been emphasized by many workers [8,9,3].

2. CALCULATION

2.1 Freundlich Adsorption Isotherms

The Freundlich adsorption isotherms equation relates the amount of the test substance adsorbed to the concentration of the test substance in solution. The Freundlich adsorption isotherm is mathematically expressed as

$$\frac{x}{m} = KC_e^{1/n}$$

Where,

x/m (mg/g) is the amount of pesticide adsorbed per gram of adsorbent;

Ce (mg/l) is the equilibrium concentration in solution;
q_{max} is the maximum adsorption capacity of the adsorbent;
K = Freundlich adsorption coefficient and
1/n= Adsorption constant

- C_s^{ads} (eq) $= K_F^{ads} \cdot C_{aq}^{ads}$ (eq)$^{1/}$n (µg/g)...(1)

or in the linear form

- $logC_s^{ads}$ (eq) $= \log K_F^{ads} + 1/\text{n} \cdot logC_{aq}^{ads}$ (eq).(2)

Where.

K_F^{ads} : Freundlich adsorption coefficient;
1/n: slope
n = regression constant;

2.2 Freundlich Desorption Isotherms

The Freundlich desorption isotherms equation relates the content of the test substance remaining adsorbed on the soil to the concentration of the test substance in solution at desorption equilibrium.

C_s^{des} (eq) $= K_F^{des} \cdot C_{aq}^{des}$ (eq)$^{1/}$n (µg/g)…(1)

or in the linear form:

- $logC_s^{des}$ (eq) $= \log K_F^{des} + 1/\text{n} \cdot logC_{aq}^{des}$ (eq).(2)

where,

K_F^{ads} : Freundlich desorption coefficient;
1/n: Desorption exponent
n = Regression constant;
$\log C_{aq}^{des}$ = mass concentration of the substance in the aqueous phase at desorption equilibrium (µg cm^{-3}).

2.3 Langmuir Adsorption Isotherms

- $\frac{X}{m} = \frac{q_{max}\, bCe}{(1+ bCe)}$

where.,

x/m (mg/g) is the amount of pesticide adsorbed per gram of adsorbent;
Ce (mg/l) is the equilibrium concentration in solution;
q_{max} is the maximum adsorption capacity of the adsorbent;
b is Langmuir constant;

Soil adsorption coefficient (Kd) measures the amount of chemical substance adsorbed onto soil per amount of water. It is also known as Freundlich solid-water distribution coefficients (Kf).

- $\text{Kd or Kf} = \frac{\text{Concentration of chemical in soil}}{\text{Concentration of chemical substance in water}}$

- $\text{Organic Carbon} - \text{Partition Co} - \text{efficient} = (\text{Koc}) = \frac{Kf}{\%OC} * 100$

- $\text{Coefficient for sorbtion to soil organic matter (Kom)} = \frac{Kf}{\%Om} * 100$

3. THERMODYNAMIC PARAMETERS

The thermodynamic parameters for the adsor ption processes were obtained by the following equations:

- $\Delta G^o = -RT \ln KF$
- $\Delta G^o = \Delta H_o - T\Delta S_o$

Where,

KF is the Freundlich constant,
T (K) is the absolutetemperature,
R is the gas constant (8.314 J/(mol·K),
ΔS_o(kJ/(mol·K) is the standard entropy change,
ΔH_o (kJ/mol)is the standard enthalpy change.
ΔH_o and ΔSo were obtainedfromthe slopes and intercepts of a linear regression of lnK vs.1/T.
ΔG^o (kJ/mol) is the standard Gibbs free energy.

3.1 Effect of Organic Matter

Adsorption of oxamyl-carbamate pesticide was higher in treatment receiving 5g sewage sludge per kg soil followed by treatment receiving 5g FYM per kg soil. Similar trends of adsorption were also observed for S-ethyl carbamate and N-phenyl carbamate pesticides [10]. Higher adsorption of azoxystorbin within the silt loam and sandy soil treated with FYM which was reflected from respective higher Freundlich coefficient (K_f) values [11]. Addition of 0.5% biochar recorded higher adsorption and desorption of acetamiprid in soil with relevancy unamended soil. They also found higher persistence of acetamiprid in organic amended soil as compared to without amended soil [12]. Soil A with little organic matter content higher desorption for simazine and atrazine herbicide and therefore the rate of desorption was comparatively fast in soil B as compared to the soil [13]. The "fast" adsorption of pesticidesalso attributed to adsorption of organic compounds to mineral surfaces [14] or partitioning into a "rubbery" fraction of the soil organic matter [15], while the "slow" adsorption can be associated to the gradual diffusion of organic compounds into soil micropores [16] or into highly cross-linked regions of soil organic matter [17]. Consistent with [18] the variability of organic carbon content of soils contributes significantly in Koc values reported for various studies and may be generate differences of up to 10 times the values reported when different experimental conditions are used.

3.2 Effect of Soil Type

The maximum adsorption (q_{max}) of alpha and beta endosulfan observed in clay soil followed by composted soil, red soil and sandy soil. While maximum desorption rate was observed in composted soil for alpha and beta endosulfan followed by clayey soil, red soil and sandy soil [19]. Adsorption of cypermethrin and deltamethrin insecticide was higher in peat soil than silt clay soil. which was reflected from respective higher Freundlich adsorption coefficient (K_{ads}) values [20]. Adsorption of atrazine was higher in silty clay loam texture having vetisols while Freundlich desorption isotherms (K_f des.) were found to extend with increasing initial concentrations of atrazine in both the soils [21]. These results are in conformity with the results reported earlier by Ma et al., Seybold et al., Gan et al. and Reddy et al [22-25]. Soil with higher OC content recorded higher pretilachlor adsorption coefficients (*logKFads*), desorption coefficients (*logKFdes*) and hysteresis values in clay loam followed by sandy loam and loamy sand soils [26]. Maznah et al. [27] studied that *1/n Fdes* of thiram recorded higher in *Inceptisols* and lower in *Ultisols* However, positive hysteresis (*H*< 1) recorded in Ultisols [27]. Lorenzo et al. [28] revealed that sulfotep and dimethoate pesticiderecorded the higher adsorption in Komchen and Chablekal soil, respectively [28].The higher value of Langmuir constant b was recorded for sulfotep and dimethoate in Mococha soil.Moreover, the upper Frendulich adsorption coefficient (K_f) value of sulfotep and dimethoate observed in Chablekal soil. Adsorption coefficients (*logKFads*) of pendi methalin and quizalo fop-p-ethyl higher in clay followed by sandy and sandy loam soil while, higher desorption coefficient (*logKFdes*) recorded in sandy loam followed by sandy and clay soil [29]. Adsorption coefficients (*logKFads*) of atrazine higher in alluvial soil followed by laterite and paddy soil while higher desorption coefficient (*logKFdes*) recorded in decreasing order: Laterite > Paddy soil > Alluvial soil [30]. Experiment on sandy and clay soils in India showed that the form of the adsorption isotherms of methyl parathion was S type [31].

3.3 Effect of pH

Bailey and White [32] showed that the adsorption behaviors of pesticides in soils affected by soil chemical properties, molecular structure, acidity and alkalinity, water solubility and other physical and chemical properties of pesticides [32]. Kumar et al. [19] observed that no adsorption of endosulfan was observed in the pH 1.5 but it increased very slowly upto pH 6 then after adsorption rate was decrease with increase pH of 6–8.while desorption was increase from pH 2 to 4 further increase in pH reduced the endosulfan desorption. But, endosulfan desorption increased again at higher pH values of 8 and 10 [19]. High adsorption coefficients K_f of simazine and atrazine herbicide in the soil was at low pH and reduced with the increase in pH of the solution [13]. Adsorption of thiram on the *Inceptisols* and *Ultisols* was high at low pH values and decreased with increasing pH values [27]. This finding is in accordance with the general trend observed for many various other pesticides [33-35].The adsorption of atrazine in laterite, paddy and alluvial soils decreased with the increasing pH value [30]. The results are consistent with Abate and Masini [36] that lower pH provides more favorable conditions for atrazine adsorption [36]. Several factors may be related to this phenomenon: Firstly, atrazine is weakly alkaline pesticide with the pKa at 1.68 [37]. Imazethapyr adsorption coefficients K_f produced low values ranging from 3.9×10^{-5} to 114.4×10^{-5} it has a significant and positive correlation with both clay content and CEC [38].

3.4 Effect of Temerature

Singh and Singh [13] observed that adsorption coefficients K_f value declined for simazine and atrazine herbicide in soil when the temperature increased from 298 K to 308 K and indicate the feasibility and spontaneous nature of adsorption process at lower temperature [13]. Kaur [26] observed that the adsorption and desorption coefficientof pretilachlor recorded higher as the temperature increased from 30 to 50 ^{0} C, indicating more favorable adsorption of pretilachlor at high temperaturewhile positive hysteresis recorded at 30 and 40 ^{0}C [26]. Maznah et al. [27] reported that adsorption process attemperature 25, 30 and 35 °C was slightly consistent and the adsorption of thiram in *Inceptisols* and *Ultisols* soil was not affected by temperature [27]. Adsorption coefficients K_f value higher in soil when the temperature increased from 298 K to 308 K and ΔG^o reduced with increasing temperature [30]. Generally, the value of Gibbs free energy change (∆Go) indicates the spontaneity of a chemical reaction. Therefore, it is possible to evaluate whether sorption is related to spontaneous interaction [39].The negative ΔG° values indicate that the H bonds were the main interaction in the adsorption process in the soil [7]. This finding is in line with that of Zahoor [40], who obtained negative ΔG° values for thiram adsorption onto activated C at various temperature levels. Decrease in ΔG value suggest the feasibility and spontaneous nature of the adsorption process [41].Temperature induced change in aqueous solubility of herbicides may also influence the adsorption process [42].

4. CONCLUSION

Soil properties play a major role on the adsorption-desorption behavior of pesticide in soil. The factors such as organic matter, clay content, pH and soil temperature also affect the soil properties. The adsorption and desorption behavior of pesticides is peculiar and it is based on the chemical physical properties of pesticides as well as the characters of matrices in which the pesticides exposed. Therefore, adsorption and desorption of pesticides varies in different condition.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
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