

EFFECTS OF BIOCHAR ON FATE OF IMAZETHAPYR IN SANDY LOAM SOIL

MAMTA KASWA

Thesis

Master of Science in Agriculture
(Soil Science and Agricultural Chemistry)



DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY

**COLLEGE OF AGRICULTURE
RANI LAKSHMI BAI CENTRAL AGRICULTURAL
UNIVERSITY,
JHANSI-284 003, UTTAR PRADESH, INDIA**

AUGUST, 2022

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SANDY LOAM SOIL**

Thesis

Submitted to the



**RANI LAKSHMI BAI CENTRAL AGRICULTURAL
UNIVERSITY, JHANSI-284 003 (U.P.), INDIA**

By

MAMTA KASWA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE IN AGRICULTURE

(Soil Science and Agricultural Chemistry)

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ICAR-Indian Grassland and Fodder Research Institute
भाकृअनुप-भारतीय चरागाह एवं चारा अनुसंधान संस्थान
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To,
The Director Education,
RLBCAU, Jhansi

Subject: Submission of M.Sc. Soil science and Agricultural Chemistry thesis of Ms. Mamta Kaswa.

Sir,

I am forwarding herewith thesis entitled “**Effects of biochar on fate of imazethapyr in sandy loam soil**” by **Ms. Mamta Kaswa** in partial fulfilment for the award of degree of M. Sc. Soil science and Agricultural Chemistry) from your university.

The work has been carried out under the supervision of **Dr. Anup Kumar**, Scientist, Division of Plant Animal Relationship at ICAR-Indian Grassland and Fodder Research Institute, Jhansi.

Thanking you

(Amaresh Chandra)



Plant Animal Relationship Division
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Dr. ANUP KUMAR
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CERTIFICATE-I

Certified that **Ms. Mamta Kaswa**, Id. No. **RLBCAU/AG/PG/0050/20** has satisfactorily pursued her course of research for a period of not less than IV semesters and that the thesis entitled “**Effects of biochar on fate of imazethapyr in sandy loam soil.**” submitted by her to the Rani Lakshmi Bai Central Agricultural University, Jhansi – 284 003 (UP) in partial fulfillment of the requirements for the award of the degree of **Master of Science in Agriculture** in the subject of **Soil Science and Agricultural Chemistry** is the result of original research work conducted by her under my supervision and is sufficiently of a high standard to warrant its presentation to the examination.

I also certify that the thesis or part thereof has not been previously submitted by her for a degree/diploma of any University.

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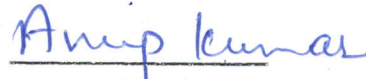
CERTIFICATE-II


This is to certify that the thesis entitled “Effects of biochar on fate of imazethapyr in sandy loam soil.” submitted by Ms. Mamta Kaswa, Id. No. RLBCAU/AG/PG/0050/20 submitted to the Rani Lakshmi Bai Central Agricultural University, Jhansi – 284 003 (UP) in partial fulfillment of the requirements for the award of the degree of **Master of Science in Agriculture** in the subject of **Soil Science and Agricultural Chemistry** has been approved by the Students’s Advisory Committee after the viva voce examination.

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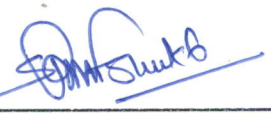
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LIST OF ABBREVIATIONS

US-EPA	United States - Environmental Protection Agency
g	gram
ha	hectare
^o C	Degree Centigrade
K	Kelvin
>	more than
<	less than
mg	milli gram
kg	kilo gram
wt	weight
ppm	parts per million
ppb	parts per billion
L	liter
Tg	teragram
Mt	million tons
Mg	mega gram
cm	centi metre
t _{1/2}	half life
h	hour
μg	micro gram
mg	milligram
mL	millilitre
d	day
%	pecentage

1. INTRODUCTION

Indian agriculture plays pivotal role in economy of the whole country and most of the farmers' family lies in the village. Modern agriculture systems are consuming large number and quantities of pesticides for maximize the food grain production to fulfill the food demand of growing populations. Pesticides are a broad group of chemicals, which are used to manage illnesses, pests, and weeds. Pesticides are regarded a regular and constant component of the agricultural system (Ahmad *et al.*, 2019). It has been observed that very little quantity of total applied pesticides reaches to the target organisms, while the remaining is releases into surrounding environments (Carriger *et al.*, 2006). Therefore, released pesticides from the extensive use of these pesticides under modern agriculture used in an inefficient manner can cause the contamination on agricultural soil and their surrounding associated ecosystems. Pesticides can contaminate air, groundwater, and other areas of the environment once they are present heavily in soil. The extent of this contamination depends on how long the pesticides are present in the soil. The higher accumulation of these toxic substances in the environment like food, soil and water may cause serious health hazard for human and other animals (Chiari *et al.*, 2017; Jallow *et al.*, 2017; Mostafalou and Abdollahi, 2017; Shahid *et al.*, 2016; Tosi and Nieh, 2019) Extensive use of pesticides in agriculture may also degrade the soil quality especially in microbial and enzymatic activity of soil. However, poor microbial community may alter the soil physico-chemical properties and reduces the crop yield (Karpouzas *et al.*, 2016; Niemi *et al.*, 2009). Globally, United States has securing first position with respect to the pesticides as manufacturers, traders, and consumers, While China, France, Japan, and Brazil are contributing after United State for pesticides consumption. Among all the pesticides herbicides is maximal uses and it share about 40% in the worldwide consumption followed by insecticides (18%) and fungicides (10%).

Herbicides are chemical substances which are used to control unwanted plants or weeds in cultivated crops field. Weeds are aggressively competed with crops for available moisture, nutrients, air, light, and other micro-environmental factors, which ultimately reducing crop yield up to 30–80 percent (Kumar and Sarkar 2020). Although herbicides boost crop production by suppression of weed growth but their negative impact is also exhibited due to indiscriminate use which can pollute the surrounding environment and pose a threat to biota (Nakatani *et al.* 2014). Once herbicides are released to

environment, they residually impair the quality of soil, water, air and sometimes its shows toxicity to crop and also residual effect on successive crop or entities and non-target organisms depending upon their persistence (Sondhia 2013).

Imazethapyr is an imidazole compound that is used as a selective herbicide for soybean and other pulse crops as pre-plant incorporation, pre-emergence and post-emergence. This herbicide compound able to control weeds by reducing the levels of three branched chain aliphatic amino acids, isoleucine, leucine and valine through the inhibition of aceto-hydroxy acid synthase. However, inhibition causes a disruption in protein synthesis which leads to interference in DNA synthesis, cell growth and eventually to weed death. (Breccia *et al.*, 2013; Zhou *et al.*, 2010). This herbicide is used to control grasses and other broad leaf weeds including barnyard grass, crabgrass, cocklebur, pigweeds and foxtails etc. The application of imazethapyr is having the negative effect on successive sensitive crops like wheat, spanich, raya, canola, barley, pea and sugarbeet (Alister and Kogan 2005). Total consumption of imazethapyr was 61.07 MT in 2016-17 which is increased to 74.00 MT in 2020-21(DPPQS, GOI). Imazethapyr has been classified as a slightly toxic compound under Class III as per the USEPA (1989). It is designed as biologically active but residues of imazethapyr are also found in crop produce, soil and water. Increasing use of such herbicide may pose serious environmental problems through off site movement and leaching which must be controlled to minimize harmful effects on non-targeted organism. Similarly, the herbicide has been reported as a harmful irritant for human can damage the respiratory track, skin, and eyes (PPDB, 2014). This herbicide is also reported to induce nuclear abnormalities such as blebbed and notched nuclei, only when tadpoles were exposed for 96 hours. In addition, imazethapyr exposure to it about 0.39–1.17 mg L⁻¹ increase the possibility to genetic damage index in tadpoles lasting for both 48 and 96 hours respectively. (Pérez-Iglesias *et al.*, 2015).

Processes related to sorption, degradation, and transport is the key factors that affect how pesticides behave in the environment. Pesticides are divided between the solid and aqueous phases of soil by the transfer process known as sorption, which has a significant impact on the other processes (Wauchope *et al.*, 2002). Soil sorption of organic contaminants is an important physico-chemical process that strongly influences contaminant transport and its fate in the surrounding environment. Sorption and bioavailability of pesticides in agricultural soils is influenced by the presence of soil organic matter and clay content. Imazethapyr is susceptible to leaching loss due to having

more water solubility (1400 mg L^{-1}) and poor soil adsorption coefficient (K_Fads). Therefore, imazethapyr is possible source of surface and groundwater contaminants from leaching losses. It has been observed that about 71% of the surface and groundwater samples is exceed the maximum imazethapyr residue limit of $0.01 \mu\text{g L}^{-1}$ (Battaglin *et al.*, 2000; Espy *et al.*, 2011). It is important to understand the kinetics of pesticide degradation since it describes the chemical concentration over time and it is used to assess the persistence of applied pesticides and their potential risks to exposed species. The environmental dispersion of pesticides is influenced by both biotic and abiotic variables. The two main processes that contribute to the abiotic breakdown of pesticides which are hydrolysis and photo-degradation. The biological mechanism which reduces severity level of pesticides from soil, and even in the most persistent ones, is known as microbial degradation. Imazethapyr is primarily degrades by microbial decomposition, which is influenced by soil physicochemical properties, environmental variability, and agricultural practices. Other factors like climatic, edaphic features and pesticide properties are also influencing the breakdown of pesticides in soil. Imazethapyr is a long-lasting herbicide with having a half-life (DT₅₀) of 7 and 513 days (Sullivan *et al.*, 1998; Punia *et al.*, 2011; Grichar *et al.*, 2012).

Biochar is a carbon-rich material prepared from the pyrolysis of plant and animal wastage under low oxygen and high temperature conditions. The application of biochar has been increasingly used for soil compartmentalization and it happening through carbon sequestration and other soil quality improvement. Biochar as an environmentally benign and low-cost sorbent has an emerged viable technique for reducing the high residue of pesticide in soil and also able to alleviate the pesticide-related health hazards problems (Ahmad *et al.*, 2014; Mohan *et al.*, 2014). *Parthenium* and *Lantana* weeds are majorly found in India, which is having wide range of adaptability to the variety of ecosystems. Whenever, these weeds are found in the cultivated fields it reduces the profibility of crop. Therefore, it can be used for two directional profits by use of weeds biomass for biochar preparation, it reduce the herbicide applications and by application of biochar in contaminated site reduce the pesticide level in soil. Soil application of biochar increases the soil quality via enhancing soil microbial activities (Irfan *et al.*, 2019), carbon sequestration (El-Naggar *et al.*, 2019b; Lehmann *et al.*, 2006), modifying soil nutrient holding capacity and their bioavailability (El-Naggar *et al.*, 2019a; Bilgili *et al.*, 2019), alteration in soil physicochemical characteristics (Su *et al.*, 2019), and establishing

mycorrhizal associations (Aggangan *et al.*, 2019; Solaiman *et al.*, 2019). Additionally, application of biochar can increase plant growth and production through improving soil structure (Jien, 2019) and nutrient availability (Yu *et al.*, 2019). Application of biochar is also reported to increase the sorption capacity of pesticides and decrease its dissipation which can consequently minimize the risk of human health hazard exposure to pesticides.

As a result, biochar has been found to be very effective in reducing the pesticide contaminations and increases the sorption phenomena in agricultural soils. This is owing due to biochar is having high surface area and nano-porosity (Abdul *et al.*, 2017; Lehmann, 2007) By altering of pesticide sorption, desorption, degradation, leaching, and bioavailability in soil system and have a significant impact on pesticide behaviour in soil system (Nag *et al.*, 2011).

The implication of biochar on pesticide behaviour is limited studied and poorly understood especially for the herbicides. Hence, we are going to investigate the effect of biochar of most majorly weed *i.e.* *Parthenium* and *Lantana*. The present investigation was undertaken with the following objectives:

1. Preparation & characterization of biochar and soil
2. Effect of biochar on sorption behaviour of imazethapyr in soil
3. Effect of biochar on leaching behaviour of imazethapyr in soil
4. Effect of biochar on dissipation of imazethapyr.

2. REVIEW OF LITERATURE

Agriculture is an important sector where 60% of the Indian population depends for their source of income and they are mostly lives in the rural background. The human populations are increasing day by day which creates huge pressure for food grain production to supply their demands in limited land resources. The crop can be damaged by certain pest like insects, fungi, bacteria, nematodes, weeds, and other pests and possible source to reduce crop productions which harm Indian agriculture. For maintaining farmers employ to keep maximum production and productivity of different crops to fulfill the food demands pesticides (insecticides, fungicides, and herbicides etc.) are using to repel various pest. Herbicides are consuming about 16% of the total pesticides use in Indian agriculture (Anonymous, 2016, Devi *et al.*, 2017). Application of herbicides removes the unwanted plants from the cultivated field and helps to increase crop production. However, indiscriminate use of herbicides having a variety of negative effects on the agriculture and associated environments (Baran *et al.*, 2011; Bassil *et al.*, 2007; Pingali *et al.*, 1994; Balabanic *et al.*, 2011).

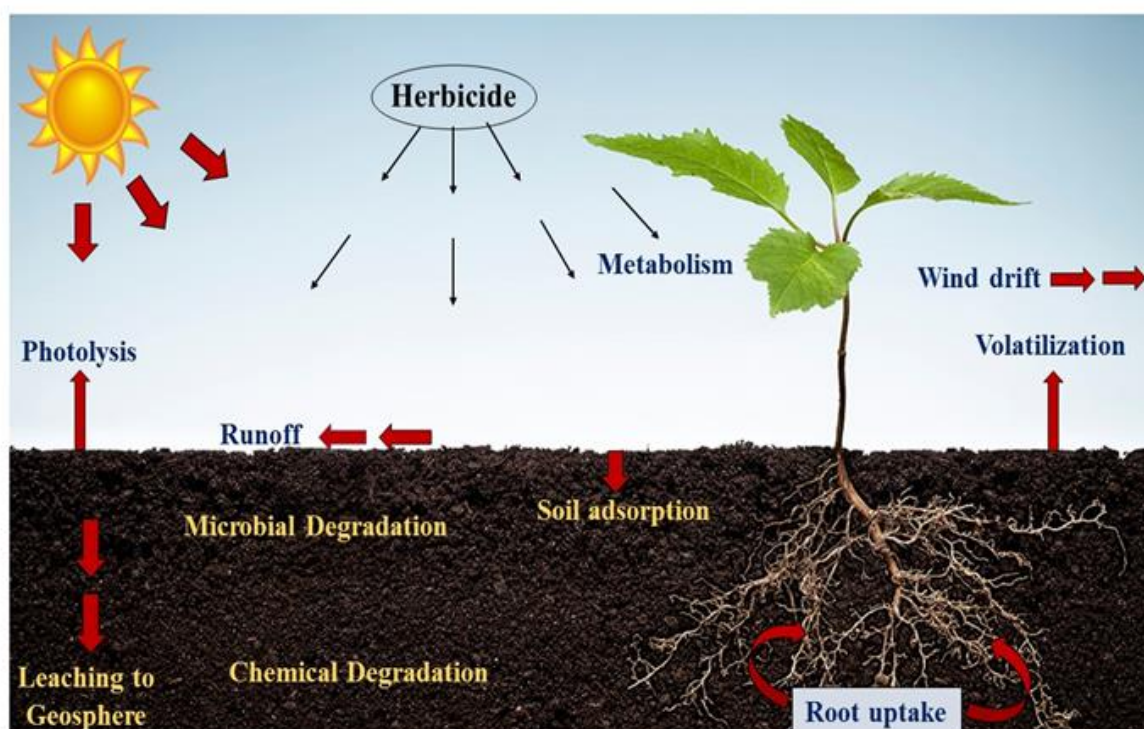


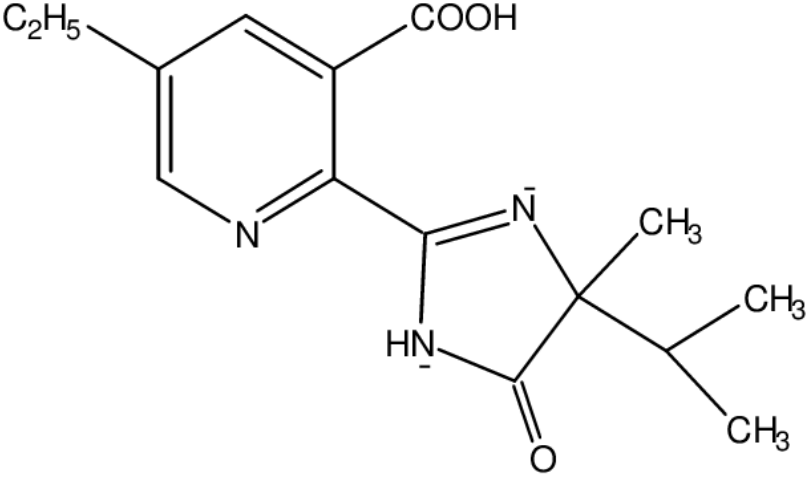
Figure.2.1 Factors affecting fate of herbicide in the environment (Ahemad and Khan., 2013)

The applied herbicides interacted with the different systems through various physical, chemical and biochemical processes like photolysis, hydrolysis, degradation, leaching, volatilization, adsorption, and other processes depicted in Fig. 2.1 and only 0.1 % herbicide compounds reach to the target weeds from the applied quantity. While, the remaining quantity of herbicides are dispersed in ecosystems and resulting degrade environments (Pimentel and Levitan, 1986).

2.1. General information about imazethapyr

Imazethapyr (5-ethyl-2-(4-methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)Pyridine-3-carboxylic acid) is an imidazole compound used as a selective herbicide in soybean and pulse crops are presented in table 2.1. Imazethapyr is locally available in the different names like Contour, Hammer, Overtop, Passport, Pivot, Pursuit, Pursuit Plus, and Resolve in market but all contains active component only is imazethapyr. It is applied as pre-plant incorporated, pre-emergence, and post-emergence. Applied herbicides inhibits weed growth by lowering levels of three branched chain aliphatic amino acids, isoleucine, leucine and valine through the inhibition of aceto-hydroxy acid synthase. This inhibition causes a disruption in protein synthesis which in turn leads to interference in DNA synthesis, cell growth and ultimately weed death (Breccia *et al.*, 2013; Zhou *et al.*, 2010).

Table 2.1: Basic profile of the Imazethapyr.

Parameter	Imazethapyr
Structure	 <p>The chemical structure of Imazethapyr consists of a pyridine ring substituted with an ethyl group (C₂H₅) at the 5-position and a carboxylic acid group (COOH) at the 3-position. The 2-position of the pyridine ring is connected to the 2-position of an imidazole ring. The imidazole ring has a carbonyl group (=O) at the 4-position and a nitrogen atom at the 1-position. The 5-position of the imidazole ring is substituted with a 2,2,4-trimethylbutyl group, which is a branched aliphatic chain with three methyl groups (CH₃) attached to the second carbon atom.</p>

Introduced in	1989
Chemical name	5-ethyl-2-(4-methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)pyridine-3-carboxylic acid
CAS Reg. No.	81335-77-5
Physical state	Colourless crystals
Chemical formula	$C_{15}H_{19}N_3O_3$
Molecular mass	289.33
Melting point (°C)	171
Boiling point (°C)	180 (decomposes)
Vapor pressure (20°C)	1.33×10^{-2}
Bulk density (g/cc)	1.11
Solubility in water (25°C)	1415 ppm
Log Kow (25°C), pH 7.0	1.49
Mode of action	Systemic herbicide which inhibits acetohydroxy acid synthase (AHAS) enzyme that helps in synthesis of branched chain amino acid (Leucine, Isoleucine and Valine)

Use	Control grasses and broad-leaved weeds including barnyard grass, crabgrass, cocklebur, pigweeds and foxtails millets
Rate of application	75-100 g a.i./ha
Formulation and application	Usually supplied as an aqueous concentrate
Applications	Soybeans, peanuts, beans and peas

Therefore, the study was conducted entitled “**Effects of biochar on fate of imazethapyr in sandy loam soil.**” to see the behavior of imazethapyr on different sorption phenomena, leaching and dissipation of applied biochar. The literature cited below based on research findings from the national and international work.

2.2. Review of literature is grouped into following sub-heads:

1. Preparation and characterization of biochar
2. Effect of biochar on sorption behaviour of imazethapyr in soil
3. Effect of biochar on leaching behaviour of imazethapyr in soil
4. Effect of biochar on dissipation of imazethapyr

2.2.1. Preparation and characterization of biochar

Brewer *et al.*, 2009 noticed that the biochar is prepared by pyrolysis of biological materials and a stable form of carbon having a capacity to adsorb pesticides and hence it reduce the bioavailability of pesticides in soils. However, biochar was also having ability to improve soil nutrient status, increase crop output, and sequester carbon (C) in the soil.

The study was conducted to synthesis and characterization of water hyacinth biochar for cadmium (Cd) removal from aqueous solutions at temperatures ranging from 300°C to 700°C. The factors for Cd removal like solution pH, contact time, and initial concentration of Cd was also investigated. The ideal pH value was 5.0 which eliminated about 90% of

the Cd. The Langmuir isotherm having maximal Cd adsorption capacities were 49.837, 36.899, and 25.826 mg g⁻¹. The biochar adsorption processes followed pseudo-second-order kinetics with an equilibrium occurring approximately 5 hours (Shen *et al.* 2016).

Tang *et al.*, 2013 studied that the characteristics of biochar and apply for the remediations of contaminated soil. Biochar has been shown to improve soil characteristics and also increasing crop biomass. They reported that heavy metals reduced in the contaminated site due to the involvement of process like electrostatic interaction and precipitation and organic pollutants by the mechanism of surface adsorption, partition, and sequestration through applying biochar in soil system has been proven to reduce pesticide efficacy.

Khorram *et al.*, 2016 studied on biochar and its impact on pesticide behavior in soil environments with their potential applications. They concluded that the biochar is regarded as a distinctive adsorbent due to its large specific surface area and largely carbonaceous composition. Whenever, soil additives containing tiny concentrations of biochar may lead to more adsorption and decrease the bioavailability of pollutants to plants, earthworms, and other soil-dwelling creatures.

Kookana, 2010 revealed that the role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils and found that the distinctive nature of biochar having high specific surface area, high carbonaceous, and aromatic nature. It has been observed that the biochars having >2000 times more effective at pesticides sorption than soil. It has also been demonstrated that adding very tiny amounts of fresh biochar to soil (0.05 % by weight) can restrict the availability and effectiveness of pesticides to plants.

Ying & Kookana, 2009 investigated that the efficiency of two different forms of biochar in lowering the bioavailability of two pesticides (chlorpyrifos and carbofuran) which were applied to the soil of onion (*Allium cepa*). The biochar was prepared from the wood chips at 450 and 850 °C (BC850) were also well mixed into the soil. They noticed that when the amount of biochar was increased in the soil loss of both pesticides appeared through degradation and sequestration. It was observed that at 35 days about 86–88% of the pesticides were lost from treated soil and only 51% of carbofuran and 44% of chlorpyrifos were lost from the soil when it supplemented with 1.0 % BC850. The total

plant residues of carbofuran and chlorpyrifos were reduced up to 10% and 25%, respectively than control treatment.

Nartey & Zhao 2014, determined the fundamental composition and characteristics of biochar and forecast its potential for use in diverse environmental applications, physical and chemical characterizations. Biochar was a promising alternative to treat soils contaminated with heavy metals and organic compounds due to huge surface area, charged surface, and functional groups by adsorption and immobilization mechanism.

Khorram *et al.*, 2018 reported that the biochar had distinctive adsorbent due to its large specific surface area and largely carbonaceous composition. However, it was unclear how organic pollutants, particularly pesticides in soil altered with biochar and affect their behaviour and environmental fate. Pesticide destiny and effects can be seen to be affected by biochar and it has also been demonstrated to alter pesticide breakdown and bioavailability to living things. Additionally, certain important facets of biochar uses in agriculture and the environment were also emphasized.

2.2.2. Effect of biochar on sorption behaviour of imazethapyr in soil

Ahmad *et al.*, 2001 investigated that the sorption of imazethapyr in 25 soils collected from Pakistan and Australia using the batch method. They concluded that soils varied widely in their intrinsic capacities to sorb herbicide as indicated by the sorption coefficients. They also noticed that soil pH was strongly correlated with imazethapyr sorption.

Yavari *et al.*, 2020 experimented on sorption behavior of polar imidazolinone herbicides in tropical paddy fields and concluded that Imidazolinones were persistent and have a high leaching potential. The adsorption–desorption of imazapic and imazapyr herbicides in various types of Malaysian agricultural soils was investigated in this study. The effects of soil characteristics on the sorption capabilities of soils were also examined. The Freundlich isotherm ($R^2 > 0.991$) were best fitted in the adsorption data due to the G values were negative and below 40 kJ/mol and the herbicide adsorptions were physical and spontaneous processes.

Yavari *et al.*, 2021 revealed that the fate of imazapyr herbicide in the soil amended with carbon sorbents and found that the use of biochar to stabilize herbicides is a cost-effective and efficient way for environment safety. The goal of this study was to see how biochar made from oil palm empty fruit bunches (EFB) and rice husk (RH) were affected imazapyr destiny in soil. The soil amendment considerably boosted soil sorption capacity (up to 2.34 folds) and reduced herbicide leaching.

Dechene *et al.*, 2014 conducted this experiment to see how a soil amendment including biochar was affected the sorption of polar herbicides and herbicide metabolites (log Kow 0.32). Three anionic and one neutral polar molecule were tested for one herbicide (imazamox) and three herbicide metabolites (methyl-desphenyl-chloridazon, metazachlor oxalic acid, and metazachlor sulfonic acid). The presence of biochar boosted the soil's sorption capacity solely in the case of the uncharged molecule methyl-desphenyl-chloridazon for which the average distribution coefficients in biochar-amended soils were 2.1–2.5 times greater than in pure soil. However, rather than a favored sorption of methyl-desphenyl-chloridazon to biochar, this effect appeared to represent an increase in soil organic carbon content after the addition of biochar. Whereas, biochar amendment did not increase the sorption capacity of the soil for the all anionic chemicals imazamox, metazachlor oxalic acid, and metazachlor sulfonic acid due to likely because of its negative net charge. Similarly, desorption experiments revealed that the biochar amendment had no effect on desorption.

Untreated, chemically, thermally, and chemical-thermally treated rice husk adsorbents were used for investigation of their ability to adsorb imazethapyr and imazamox from aqueous solution. The pseudo second order kinetic model accurately represented the adsorption kinetics of imazethapyr and imazamox on untreated and treated rice husk adsorbents and the adsorption isotherms suited in the Langmuir model as well. Treated rice husk adsorbents had a larger potential to adsorb imazethapyr and imazamox than untreated rice husk. Imazethapyr (0.636 10³ to 166.514 10³ g g⁻¹) adsorption potential was higher in the synthesized adsorbents than imazamox (0.158 10³ to 131.835 10³ g). Imazethapyr and imazamox desorption rates from rice husk adsorbents ranging from 92.82 to 99.34 %. Finally, they concluded that the rice husk has the potential to be a useful and low-cost adsorbent for removing imazethapyr and imazamox from water contaminations (Kaur *et al.*, 2020)

Yavari *et al.*, 2017 observed that the biochar a biomass-derived solid substance which was prepared from the pyrolyzing oil palm empty fruit bunches (EFB) and rice husk (RH). However, they recorded the impacts of three pyrolysis factors (temperature, heating rate, and retention time) on biochar ability to remove imazapic and imazapyr herbicides from soil. The findings revealed that when the temperature was reduced up to 300 °C sorption capacity was improved in both biochar which owing to increased biochar efficient functionality in polar molecule sorption. The sorption capabilities of both biochar were maximized under ideal conditions of 3°C/min heating was reported and for EFB and RH biochar retention times of between 1 h and 3 h were determined to be the best. The chemical composition and greater polarity index (0.42) of EFB biochar proved more effective in removing herbicides particularly imazapyr than RH biochar (0.39). Furthermore, EFB biochar had greater cation exchange capacity (CEC) values (83.90 cmolc/kg) compared to RH biochar (70.73 cmolc/kg) which indicated a stronger surface polarity efficient in polar herbicide sorption.

The experiment was conducted to determine biochar sorption behaviour on the highest temperature treatment of pyrolysis factor. The pyrolysis peak temperature rise to causes the expansion of microporosity and surface area, increase in biochar organic carbon content and hydrophobicity. Biochar is now suitable for the immobilization of organic pollutants due to these improvements was noticed. After the pyrolysis temperatures, heating rate, gas pressure, and reaction retention time were successively key pyrolysis variables that affect biochar sorptive characteristics (Yavari *et al.*, 2015).

Marinho *et al.*, 2018 studied on the sorption-desorption of imazethapyr and imazapic in six agricultural soils. High-performance liquid chromatography and the batch equilibrium method were applied in this investigation. Imazapic and imazethapyr K_f values were found between 0.43 and 2.72 mg_l⁻¹ n kg_l⁻¹ Ln and 0.38 to 2.52 mg_l⁻¹ n kg_l⁻¹ Ln, respectively which indicated modest sorption in the studied soils. Lower desorption (50%) was also seen in the soils of Cambisol, Alisol, and Dystric Gleysol highlighting the possibility that these herbicides could harm the sensitive crops grown in rotation.

The effects of maize stalk biochar on the persistence and sorption behavior of flubendiamide in two distinct Indian soils were investigated. At a fortification level of 10 g g⁻¹ West Bengal soil were reported more persistence (178.6 days) than Sikkim soil (165.3 days). The Half-life (T_{1/2}) values for biochar amended Sikkim and West Bengal

soil were observed as 103.5 and 117.4 days, respectively. The results of a sorption investigation using the batch equilibrium method and showed that the soils of Sikkim and West Bengal had adsorption rates of 6.22 %, 0.16 % and 5.26 % 0.16 %, respectively after 4 hours of equilibrium time. Whereas, Sikkim soil that had been modified with biochar showed more adsorption than West Bengal soil. Desorption values that were slower than adsorption values suggested a hysteresis effect with hysteresis coefficients (H1) in two test soils ranging from 0.025 to 0.151(Das & Mukherjee, 2020).

Eucalyptus bark (EBBC), corn cob (CCBC), bamboo chips (BCBC), rice husk (RHBC), rice straw (RSBC), and acid treated RSBC (T-RSBC) biochar were described for their physico-chemical properties and the atrazine and imidacloprid sorption behaviour was investigated. A kinetics analysis revealed that the modified Elovich model was a good fit for the sorption of atrazine and imidacloprid with applied biochar. While the exception of atrazine adsorption on RSBC which was best explained by the pseudo second order model was observed. The RSBC displayed the highest levels of atrazine (37.5-70.7%) and imidacloprid (39.9-77.8%) sorption among the five typical biochar. The sorption of both pesticides in T-RSBC was further improved by the phosphoric acid treatment of RSBC. The percent adsorption decreased with a rise in pesticide concentration in solution where the Freundlich adsorption isotherms were extremely nonlinear. Their aromaticity, polarity, pore width, pH, and weak acid percentage had an impact on the pesticide adsorption on the biochar was reported. As a result, rice straw biochar can be used as adsorbents for the purification of pesticide industry waste water and have significant environmental effects (Mandal *et al.*, 2017).

Utilizing two pretreatment methods without and with ammonium dihydrogen phosphate (ADP), biochar (CS450 and ADPCS450) were generated in this study using maize straw. Elemental analysis, specific surface area (SSA), and Fourier transform infrared spectra were used to compare the characteristics of the two biochar (FTIR). In comparison to CS450, ADPCS450 produced more residue and had a significantly greater specific surface area. The sorption behavior of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was studied using the Freundlich, Langmuir, and Redlich-Peterson models. However, the results best suited in the Redlich-Peterson equation. The isothermal sorption parameters atrazine's had capacity to bind to ADPCS450 was significantly higher than that of CS450 where acidic environments and high temperature were also favored atrazine sorption as well (Zhao *et al.*, 2013).

Ren *et al.*, 2018 investigated on sorption behaviours of atrazine and phenanthrene (Phen) on soil-biochar mixes aged for various lengths of time. Biochar were made from pig manure at two different temperatures. In comparison untreated biochar treated soils with biochar were showed a considerable increase in the sorption of atrazine (up to 23.4 times at $C_e = 0.01$ S w) and Phen (up to 3.12 times at $C_e = 0.01$ S w). With the soil-biochar mixes changed their physical and chemical characteristics which in turn had an impact on their sorption capacity. The sorption of atrazine and phen in black soil (BS) and fluvo-aquic soil (FS) was increased to varying degrees after the biochar generated at 300 °C (BC300) was aged in soil except phen's sorption on BS. However, the sorption of atrazine on the two soils significantly decreased when the biochar was generated at 700 °C (BC700) but it was still 56.3 percent higher than that on the original soil.

A silt loam soil was treated with the herbicides of aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropyl-4-pyrimidinacarbonylic acid), bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4 (3H)-one 2,2-dioxide), and the fungicide pyraclostrobin (methyl 2-[1-(4-chlorophenyl) Bentazone and aminocyclopyrachlor were almost entirely absorbed by soils that had been treated with biochar made from wood pellets. As reported amended soil with biochar derived from macadamia nut shells showed decreased herbicide sorption, which was explained by the competition between the herbicides and dissolved organic carbon (DOC) from the biochar for sorption sites. However, pyraclostrobin has a high level of soil sorption, and adding biochar to the soil had no further impact on its sorption. The sorption of highly mobile pesticides in soil, however, can be increased by biochar with high surface areas and low DOC levels (Cabrera *et al.*, 2014).

Chen & Yuan, 2011 recorded that the pine needle biochar was prepared at various pyrolytic temperatures at 100°C, 300°C, 400°C, and 700°C (P100 - P700) and added in paddy soil. Different effects of biochar were imposed on the sorption of PAHs by biochar-amended soil. However, P100 increased the sorption isotherm's linearity while, the addition of more biochar to the soil increased the nonlinearity of the sorption isotherm for P300, P400, and P700 treated soil. P300 content was reported to increase sorption affinity as 0.5 percent and 0.1 percent in P400 and P700. Experimental finding were projected sorption of soil modified with P100 and P300 was accurate and actual sorption was lower than expected for P400 and P700 treated soil.

Ahmad *et al.*, 2009 used batch equilibration method for study the sorption properties of two widely used herbicides i.e. atrazine and imazethapyr in 101 soils having both allophanic and non-allophanic clays in New Zealand. As the K_d values for atrazine and imazethapyr were varied from 0.7 to 52.1 and from 0.1 to 11.3 L kg⁻¹, respectively. Atrazine had an average soil sorption coefficient or K_{oc} that varied more than imazethapyr which had a mean K_{oc} of 13.2 L kg⁻¹.

Manna & Singh 2015 explained that how wheat and rice biochar were affected the sorption of pyrazosulfuron-ethyl in a sandy loam soil. Pyrazosulfuron-ethyl had a low adsorption in the soil (3.5-8.6%), however adding biochar improved the herbicide adsorption with varying results depending on the feedstock and pyrolysis temperature. Pyrazosulfuron-ethyl was more easily adsorbable by biochar made at 600°C compared to 400°C. Pyrazosulfuron-ethyl sorption and desorption showed strong correlations with biochar content. The pyrazosulfuron-ethyl sorption process was exothermic, spontaneous, and physical in character as their free energy change (G). The half-lives of the herbicides in the control was 0.5 percent WBC600- and 0.5 percent RBC600-amended rice planted soils were 7, 8.6, and 10.4 days, respectively with respect to persistence studies. The herbicides were not significantly affected by the biochar (0.5 percent) amendment on herbicide degradation was found.

This study looked at how the biochar amendment to the soil affected the adsorption, desorption, and leaching of the chemical fomesafen. Hardwood biochar (B4) had the highest fomesafen adsorption coefficient ($k_{fads} = 20.67$) was observed when put to the soil. In contrast, the soil amended with 2 percent rice straw biochar (B1) had the lowest adsorption coefficient ($k_{fads} = 16.64$) was recorded by Khorram *et al.*, 2018.

2.2.3. Effect of biochar on leaching behaviour of imazethapyr in soil

This research was conducted to examine how imazapic, imazapyr, and a combination leach from charcoal. The percentages of pesticides that leached into the soil were dramatically reduced by adding biochar made from rice husk and empty fruit bunches from oil palm trees. However, Imazapic was leached by 16 percent from soil devoid of charcoal while, 4.3% for rice husk-modified soils and 3.6% for soils amended with empty fruit bunches. Imazapyr was leached out of soil in the greatest concentrations (14.2%) from non-modified soil followed by soil amended with charcoal and rice husk (4.0%) and empty fruit bunch (2.8%). Biochar made from rice husk and empty fruit bunches can lower the

herbicide leaching to 4.2 and 3.0 percent, respectively. The top 7.5 cm of soil modified with biochar retained the highest percentages of the herbicides. It was also determined that applying biochar could lessen the leaching of imidazolinones and reduce the environmental damage (Yavari *et al.*, 2021).

Yavari *et al.*, 2021 experimented that the soil amendment greatly increased soil sorption capacity (up to 2.34 times) and decreased herbicide leaching. In soil modified with EFB biochar and reported lowest percentage of leached herbicide (2.8%) and maximum percentage of retained herbicide (97.1%) were attained. The photo-degradation rate was dramatically reduced with a half-life of 53.3 days in soil amended with EFB biochar compared to 38.5 days in non-amended soil. However, the application of biochar led to an increase in the bio-degradation of herbicides.

In columns of homogenized packed soil and the addition of pine chip biochar (commercially pyrolyzed between 300 and 550 °C) decreased cumulative atrazine leaching by 52% ($p = 0.0298$). Leaching of atrazine was not significantly ($p > 0.05$) reduced by biochar additions in columns of undisturbed soil. In a field experiment the mean peak groundwater atrazine concentrations were reported 53 percent lower after additions of 10 t ha⁻¹ acidified biochar ($p = 0.0056$) compared to no additions of biochar. They concluded that the use of biochar has the potential to lower peak atrazine leaching but that heterogeneous soil characteristics, particularly preferential flow pathways, may mitigate this effect were recorded by Delwiche *et al.*, 2014.

Sondhia, 2013 studied on leaching behavior of imazethapyr in soil columns under natural rainfall conditions and founded that the imazethapyr could leach in clay loam soil up to the depth of 70 cm when columns were arranged randomly and allowed to receive approximately 850 mm rain for three months with imazethapyr application rate of 100 and 200 g/ha on the soil columns.

Majumdar *et al.*, 2007 evaluated that the impact of fly ash and organic manure amendments on the downward mobility of metribuzin in sandy loam soil columns. Metribuzin retention in the soil was improved by applying animal manure (T-1(OM) and T-2(OM)) and fly ash (T-1(FA) and T-2(FA)) at 2.5 percent and 5.0 percent levels, respectively. This study found that fly ash and animal dung were both very effective at lowering the mobility of metribuzin in packed soil columns of a sandy loam soil.

Six biochar were made from various feedstocks compared to other sorbents, including activated carbon, an Arizona montmorillonite modified with hexadecyltrimethylammonium organic cation (SA-HDTMA) and an agricultural organic residue from the production of olive oil used to see how they affected the sorption and leaching of fluometuron and 4-chloro-2-methylphenoxyacetic acid (MCPA) (OOW). The batch equilibration technique experiments was conducted after soil amended at a rate of 2 percent (w/w). The findings showed that not all biochar amendments was boost sorption and reported lessen fluometuron and MCPA leaching. The amount and make-up of the organic carbon (OC) content of the amendment particularly in the soluble component (DOC) can also have an impact on sorption and leaching of these herbicides was observed (Cabrera *et al.*, 2011).

The effects of charcoal amendment on the adsorption, leaching, and degradation of the herbicide isoproturon in soils were investigated by Wang *et al.*, 2011. All of the adsorption data matched with the Freundlich empirical equation accurately. It was discovered that the pace of charcoal amendment increased the amount of isoproturon that soils could adsorb (correlation coefficient $r = 0.957$, $P 0.01$). The retention of isoproturon in soils rose with an increase in the charcoal content of soil samples. Whereas the amount of isoproturon in leachate reduced with an increase in the amount of charcoal addition to the soil column. The main mechanism for isoproturon dissipation from soil was still biodegradation. The biodegradation of isoproturon in soils was significantly slowed down by charcoal amendment and this study concluded with adding of charcoal to soil may be a useful management technique for lowering pesticide leaching and increasing its persistence in soils.

Rani *et al.*, 2014 evaluated that the mobility of pesticides like chlorpyrifos and cypermethrin in sandy loam soil at two application rates of 25 and 50 g with a simulated rainfall of 300 mm. Gas-liquid chromatography was used to estimate and gas chromatography-mass spectrometry to confirm the presence of chlorpyrifos and cypermethrin residues in soil and leachate, respectively. The top 10 cm of soil contained the highest concentration of both insecticides was observed. However, the soil was found to be spread with chlorpyrifos up to a depth of 35 cm and cypermethrin up to 15 cm. Results showed that both insecticides had minimal mobility under conditions of saturated moisture and might not pollute ground water. The leachate fractions contained no pesticide residues of any kind.

Chen *et al.*, 2011 studied on the use of rice straw biochar simultaneously as the sustained release carrier of herbicides and soil amendment for their reduced leaching. The rice straw charcoal (RS350) was served as a vehicle for the incorporation of herbicides. Additionally, depending on the depth (50 or 100 mm) of the biochar-amended soil horizon, the RS350 biochar dramatically decreased the leached amount of herbicides by 25.4 percent - 40.7 percent for acetochlor and by 30.2 percent - 45.5 percent for 2,4-D. It is possible to increase both herbicides' potency due to the high retention of those substances in the topsoil treated with biochar. They found that this was viable method for employing low temperature biochar to lessen herbicide leaching while maintaining their efficiency.

Using a ^{14}C labelling method by Cheng *et al.*, (2017) investigated how biochar and straw affected the simazine behaviour in a soil. A sandy loam soil was amended with biochar, which was created by thermally treating wheat straw at four different temperatures (250, 350, 450, and 550°C). The biochar soil had minimal samizine leaching from 21.8 percent to 42.6 percent due to the simazine sorption in the soil from 83.9 percent to 87.5 percent, which was significantly greater than the 43.0 percent in the unamended soil and the 35.7 percent in the soil supplemented with unprocessed straw. They suggested that the use of biochar can greatly increase simazine adsorption and decrease leaching, both of which are advantageous for reducing environmental pollution.

Zhang *et al.*, 2013 assesed that the adsorption and other physicochemical processes utilized biochar to lessen the bioavailability and leachability of heavy metals and organic contaminants in soils. Typically an alkaline substance, biochar can raise soil pH and aid in the stability of heavy metals. Applying biochar to clean up contaminated soils could offer a fresh approach to the problem of soil contamination. This document gives an overview of the effects of biochar on the mobility and environmental destiny of heavy metals and organic contaminants in contaminated soils as well as the implications for soil restoration.

2.2.4. Effect of biochar on dissipation of imazethapyr

The study was compare oil palm EFB and rice husk (RH) biomasses as biochar feedstocks for imidazolinones-contaminated soil remediation. During a 70-day incubation period degradation of imazapic, imazapyr, and a mixture of the two (Onduty®) was studied in the presence of tailored biochar in the soil. The polar herbicides were shown to be resistant to hydrolysis degradation and biochar amendment had a greater impact on

imazapyr photodegradation. The biodegradation of imidazolinones on the other hand was greatly accelerated in the presence of EFB and RH biochar in soil with the higher effects as reported by Yavari *et al.*, 2019.

Huang *et al.*, 2018 experimented an alluvial soil and apply 0.2 percent and 0.5 percent (w/w) of biochar made from sugarcane tops in paddy field. The sorption coefficients (K_d) of atrazine ($C_e = 10 \text{ mg L}^{-1}$) were increased after the addition of 0.2 percent and 0.5 percent biochar by 26.97 percent and 79.58 percent, respectively in the moist soil with a low level of total organic carbon (TOC) and by 31.43 percent and 60.06 percent, respectively in the paddy soil with a high level of TOC. The Deisopropylatrazine and desethylatrazine, atrazine breakdown products were decreased after reaching 3.2 and 1 mg kg^{-1} , respectively.

At lower application rates (0.0375 and 0.187 g g^{-1}) in all soils and tested temperatures, dissipation followed single first-order kinetics with a half-life ranging from 30.15 to 52.16 days. Although dissipation followed biphasic first-order kinetics at higher application rates (0.8 and 1.5 g g^{-1}). The half-lives varied between 6.57 and 7.79 days ($p > 0.05$) during the initial phase and 93.74-152.83 days ($p < 0.05$) during the final phase. Alkaline soils ($\text{pH} = 8.0\text{--}8.8$), neutral soils ($\text{pH} = 7.4$) and acidic soils ($\text{pH} = 5.0$) had the fastest dissipation rates. Imazethapyr dissipated more quickly after farmyard manure amendment and temperature rise were also observed (Kaur & Kaur, 2022).

Janaki, *et al.*, 2015 evaluated that the Triazines, isoxazolidinones, imidazolinones, and a few sulfonylureas were persistent herbicides and five main categories like cultural and mechanical practices were increased degradation, deactivation, lowering the availability in soil. The combining mechanical and cultural management approaches with herbicides to control weeds was a valid protective measure because the safeners have different behaviours in soil that affect the persistence of the herbicide. Biostimulation, when used in conjunction with other tools like crop rotation and increasing the organic matter content was undoubtedly a promising method for managing the persistence of herbicides and minimising their residue in the soil even though it necessitates extensive field evaluation studies.

Cheng *et al.*, 2017 used a ^{14}C labelling method to investigate how biochar and straw affected the behaviour of simazine in a soil. At four different, contrasting temperatures (250, 350, 450, and 550°C) was applied for wheat straw was thermally

treated to form biochar which was then mixed with sandy loam soil. These findings showed that the simazine adsorption and leaching can both be greatly increased by the application of biochar and advantageous for reducing environmental pollution. The biochar qualities have a significant impact on the simazine behaviours in the soil and lessen simazine pollution in comparison to straw.

Butachlor, pretilachlor, and 2,4-D dispersed by first order kinetics in long-term tests on rice with half-lives of 6.0-11.8, 9.9-10.8, and 6.5-11.4 days, respectively. However, herbicides such as traizines, dinitroanilines, acetoanilide, imidazolinones, diethyl-ether, pyrimidinyloxybenzoic acid, phenoxy, and propionic acid lasted between 60 and 150 days in the soil. Atrazine, pendimethalin, and metolachlor each had soil half-lives ranged between 31.8 to 44.9, 12.2 to 30.1, and 16.0 to 38.5 days, respectively. Imazethapyr is followed by atrazine, pendimethalin, metolachlor, metribuzin, alachlor, butachlor, pretilachlor, oxyfluorfen, and then imazethapyr. 99.2% of the crop samples tested for pesticide residues had levels below the MRL. It was determined that Tamil Nadu had very low amounts of pesticide pollution in its soil, crops, and water was observed (Janaki *et al.*, 2019).

Lonappan *et al.*, 2018 studied on the impact of biochar amendment in agricultural soils with their sorption, desorption, and degradation of pesticides along with the material's primary characteristic such as porosity and surface area, pH, surface functional groups, carbon content, aromatic structure, and mineralogical composition. Furthermore, by analysing the bioavailability of pesticide residues in the soil and assess the impact of other contaminants on the removal of pesticides by biochar in soils was influence of pesticide properties on its behaviour in biochar-amended soils. The combined effect of biochar and soil microorganisms on pesticide degradation and the widespread application of biochar in agricultural soils for multifunction an insight into future research directions has been provided.

Jones *et al.*, 2011 investigated that the effect of biochar type, duration after incorporation into the soil, dose rate, and particle size on the sorption, biodegradation, and leaching of the herbicide simazine was assessed in this study. The amount of sorption, leaching, and the rate of simazine mineralization were negatively linked with the size of the biochar particles. The sorption and mineralization of simazine were not affected by the presence of aged biochar in the field after two years which indicated that biochar may have

long-lasting effects on herbicide behaviour. They concluded that applying biochar to the soil will decrease the foliar pesticide dissipation, reducing the risk of environmental contamination and human exposure through the food chain but reduce the efficacy of soil-applied herbicides was also recorded.

This study looked into how two different forms of biochar was affected the bioavailability of pesticides that were applied to the soil and sprayed to Chinese chives (*Allium tuberosum*), namely chlorpyrifos and fipronil and how the pesticides dissipated in the biochar-amended soils. In order to obtain 0, 0.1, 0.5, and 1 percent by soil dry weight, the biochars (BC450 and BC850) made from burning cotton (*Gossypium spp.*) straw chips at two different temperatures (450 and 850 °C) were thoroughly mixed into the soil. In the biochar-amended soils supplemented with 50 mg kg⁻¹ of each pesticide and Chinese chives were grown for 5 weeks. As the amount of biochar was increased in the soil the loss of both pesticides in the soil fell noticeably. As a result, it was discovered that biochar BC850 was successful in lowering the bioavailability of both pesticides from the soil and contaminated soils biochar can be used to store pesticide residues and inhibit plant absorption was recorded by Yang *et al.*, 2010.

Zhelezova *et al.*, 2017 investigated that how ageing of the biochar was influenced the adsorption and breakdown of two herbicides, glyphosate (N-(phosphonomethyl)-glycine) and diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) in soil. A wood-based biochar that had been added at 0, 1, 10, 20, and 30% w/w to one sandy and one clayey soil. Biochar amendment improved the adsorption of diuron in both soils while reducing the adsorption of glyphosate in the sandy soil. Compared to newly modified soil containing biochar, the adsorption of both herbicides was reduced over time. Ageing in any of the soils or the addition of biochar did not consistently change the rates of herbicide degradation. However, glyphosate half-lives corresponded with the clayey soil and Freundlich Kf values suggested that there was availability constrained degradation.

Kumar & Singh, 2020 studied on the impact of rice straw ash (RSA) and wheat straw ash (WSA) on the leaching, degradation, and bioactivity of sulfosulfuron in soils. Both types of ash decreased the downward mobility of their respective herbicides which depends on the type of soil and ash dosage. Pretilachlor degradation tests showed that the WSA accelerated degradation and effect was more pronounced in the flooded soil. In the sandy loam soil was observed that the impact of RSA on sulfosulfuron

decomposition was substantial. These findings were also corroborated by a wheat pot culture investigation. By observing the effect of the WSA on mustard seedlings and the effect of the WSA on the bioavailability of sulfosulfuron was also tested and the results revealed that even 0.1 percent WSA lowered herbicide availability.

Janaki *et al.*, 2012 evaluated that the pretilachlor persistence and degradation in sandy clay loam and clay loam soils from 2007 to 2009 at two degrees of treatment. They demonstrated that pretilachlor and other herbicides dissipated in soil according to first order kinetics. They discovered that the pretilachlor was half-life of 12.44 days. Additionally, they also noticed that more than 98 percent of soil moisture disappeared throughout the crop harvest time.

Curran *et al.*, 1992 assessed a number of imidazolinone herbicides in solution and on soil undergo photolytic degradation. After 48 hours Imazaquin, Imazethapyr, and Imazapyr were totally deteriorated under ultraviolet light. Whereas, Imazamethabenz and Atrazine only degraded by 87 and 8%, respectively. In descending order imazaquin was more photosensitive than imazethapyr, imazapyr, imazamethabenz, and atrazine. They also tested soil in which 48 hours of exposure to damp sand resulted in a loss of imazaquin and imazethapyr of 45% and 52%, respectively. Herbicide dissipation on air-dry sand, field capacity, and air-dry silty clay loam was frequently reported less than 10% and Atrazine did not appear to be photolyzed. This study showed that the in solution, imidazolinone herbicides photolyze rapidly due to moist, coarse-textured soils.

Morrica *et al.*, 2002 experimented that on degradation of imazosulfuron in four different soils under aerobic laboratory settings to estimate its environmental destiny. Tested soils were treated with this herbicide at a final dosage of 0.2 mg kg⁻¹ (100 g ha⁻¹) before being extracted with methylene chloride and analysed using reversed-phase liquid chromatography (RP-HPLC) using a C18 column and UV detection and 84.3 to 99.8 percent of the recovered spiking soils were retrieved (RDS 0.0-4.9 percent; n = 4). The range for measurement was recorded 0.002 to 0.004 mg kg⁻¹. The *t*_{1/2} of imazosulfuron in each of the examined soils was determined which was varied between 1 and 50 days under aerobic settings.

3. MATERIALS AND METHODS

Details of the materials dealt with and the methods adopted, during the course of present investigation in order to achieve objectives of the present study are given below:

3.1. Pesticide

Analytical grade imazethapyr (> 98% purity) was purchased from M/S Sigma Aldrich chemicals Pvt Ltd, Bangalore, India.

3.2. Chemicals

HPLC grade acetonitrile, methanol and solvents (analytical reagents) like dichloromethane, acetonitrile and acetone were purchased from the Himedia. Reagents like calcium chloride and HPLC grade water were purchased from the SD Fine Chemicals Ltd., Mumbai.

3.3. Glass and plastic wares

Erlenmeyer flasks, round bottom flasks, beakers, funnels, volumetric flasks, test tubes, separating funnel, petri-plates, micro-centrifuge tubes, pipette tips *etc.* were locally purchased. 0.45 μ PTFE filter used for filtration was purchased from Rankem India ltd.

3.4. Soil

Soil from ICAR-Indian Grassland and Fodder Research Institute farm was collected from the 0–15 cm depth, dried in shade, ground, sieved through 2 mm sieve and stored in polythene bags which was further placed in metallic container at room temperature. The physico-chemical properties of the soil (Table 3.1) were determined using standard analytical procedures: pH was measured at 1:1.25 soil to water ratio using Control Dynamics pH meter (Systronics μ pH system 361)) equipped with calomel glass electrode assembly (Jackson, 1967); organic carbon (OC) content through

Walkley and Black method (Black, 1965); and soil mechanical fractions using the Bouyoucos hydrometer method (Jackson, 1967).

Table 3.1. Physico-chemical properties of the soil

Location	Name	OC%	Sand %	Silt %	Clay %	EC (dS/m)	pH
ICAR-IGFRI Farm	Sandy loam soil	0.65	58	30	12	0.18	7.40

3.5. Preparation of standard solution

Imazethapyr (51.02 mg, 98% purity) was weighed, transferred into a 50 mL capacity volumetric flask and dissolved in ~5 mL acetonitrile (HPLC grade). The volume was made up to the mark with additional acetonitrile. This gave a stock solution of 1000 $\mu\text{g mL}^{-1}$.

Working standard solutions of lower concentrations were prepared from the stock solution by serial dilution. One millilitre of the primary stock solution (1000 $\mu\text{g mL}^{-1}$) was taken in a 10 mL volumetric flask and volume was made up with acetonitrile to give a standard solution of 100 $\mu\text{g mL}^{-1}$ concentration. Similarly, serial dilution was done to get working standards of lower concentration. Standard curve of atrazine was prepared using serial dilutions method from 100 $\mu\text{g mL}^{-1}$ to make 0.1, 1, 2, 4, 6, 8 and 10 $\mu\text{g mL}^{-1}$ respectively.

3.6. High performance liquid chromatography (HPLC) analysis

Imazethapyr was analyzed using HPLC (Young Ling 9100 HPLC System) equipped with Vacuum Degasser, Binary Pump, PDA detector and using Reverse phase Chromatopak 30 cm C-18 stainless steel column [250 mm \times 4 mm (i.d.)], acetonitrile: 0.1% aqueous o-phosphoric acid (55:45) as a mobile phase at a flow rate of 1 mL min^{-1} at wave length of 250 nm. Under these conditions the retention time of imazethapyr was 2.88 min.

3.7. Recovery experiments and detection limit of instrument

3.7.1. Recovery of imazethapyr from water

Recovery of imazethapyr was done at two fortification levels in triplicate for 5 and 0.5 $\mu\text{g mL}^{-1}$. For this, 50 mL oak ridge tube was taken and requisite amount (for 5 and 0.5 $\mu\text{g mL}^{-1}$ an amount of 1.25 mL and 0.125 mL of 100 $\mu\text{g mL}^{-1}$ working standard solution in acetone) amount of imazethapyr was added into it. The samples were then left for 30 minutes to evaporate solvent and then 25 mL of water was added into it. Further, tubes were shaken on horizontal shaker for 30 minutes. As a control, 2 mL each of water mixed - imazethapyr was taken. Further, pH of 20 ml sample was reduced to 2 using 6 N hydrochloric acid (HCl) and then 10 mL of sample was extracted using 10 mL of dichloromethane (DCM) to partition. The organic fraction was taken out from separatory funnel dried over anhydrous sodium sulphate. The aqueous fraction was again extracted using 10+10 mL DCM and further dried over anhydrous sodium sulphate. The three organic fraction was mixed and was dried at room temperature. The residue was re-dissolved in 2 mL of acetonitrile and further proceeded for high performance liquid chromatography (HPLC) analysis. On the basis of results obtained, 92.12% and 94.08% of imazethapyr were recovered (Table 3.2) (Sondhia, 2008).

Table 3.2. Recovery of imazethapyr from water

Fortification ($\mu\text{g mL}^{-1}$)	Imazethapyr recovered ($\mu\text{g ML}^{-1}$)			
	R1	R2	R3	Mean \pm SD (% recovered)
0.385	0.373	0.328	0.363	0.355 \pm 0.024 (92.12%)
4.874	4.639	4.445	4.672	4.585 \pm 0.123 (94.08%)

3.7.2. Recovery of imazethapyr from soil

Recovery of imazethapyr was done with modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) as depicted by Marinho *et al.*, 2019 with slight modifications. The recovery of imazethapyr was done at two fortification levels in triplicate for 5 and 0.5 $\mu\text{g mL}^{-1}$. 5 g of soil was taken in 50 mL oak ridge tube and requisite amount (for 5 and 0.5 $\mu\text{g mL}^{-1}$ an amount of 0.25 mL and 0.025 mL of 100 $\mu\text{g mL}^{-1}$ working standard solution in acetone) of imazethapyr was added into it. Then tubes were left for half an hour for evaporation of solvent. Soils were thoroughly mixed and 1.5 mL of distilled water, 10 mL of HPLC grade acetonitrile (ACN), 4 g of anhydrous magnesium sulphate (MgSO_4), 1 g fine ground sodium chloride (NaCl), 1g tri sodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) and 0.5 g disodium hydrogen citrate ($\text{Na}_2\text{C}_6\text{H}_6\text{O}_7 \cdot 1.5\text{H}_2\text{O}$) were added to each tubes and vortexed for 5 min. Further, samples were centrifuged at 5000 rpm (1396 x g) for 5 min and 1 mL of sample from each tube was withdrawn for imazethapyr analysis. Simultaneously, another 1 mL of supernatant sample was taken in 2 mL centrifuge tube and 150 mg of anhydrous MgSO_4 and 50 mg of primary secondary amine (PSA) were added. The sample was vortexed and centrifuged at 10000 rpm (5585 x g) for 5 min. The supernatant were separated and analyzed for imazethapyr by HPLC. Results of recovery study are shown in Table 3.3 and suggested that recovery of imazethapyr without and with PSA 85.37% & 87.81% and 40.00% & 49.58% for 0.5 and 5 $\mu\text{g mL}^{-1}$, respectively. Thus, addition of PSA significantly decreased imazethapyr recovery (Saha *et al.*, 2014).

3.8. Biochars

3.8.1. Preparation of biochars

Weed biomass of *Parthenium hysterophorus* L. and *Lantana camara* L. were collected from Central Research Farm, ICAR-Indian Grassland and Fodder Research Institute, Jhansi- 248 003 (U.P.), India. The biomass of both weeds was cut into small pieces (30-50 mm) and used for preparation of biochar. All biomass was heated at a temperature of $\sim 400^\circ\text{C}$ for 2 hours in a cylindrical low cost portable biochar kiln, using

Table 3.3. Recovery of imazethapyr from soil

Fortification ($\mu\text{g mL}^{-1}$)	Imazethapyr recovered ($\mu\text{g mL}^{-1}$)			
	Without PSA			
	R1	R2	R3	Mean \pm SD (% recovered)
0.385	0.352	0.311	0.323	0.329 \pm 0.210 (85.37%)
4.874	4.211	4.019	4.61	4.280 \pm 0.301 (87.81%)
	With PSA			
0.385	0.153	0.185	0.124	0.154 \pm 0.031 (40.00%)
4.874	2.159	2.647	2.443	2.416 \pm 0.245 (49.58%)

the methodology as described by Venkatesh *et al.* (2018). After cooling, the biochar was crushed manually and ground to pass through a 2 mm sieve.

3.8.2. Characterization of biochar/FYM

Biochars were characterized for pH, electrical conductivity, water holding capacity (Keen and Raczkowski, 1921), bulk density (Veihmeyer and Hendrickson, 1948), cation exchange capacity (Mukherjee *et al.*, 2011) total carbon, nitrogen, phosphorus and potassium. Total carbon in biochar was determined wet oxidation diffusion method (Snyder and Trofymow, 1984). Total nitrogen, phosphorus and potassium were determined by di-acid digestion method (Gupta, 2007). Point of zero charge was determined as per Trivedi *et al.* (2016).

3.8.2.1. Point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) is the pH at which the electrical surface charge of biochar is zero. The 0.1N KNO_3 aqueous solution (45 mL) was taken in a series of

100 mL Erlenmeyer flasks and the pH_0 values were roughly adjusted from 2 to 12 by adding either 0.1 N HCl or 0.1 N NaOH. Finally, volume in each flask was made to 50 mL by adding KNO_3 solution of the same and initial pH (pH_0) value of the solution was accurately noted. Then, 1 g of each biochar (PB or LB) was added to each flask and maintained in an isothermal condition. The flasks were closed and shaken at 30°C in an orbital incubator shaker. The final pH (pH_f) values of the fluid were noted after 48h incubation and the difference between the pH_0 and pH_f gave ΔpH , which was plotted against pH_0 values. The point at which the curve crosses the line $\text{pH}_0 = \text{pH}_f$ gave the pH_{pzc} .

3.9. Kinetics studies

The kinetics of imazethapyr in sandy loam soil were studied by batch sorption method. To study kinetics of imazethapyr sorption in sandy loam soil (5 g, oven dry basis) alone and with 0.2% & 0.5% each of *Parthenium* biochar (PB), *Lantana* biochar (LB) and farm yard manure (FYM) was taken in 50 mL oak ridge tubes. A fortification level of $5 \mu\text{g mL}^{-1}$ imazethapyr was done for all the treatments using working standard solution of $100 \mu\text{g mL}^{-1}$ concentration in acetone and solvent was evaporated. Further, 0.01 M CaCl_2 (10 mL) was added into each tube and no herbicide controls were also maintained as each treatment was replicate thrice. Samples were equilibrated for different time period viz.: 0, 15, 30 min, 1, 2, 4, 8, 12, 24 and 48 h for imazethapyr sorption. After equilibration, soil suspension was centrifuged using Remi C24 centrifuge at 5000 rpm ($1396 \times g$) for 5 min. imazethapyr residues in the supernatant were quantified using the HPLC. The amount of herbicide that are adsorbed by the sorbent was calculated using the difference of initial and final concentration of the herbicide in the supernatant. Also, calculation of mass balance indicated that there were no sorption of herbicides on tube surface and they were stable during the equilibration period.

3.10. Adsorption-desorption studies

Adsorption of imazethapyr in sandy loam soil was studied using batch method. Adsorption of imazethapyr was studied at 1:2 soil:solution ratio. Sandy loam soil (5 g,

oven dry basis) alone and with 0.2% & 0.5% each of *Parthenium* biochar (PB), *Lantana* biochar (LB) and farm yard manure (FYM) and 0.01 M CaCl₂ solution of imazethapyr (10 mL) were mixed in 50 mL oak ridge test tubes. The initial concentrations of imazethapyr used for sorption study were 1, 2, 3, 4 and 5 µg mL⁻¹. Sorption of each concentration was replicated three times. For every treatment blanks, one without soil and other without imazethapyr, were maintained as control. Tubes containing samples were equilibrated on an orbital shaker for 24h at room temperature. After equilibration, the soil suspension was centrifuged at 5000 rpm (1396 x g) for 5 min and imazethapyr residues were quantified using HPLC with prior filtration through 0.45µ PTFE syringe filter. The amount of herbicide adsorbed by the sandy loam soil/soil-amendment mixture (PB, LB and FYM) was calculated from the difference of initial and final concentration of herbicide in the supernatant.

Desorption of imazethapyr was studied in the same soil as used for the adsorption and only two concentrations (highest & lowest) of pesticide were used for desorption. After adsorption 5 mL of sample was withdrawn from the every tube and same 5 mL of fresh 0.01 M CaCl₂ solution were added. Tubes were again shaken to attain equilibrium. After equilibration, the soil suspension was centrifuged at 5000 rpm (1396 x g) for 5 min and 5 mL of supernatant was removed and replaced with fresh 5 mL of 0.01 M CaCl₂ solution. A total of three desorption cycles were performed for one sample. Imazethapyr residues were quantified in the supernatant solution after each desorption and amount of imazethapyr desorbed by the soil/soil-amendment mixture was calculated from the difference of initial and final concentration of herbicide in the supernatant.

3.11. Theory

3.11.1. Model Validation Criteria

Partition coefficient (K_d): The K_d values for herbicide adsorption on the sandy loam soil was calculated from the equation:

$$K_d = q_e/C_e$$

The adsorption models, which predicted the imazethapyr adsorption in approximation to the observed partition coefficient, were short listed and were further analyzed for the best suited model.

The adjusted coefficient of determination (r^2_{Adj}): A measure of the variability of the non-linear model is explained by the r^2_{Adj} values.

$$r^2_{Adj} = 1 - (1 - r^2) \cdot \left(\frac{n-1}{n-p}\right)$$

3.11.2. Temporal adsorption kinetics models

In the kinetic models, it is normally assumed that the overall rate of adsorption is exclusively controlled by the adsorption rate of the solute on the surface of the adsorbent, and the intraparticle diffusion and external mass transport can be neglected. Moreover, it is considered that the adsorption rate of a solute on the surface can be represented in the same manner as the rate of a chemical reaction (Ocampo-Perez *et al.*, 2011). The adsorption kinetics is modeled using pseudo-first-order (PFO) (Lagergren, 1898), pseudo-second order (PSO) (Ho and McKay, 1999; Ho, 2004) modified Elovich (Chien and Clayton, 1980) and intra-particle diffusion (IPD) models (Weber and Morris, 1963). The kinetics of adsorption process for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$. The parameter q_e is the amount of pesticide adsorbed at equilibrium (mg kg^{-1}) and q_t is the amount of pesticide adsorbed at time t (mg kg^{-1}).

The Lagergren pseudo-first order model: This model considers that the rate of change of pesticide uptake with time is directly proportional to difference in amount of solute adsorbed at equilibrium time. It is expressed by following equation

$$\frac{dq_t}{dt} = K_1\{q_e - q_t\}$$

After integration and linearization the above equation becomes

$$\text{Log}\{q_e - q_t\} = \log q_e - \left\{\frac{K_1}{2.303}\right\} t$$

K_1 is Lagergren rate constant of the pseudo first order adsorption (h^{-1}) and can be determined from the slope of the plot of $\log (q_e - q_t)$ versus time.

Irreversible pseudo-second-order model: The pseudo second order kinetics model is expressed by following equation

$$\frac{dq_t}{dt} = K_2\{q_e - q_t\}^2$$

After integration and linearization following equation is obtained

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left\{ \frac{1}{q_e} \right\} t$$

K_2 = Rate constant for pseudo second order adsorption ($Kg\ mg^{-1}\ h^{-1}$) can be determined experimentally from the slope and intercept of t/q_t versus t plot.

The modified Elovich model equation: The Elovich equation is expressed as follows:

$$\frac{dq_t}{dt} = \alpha \times \exp(-\beta q_t)$$

α =Initial sorption rate ($mg\ Kg^{-1}\ h^{-1}$)

β =Desorption constant ($Kg\ mg^{-1}$)

To simplify the Elovich equation, it has been assumed that $\alpha_E \beta_E t \gg 1$ (Chien and Clayton, 1980) and above equation becomes

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

The constants α and β were calculated from the graph plotted between q_t and $\ln t$.

Intra-particle diffusional model: It is well documented in the literature that the overall adsorption rate in a porous adsorbent must consider the three following steps: surface adsorption and external diffusion (boundary layer diffusion), gradual adsorption step where the intra-particle diffusion is rate controlled and adsorption on an active site

inside the pores or the final equilibrium step where the intra-particle diffusion starts to slow down due to the low solute concentration in the solution. The overall rate of adsorption is controlled by either film or intra-particle diffusion, or a combination of both mechanisms.

The rate parameter for intra-particle diffusion was determined using following equation:

$$q_t = \left[K_{\text{int}} \times t \exp\left(\frac{1}{2}\right) \right] + C$$

C = Intercept

K_{int} = Intra-particle diffusion rate constant (mg Kg⁻¹h^{-1/2})

The intercept (C) and rate constant (K_{int}) were calculated from the graph plotted between q_t and $t^{1/2}$.

3.11.3. Adsorption desorption models

Mathematical equations fitted to isotherm data to summarize the relationship between equilibrium concentration, amount adsorbed/desorbed and other parameters including thermodynamic parameters.

3.11.3.1. Calculation of amount of pesticide adsorbed

The amount of herbicide adsorbed on adsorbate after equilibrium was calculated as the difference between the initial and final equilibrium solution concentrations by the following equation

$$q_e = (C_i - C_e) \times \left(\frac{v}{m}\right)$$

q_e = Amount of herbicide adsorbed by adsorbate (mg Kg⁻¹) at equilibrium

C_i = Initial aqueous concentration of herbicide

C_e = Final aqueous concentration of herbicide

v = Solution volume (mL)

m = Mass of the soil (g)

Table 3.4. Lists of adsorption isotherms models analyzed for optimization studies.

Isotherms	Nonlinear form	Reference
2-Parameter		
<i>Langmuir</i>	$q_e = \frac{Q_0 b_L C_e}{1 + b_L C_e}$	Langmuir, 1916
<i>Freundlich</i>	$q_e = K_F C_e^{1/n}$	Freundlich, 1906
<i>Temkin</i>	$q_e = \frac{RT}{b_{Tem}} \ln A_{Tem} C_e$	Temkin & Pyzhev, 1940

3.11.3.2. Linear form of adsorption isotherms

Nonlinear Freundlich isotherm can be converted in to linear form by logarithm of nonlinear equation as depicted in table 3.4:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

The Freundlich constants K_F and $1/n$ were determined from intercept and slope of Freundlich isotherm obtained by plotting $\log q_e$ vs. $\log C_e$.

A desorption hysteresis coefficient (H) was calculated as the ratio between desorption and adsorption isotherm slopes and indicates the greater or lesser irreversibility of adsorption.

$$H = \left(\frac{1}{n_{desorb}}\right) / \left(\frac{1}{n_{adsorb}}\right)$$

A value of 1 means that desorption proceeds as fast as adsorption does and no hysteresis occurs. However, a value of $H < 1$ indicates that the rate of desorption is slower than the rate of adsorption and hysteresis takes place (Pusino *et al.*, 2004). In case of $H > 1$, greater desorption or negative hysteresis takes place.

The nonlinear form of the Langmuir equation can be linearized and represented by the following equation

$$\frac{1}{qe} = \frac{1}{Q_0} + \frac{1}{Q_0 b_L C_e}$$

b_L = Langmuir adsorption/desorption constant ((L mg⁻¹))

Q_0 = Maximum monolayer coverage capacity (mg g⁻¹)

Isotherm constants were calculated from the graph plotted between $1/qe$ and $1/C_e$ and constants were calculated.

The linearized form of the Temkin isotherm is expressed as follows

$$C_S = B \ln A_{Tem} + B \ln C_e$$

Where, $B = RT/b_{Tem}$

A_{Tem} = Temkin isotherm equilibrium binding constant (L g⁻¹)

b_{Tem} = Temkin isotherm constant

R = Universal gas constant (8.314 J K⁻¹ mol⁻¹)

T = Temperature (K)

B = Constant related to heat of adsorption/desorption (J mol⁻¹)

Isotherm was plotted between qe and $\ln C_e$ and constants were calculated.

3.11.3.3. Thermodynamic studies

The Gibb's free energy (ΔG) denotes spontaneity of the reaction. If (ΔG) for a reaction is negative than the reaction will be spontaneous and these reactions are

occurred naturally in the environment and vice versa. The ΔG is used as a measure of the extent of the driving force in the adsorption process. The greater the absolute magnitude of ΔG , the greater is the extent to which the adsorption reaction may take place. The ΔG for sorption was calculated using the K_F values with following equation:

$$\Delta G = -RT \ln K_F$$

where,

ΔG = The Gibb's free energy change ($\text{KJ K}^{-1} \text{mol}^{-1}$)

K_F = Freundlich constant

R = Universal gas constant ($8.314 \times 10^{-3} \text{KJ K}^{-1} \text{mol}^{-1}$)

T = Absolute temperature (K)

3.12. Effect of biochar/FYM on leaching behavior of imazethapyr in soil packed columns

Columns [sandy loam soil- 300 mm (l) x 59 mm (i.d.), were formed using polyvinyl chloride (PVC) pipes, which was fixed upon Buchner funnel fitted with 60 μm nylon membrane to reduce the dead end volume. Columns (in duplicate) were packed by adding small portion of soil (around 50 g) and compacting the soil with equal force through iron rod fitted with flat iron bottom so as to get the columns of uniform packing. The columns were packed to a bulk density of 1.38 kg L^{-1} for control soil where no amendments were used soil. The pore volume of the control sandy loam soil which was determined using the difference of mass of the soil in fully saturated column and oven dry mass of the soil was 411 mL. To study the effect of biochar/FYM amendment on the leaching behavior of imazethapyr, PB, LB and FYM was mixed thoroughly at 0.2% & 0.5% level to soil in the upper 15 cm (plough layer) section of the sandy loam soil column. The pore volume and bulk densities of sandy loam soil and soil with amendments were shown in table 3.5.

Table 3.5. Pore volume and bulk density of soil/soil+PB/soil+LB/soil+FYM filled in column

Amendment	Pore volume (mL)	Bulk density (KgL⁻¹)
Soil alone	411.41	1.383
0.2 % PB	389.54	1.384
0.5 % PB	387.86	1.386
0.2 % LB	374.75	1.384
0.5 % LB	395.50	1.386
0.2 % FYM	389.36	1.384
0.5 % FYM	371.12	1.386

One day before the imazethapyr application the columns were pretreated with 400 mL of distilled water to minimize the variation in the soil water content between the columns. The water was allowed to drain naturally. 50 µg of imazethapyr was applied to the column surface in 0.1 mL of acetone in a drop wise manner so as to cover the entire column surface. After application of imazethapyr the columns were left overnight. Before leaching, the column surface was covered with 0.5 cm thick layer of acid washed sand (DOC free) to minimize the disturbance of soil surface and to allow even distribution of water. One day after herbicide application, the columns were leached with 365 mL (118 mm rainfall) distilled water. The water was applied on the column surface and the natural drainage was allowed. This application rate allowed a water head of approximately 1 cm on the soil surface throughout the leaching. The leachate fractions were collected in approximately 50 mL portions and were analyzed of imazethapyr residues using HPLC.

3.13. Effect of biochar/FYM on dissipation behavior of imazethapyr

Degradation of imazethapyr in sandy loam soil was studied under field capacity condition at 27±2 °C in laboratory conditions. The soil (50g) or 0.2 and 0.5% PB, LB

and FYM mixed soils were taken in 250 mL sterilized Erlenmeyer flask and samples were supplemented with sterile distilled water so as to maintain 60% water holding capacity. Samples were fortified with 3 $\mu\text{g g}^{-1}$ imazethapyr in 0.1 mL acetone. Imazethapyr untreated samples were served as control. Each treatment was replicated thrice and water lost during incubation in BOD was maintained by adding water every week. The soil samples for imazethapyr degradation were withdrawn at regular intervals for further extraction and analysis through HPLC.

4. RESULTS AND DISCUSSION

4.1 Characterization of biochar and farm yard manure

The *Parthenium* biochar (PB), *Lantana* biochar (LB) and farm yard manure (FYM) were characterized for its physio-chemical properties (Table 4.1).

Table 4.1: Characterization of *Parthenium* biochar (PB), *Lantana* biochar (LB) and farm yard manure (FYM)

Parameters	<i>Parthenium</i> biochar	<i>Lantana</i> biochar	Farm yard manure
pH (1:5 Biochar: water suspension)	9.52	10.25	7.80
Electrical conductivity (dS/ m)	7.5	8.5	1.80
Water holding capacity (%)	550	425	-
Bulk density (Mg/ m ³)	0.38	0.47	0.36
Cation exchange capacity (cmol (p+)/ kg)	30.5	27.5	-
Total carbon (%)	33	35	15.45
Total nitrogen (%)	2.02	2.25	1.25
Total phosphorus (%)	0.27	0.35	1.2
Total potassium (%)	1.59	1.95	0.74
Point of zero charge	8.85	9.87	-

Both biochars (Figure 4.1) are of alkaline nature with LB having slightly higher pH than PB whereas FYM is almost neutral in nature. Similar effects are seen for electrical conductivity, total C%, N%, P%, K% and point of zero charge (Table 4.1). The point of zero charge (pH_{zpc}) is a measure of charge on adsorbent of both biochars did not show much variation (PB – 8.85; LB -9.87). At $pH < pH_{zpc}$, the surface of the adsorbent is positively charged and favours the uptake of negatively charged adsorbate with the increased electro-static force of attraction, besides at $pH > pH_{zpc}$, the surface

becomes negatively charged and preferable for adsorption of positively charged adsorbate. The alkaline pH_{zpc} of biochars can be depicted to the presence of alkali metal oxides. The pH_{zpc} has an important role in influencing the sorption of ionizable or polar herbicides. Sorption of negatively charged molecules are favored when $pH < pH_{zpc}$ because of the positive charged, whereas when $pH > pH_{zpc}$, the surface were negatively charged and was favorable for positively charged molecule adsorption of (Deokar and Mandavgane, 2015). The cation exchange capacity and water holding capacity is higher for PB when compared with LB. % C was nearly half for FYM when it is compared with biochars. This may be the reason for low sorption of imazethapyr as compared to others.



Figure 4.1. Lantana biochar(A) and Parthenium biochar (B) before (I) and after grinding and sieving (II)

4.3. Kinetics of imazethapyr adsorption

The kinetics of imazethapyr adsorption was studied in the sandy loam soil of Bundelkhand region, with various treatment combinations *viz.* soil alone, 0.2% and 0.5% each of PB, LB and FYM with sandy loam soil. The results of kinetics study

showed that for all treatments used for kinetics study rate of adsorption was increased with increase in the contact time with adsorbent, which decreased drastically after half an hour of shaking in orbital shaker (Table 4.2). The adsorption rate for all treatments proceeded at faster rate during first half hour. The % sorption at half an hour shaking for control, 0.2% PB and 0.5% PB were 8.46%, 6.82% and 10.29% respectively (Table 4.2 & 4.3). Similarly, % sorption at half an hour shaking for 0.2% LB & FYM and 0.5% LB and FYM mixed sandy loam soil were 10.99%, 4.11%, 16.57% and 5.40% respectively (Table 4.4 & 4.5). The rate of imazethapyr adsorption decreases as the time progress and achieved nearly constant value after lapse of 24 h. At equilibration time i.e. after 24 h of shaking % sorption where 17.68%, 21.85% & 26.77% for sandy loam soil alone, 0.2% PB mixed and 0.5% PB mixed sandy loam soil respectively (Table 4.2 & 4.3). Whereas, for 0.2% and 0.5% LB and FYM amended sandy loam soil adsorption % where 26.91%, 15.28%, 34.45% and 20.50% respectively (Table 4.4 & 4.5). Thus, 24h equilibration was considered as the equilibration time for imazethapyr adsorption in all the treatment combination with soil.

Table 4.2. Temporal Kinetics of imazethapyr sorption in soil alone

Time (h)	Imazethapyr recovered in solution ($\mu\text{g mL}^{-1}$)			
	Control (Soil alone)			Mean \pm S.D. (% sorbed)
	R1	R2	R3	
0	2.81	2.78	2.80	2.80 \pm 0.017 (0.00)
0.25	2.58	2.63	2.61	2.61 \pm 0.024 (6.85)
0.5	2.57	2.60	2.52	2.56 \pm 0.036 (8.46)
1	2.51	2.53	2.52	2.52 \pm 0.009 (9.99)
2	2.48	2.51	2.50	2.50 \pm 0.015 (10.74)
4	2.48	2.49	2.48	2.48 \pm 0.006 (11.31)
8	2.43	2.43	2.41	2.42 \pm 0.013 (13.46)
12	2.39	2.39	2.39	2.39 \pm 0.002 (14.67)
24	2.34	2.32	2.32	2.33 \pm 0.010 (16.86)
48	2.30	2.29	2.32	2.30 \pm 0.013 (17.68)

Table 4.3. Temporal kinetics of imazethpyr sorption in 0.2% and 0.5% PB mixed sandy loam soil

time (h)	Imazethapyr recovered in solution ($\mu\text{g mL}^{-1}$)							
	0.2 % PB				0.5 % PB			
	R1	R2	R3	Mean \pm S.D. (% Sorbed)	R1	R2	R3	Mean \pm S.D. (% Sorbed)
0	3.80	3.83	3.85	3.82 \pm 0.026 (0.00)	3.80	3.83	3.85	3.82 \pm 0.026 (0.00)
0.25	3.53	3.58	3.56	3.56 \pm 0.025 (6.93)	3.58	3.52	3.52	3.54 \pm 0.037 (7.39)
0.5	3.59	3.54	3.56	3.56 \pm 0.023 (6.82)	3.44	3.41	3.45	3.43 \pm 0.021 (10.29)
1	3.45	3.50	3.42	3.46 \pm 0.043 (9.62)	3.37	3.39	3.39	3.38 \pm 0.009 (11.49)
2	3.46	3.44	3.42	3.44 \pm 0.017 (10.06)	3.36	3.37	3.32	3.35 \pm 0.027 (12.33)
4	3.27	3.20	3.24	3.24 \pm 0.036 (15.27)	3.19	3.22	3.17	3.19 \pm 0.026 (16.53)
8	3.34	3.20	3.19	3.24 \pm 0.081 (15.22)	3.10	3.10	3.15	3.12 \pm 0.027 (18.49)
12	3.17	3.14	3.20	3.17 \pm 0.028 (17.11)	3.01	3.06	3.00	3.02 \pm 0.035 (20.90)
24	3.09	3.06	3.08	3.08 \pm 0.013 (19.52)	2.96	2.88	2.91	2.92 \pm 0.040 (23.72)
48	3.05	2.99	2.92	2.99 \pm 0.061 (21.85)	2.84	2.75	2.81	2.80 \pm 0.042 (26.77)

Table 4.4. Temporal kinetics of imazethpyr sorption in 0.2% and 0.5% LB mixed sandy loam soil

time (h)	Imazethapyr recovered in solution ($\mu\text{g mL}^{-1}$)							
	0.2%LB				0.5 % LB			
	R1	R2	R3	Mean \pm S.D. (% Sorbed)	R1	R2	R3	Mean \pm S.D. (% Sorbed)
0	3.61	3.52	3.62	3.58 \pm 0.052 (0.00)	3.61	3.52	3.62	3.58 \pm 0.052 (0.00)
0.25	3.27	3.26	3.25	3.26 \pm 0.011 (9.01)	3.08	3.03	3.02	3.04 \pm 0.032 (15.10)
0.5	3.19	3.19	3.19	3.19 \pm 0.002 (10.99)	3.00	3.00	2.97	2.99 \pm 0.014 (16.57)
1	3.17	3.10	3.11	3.13 \pm 0.034 (12.75)	2.90	2.88	2.87	2.88 \pm 0.018 (19.52)
2	3.03	3.02	3.04	3.03 \pm 0.011 (15.33)	2.81	2.81	2.78	2.80 \pm 0.018 (21.90)
4	2.90	2.89	2.94	2.91 \pm 0.026 (18.75)	2.64	2.69	2.66	2.67 \pm 0.027 (25.60)
8	2.87	2.90	2.86	2.88 \pm 0.020 (19.74)	2.62	2.56	2.60	2.59 \pm 0.032 (27.65)

12	2.80	2.75	2.83	2.80±0.043 (21.97)	2.44	2.50	2.49	2.48±0.030 (30.86)
24	2.71	2.70	2.72	2.71±0.009 (24.45)	2.45	2.39	2.41	2.42±0.029 (32.53)
48	2.64	2.59	2.63	2.62±0.026 (26.91)	2.36	2.35	2.33	2.35±0.017 (34.45)

Table 4.5. Temporal kinetics of imazethapyr sorption in 0.2% and 0.5% FYM mixed sandy loam soil

time (h)	Imazethapyr recovered in solution ($\mu\text{g mL}^{-1}$)							
	0.2% FYM				0.5 % FYM			
	R1	R2	R3	Mean±S.D. (% Sorbed)	R1	R2	R3	Mean±S.D (%Sorbed)
0	3.19	3.11	3.18	3.16±0.040 (0.00)	3.19	3.11	3.18	3.16±0.040 (0.00)
0.25	3.07	3.08	3.10	3.08±0.016 (2.39)	3.06	3.07	3.06	3.07±0.003 (2.96)
0.5	3.08	3.01	3.00	3.03±0.043 (4.11)	2.99	3.01	2.97	2.99±0.023 (5.40)
1	2.98	2.97	2.98	2.98±0.004 (5.77)	2.92	2.87	2.95	2.91±0.037 (7.83)
2	2.95	2.96	2.93	2.95±0.017 (6.65)	2.90	2.89	2.89	2.89±0.008 (8.38)
4	2.86	2.87	2.88	2.87±0.008 (9.14)	2.79	2.81	2.77	2.79±0.023 (11.67)
8	2.79	2.81	2.81	2.81±0.009 (11.19)	2.75	2.72	2.72	2.73±0.019 (13.56)
12	2.78	2.78	2.78	2.78±0.002 (12.02)	2.61	2.60	2.63	2.61±0.172 (17.24)
24	2.72	2.73	2.68	2.71±0.023 (14.27)	2.55	2.60	2.61	2.59±0.033 (18.04)
48	2.70	2.64	2.69	2.68±0.031 (15.28)	2.55	2.48	2.50	2.51±0.038 (20.50)

Further, the kinetics data were fitted to the linear form of the pseudo first order, pseudo second order, modified Elovich and the intraparticle models and constants for the kinetics of imazethapyr adsorption in various treatment combinations *viz.* sandy loam soil alone, 0.2% & 0.5% PB, 0.2% and 0.5% LB and 0.2% & 0.5% FYM with sandy loam soil were calculated (Figure 4.2, 4.3 and 4.4; and Table 4.6). Among the three kinetics models fitted, the values for r^2_{Adj} were highest for the pseudo second order model (Soil alone – 0.995; Soil+ 0.2% PB- 0.992; soil + 0.5% PB- 0.991, Soil+ 0.2% LB- 0.994; soil + 0.5% LB- 0.998, Soil+ 0.2% FYM- 0.994; soil + 0.5% FYM- 0.989).

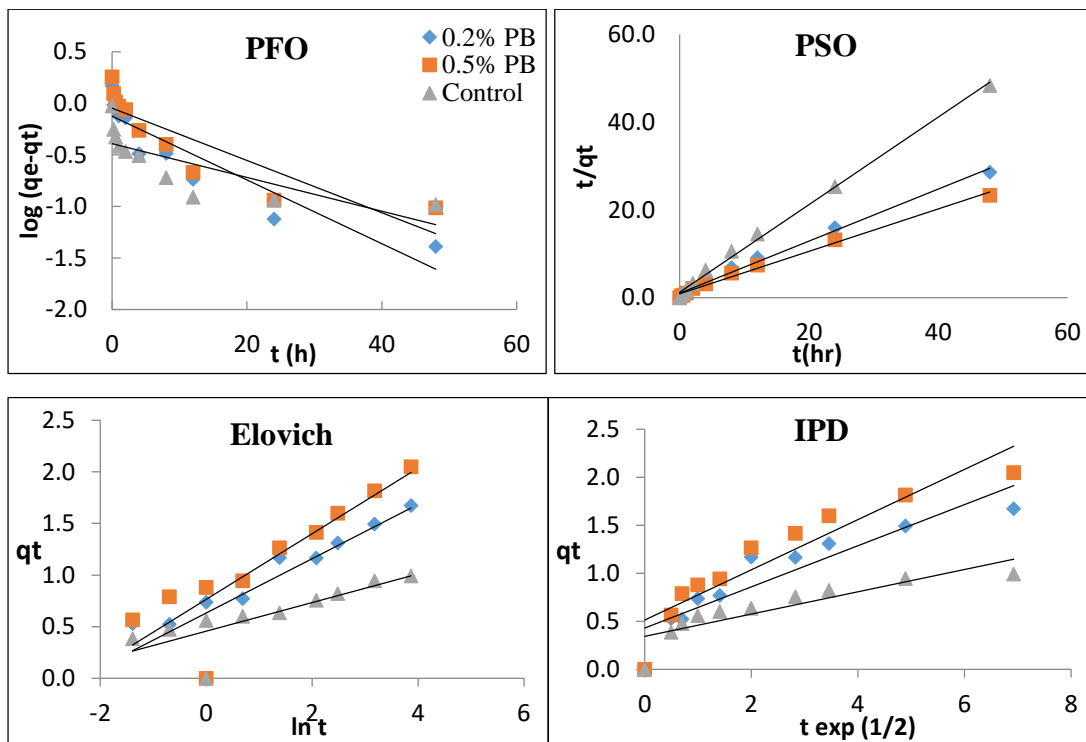


Figure 4.2. Linear plots of pseudo-first-order (PFO), pseudo-second order (PSO), modified Elovich and intra-particle diffusion (IPD) models for imazethapyr in control, 0.2% and 0.5% PB-mixed sandy loam soil.

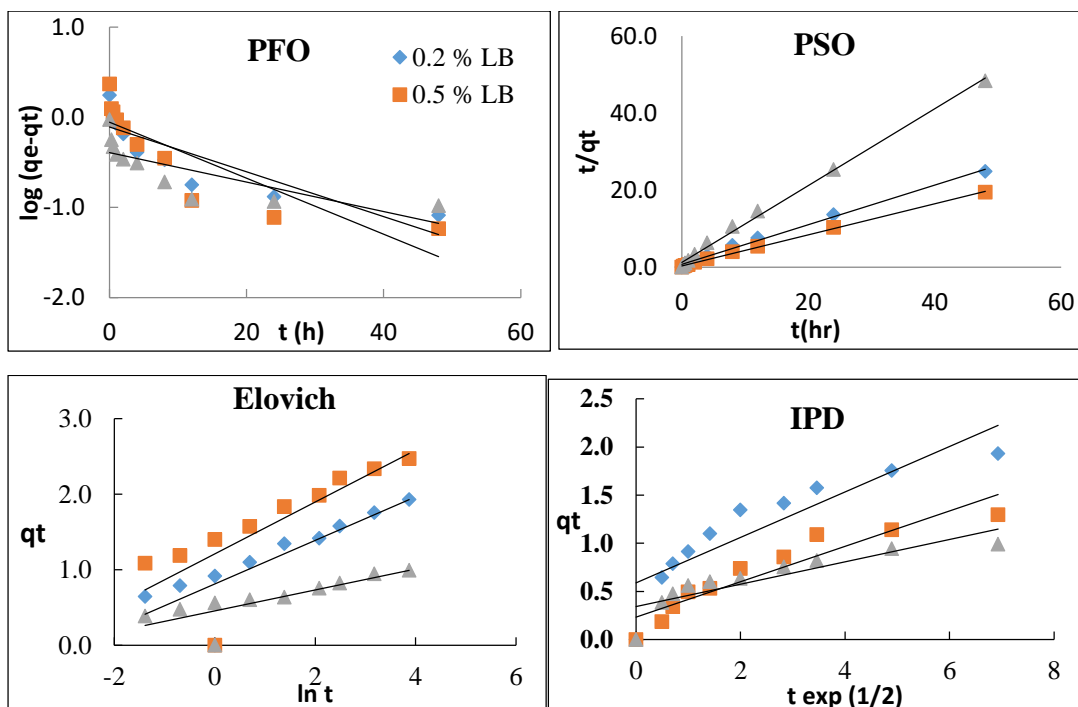


Figure 4.3. Linear plots of pseudo-first-order (PFO), pseudo-second order (PSO), modified Elovich and intra-particle diffusion (IPD) models for imazethapyr in control, 0.2% and 0.5% LB -mixed sandy loam soil.

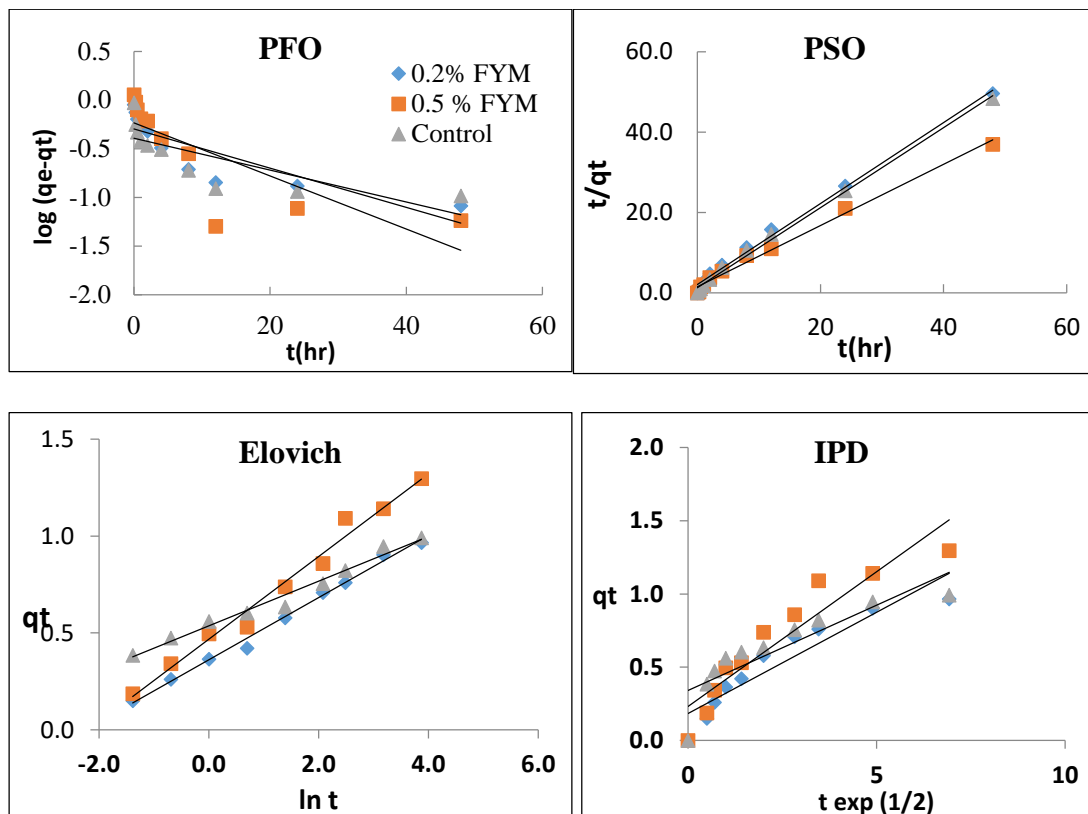


Figure 4.4. Linear plots of pseudo-first-order (PFO), pseudo-second order (PSO), modified Elovich and intra-particle diffusion (IPD) models for imazethapyr in control, 0.2% and 0.5% FYM -mixed sandy loam soil.

A best fit to the PSO kinetic model indicated that rate of adsorption was dependent more on the availability of the adsorption sites than on the concentration of the pesticide in solution (Liu, 2008). The intra particle diffusion graph was not passing through the origin suggesting that intraparticle diffusion was not the only rate determining step and the boundary layer diffusion might also affected adsorption to some degree. Establishing the linear fitting of the kinetics data in PFO, PSO and the modified Elovich models suggested that the PSO model was best explained model for imazethapyr adsorption in the PB/LB/FYM-mixed sandy loam soil. The PSO model suggests that the adsorption rate is dependent more on the availability of the adsorption sites than on the concentration of the herbicide in solution.

Table 4.6. Rate constants k (min^{-1}), k_2 ($\text{Kg mg}^{-1} \text{min}^{-1}$), model parameters and r^2_{Adj} of the studied kinetic models for imazethapyr in control, 0.2% and 0.5% PB, LB and FYM mixed sandy loam soil following linear fitting of model

Adsorbent	Pseudo-First Order				Pseudo-Second Order				Modified Elovich			Intra-Particle diffusion		
	$q_{e, \text{cal}}$	$q_{e, \text{exp}}$	k	r^2_{Adj}	$q_{e, \text{cal}}$	$q_{e, \text{exp}}$	k_2	r^2_{Adj}	α_E	β_E	r^2_{Adj}	k_i	C	r^2_{Adj}
Soil alone	0.408	0.946	0.038	0.541	1.003	0.946	0.789	0.995	0.279	7.215	0.617	0.116	0.341	0.724
0.2% PB	0.751	1.495	0.071	0.822	1.687	1.495	0.338	0.992	0.687	3.799	0.746	0.214	0.429	0.809
0.5% PB	0.898	1.817	0.058	0.734	2.067	1.817	0.261	0.991	0.828	3.146	0.753	0.262	0.513	0.837
0.2% LB	0.779	1.755	0.057	0.716	1.941	1.755	0.364	0.994	0.656	3.460	0.698	0.236	0.587	0.764
0.5% LB	0.880	2.335	0.072	0.701	2.489	2.335	0.417	0.998	0.661	2.910	0.587	0.184	0.632	0.857
0.2% FYM	0.955	0.903	0.047	0.681	0.992	0.903	0.491	0.994	0.660	5.675	0.858	0.138	0.184	0.850
0.5% FYM	0.939	1.142	0.063	0.588	1.314	1.142	0.378	0.989	0.904	4.283	0.856	0.184	0.232	0.857

4.4. Adsorption-desorption studies of imazethapyr

4.4.1. Adsorption

Adsorption of imazethapyr with various treatments *viz.* sandy loam soil alone, 0.2% & 0.5% PB, 0.2% and 0.5% LB and 0.2% & 0.5% FYM with sandy loam soil was studied at 1:2 adsorbent:solution ratio at five different concentrations of imazethapyr varying in between 1 and 5 $\mu\text{g mL}^{-1}$. Results showed that in soil alone i.e. where no any amendments used in sandy loam soil showed adsorption in the range 9.82% to 14.66% (Table 4.7). Whereas, 0.2% and 0.5% PB mixed sandy loam soil

Table 4.7. Adsorption of imazethapyr in *Parthenium* biochar (PB) mixed sandy loam soil

Initial conc. ($\mu\text{g mL}^{-1}$)	Equilibrium conc. ($\mu\text{g mL}^{-1}$)				Amount sorbed ($\mu\text{g g}^{-1}$)	% Adsorption
	R1	R2	R3	Mean \pm S.D		
Control						
1.050	0.918	0.913	0.922	0.918 \pm 0.0045	0.348	12.60
1.962	1.622	1.641	1.647	1.637 \pm 0.0131	0.548	16.58
2.949	2.654	2.661	2.663	2.659 \pm 0.0047	0.748	9.82
4.241	3.639	3.606	3.612	3.619 \pm 0.0176	1.005	14.66
5.123	4.494	4.499	4.493	4.495 \pm 0.0032	1.255	12.25
0.2 % PB						
1.398	1.104	1.108	1.137	1.116 \pm 0.0180	0.685	20.14
2.537	1.999	1.998	2.037	2.011 \pm 0.0222	1.051	20.72
4.049	3.384	3.380	3.353	3.372 \pm 0.0169	1.353	16.71
5.555	5.239	4.582	4.661	4.827 \pm 0.3587	1.748	13.10
7.019	5.992	5.850	5.973	5.938 \pm 0.0771	2.161	15.39
0.5 % PB						
1.398	1.009	0.865	0.988	0.954 \pm 0.0778	0.888	31.75
2.537	1.837	1.903	1.798	1.846 \pm 0.0531	1.382	27.23
4.049	3.030	3.028	3.042	3.033 \pm 0.0076	2.031	25.08
5.555	4.284	4.295	4.104	4.228 \pm 0.1072	2.655	23.89
7.019	6.155	5.619	5.498	5.757 \pm 0.3497	2.956	17.97

shows adsorption range 13.10% to 20.72% and 17.97%-31.75% respectively (Table 4.7). Similarly 0.2% and 0.5% LB mixed sandy loam soil showed adsorption range of 17.97%-38.38% and 29.21% - 51.21% respectively (Table 4.8). In case of 0.2% and 0.5% FYM mixed sandy loam soil adsorption ranges between 29.32-44.42% and 36.20-45.68% respectively (Table 4.9). Low adsorption of imazethapyr may be due to

Table 4.8. Adsorption of imazethapyr in *Lantana* biochar (LB) mixed sandy loam soil

Initial conc. ($\mu\text{g mL}^{-1}$)	Equilibrium conc. ($\mu\text{g mL}^{-1}$)				Amount sorbed ($\mu\text{g g}^{-1}$)	% Adsorption
	R1	R2	R3	Mean \pm S.D		
Control						
1.050	0.918	0.913	0.922	0.918 \pm 0.0045	0.348	12.60
1.962	1.622	1.641	1.647	1.637 \pm 0.0131	0.548	16.58
2.949	2.654	2.661	2.663	2.659 \pm 0.0047	0.748	9.82
4.241	3.639	3.606	3.612	3.619 \pm 0.0176	1.005	14.66
5.123	4.494	4.499	4.493	4.495 \pm 0.0032	1.255	12.25
0.2 % LB						
1.398	0.842	0.921	0.821	0.861 \pm 0.0527	1.073	38.38
2.537	1.953	1.957	2.030	1.980 \pm 0.0433	1.421	21.95
4.049	3.465	3.161	3.214	3.280 \pm 0.1624	1.738	18.99
5.555	4.582	4.385	4.560	4.509 \pm 0.1079	2.092	18.82
7.019	5.637	5.789	5.847	5.758 \pm 0.1084	2.523	17.97
0.5 % LB						
1.398	0.655	0.708	0.683	0.682 \pm 0.0265	1.432	51.21
2.537	1.712	1.538	1.390	1.547 \pm 0.1612	1.981	39.03
4.049	2.618	2.587	2.567	2.591 \pm 0.0257	2.917	36.01
5.555	3.792	3.907	3.816	3.838 \pm 0.0607	3.433	30.90
7.019	4.710	5.183	5.012	4.968 \pm 0.2395	4.101	29.21

Table 4.9. Adsorption of imazethapyr in FYM mixed sandy loam soil

Initial conc. ($\mu\text{g mL}^{-1}$)	Equilibrium conc. ($\mu\text{g mL}^{-1}$)				Amount sorbed ($\mu\text{g g}^{-1}$)	% Adsorption
	R1	R2	R3	Mean \pm S.D		
Control						
1.050	0.918	0.913	0.922	0.918 \pm 0.0045	0.348	12.60
1.962	1.622	1.641	1.647	1.637 \pm 0.0131	0.548	16.58
2.949	2.654	2.661	2.663	2.659 \pm 0.0047	0.748	9.82
4.241	3.639	3.606	3.612	3.619 \pm 0.0176	1.005	14.66
5.123	4.494	4.499	4.493	4.495 \pm 0.0032	1.255	12.25
0.2 % FYM						
1.398	1.027	1.049	1.052	1.043 \pm 0.0137	0.711	25.41
2.537	2.369	2.378	2.192	2.313 \pm 0.1049	1.328	8.82
4.049	3.616	3.871	3.735	3.741 \pm 0.1276	1.805	7.61
5.555	5.097	5.146	5.134	5.126 \pm 0.0255	2.403	7.72
7.019	6.625	6.658	6.552	6.612 \pm 0.0542	3.241	5.80
0.5 % FYM						
1.398	1.014	1.020	0.972	1.002 \pm 0.0262	0.792	28.32
2.537	2.129	2.246	2.239	2.205 \pm 0.0656	1.524	13.09
4.049	3.658	3.706	3.637	3.667 \pm 0.0354	2.421	9.43
5.555	4.915	4.924	4.937	4.925 \pm 0.0111	3.124	11.33
7.019	6.426	6.542	6.669	6.546 \pm 0.1215	4.125	6.74

hydrophobicity of the imazethapyr as which is represented by K_{ow} (Octanol water coefficient) values to depict the sorption of imazethapyr onto biochar/FYM amended sandy loam soils (Calvet 1989; Ahmad *et al.* 2001). The Adsorption of imazethapyr is directly proportional to total carbon of the adsorbate (Loux *et al.* 1989). Our results of adsorption also follows same pattern of adsorption i.e. highest adsorption was shown in LB amended soil because of higher total C% in comparison with other amendments (PB & FYM). Further, Kibe *et al.* (2000) suggested that there were no correlation between the Freundlich adsorption constant and soil organic carbon contents & cation exchange capacity of the soils. Further, imazethapyr adsorption data were fitted to the linear form of adsorption isotherms (Freundlich, Langmuir and

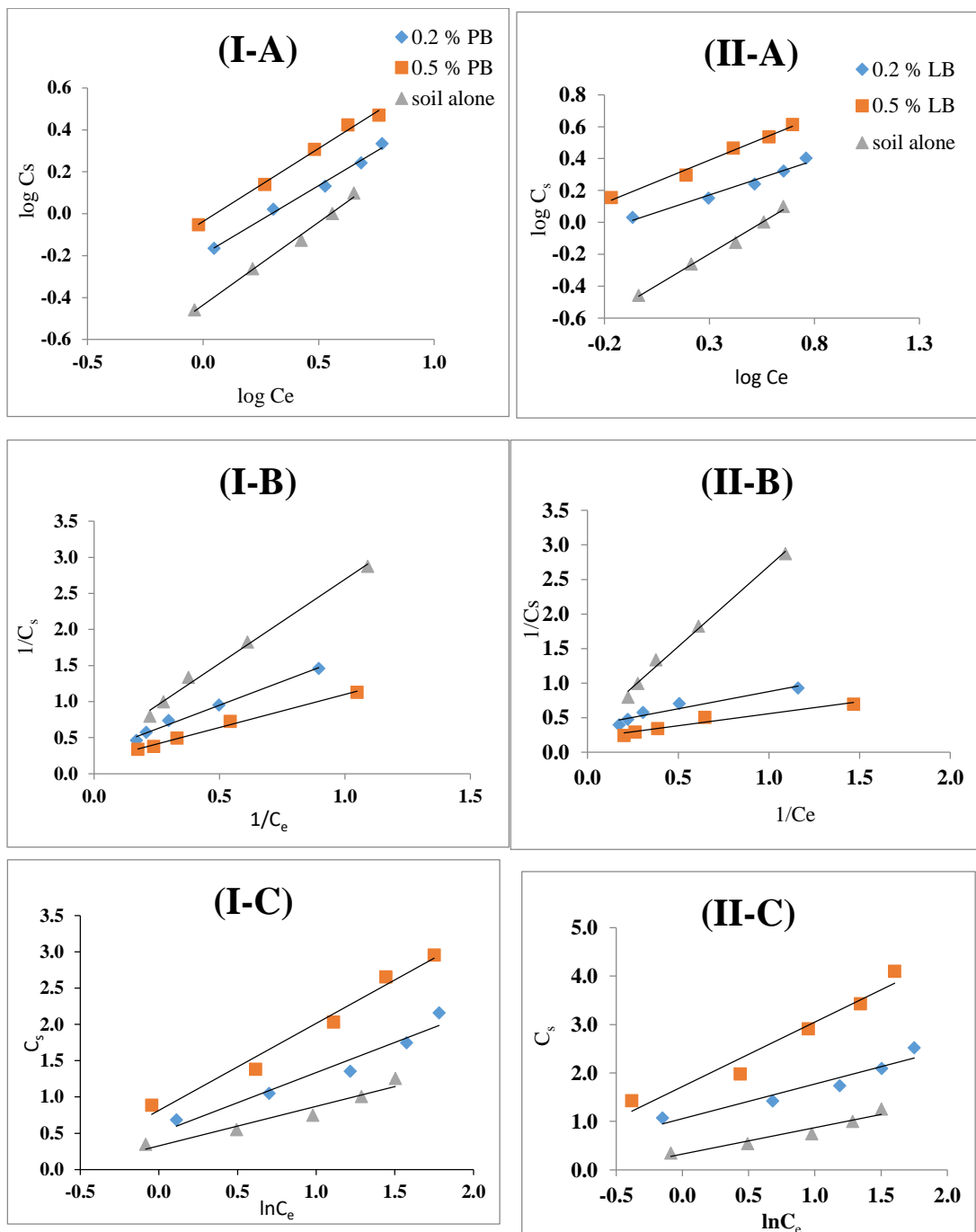


Figure 4.5. Adsorption isotherms for imazethapyr adsorption in the PB (I) and LB (II) mixed sandy loam soil [(A) Freundlich (B) Langmuir (C) Temkin isotherm]

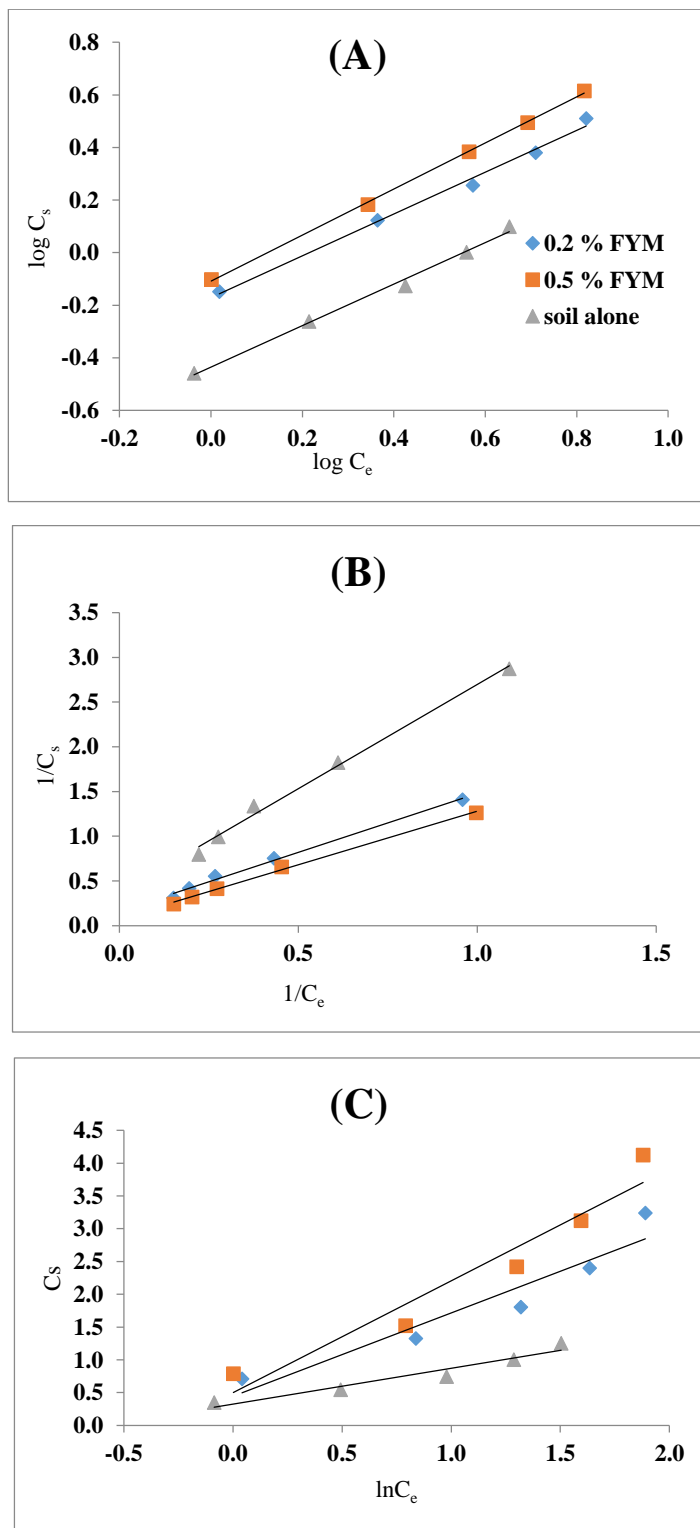


Figure 4.6. Adsorption isotherms for imazethapyr adsorption in the FYM mixed sandy loam soil [(A) Freundlich (B) Langmuir (C) Temkin isotherm]

Temkin, Figure 4.5 & 4.6) and adsorption constants were calculated (Table 4.10). Imazethapyr adsorption data were best fitted to the Freundlich adsorption isotherm as, in general, the value of coefficient of correlation (r^2) and the r^2_{Adj} were highest for the

Table 4.10. Adsorption constants for imazethapyr adsorption in control, 0.2% and 0.5% PB, LB and FYM mixed sandy loam soil

Model	Para meter	Control	0.2% PB	0.5% PB	0.2% LB	0.5% LB	0.2% FYM	0.5% FYM
Freundlich	K_d	0.248	0.291	0.445	0.289	0.622	0.440	0.599
	K_F	0.923	1.064	1.586	1.099	1.694	1.282	1.484
	1/n_{ads}	0.789	0.658	0.696	0.435	0.537	0.795	0.877
	r²	0.994	0.991	0.993	0.994	0.997	0.993	0.999
	r²_{Adj}	0.992	0.999	0.991	0.995	0.993	0.990	0.999
	ΔG	-0.086	-0.093	-0.491	-0.105	-0.589	-0.239	-0.479
Langmuir	Q₀	2.749	3.400	5.385	2.627	4.785	6.231	12.270
	K_L	0.156	0.224	0.203	0.762	0.597	0.122	0.068
	r²	0.993	0.990	0.994	0.927	0.951	0.993	0.998
	r²_{Adj}	0.991	0.987	0.992	0.903	0.935	0.991	0.997
Temkin	b_{Tem}	0.545	0.829	1.198	0.718	1.331	1.272	1.708
	A_{Tem}	1.817	1.845	1.977	4.349	3.640	1.415	1.337
	r²	0.939	0.947	0.976	0.917	0.952	0.908	0.933
	r²_{Adj}	0.918	0.930	0.967	0.889	0.936	0.877	0.910

ΔG- Gibbs free energy ((KJK⁻¹ mol⁻¹)

Freundlich isotherm. The K_F value for adsorption of imazethapyr in the control soil (no amendment), 0.2% & 0.5% PB mixed sandy loam soil were 0.923, 1.064 and 1.586 respectively. Whereas, K_F values for 0.2% and 0.5% LB mixed sandy loam soil were 1.099 and 1.694 respectively. Similarly, the values of K_F were 1.282 and 1.484 for 0.2% and 0.5% FYM were 1.282 and 1.484 respectively. Thus, K_F values increased with increase in level of the biochar and FYM amendment in sandy loam soil. These results suggested that amendments (PB, LB & FYM) were significantly effective in enhancing atrazine adsorption in PB, LB & FYM amendment in sandy loam soil. The value of slope (1/n_{ads}, measure of intensity of adsorption) for control sandy loam soil where no any amendment was used is 0.789 that suggests L-type of adsorption. Whereas, for 0.2% and 0.5% PB amended sandy loam soil the values were 0.658 and 0.696 respectively. Similarly, the values of 1/n_{ads} were 0.435, 0.537, 0.795 and 0.877 for 0.2% & 0.5% LB and 0.2% and 0.5% FYM amended sandy loam soil (Table 4.10). Further, the values of 1/n_{ads} increased with increasing the amount of amendment (PB, LB and FYM) suggesting adsorption was shifting towards linearity. This study

suggested that imazethapyr adsorption in all amendment combinations have L-type of adsorption and with increasing the amendment application isotherms shifted towards the linear isotherm (Kumar *et al.* 2019).

The effect of soil amendments (PB, LB and FYM) on change in the free energy (ΔG) for imazethapyr adsorption was calculated using the equation $\Delta G = -RT \ln K_F$ as mentioned previously (Table 4.10). The negative values of ΔG showed that adsorption of imazethapyr were spontaneous in nature and with increasing the rate of amendment from 0.2% to 0.5% negative values of ΔG increases indicating that with increase in the amendment rate degree of spontaneity increases i.e. ease to complete the work increases (Kumar *et al.* 2019).

4.4.2. Desorption

Adsorption reversibility plays a significant role in predicting the mobility of the herbicides in the soil profile. Desorption of imazethapyr in sandy loam soil/amendment mixed sandy loam soil was studied at lowest and highest concentration after adsorption and 3 desorption cycles were performed. The results of imazethapyr desorbed in sandy loam soil alone / 0.2% and 0.5% each of PB, LB and FYM mixed sandy loam soil during three desorption cycles are represented in Table 4.11, 4.12 and 4.13. On the basis of results obtained, it is concluded that initial concentration of imazethapyr affected its desorption which decreases with every proceeding desorption cycle. Percent imazethapyr desorption from the sandy loam soil alone was 24.992% and 47.888% at the lower and the higher concentration, respectively. Addition of the amendments to sandy loam soil increased imazethapyr retention and lower amounts were desorbed. Further, desorption decreased with increase in the level of PB/LB/FYM amendment. Thus, 0.2% and 0.5% PB amendment resulted in 22.37% and 25.41%, 18.77% and 22.47% desorption at lower and higher concentration, respectively (Table 4.11). Similarly, 0.2% and 0.5% LB amendment resulted in 27.49% and 36.11%, 17.33% and 36.37% desorption at lower and higher concentration, respectively (Table 4.12). Further, 0.2% and 0.5% FYM amendment resulted in 15.61% and 23.87%, 12.00% and 18.55% desorption at lower and higher concentration, respectively (Table 4.13).

Table 4.11. Desorption of imazethapyr from the *Parthenium* biochar (PB) mixed sandy loam soil

Desorption cycle	Equilibrium concentration ($\mu\text{g mL}^{-1}$)				Amount Desorbed ($\mu\text{g g}^{-1}$)	% Desorption
	R1	R2	R3	Mean \pm S.D		
Control						
1.050 $\mu\text{g mL}^{-1}$						
I	0.475	0.467	0.486	0.476 \pm 0.0095	0.136	
II	0.276	0.265	0.266	0.269 \pm 0.0061	0.084	
III	0.140	0.150	0.145	0.145 \pm 0.0050	0.033	
Total					0.253	24.992
5.123 $\mu\text{g mL}^{-1}$						
I	2.420	2.420	2.432	2.424 \pm 0.0069	0.761	
II	1.298	1.272	1.280	1.283 \pm 0.0133	0.052	
III	0.683	0.695	0.693	0.690 \pm 0.0064	0.070	
Total					0.883	47.888
0.2 % PB						
1.398						
I	0.531	0.509	0.538	0.526 \pm 0.0151	0.068	
II	0.239	0.294	0.275	0.269 \pm 0.0279	0.044	
III	0.148	0.141	0.150	0.146 \pm 0.0047	0.012	
Total					0.124	22.336
7.019 $\mu\text{g mL}^{-1}$						
I	2.841	2.807	2.969	2.872 \pm 0.0854	0.097	
II	1.351	1.591	1.400	1.447 \pm 0.1268	0.011	
III	0.562	0.751	0.631	0.648 \pm 0.0956	0.076	
Total					0.184	25.405
0.5 % PB						
1.398 $\mu\text{g mL}^{-1}$						
I	0.471	0.415	0.436	0.441 \pm 0.0283	0.036	
II	0.246	0.231	0.238	0.238 \pm 0.0075	0.018	
III	0.129	0.126	0.153	0.136 \pm 0.0148	0.034	
Total					0.088	18.874
7.019 $\mu\text{g mL}^{-1}$						
I	2.523	2.642	2.599	2.588 \pm 0.0603	1.438	
II	1.109	1.345	1.289	1.248 \pm 0.1233	0.018	
III	0.477	0.529	0.565	0.524 \pm 0.0442	0.017	
Total					1.473	22.472

Table 4.12. Desorption of imazethapyr from the *Lantana* biochar (LB) mixed sandy loam soil

Desorption cycle	Equilibrium concentration ($\mu\text{g mL}^{-1}$)				Amount Desorbed ($\mu\text{g g}^{-1}$)	% Desorption
	R1	R2	R3	Mean \pm S.D		
Control						
1.050 $\mu\text{g mL}^{-1}$						
I	0.475	0.467	0.486	0.476 \pm 0.0095	0.136	
II	0.276	0.265	0.266	0.269 \pm 0.0061	0.084	
III	0.140	0.150	0.145	0.145 \pm 0.0050	0.033	
Total					0.253	24.992
5.123						
I	2.420	2.420	2.432	2.424 \pm 0.0069	0.761	
II	1.298	1.272	1.280	1.283 \pm 0.0133	0.052	
III	0.683	0.695	0.693	0.690 \pm 0.0064	0.070	
Total					0.883	47.888
0.2 % LB						
1.398						
I	0.490	0.454	0.421	0.455 \pm 0.0345	0.086	
II	0.236	0.259	0.231	0.242 \pm 0.0149	0.019	
III	0.104	0.132	0.116	0.117 \pm 0.0140	0.007	
Total					0.112	27.493
7.019						
I	3.104	3.049	2.872	3.008 \pm 0.1212	0.129	
II	1.481	1.610	1.577	1.556 \pm 0.0670	0.052	
III	0.689	0.736	0.699	0.708 \pm 0.0248	0.070	
Total					0.251	36.108
0.5 % LB						
1.398						
I	0.366	0.372	0.339	0.359 \pm 0.0176	0.122	
II	0.204	0.190	0.187	0.194 \pm 0.0091	0.069	
III	0.132	0.122	0.118	0.124 \pm 0.0072	0.057	
Total					0.248	17.331
7.019						
I	2.428	2.663	2.658	2.583 \pm 0.1343	0.858	
II	1.296	1.449	1.399	1.381 \pm 0.0780	0.484	
III	0.601	0.680	0.605	0.629 \pm 0.0445	0.149	
Total					1.492	36.372

Table 4.13. Desorption of imazethapyr from the farm yard manure (FYM) mixed sandy loam soil

Desorption cycle	Equilibrium concentration ($\mu\text{g mL}^{-1}$)				Amount Desorbed ($\mu\text{g g}^{-1}$)	% Desorption
	R1	R2	R3	Mean \pm S.D		
Control						
1.050						
I	0.475	0.467	0.486	0.476 \pm 0.0095	0.136	
II	0.276	0.265	0.266	0.269 \pm 0.0061	0.084	
III	0.140	0.150	0.145	0.145 \pm 0.0050	0.033	
Total					0.253	24.992
5.123						
I	2.420	2.420	2.432	2.424 \pm 0.0069	0.761	
II	1.298	1.272	1.280	1.283 \pm 0.0133	0.052	
III	0.683	0.695	0.693	0.690 \pm 0.0064	0.070	
Total					0.883	47.888
0.2 % FYM						
1.398						
I	0.655	0.568	0.492	0.572 \pm 0.0816	0.051	
II	0.384	0.361	0.231	0.325 \pm 0.0825	0.039	
III	0.208	0.185	0.159	0.184 \pm 0.0245	0.022	
Total					0.112	15.612
7.019						
I	3.695	3.522	3.551	3.589 \pm 0.0927	0.283	
II	1.608	1.251	1.397	1.419 \pm 0.1795	0.376	
III	0.888	0.712	0.751	0.784 \pm 0.0924	0.075	
Total					0.734	23.866
0.5 % FYM						
1.398						
I	0.474	0.494	0.507	0.492 \pm 0.0166	0.009	
II	0.326	0.299	0.328	0.318 \pm 0.0162	0.072	
III	0.191	0.170	0.176	0.179 \pm 0.0108	0.020	
Total					0.101	11.995
7.019						
I	3.436	3.330	3.486	3.417 \pm 0.0797	0.144	
II	1.103	1.132	1.317	1.184 \pm 0.1161	0.525	
III	0.788	0.782	0.751	0.774 \pm 0.0199	0.182	
Total					0.851	18.545

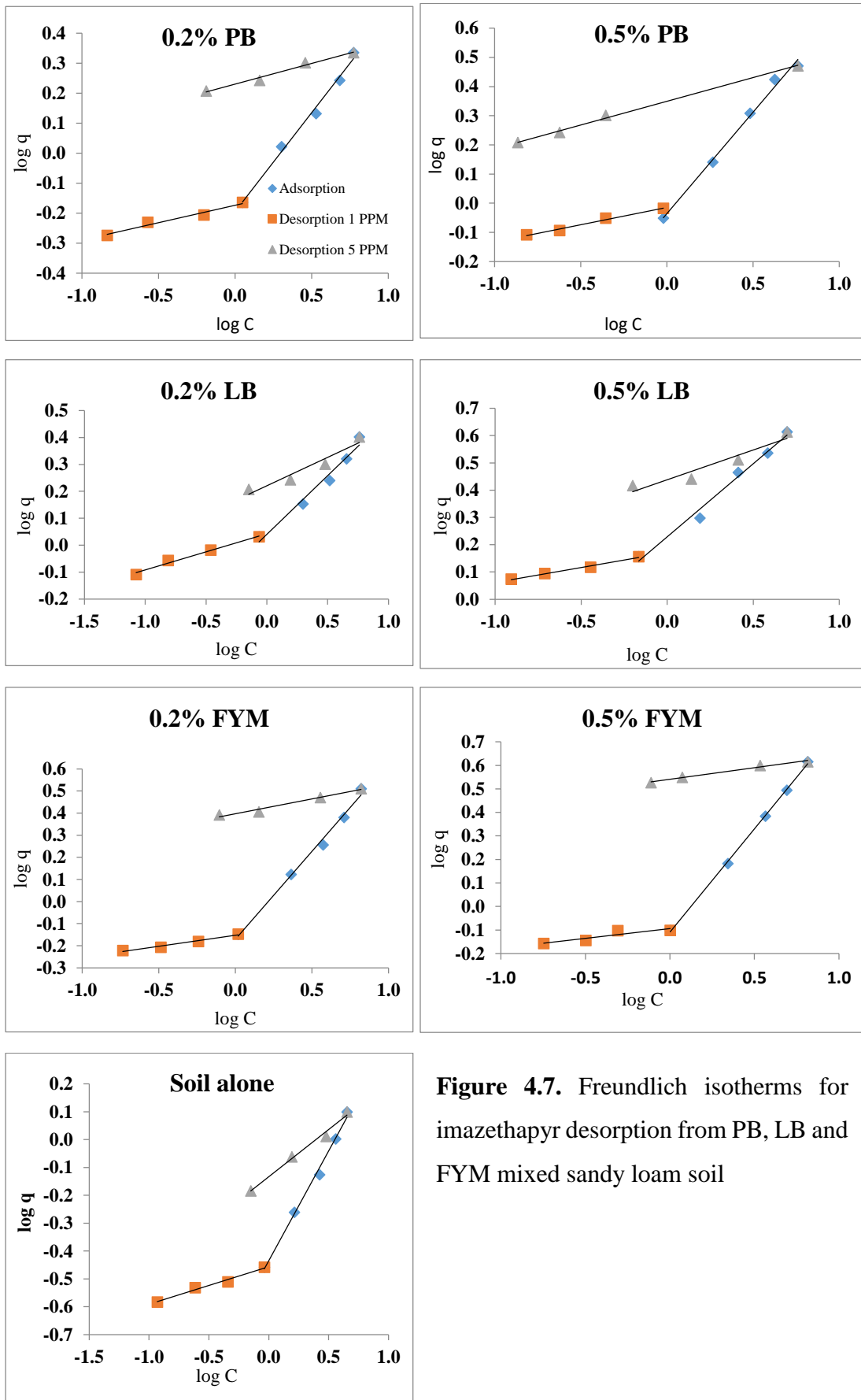


Figure 4.7. Freundlich isotherms for imazethapyr desorption from PB, LB and FYM mixed sandy loam soil

Table 4.14. Freundlich parameters for desorption of imazethapyr from the soil alone/*Parthenium* biochar (PB), *Lantana* biochar (LB) and farmyard manure (FYM) mixed sandy loam soil

Treatment		K_F	$1/n$	r^2_{Adj}	H	ΔG
Control	Lower	1.364	0.134	0.975	0.170	-1.040
	Higher	2.861	0.339	0.986	0.430	-1.349
0.2 % PB	Lower	1.489	0.116	0.962	0.176	-0.439
	Higher	1.698	0.138	0.976	0.210	-0.840
0.5 % PB	Lower	1.033	0.119	0.985	0.171	-0.036
	Higher	2.234	0.162	0.996	0.233	-0.885
0.2% LB	Lower	1.103	0.134	0.982	0.308	-0.109
	Higher	1.663	0.210	0.905	0.483	-0.568
0.5% LB	Lower	1.483	0.110	0.986	0.205	-0.440
	Higher	2.741	0.219	0.980	0.408	-1.526
0.2% FYM	Lower	1.424	0.099	0.974	0.125	-0.400
	Higher	2.496	0.134	0.964	0.169	-0.991
0.5% FYM	Lower	1.243	0.082	0.972	0.094	-0.246
	Higher	3.520	0.098	0.977	0.112	-1.423

H (Hysteresis)- $1/n_{des}/1/n_{ads}$; ΔG - Gibbs free energy (($KJK^{-1} mol^{-1}$))

The desorption data was fitted to the best fitted adsorption isotherm i.e. the Freundlich isotherm and graphs are presented in Figure 4.4 while adsorption constant are shown in Table 4.14. The K_F values for imazethapyr desorption in amendment mixed soil increased with increase in the level of amendment suggesting that lesser amounts of herbicide were desorbed at higher PB, LB and FYM amendment. The K_F values in any treatment were higher for desorption done at higher concentration than at lower concentration suggesting that net amount of imazethapyr remain sorbed was more at higher concentration. The Freundlich $1/n_{des}$, which is an indication for nonlinearity in the desorption isotherms, were lower than the $1/n_{ads}$ values and hysteresis (H) was observed. The ratio of slope of desorption and adsorption ($1/n_{des}$)/($1/n_{ads}$) gives hysteresis (H) constant. The value of $H < 1$ shows the rate of desorption is slower than the rate of adsorption (positive hysteresis) while, $H > 1$ confers rate of desorption is higher than rate of adsorption (negative hysteresis) (Pusino *et al.*, 2004). The H values varied from 0.170-0.430 for control soil where no

any amendments were used. Whereas, H values for 0.2% PB and 0.5% PB at lower and higher levels of imazethapyr ranged 0.176-0.210 and 0.171-0.233 respectively. However, the values of H for 0.2% and 0.5% LB at lower and higher herbicide levels ranged 0.176-0.210 and 0.171-0.233 respectively. Similarly, H values for 0.2% FYM and 0.5% FYM at lower and higher levels of imazethapyr ranged 0.125-0.169 and 0.094-0.112 respectively. Also on the basis of values of H it is concluded that sorption of imazethapyr follows the positive hysteresis in all amendments. Further, H values were more at the higher pesticide concentration than at the lower concentration suggesting that hysteresis was more at the higher pesticide concentration. The values of Gibb's free energy were negative for all the desorption treatments which indicates that desorption of imazethapyr are spontaneous in nature. Further, at higher concentration of herbicide negative values of ΔG increases indicating that with increase in the concentration degree of spontaneity increases i.e. ease to complete the work increases (Kumar *et al.* 2019).

4.5. Effect of biochars on leaching behavior of imazethapyr in soil

The effect of the *Parthenium* biochar (PB), *Lantana* biochar (LB) and farm yard manure (FYM) on leaching behavior of imazethapyr was studied in the packed columns (sandy loam soil – 30 cm length, 118 mm irrigation) (Tables 4.15 to 4.18). As imazethapyr showed very less adsorption on to all treatments, leaching was high (Sondhia, 2013). Leaching (breakthrough and cumulative) curves of imazethapyr in the control (no amendment), 0.2 and 0.5% each of PB, LB and FYM- mixed soil columns are shown in Figure 4.8. Results suggested that in all the columns breakthrough of imazethapyr was observed in 1st fraction of the leachate. It may be because of low adsorption in soils/soil-amendments (Sondhia, 2013). For control soil where no amendment was used, the maximum concentration of herbicide was observed in 152.090 mL (0.36 pore volume) fraction. Amendment of the 0.2% and 0.5% of PB to soil reduced leaching losses of imazethapyr and maximum concentration was observed in 101.070 mL (0.25 pore volume) and 103.075 mL (0.26 pore volume) respectively. Similarly, for 0.2% and 0.5% LB amended sandy loam soil column, maximum concentration was observed in 102.935 mL (0.27 pore volume) and 100.905 mL (0.25 pore volume) respectively. Similarly, for 0.2% and 0.5% FYM amended sandy loam soil packed soil, maximum amount of imazethapyr was observed

Table 4.15. Leachate parameters for imazethapyr from control sandy loam soil packed columns

Fraction	Control			
	Column A		Column B	
	Leachate (mL)	Imazethapyr (µg)	Leachate (mL)	Imazethapyr (µg)
1	50.54	3.065	51.05	4.919
2	51.36	4.574	50.57	4.553
3	49.29	6.833	51.37	6.655
4	54.47	4.961	42.98	4.962
5	54.00	4.626	52.33	4.651
6	60.43	3.901	48.62	4.538
7	17.68	4.736	33.67	3.407
Total	337.77	32.70	330.59	33.69

Table 4.16. Leachate parameters for imazethapyr from 0.2% and 0.5% each of PB sandy loam soil mixed packed columns

Fraction	0.2 % PB			
	Column A		Column B	
	Leachate (mL)	Imazethapyr (µg)	Leachate (mL)	Imazethapyr (µg)
1	49.18	2.050	50.36	2.150
2	49.75	6.041	52.85	6.060
3	50.49	4.674	49.98	4.318
4	50.07	3.654	49.97	3.620
5	51.34	2.692	49.97	2.609
6	48.66	2.082	45.94	2.085
7	20.22	1.865	56.45	1.870
Total	319.71	23.06	355.52	22.71
Fraction	0.5% PB			
	Column A		Column B	
	Leachate (mL)	Imazethapyr (µg)	Leachate (mL)	Imazethapyr (µg)
1	49.96	1.816	51.64	1.825
2	52.07	4.045	52.48	4.056
3	51.52	2.894	51.44	2.987
4	51.63	1.114	50.47	1.096
5	56.80	0.524	49.18	0.983
6	53.64	0.546	49.06	0.927
7	35.76	0.647	44.44	0.746
Total	351.38	11.59	348.71	12.62

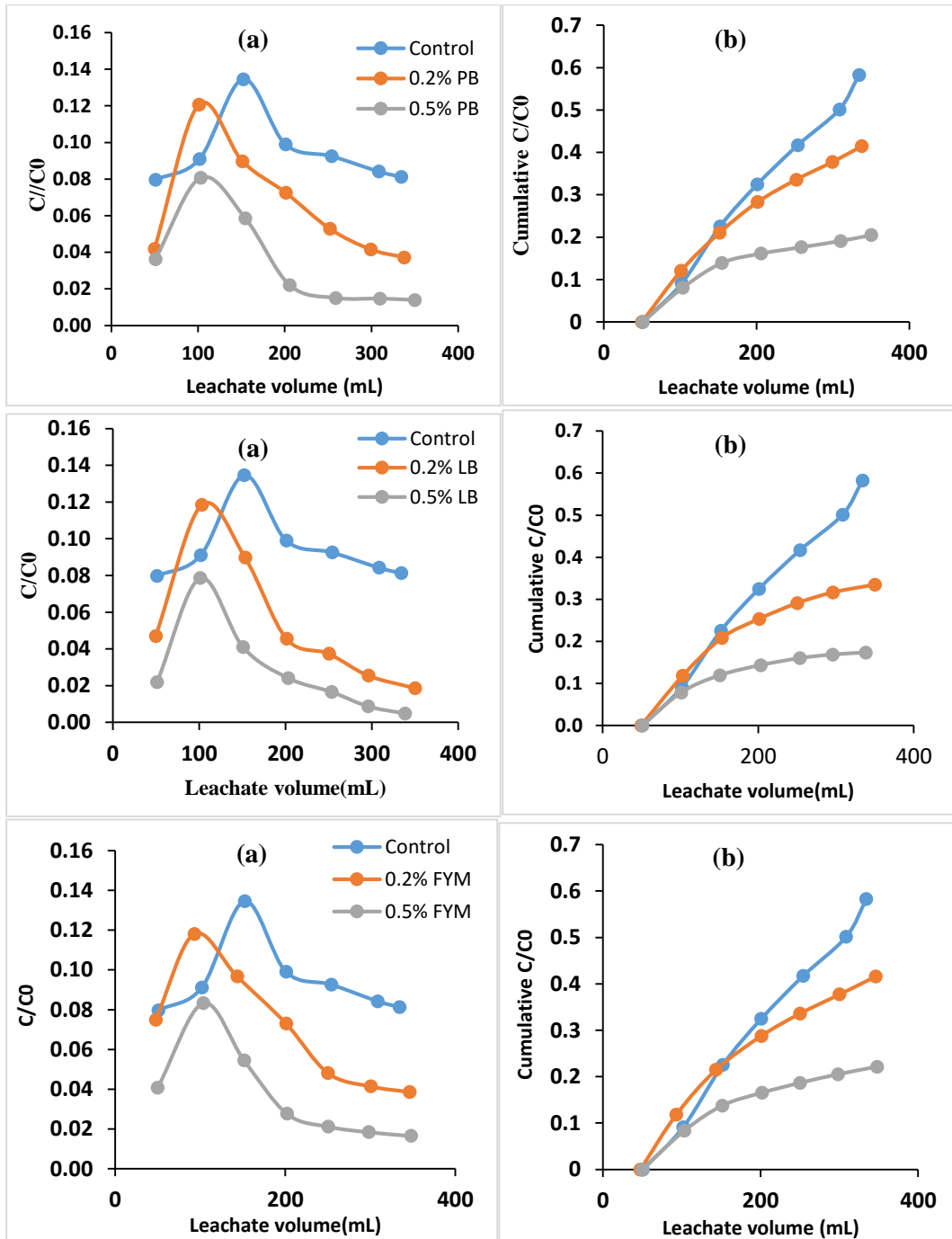


Figure 4.8. Imazethapyr breakthrough (a) and cumulative (b) leaching curves in control, *Pathenium* biochar (PB), *Lantana* biochar (LB) and farmyard manure (FYM) mixed sandy loam soil columns.

Table 4.17. Leachate parameters for imazethapyr from 0.2% and 0.5% each of LB mixed sandy loam soil packed columns

Fraction	0.2 % LB			
	Column A		Column B	
	Leachate (mL)	Imazethapyr (µg)	Leachate (mL)	Imazethapyr (µg)
1	48.68	2.154	50.34	2.548
2	50.93	5.984	55.92	5.886
3	49.04	4.542	51.47	4.456
4	47.33	2.012	48.93	2.546
5	49.16	1.886	48.58	1.859
6	41.37	1.058	50.09	1.491
7	62.38	0.910	45.80	0.955
Total	348.89	18.55	351.13	19.74
	0.5% LB			
1	50.55	1.084	51.40	1.106
2	49.14	3.986	50.72	3.885
3	48.78	2.102	50.75	2.002
4	54.12	1.156	50.56	1.256
5	50.98	0.827	49.53	0.831
6	35.02	0.429	49.49	0.440
7	52.48	0.245	32.90	0.234
Total	341.07	9.83	335.35	9.75

Table 4.18. Leachate parameters for imazethapyr from 0.2% and 0.5% each of FYM mixed sandy loam soil packed columns

Fraction	0.2 % FYM			
	Column A		Column B	
	Leachate (mL)	Imazethapyr (µg)	Leachate (mL)	Imazethapyr (µg)
1	47.06	3.654	47.84	3.856
2	46.47	5.846	44.52	5.992
3	50.63	4.895	50.37	4.796
4	47.78	3.620	67.21	3.697
5	48.78	2.256	49.33	2.569
6	49.96	2.023	50.57	2.123
7	59.12	1.912	32.35	1.956
Total	349.80	24.21	342.19	24.99

0.5% FYM				
1	50.16	2.025	49.35	2.056
2	50.30	4.159	56.76	4.186
3	48.22	2.559	48.38	2.896
4	49.24	1.557	51.50	1.213
5	48.95	0.998	47.56	1.125
6	48.11	0.856	47.72	0.986
7	50.24	0.668	49.31	0.986
Total	345.22	12.82	350.58	13.45

in 92.945mL (0.23 pore volume) and 103.285 mL (0.27 pore volume) respectively. Further, the PB, LB and FYM amendments reduced the maximum concentration (C/C_0) of imazethapyr in the leachate. The values of maximum concentration (C/C_0) of imazethapyr in control, 0.2% and 0.5% each of PB, LB and FYM were 0.583, 0.415, 0.205, 0.335, 0.174, 0.416 and 0.221 respectively. However, downward mobility behavior of imazethapyr in soil was well explained by the partition coefficient (K_d) values which are higher in the LB mixtures. Sondia, 2013 also found similar results for leaching of imazethapyr and she concluded that it is highly leachable and can leach below 70 cm of columns.

4.6. Effect of biochar on dissipation of imazethapyr

Soil physico-chemical properties such as soil type, pH, moisture status, organic carbon content, biological parameters such as microorganism's nature etc. and intentional and unintentional addition of external materials affect the fate of soil applied pesticides. Joseph *et al.* (2010) reported that soil amendments affect some basic reactions *viz.* adsorption-desorption, dissolution-precipitation, redox reaction and acid-base reactions, that affect fate of soil applied herbicide or xenobiotics.

Effect of *Parthenium* biochar (PB), *Lantana* biochar (LB) and farm yard manure (FYM) on dissipation of imazethapyr was studied in the sandy loam soil under laboratory condition. Soil was mixed with 0.2 and 0.5% each of PB, LB and FYM and soil without any amendment served as control. Study was performed under 60% water holding capacity (field capacity) at 27 ± 2 °C. Table 4.19 to 4.22 represents persistence of imazethapyr in sandy loam soil with different amendment conditions. Results suggested that herbicide was slightly persistent in nature and degraded at relatively

Table 4.19. Persistence of imazethapyr in sandy loam soil alone

Incubation (Days)	Soil alone			
	R1	R2	R3	Mean±SD (%remained)
0	2.20	2.20	2.20	2.20±0.000 (100.00)
2	1.82	1.83	1.85	1.83±0.012 (83.23)
4	1.72	1.72	1.76	1.73±0.021 (78.71)
8	1.32	1.34	1.36	1.34±0.02 (60.97)
16	1.07	1.02	1.03	1.04±0.026 (47.40)
24	0.81	0.85	0.80	0.82±0.028 (37.38)

Table 4.20. Persistence of imazethapyr in *Parthenium* biochar (PB) mixed sandy loam soil

Incubation (Days)	0.2 % PB				0.5 % PB			
	R1	R2	R3	Mean±SD (% remained)	R1	R2	R3	Mean±SD (% remained)
0	2.34	2.34	2.34	2.34±0.000 (100.00)	2.34	2.34	2.34	2.34±0.00 (100.00)
2	2.03	2.08	2.05	2.056±0.026 (87.76)	1.84	1.82	1.83	1.83±0.01 (78.22)
4	1.71	1.77	1.79	1.76±0.037 (74.93)	1.64	1.65	1.66	1.65±0.01 (70.47)
8	1.32	1.34	1.32	1.33±0.014 (56.59)	1.12	1.11	1.16	1.13±0.023 (48.24)
16	0.96	0.90	0.94	0.94±0.030 (39.99)	0.71	0.73	0.80	0.74±0.045 (31.70)
24	0.54	0.52	0.55	0.54±0.017 (23.03)	0.40	0.45	0.49	0.45±0.046 (19.18)

Table 4.21. Persistence of imazethapyr in *Lantana* biochar (PB) mixed sandy loam soil

Incubation (Days)	0.2 % LB				0.5 % LB			
	R1	R2	R3	Mean±SD (%remained)	R1	R2	R3	Mean±SD (%remained)
0	1.89	1.89	1.89	1.89±0.00 (100.00)	1.89	1.89	1.89	1.89±0.00 (100.00)
2	1.54	1.55	1.59	1.56±0.029 (82.55)	1.43	1.45	1.48	1.45±0.028 (76.82)
4	1.29	1.25	1.20	1.24±0.043 (65.91)	1.10	1.15	1.11	1.12±0.029 (59.28)
8	0.97	0.94	0.97	0.96±0.012 (50.71)	0.87	0.88	0.85	0.86±0.018 (45.69)
16	0.67	0.65	0.72	0.68±0.035 (35.84)	0.42	0.44	0.45	0.44±0.015 (23.13)
24	0.52	0.51	0.54	0.52±0.017 (27.76)	0.35	0.35	0.33	0.34±0.009 (18.12)

Table 4.22. Persistence of imazethapyr in FYM biochar (PB) mixed sandy loam soil

Incubation (Days)	0.2 % FYM				0.5 % FYM			
	R1	R2	R3	Mean±SD (%remained)	R1	R2	R3	Mean±SD (%remained)
0	1.89	1.89	1.89	1.89±0.00 (100.00)	1.89	1.89	1.89	1.89±0.00 (100.00)
2	1.45	1.48	1.45	1.46±0.02 (77.22)	1.34	0.93	1.15	1.14±0.21 (60.25)
4	1.23	1.10	1.12	1.15±0.04 (60.66)	0.80	1.06	1.20	1.02±0.20 (53.83)
8	0.92	0.90	0.99	0.94±0.07 (49.52)	0.95	0.72	0.86	0.84±0.12 (44.54)
16	0.77	0.67	0.63	0.69±0.07 (36.24)	0.66	0.52	0.56	0.58±0.07 (30.64)
24	0.42	0.40	0.40	0.40±0.01 (21.47)	0.34	0.34	0.35	0.34±0.01 (18.09)

faster rate in the sandy loam soil. After 24 days of incubation 37.38% of herbicide was recovered from control soil. Whereas, 23.03% and 19.18% of imazethapyr were recovered from 0.2% and 0.5% PB mixed sandy loam soil. Similarly, from 0.2% & 0.5% each of LB and FYM mixed sandy loam soil 27.76% 18.12%, 21.47% and 18.09% herbicide were recovered respectively.

The data of degradation from all the treatments combinations were fitted to the first order kinetic equation:

$$C_t = C_0 e^{-K_{obs}t}$$

where, C_0 is the apparent initial concentration of imazethapyr ($\mu\text{g g}^{-1}$), C_t is the concentration ($\mu\text{g g}^{-1}$) after a lapse of time t (days), and K_{obs} is the observed degradation rate constant. The half-life ($t_{1/2}$) for dissipation of herbicide were calculated from the K_{obs} value using following formula:

$$t_{1/2} = \left(\frac{0.693}{K_{obs}} \right)$$

Table 4.23. Degradation constants (K_{obs}) and half-life ($t_{1/2}$) values for imazethapyr in control and *Parthenium* biochar (PB), *Lantana* biochar (LB) and FYM mixed sandy loam soil

Treatment	k_{obs}	r²_{Adj}	T_{1/2}(Days)
Control	0.040	0.967	17.325
0.2 % PB	0.059	0.992	11.746
0.5 % PB	0.067	0.987	10.340
0.2 % LB	0.052	0.946	13.327
0.5 % LB	0.071	0.955	9.760
0.2 % FYM	0.059	0.963	11.745
0.5 % FYM	0.062	0.931	11.177

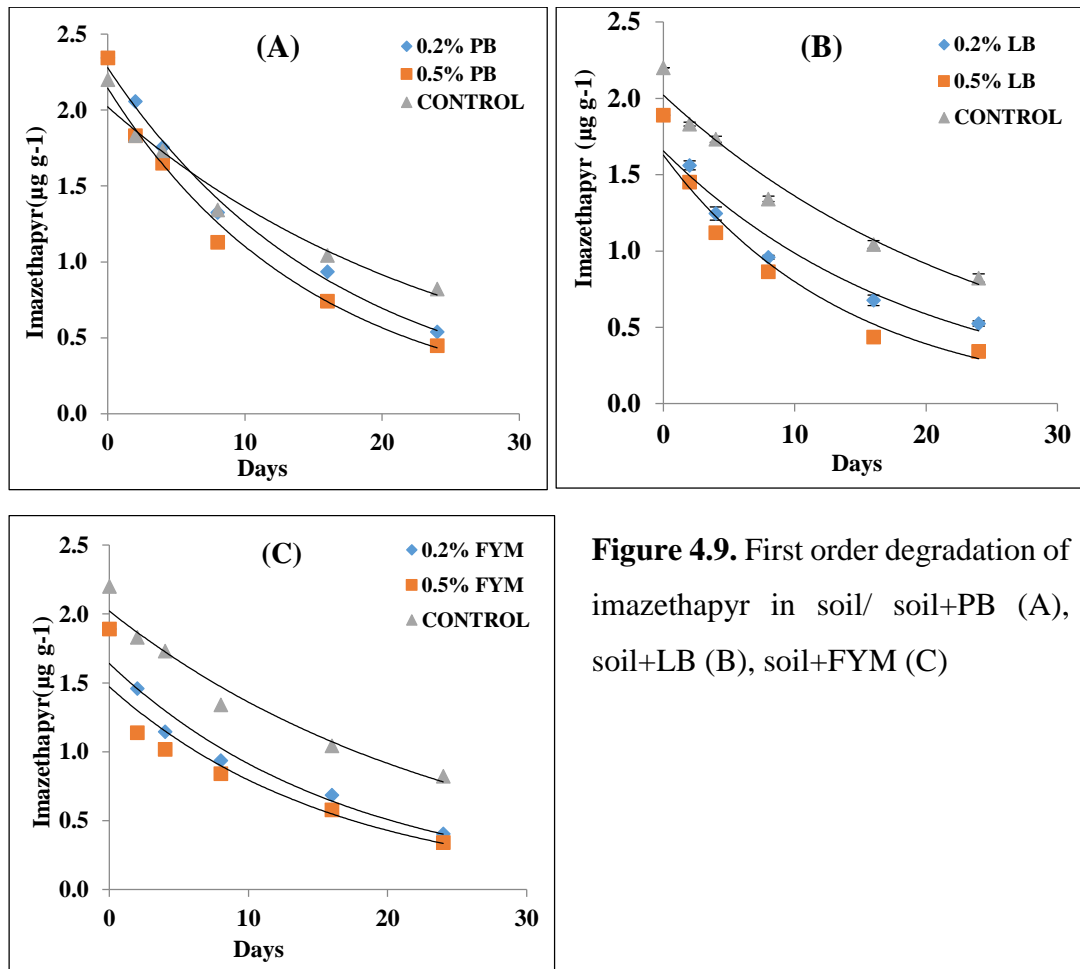


Figure 4.9. First order degradation of imazethapyr in soil/ soil+PB (A), soil+LB (B), soil+FYM (C)

The imazethapyr persistence data were best fitted to the first order degradation equation as r^2_{Adj} (Table 4.23, Figure 4.9) were higher than 0.9 for most of the cases. The half-life ($t_{1/2}$) values for imazethapyr degradation in the control (no amendment) sandy loam soil under was 17.325 days. The values of half-life ($t_{1/2}$) in 0.2% and 0.5% PB amended sandy loam soil were 11.746 and 10.340 days respectively. Similarly, the values of half-life ($t_{1/2}$) in 0.2% and 0.5% LB amended sandy loam soil were 13.327 and 9.760 days respectively. However, the values were 11.745 and 11.177 days for half-life ($t_{1/2}$) in 0.2% and 0.5% FYM amended sandy loam soil respectively. Fastest degradation was shown in LB amended soil as compared to other amendments. It may be due to higher pH and presence of indigenous microorganisms present in soils. (Kaur & Kaur, 2021; Goetz *et al.* 1990).

5. SUMMARY AND CONCLUSIONS

After green revolution use of pesticide has increased many folds. Injudicious use of such chemicals leads to environmental toxicity. After application of such chemicals, they get distributed in various components of environment via sorption, degradation, translocation volatilization and leaching. Physico-chemical properties of soil and herbicide, along with climatic drivers, influence the participation of the pesticide in the environment. To cope up with such issues with imazethapyr, an herbicide mostly used for pulse production and has harmful effect to non-target biotic and abiotic ecosystems, present study deals with its fate in the environment and further amendment with *Parthenium* & *Lantana* biochar and farm yard manure (FYM) on its fate under laboratory conditions.

Preparation of biochar with *Parthenium* & *Lantana* (an obnoxious weed) through pit method resulted in biochar with considerable amount of unburnt carbon, have exhibited high potential to adsorb chemicals. (Majumdar and Singh, 2007; Ghosh and Singh, 2013; Deokar *et al.*, 2016 a, b); therefore, might affect physical, chemical and biological detoxification of herbicides towards weed control (Singh *et al.*, 2013a, b; Ghosh *et al.*, 2016).

According to ICRISAT Happenings Newsletter 2022 production of pulses was increased from 13.38 million metric tons in 2005-06 to 25.58 million metric tons in 2020-21. (ICRISAT, 2022). This leads to increase in the use of pesticides that includes one of the herbicide imazethapyr to many folds. Imazethapyr is an imidazolinone group of herbicide which is widely used for control of grasses and broadleaf weeds in a variety of crops and is registered in many countries. Practically, no information is available on the effect of *Parthenium* & *Lantana* biochar and farm yard manure (FYM) on the fate of imazethapyr. Therefore, a study entitled “**Effects of biochar on fate of imazethapyr in sandy loam soil**” was conducted.

The PB, LB and FYM differed in their physico-chemical properties. In general, biochar contained a significant amount of unburnt carbon, alkaline in nature and high

cation exchange capacity. Whereas FYM contains almost half of carbon content as compared to biochars and are almost neutral in nature.

The kinetics of imazethapyr adsorption in 0.2% and 0.5% each of PB, LB and FYM mixed sandy loam soil was studied. The pseudo second order model best explained imazethapyr adsorption on to PB/LB/FYM amended sandy loam soil, suggesting that rate of adsorption was more dependent on the availability of the adsorption sites than on the concentration of the imazethapyr in solution. The intra particle diffusion graph had not passed through the origin indicating that the intraparticle diffusion was not only the rate determining step but boundary layer diffusion also might have played a role in the adsorption to some degree.

The sorption of imazethapyr in 0.2% and 0.5% each of PB, LB and FYM mixed sandy loam soil was studied. Results reveals that herbicide was more sorbed to LB. The sequence for sorption of imazethapyr in amended soil are soil alone < FYM < PB < LB mixed sandy loam soil with varied rate of amendments. Imazethapyr adsorption in the soil/soil + amendment mixtures was well explained through Freundlich adsorption isotherm and adsorption was highly nonlinear. The $1/n$ values for sandy loam soil alone was 0.789, whereas it was varied between 0.658 and 0.696 (0.2% & 0.5% PB mixed sandy loam soil) or 0.435 and 0.537 (0.2% & 0.5% LB mixed sandy loam soil) or 0.795 and 0.877 (0.2% & 0.5% FYM mixed sandy loam soil). Both adsorption and desorption parameters correlated well with the amendments content in soil.

The leaching of imazethapyr in 0.2% and 0.5% each of PB, LB and FYM mixed sandy loam soil was studied. Due to lesser sorption of onto the soils/soil+amendments, imazethapyr was more mobile in all treatments and was detected in the leachate. Addition of the amendments reduced the leaching losses and effect was more in the LB mixed sandy loam soil as compared to sandy loam soil alone and PB and FYM amended sandy loam soil.

The degradation of imazethapyr in 0.2% and 0.5% each of PB, LB and FYM mixed sandy loam soil was studied. Degradation of imazethapyr was fastest in LB

amended sandy loam soil as compared to sandy loam soil alone and PB and FYM amended sandy loam soil.

The present study suggested that addition of amendments (PB, LB and FYM) greatly affected behavior of imazethapyr in soil. The biochars increased adsorption, reduced leaching and increased degradation of imazethapyr. However, these effects varied with nature and dose of amendment and soil type. These findings are relevant in assessing the fate of imazethapyr applied in fields where there are *Parthenium* and *Lantana* weeds and farmers practices burning of it and ploughing into soil.

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ABSTRACT


Imazethapyr is a common herbicide mostly used in pulses and during seed production of berseem. *Parthenium historophorous* and *Lantana camara* are obnoxious weeds which are found everywhere inside and also outside of the cropped area. The preparation of biochar from them and adding into the soil will results in change in the physico-chemical properties of soil as they are alkaline in nature and contain considerable portion of unburnt carbon. Biochars have exhibited potential to adsorb pesticides; therefore might affect chemical and biological degradation and bioefficacy of herbicide. Therefore, the present study summarizes the effect of *Parthenium* biochar (PB), *Lantana* biochar (LB) and farmyard manure (FYM) on the adsorption, leaching and degradation behavior of imazethapyr in the sandy loam soil.


The PB, LB and FYM were characterized for their physico-chemical properties and adsorption of imazethapyr from soil/biochar/FYM mixed soil was evaluated. Kinetics study suggested that the pseudo second order model best explained the imazethapyr adsorption on all three amendments. Imazethapyr was sorbed onto the amendments in the order of FYM (5.80-28.32%) < PB (13.10-27.08%) < LB (17.97-51.21%). The Freundlich isotherms were the best models to predict imazethapyr adsorption onto the biochars and FYM.

The amendments (PB, LB and FYM) affected downward mobility of imazethapyr in soil, but effect varied with varied level of amendment. Compared to FYM and PB, herbicide was least leached in LB amended sandy loam soil. Higher herbicide adsorption in biochar mixed soil contributed to their reduced leaching/downward mobility.

Amendments (PB, LB and FYM) affected imazethapyr degradation also but its effect varied with varied level of amendment. Highest degradation of imazethapyr was shown in LB ($t_{1/2}$ - 9.76-13.32 days) followed by PB ($t_{1/2}$ - 10.34-11.75 days) and FYM ($t_{1/2}$ - 11.18-11.75 days). The amendment enhanced imazethapyr degradation at both levels. These findings are relevant in assessing the fate of imazethapyr applied in soil.

Keywords: Imazethapyr, *Parthenium* biochar, *Lantana* biochar, Farm yard manure, Sorption, Degradation, Leaching


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शोध शीर्षक : रेतीली दोमट मृदा में इमाजेथापायर के हथ पर बायोचार का प्रभाव

सारांश

इमाजेथापायर एक आम शाकनाशी है जिसका उपयोग ज्यादातर दालों में और बरसीम के बीज उत्पादन के दौरान किया जाता है। पार्थेनियम हिस्टोरोफोरस और लैंटाना कैमरा हानिकारक खरपतवार हैं जो फसली क्षेत्र के अंदर और बाहर हर जगह पाए जाते हैं। इनसे बायोचार तैयार करके मिट्टी में मिलाने से मिट्टी के भौतिक-रासायनिक गुणों में परिवर्तन होता है क्योंकि ये प्रकृति में क्षारीय होते हैं और इनमें बिना जले कार्बन का काफी हिस्सा होता है। बायोचार नाशीजीवनाशियों के अधिशोषण की उच्च क्षमता दर्शाता है। ये शाकनाशी की रासायनिक और जैविक निम्नीकरण और जैव-प्रभाविता को प्रभावित कर सकता है। इसलिए, वर्तमान अध्ययन रेतीले दोमट मिट्टी में इमेजेथापायर के शोषण, क्षरण और निम्नीकरण व्यवहार पर पार्थेनियम बायोचार (पी बी), लैंटाना बायोचार (एल बी) और फार्मयार्ड खाद (एफ वाई एम) के प्रभाव को प्रस्तुत करता है।

पी बी, एल बी और एफ वाई एम के भौतिक-रासायनिक गुणों के लिए उनका अभिलक्षण किया गया है और मिट्टी/बायोचार/एफ वाई एम मिश्रित मिट्टी से इमेजेथापायर के शोषण-व्यवहार का मूल्यांकन किया गया। गतिकी संबंधी अध्ययन से सुझाव मिलता है कि पीएसओ मॉडल, तीनों प्रकार के संशोधनों पर इमेजेथापायर - शोषण की सर्वोत्तम ढंग से व्याख्या करता है। इमाजेथापायर को एफ वाई एम (5.80-28.32%) < पी बी (13.10-27.08%) < एल बी (17.97-51.21%) के क्रम में संशोधनों में शामिल किया गया। बायोचार और एफ वाई एम पर इमाजेथापायर अधिशोषण के पूर्वानुमान हेतु फ्रैडलिक समताप सर्वश्रेष्ठ मॉडल था।

संशोधनों (पी बी, एल बी और एफ वाई एम) ने मिट्टी में इमेजेथापायर की नीचे की ओर गतिशीलता को प्रभावित किया, लेकिन विभिन्न स्तरों के संशोधन के साथ प्रभाव अलग-अलग था। एफ वाई एम और पी बी की तुलना में, एल बी मिश्रित रेतीली दोमट मिट्टी में शाकनाशी का क्षरण कम पाया गया। एल बी बायोचार मिश्रित मिट्टी में उच्च शाकनाशी अधिशोषण से, शाकनाशी के क्षरण में कमी पायी गयी।

संशोधनों (पी बी, एल बी और एफ वाई एम) ने इमेजेथापायर निम्नीकरण को भी प्रभावित किया लेकिन इसका प्रभाव विभिन्न स्तरों के संशोधन के साथ अलग-अलग था। इमाजेथापायर का उच्चतम निम्नीकरण एलबी (t1/2- 9.76-13.32 दिन) में दिखा, इसके बाद पी बी (t1/2- 10.34-11.75 दिन) और एफ वाई एम (t1/2- 11.18-11.75 दिन) में दिखा। संशोधन ने दोनों स्तरों पर इमाजेथापायर गिरावट को बढ़ाया। ये परिणाम, मिट्टी में अनुप्रयुक्त इमाजेथापायर के हथ का आकलन करने में उपयोगी हैं।

डॉ. अनुप कुमार

सलाहकार

ममता

ममता कसवा

शोधकर्ता

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PAR DIVISION

ICAR-IGFRI, JHANSI

Dr. Anup Kumar

Chromatogram Info:

File Name	: D:\YLClarity\Pesticides\Data\IMAZE STD 1PPM R1_10_24_2011 9_10_26 AM_312.PRM	File Created	: 10/24/2011 9:14:29 AM
Origin	: Acquired, Acquisition started 10/24/2011 9:10:26 AM	Acquired Date	: 10/24/2011 9:14:28 AM
Project	: D:\YLClarity\Projects\Pesticides.PRJ	By	: ANUP

Printed Version Info:

Printed Version	: 4/22/2022 3:58:24 PM Recent (Linked Calibration)	Printed Date	: 7/27/2022 11:39:01 AM
Report Style	: D:\YLClarity\Common\Chromatogram.sty	By	: ANUP
Calibration File	: D:\YLClarity\Pesticides\Calib\IMAZETHYPR.CAL		

Sample Info:

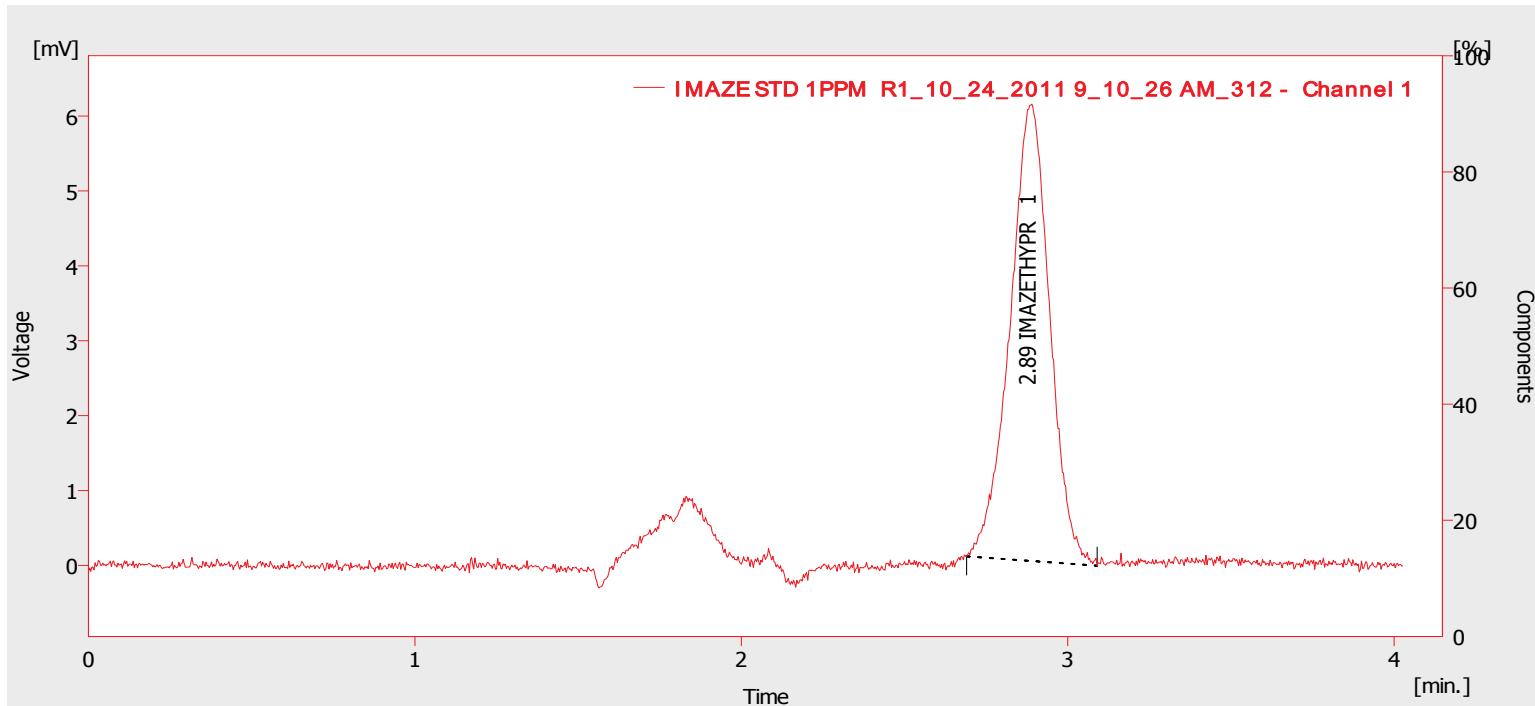
Sample ID	: IMAZE STD 1PPM R1	Amount [ppm]	: 20
Sample	:	ISTD Amount	: 0
Inj. Volume [mL]	: 0.02	Dilution	: 1

Method	: IMAZETHAPYR	By	: ANUP
Description	:		
Created	: 8/27/2021 6:28 PM	Modified	: 4/22/2022 3:58 PM

Column	:	Detection	:
Mobile Phase	:	Temperature	:
Flow Rate	:	Pressure	:
Note	:		

Autostop	: 4.00 min	External Start	: Start Only, Down
Detector 1	: Channel 1	Range 1	: Bipolar, 5000 mV, 5 Samp. per Sec.
Subtraction Chromatogram	: (None)	Matching	: No Change

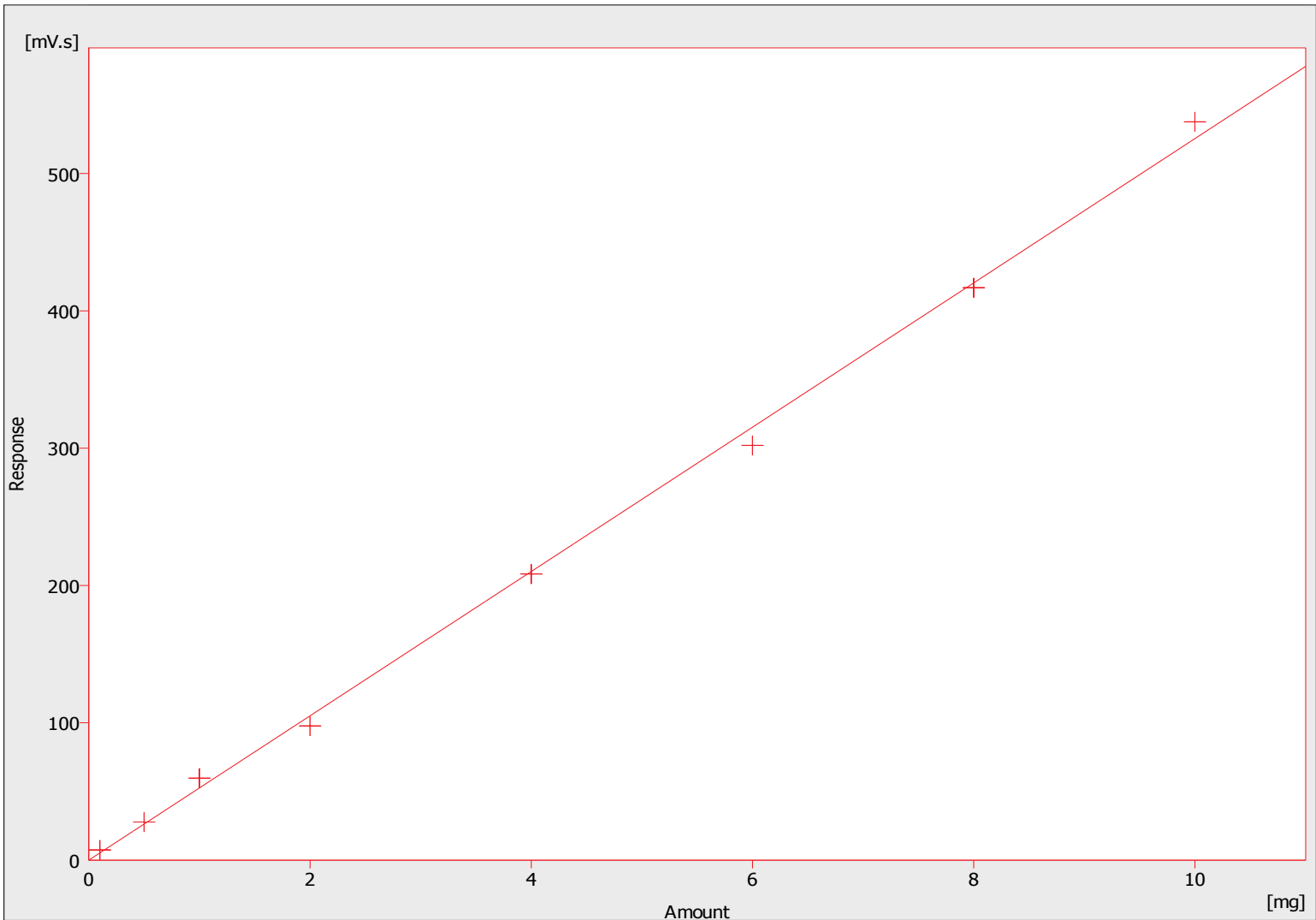
Base	: Area	Calibration File	: IMAZETHYPR	Calculation	: ESTD
Scale Factor	: Not Used	Units After Scaling	: Not Used	Uncal. Response	: 0
Unretained Time	: 0.00 min	Column Length	: 50.00 mm	Column Calc.	: From Width at 50% of Height
Result Table Reports	: All Peaks	Hide ISTD Peak	: Enabled		



IMAZETHYPR - Signal 1 - 2.847 min.

Peak Type : Ordnr
 Is or Uses ISTD : Is ISTD5
 Left Window : 0.2 min.
 Right Window : 0.2 min.
 Response Base : Area
 Curve Fit Type : Linear
 Origin : Curve from Zero
 Weighting Method : None
 Subst. Equation : $Y = 52.54742 * X$
 Correlation Coef. : 0.9992642
 Residuum : 7.09305 [mV.s]
 Linearisation X : None
 Linearisation Y : None

	Response	Amount	Resp. Factor	Rec No.	Used
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2	27.6804	0.5000	0.0181	1	<input checked="" type="checkbox"/>
3	59.6747	1.0000	0.0168	1	<input checked="" type="checkbox"/>
4	97.6701	2.0000	0.0205	1	<input checked="" type="checkbox"/>
5	208.3542	4.0000	0.0192	1	<input checked="" type="checkbox"/>
6	302.0198	6.0000	0.0199	1	<input checked="" type="checkbox"/>
7	416.8517	8.0000	0.0192	1	<input checked="" type="checkbox"/>
8	537.6703	10.0000	0.0186	1	<input checked="" type="checkbox"/>
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Academic Qualification

Degree	Board/University	Institution/School	Year of Passing	Percentage
M.Sc.(Agri.) Soil Science & Ag. Chemistry	RLBCAU, Jhansi	College of Agriculture	2022	88.10%
B.Sc. (Hons.) Agriculture	SKNAU, Jobner	College of Agriculture Kumher , Bharatpur	2020	72.50 %
Intermediate/10+2	BSER Ajmer	Deep Bal Bharti Sr. Sec.School Bhainsawa, Jaipur	2016	83.40 %
High School/10 th	BSER Ajmer	Shri Laxmi Vidhya Peeth Sr. SS, Jhamri Talai Pachar,Jaipur	2014	77.33 %

DECLARATION

I do hereby declare that all information given above is true to the best of my knowledge and belief.

Place: Jhansi

Your truly
Mamta
Mamta Kaswa