BEHAVIOUR OF PESTICIDES IN AGRICULTURAL SOILS: ASSESSMENT AND BIOCHAR-BASED CONTROL APPROACH

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Prasanta Majee

Dedicated to my parents

Abstract

The World Health Organization defines pesticides as chemical substances used to prevent, destroy, or mitigate pests, including vectors of disease and unwanted species harmful to food production and other commodities. While pesticides are crucial in modern agriculture for protecting crops and enhancing food production, their overuse can harm human health, the environment, and non-target species. Pesticide use raises environmental risks, especially regarding groundwater and surface water contamination. This necessitates a thorough understanding of pesticide behaviour in agricultural lands to address human health and environmental sustainability. Sorption characteristics of organic chemicals vary with location, influenced by factors like clay content, organic matter, and microbial presence. Understanding these characteristics is vital for developing effective remediation measures and pesticide management strategies.

In the specific context of Telangana state, where pesticide usage has increased dramatically in recent years, there is a heightened risk of groundwater contamination with persistent organic pollutants. Imidacloprid and Atrazine are the two majorly used pesticides in this region. Therefore, this research aims to investigate the sorption, desorption, and leachability of widely used pesticides in the black cotton soils and red soil of the Telangana region. The objective is to provide a comprehensive assessment of the potential risks associated with groundwater pollution from these pesticides, offering valuable insights for tailored environmental management.

Additionally, the study seeks to explore the efficacy of biochar derived from locally available cotton stalks in enhancing pesticide sorption. This aspect of the research is essential for developing targeted remedial measures against pesticide pollution and implementing effective pesticide management practices specifically tailored to the unique characteristics of the Telangana region. By shedding light on the sorption, desorption, and leaching behaviour of Imidacloprid and Atrazine, this research aims to empower policymakers with the knowledge necessary to formulate targeted strategies for environmental conservation and sustainable agricultural practices, thereby ensuring a harmonious balance between agricultural productivity and environmental preservation.

The first phase of the study assesses the sorption desorption behaviour of insecticide Imidacloprid and herbicide Atrazine in four different agricultural soils (BC-1, BC-2, BC-3, RS) of Telangana region. The study reported that both the pesticides were weakly sorbed on the investigated soils. The sorption kinetics for both the pesticides were observed to occur in two stages- the quick initial adsorption stage, where 90% of the pesticide's adsorption capacity reached within first few hours due to the rapid filling of empty spaces in soil particles, and the slow equilibrium stage. Pseudo second order kinetic model demonstrated the best fit to the experimental data. Analysis of isotherm models indicated that the Freundlich isotherm model provided the best fit compared to Langmuir or Temkin isotherm models. Among the soil samples, BC-2 soil exhibited the highest Freundlich coefficient value (K_f), followed by BC-3, BC-1, and red soil. A strong positive correlation ($r>0.9$) was observed between clay content and the K_f value, indicating that clay content significantly influences Imidacloprid adsorption to the soil. Interestingly, despite having a higher organic carbon content (0.57%), red soil showed a lower affinity for Imidacloprid compared to other soils, possibly due to the relatively low quantity of organic carbon present. Both temperature and pH exert significant influences on the sorption behaviour of Imidacloprid in the examined soils. As temperature rises, the sorption of Imidacloprid decreases, possibly due to increased solubility at higher temperatures. Additionally, lower pH levels demonstrate favourable conditions for sorption, as they facilitate the protonation of the solution, thereby increasing the cationic charge of the pesticide molecules.

The second phase of the study focused on the degradation of Imidacloprid and Atrazine in soil to assess their persistence. The study reported that the half-life of Imidacloprid ranged from 67 to 83 days in the investigated soils, whereas the half-life of Atrazine ranged from 44 to 57 days. Imidacloprid showed greater persistence in the investigated soils compared to Atrazine. The Groundwater Ubiquity Score (GUS) index is employed to evaluate the leachability of pesticides in the soils under investigation. This screening method utilizes the K_{OC} value and half-life ($T_{1/2}$, days) of pesticides to assess the probability of groundwater contamination. The GUS values for Imidacloprid ranged from 2.25 to 2.62 in black cotton soils, while in red soil, it was reported as 3.72. For Atrazine, GUS values ranged from 2.01 to 2.41 in black cotton soils, and in red soil, it was 3.16. GUS values falling between 1.8 and 2.8 in all black cotton soils suggest that both pesticides fall into the potentially mobile category. However, in red soil, where the values exceeded 2.8 for both pesticides, they are considered highly mobile. The results of the soil column leaching study corroborated these findings, as both Imidacloprid and Atrazine were

detected in the leachate sample and migrated to the deeper sections of the column. The presence of pesticides in the deeper layer of the soil matrix could make the pesticides more persistent due to the absence of microorganisms, ultimately leading to groundwater contamination.

The final phase of the study investigated the efficacy of cotton stalk biochar as soil amendments to improve pesticide sorption capacity in soils and reduce the mobility. The results indicate that the introduction of 0.5% and 1% cotton biochar (CBC) into the soil significantly enhanced the K_f values of Imidacloprid and Atrazine sorption across all the examined soils. The improved sorption capacity is a direct outcome of the augmented surface area and additional sorption sites resulting from the addition of CBC to the soil. Pesticide degradation study in biochar amended soils revealed that the addition of biochar to the soil had a slight effect on the half-life of Imidacloprid and Atrazine, with all cases showing a modest increase. With the incorporation of biochar, GUS values notably declined, falling below the threshold of 1.8 suggests a significant reduction in the mobility of both Imidacloprid and Atrazine within the investigated soils. The soil column leaching study revealed that biochar amended soil can retain pesticides in the top layers of the soil matrix for both Imidacloprid and Atrazine.

Overall, it can be concluded from the findings of the present study that the sorption capacity of both Imidacloprid and Atrazine was notably low in all three black cotton soils and red soil. Clay content, temperature and pH was identified as the primary factor influencing pesticide sorption, while soil organic matter showed a negative correlation with the sorption coefficient due to its limited availability in the soil. Imidacloprid's prolonged half-life compared to Atrazine indicates its greater persistence in all investigated soils. The calculated GUS value categorized both Atrazine and Imidacloprid as falling within the highly mobile to mobile category, highlighting the region’s vulnerability to groundwater contamination from pesticides. The study underscored the high susceptibility of groundwater in this specific area of the Telangana region to contamination, emphasizing the urgent need for proactive measures to prevent potential catastrophes. The incorporation of cotton stalk biochar into the soils emerged as a promising strategy to mitigate the leaching potential of both pesticides, offering a potential solution to reduce environmental risks associated with pesticide use.

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Chapter 1

Introduction

1.1 General

A pesticide refers to a substance or combination of substances designed to prevent, eradicate, or manage pests, including vectors of human or animal diseases, and unwanted plant or animal species that cause harm or interfere with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products, or animal feedstuffs. Additionally, pesticides may be administered to animals to control insects, arachnids, or other pests on or within their bodies (FAO, 2006). Essentially, pesticides function as plant protection products.

Pesticides offer several benefits in crop management, such as preserving yields and materials and reducing the incidence of pests and diseases by controlling harmful phytopathogens (Özkara et al., 2016). In India, an agriculture-centric economy, the widespread use of chemical pesticides has been encouraged to mitigate losses caused by various insects and weeds. Estimates indicate that approximately 40% of crops in developing countries are destroyed by insects, weeds, and diseases while still in the fields (Aktar et al., 2009). Pesticides are perceived as instrumental in enhancing agricultural output, becoming an integral part of cultivation practices.

The use of agrochemicals has substantially increased in recent decades for intensive agriculture, encompassing organophosphorus, organochlorine, carbamate, triazenes, and other chemicals based on their structural composition. Farmers favour these chemicals for their effectiveness in protecting crops against insects or weeds, leading to increased yields. However, due to insufficient knowledge regarding proper pesticide management and the adverse environmental impacts of these substances, farmers often apply more than necessary. This excessive use results in detrimental effects on groundwater quality and soil ecosystems.

The escalating utilization of pesticides contributes significantly to surface water and groundwater pollution. The behaviour of pesticides in soils is primarily influenced by the sorption-desorption process. Their harmfulness and persistence in the environment depend on their sorption characteristics. Understanding these sorption qualities is crucial for predicting the mobility of pesticides within the soil matrix.

1.2 Classification of Pesticides

There are multiple approaches to categorizing pesticides. The selection of a classification system depends on the intended purpose of the classification and the information required to make well-informed decisions regarding the utilization and control of pesticides. Other criteria used to categorize pesticides includes their properties or chemical structure, intended use, and potential risks to human health and the environment.

Chemical Structure: Based on their chemical structure, pesticides can be broadly divided into three groups: organochlorines, organophosphates, and carbamates. The first generation of synthetic pesticides, known as organochlorines, was widely used in the mid-20th century. They have a distinctive chemical composition that consists of several chlorine atoms and carbon atoms. However, due to their persistence in the environment and potential health risks, organochlorines are now largely prohibited and restricted in use. Nowadays, carbamates and organophosphates are used more frequently and have different chemical structures. Organophosphates and carbamates both contain a carbamate group and an atom of phosphorus. Compared to organochlorines, both classes of pesticides are thought to be less environmentally persistent.

Target Organism: Pesticides can also be categorized based on the crop or pest they are intended to control. Insecticides, for instance, can be categorized according to the insect pests they aim to control, such as agricultural insecticides or mosquito control insecticides. Similarly, herbicides can be categorized according to the plant or weed they target, such as herbicides for corn or herbicides for lawns. Fungicides are chemicals applied to inhibit or kill fungi, rodenticides are used to eliminate rodents and fumigants are used to kill pest living in soil by forming a gas (Jayaraj et al., 2016; Rani et al., 2021; Rasool et al., 2022).

Based on Toxicity: The World Health Organization (WHO) classifies pesticides into five categories based on their acute toxicity to humans:

Class Ia: Extremely hazardous pesticides

Class Ib: Highly hazardous pesticides

Class II: Moderately hazardous pesticides

Class III: Slightly hazardous pesticides

Class U: Pesticides unlikely to present acute hazards in normal use.

This classification system primarily concerned with the acute toxicity of pesticides, assessing their potential to cause harm after a single exposure over a short duration. However, it does not account for the long-term or persistent effects of pesticide exposure.

1.3 Pesticide Consumption Scenario

1.3.1 World Scenario

Global pesticide production reached an estimated 4.1 million tonnes in 2018, with China emerging as the leading producer (1.8 million tonnes), followed by the United States (0.6 million tonnes), India (0.4 million tonnes), Germany (0.3 million tonnes), and France (0.2 million tonnes) (FAO, 2020). Overtime, worldwide pesticide consumption has surged, escalating from approximately 1.7 million tonnes in 1990 to around 3 million tonnes in 2020 (FAO, 2022). The escalation can be attributed to several factors including population growth, increased food demand, intensified crop cultivation, and the emergence of pest resistance. Notably, China, the United States, and Brazil stand as the largest consumers of pesticides, collectively representing over 40% of global usage (Donley, 2019). However, pesticides usage per hectare of cropland varies significantly across regions and nations, ranging from less than 1 kg/ha in Africa to exceeding 10 kg/ha in Japan and Korea (FAO, 2020).

Currently, approximately 3 million tonnes of pesticides are employed, with herbicides accounting for 47.5%, insecticides for 29.5%, fungicides for 17.5%, and other pesticides for 5.5% of the total pesticide usage (Sharma et al., 2019). The top ten pesticide-consuming nations worldwide include China, the USA, Argentina, Thailand, Brazil, Italy, France, Canada, Japan, and India (Sharma et al., 2019; Yatoo et al., 2022).

The average global consumption of agricultural pesticides has risen from 1.2 kilograms per hectare of cropland in 1990 to over 1.8 kilograms per hectare in 2020 (Sharma et al., 2019). Notably, the leading countries in pesticide consumption per unit area in 2019 were Japan (11.9 kg/ha), Netherlands (9.4 kg/ha), Belgium (6.8 kg/ha), South Korea (6.6 kg/ha), and Italy (6.5 kg/ha)(Sharma et al., 2019).

1.3.2 Indian Scenario

India holds the position of being the world's fourth-largest provider of pesticides. While India has a production capacity of 139 kilotonnes annually, its effective production has averaged approximately 80 kilotonnes per year during the last 15 years. However, there has been a noticeable rise in the yearly utilisation of pesticides, with figures climbing from 39.77 kilotonnes in 2005-2006 to 58.16 kilotonnes in 2018 (Nayak and Solanki, 2021). The extent of pesticide consumption in India exhibits regional disparities owing to diverse cultivation practices. Uttar Pradesh, Maharashtra, Telangana, Punjab, Haryana, and West Bengal emerge as the states with the highest pesticide consumption (Table 1.1), while the northeastern states and the southern state of Goa report relatively lower levels of pesticide usage (Devi et al., 2017). In India, the pattern of pesticide application deviates notably from the global trend. Insecticides dominate pesticide usage, accounting for 65%, whereas the global average is 44%. Conversely, herbicides and fungicides usage in India stands at 10% each, significantly lower compared to the global utilization of 30% herbicides and 21% fungicides (Devi et al., 2017; Rani et al., 2021). The primary crops contributing to pesticide consumption (Fig. 1.1) are cotton (40–50%) and rice (22%). However, concerning cultivated area, coarse grains and oilseeds occupy the largest portion at 58%, followed by rice (24%), vegetables and fruits (18%), cotton (5%), and sugarcane (2%) (Abhilash and Singh, 2009).

In India, organochlorine pesticides (OCPs) hold the majority share, constituting 40% of total pesticide usage. Organophosphates (OPs) follow closely behind, accounting for 30% of total pesticide use, while carbamates make up 15%, synthetic pyrethroids (SPs) 10%, and botanicals and other pesticides collectively contribute 5%. OCPs have gained prominence in agriculture due to their notable efficacy, wide applicability, and cost-effectiveness. However, their toxic nature, persistence in the environment, tendency to accumulate in fatty tissues, ability to travel long distances, and adverse impacts on various organisms, including humans, have prompted India to impose bans or restrictions on several pesticides.

Table 1. 1 Statistics of state-wise consumption of chemical pesticide.

States	**2015-16**	**2016-17**	**2017-18**	**2018-19**	**2019-20**	**2020-21**	**2021-22**
Maharashtra	11,655	13,496	15,568	11,746	12,783	13243	13175
Uttar Pradesh	10,457	10,614	10,824	11,049	12,217	11557	11688
Punjab	5.743	5,843	5,835	5,543	4995	5193	5376
Telangana	993	3,436	4,866	4,894	4,915	4986	5090
Haryana	4,100	4,050	4,025	4,015	4,200	4050	4066
West Bengal	3,712	2,624	2,982	3,190	3,630	3630	3630
Rajasthan	2,475	2,269	2,307	2,290	2088	2330	2104
Tamil Nadu	2,096	2,092	1.929	1,901	1,895	1834	1851
Gujarat	1,980	1,713	1,692	1,608	1,784	1573	1869
Karnataka	1,434	1,288	1,502	1,524	1568	1930	1930
Andhra Pradesh	2,713	2,015	1,738	1,689	1559	1559	1759
Chhattisgarh	1,625	1,660	1,685	1,770	1672	1639	1740
Bihar	831	790	840	850	995	995	995
Madhya Pradesh	732	694	502	540	563	691	654
Kerala	1,123	895	1067	995	656	585	554
North Eastern States	544	684	617	657	850	503	494
All India*	56,720	58,634	63,406	59,670	56,370	56298	56975

(Quantity: MT Tech. Grade)

(Source: Ministry of Agriculture and Farmers Welfare, GOI)

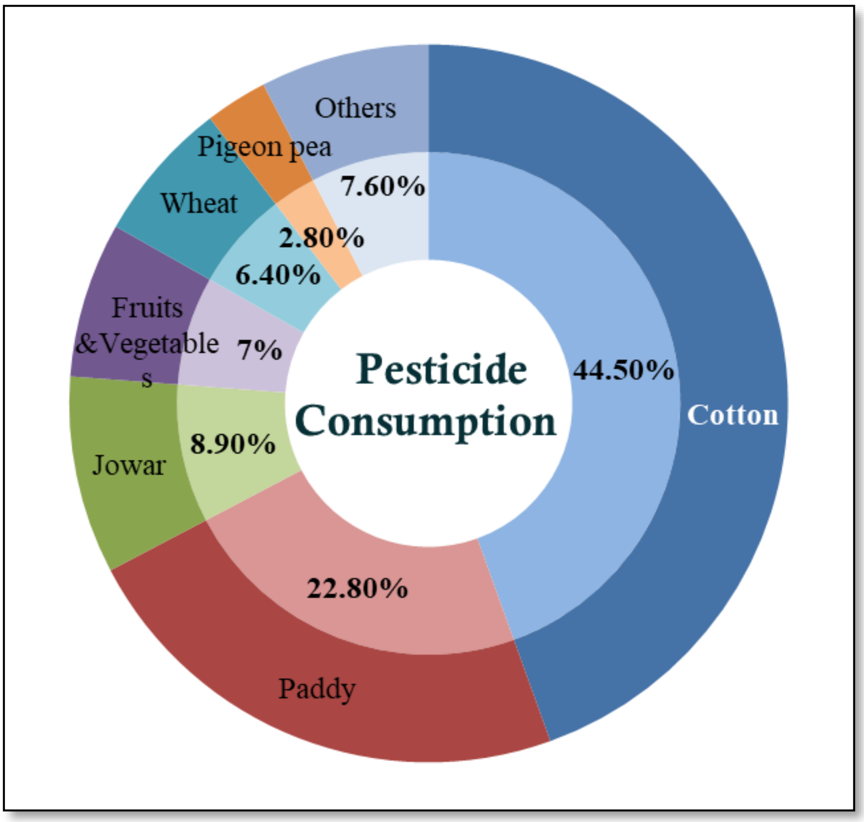

Fig. 1. 1 Crop-wise pesticide consumption in India

1.3.3 Pesticide Consumption in Telangana State

Telangana relies heavily on agriculture, with approximately 60% of its rural workforce engaged in agricultural and allied activities during the 2020-21 period (Agriculture Action Plan report 2021-2022, Department of Agriculture, Govt of Telangana). The primary crops cultivated in the state include Rice, Cotton, and Maize, collectively contributing to nearly 75% of the total agricultural output in 2020 (Agriculture Action Plan report 2021-2022, Department of Agriculture, Govt of Telangana). Other noteworthy crops include pulses, peanuts, chilies, and sugarcane.

The data presented in Table 1.1 indicates a substantial surge in the consumption of chemical pesticides in Telangana, escalating from 993 metric tonnes in 2015-16 to 5090 metric tonnes in 2021-22—a remarkable 5-fold increase over six years. In 2020-21, Telangana ranked fourth in the country for the highest consumption of chemical pesticides, following Maharashtra, Uttar Pradesh, and Punjab.

Remarkably, the consumption of chemical pesticides in Telangana constituted 7.7% of the total national consumption in 2020-21, despite the state's population accounting for only 2.97% of the total population in India in 2021. One significant factor contributing to this surge is the expansion of cotton cultivation, which necessitates extensive pesticide use. Cotton cultivation covered 18.78 lakh hectares in 2021-22, making it a major crop in Telangana (Cotton outlook-2021).

The report by Ministry of Agriculture and Farmers Welfare highlights a substantial increase in pesticide consumption in Telangana, rising from 3,400 metric tonnes in 2016-17 to nearly 5,000 metric tonnes in 2020-21. This escalation can be attributed to the expansion of the cotton area, alongside factors such as pest resistance, inadequate regulation, and limited awareness among farmers (Gaurav et al., 2018). According to the same report, the total consumption of chemical pesticides in Telangana during 2020-21 reached 4,996 metric tonnes. Additionally, the report provides a breakdown of pesticide consumption, distinguishing between indigenous and imported pesticides. Glyphosate, chlorpyrifos, acephate, Imidacloprid, and profenofos were among the most consumed indigenous pesticides, while thiamethoxam, lambda-cyhalothrin, emamectin benzoate, sulphur, and tricyclazole were noted as the most consumed imported pesticides. These pesticides belong to various chemical classes and target different types of pests.

1.4 Health Impacts Associated with Pesticides

As the world's population already surpasses the 8 billion mark and is estimated to grow by 10 billion by 2050, with limited land resources, there is peer pressure on the agricultural sector. Fertilizers and pesticides can be beneficial for the agriculture sector by increasing crop yields and protecting crops from damage caused by pests and diseases. Without pesticides, it is estimated that up to 40-50% of crops could be lost to pests (Oerke, 2006), which would have a significant impact on global food security. However, it's important to note that overuse of pesticides can have negative impacts on human health, the environment, soil quality, crop yield (AL-Ahmadi, 2019), microbial biodiversity (Megharaj, 2002) and enzymatic activity (Baxter and Cummings, 2008) and other non-target species which are beneficial to the soil ecosystem. After application, pesticide residues remain both on plant and soil surfaces (Vašíčková et al., 2019). These residues can cause ecotoxicity in various environmental systems such as food webs, freshwater bodies, and air posing risk to human health through different exposure pathways (Arias-Estévez et al., 2008; Calatayud-Vernich et al., 2017; Cengiz et al., 2018). Some sources contend that just 1% or even less of pesticides actually reach their intended target organisms, while the remainder of pesticides contaminate the nearby ecosystem and stay persistent in the soil, polluting other elements of the environment (Aktar et al., 2009; Meena and Mishra, 2020; Rajmohan et al., 2020). The unregulated use of pesticides resulted to the emergence of pest resistance, pest resurgence, and secondary outbreaks, contributing to elevated crop losses. Consequently, farmers resort to increased pesticide usage beyond conventional methods in their attempts to manage pests, inadvertently causing environmental contamination. The application of pesticides in India presents various concerns regarding ecological and health issues. Pesticides have the capability to contaminate soil and water, posing potential risks to ecosystems. Moreover, the ingestion or inhalation of pesticides can significantly impact human well-being. Furthermore, the indiscriminate usage of pesticides can contribute to the emergence of pest resistance, creating challenges in future pest management endeavours. Additionally, overuse can lead to the development of pesticide-resistant pests, which further increases the need for more pesticides. Exposure to pesticides and other chemicals used in agriculture and industry can lead to health problems in humans and non-target species such as amphibians, fish, birds, and others (Aiyesanmi and Idowu, 2012). These chemicals can contaminate soil, water, and air and can have harmful effects on the health of humans and other living organisms. Several studies have indicated that prolonged exposure to pesticides can elevate the likelihood of specific chronic illnesses, including cancer, neurological disorders, and reproductive issues. Additionally, exposure to pesticides can cause acute health problems, such as respiratory issues and skin irritation (Azmi et al., 2006; Keifer and Firestone, 2007; Singh et al., 2011).

1.5 Benefits of Biochar in Agricultural Soils

In recent years, biochar has emerged as an effective organic amendment for enhancing soil quality and promoting sustainable agriculture. Its widespread adoption by researchers and farmers is driven by its ability to address critical environmental and agricultural challenges. One of the key benefits of biochar is its ability to reduce pesticide mobility in soils, thereby minimizing the risk of groundwater contamination. This is particularly important in regions where excessive pesticide use has raised concerns about long-term soil health and water quality.

Biochar is a highly porous material with a large surface area, produced through the thermochemical conversion of various types of biomasses under oxygen-limited conditions, a process known as pyrolysis. Feedstocks used for biochar production can include a wide range of organic materials such as agricultural residues (e.g., crop stalks, husks), wood, sewage sludge, and food waste. These diverse feedstocks make biochar a versatile option, as different types of biomasses can be used depending on local availability and environmental goals. One of the most significant agricultural benefits of biochar is its ability to improve soil water retention. By enhancing the soil's capacity to hold water, biochar helps crop thrive during periods of drought or water scarcity, reducing the need for excessive irrigation. In addition to increasing water retention, biochar plays a vital role in minimizing nutrient leaching. When nutrients such as nitrogen and phosphorous leach away from the root zone, they become unavailable to plants and can contribute to water pollution. By preventing this loss, biochar ensures that nutrients remain in the soil longer, promoting healthier plant growth and higher yields.

Moreover, biochar contributes to soil fertility by stimulating microbial activity. The highly porous structure of biochar provides a favourable habitat for beneficial microorganisms, which play a crucial role in nutrient cycling, organic matter decomposition, and overall soil health. Enhanced microbial activity translates to improved soil structure, better nutrient availability, and greater resilience against soil-borne diseases, further contributing to increased crop productivity. Biochar's unique physicochemical properties also make it highly effective in retaining organic contaminants such as pesticides and heavy metals. The abundance of functional groups, such as carboxyl, hydroxyl, and carbonyl groups, on its surface enables biochar to adsorb and immobilize these harmful substances, reducing their mobility and preventing them from contaminating water resources. This makes biochar an ideal solution for managing polluted soils and safeguarding ecosystems.

1.6 Problem Statement

The Green Revolution in India has been instrumental in addressing the critical issue of hunger through the adoption of advanced technologies and agrochemicals. This transformative initiative has significantly bolstered the agricultural sector, with pesticides playing a pivotal role in elevating productivity and curbing crop losses. However, the multifaceted impacts of these chemicals on natural resources have raised substantial concerns. Despite their undeniable benefits, the adverse effects on human health and the environment necessitate a comprehensive understanding of the fate of pesticides, especially when applied on a large scale across croplands.

While pesticides have garnered credit for enhancing agricultural outputs and reducing losses, the escalating apprehensions surrounding their implications have prompted a re-evaluation of their usage. The pressing need to fathom the destiny of pesticides in extensive cropland applications has become imperative in the face of growing concerns about their impact on human health and the environment. This urgency underscores the importance of assessing the behaviour of pesticides in soil, aiming to ensure the judicious and safe use of these highly demanded agrochemicals.

Despite numerous studies revealing potential risks associated with pesticide exposure for both farmers and end-users, the global pesticides market continues to experience substantial growth, particularly in developing countries. Therefore, understanding the intricate behaviour of pesticides in various environmental compartments, notably within the soil, is indispensable. This knowledge serves as the foundation for developing nuanced strategies to mitigate potential adverse effects and safeguard the limited natural resources.

In the specific context of Telangana state, where pesticide usage has surged fivefold over the past five years, there is a heightened risk of groundwater contamination with persistent organic pollutants (PoPs). Consequently, this research aims to delve into the sorption, desorption, and leachability of widely used pesticides in the black cotton soils and red soil of the Telangana region. The goal is to provide a comprehensive assessment of the potential risks associated with groundwater pollution stemming from these pesticides, offering valuable insights for tailored environmental management.

Moreover, the study seeks to explore the efficacy of biochar derived from locally available cotton stalks in augmenting pesticide sorption. This facet of the research is crucial for developing targeted remedial measures against pesticide pollution and implementing effective pesticide management practices specifically tailored to the unique characteristics of the Telangana region. By shedding light on the sorption, desorption, and leaching behaviour of pesticides, this research aims to empower policymakers with the knowledge necessary to formulate targeted strategies for environmental conservation and sustainable agricultural practices, ensuring a harmonious balance between agricultural productivity and environmental preservation.

1.7 Objectives

The main objective of the study is to investigate the sorption-desorption and leaching of Imidacloprid and Atrazine in black cotton soils and red soil of Telangana state. The specific objectives of the present study are listed as follows:

- To investigate the sorption- desorption behaviour of Imidacloprid and Atrazine in different agricultural soils of Telangana state.
- To examine the effect of temperature and pH on pesticide sorption-desorption in the soils under investigation.
- To investigate degradation and leaching potential of pesticides in the chosen soils.
- To explore the influence of cotton stalk biochar on the sorption- desorption behaviour of pesticides in the soils.
- To assess the leaching potential of pesticides in soils amended with biochar.

To accomplish the outlined objectives, a series of experiments were undertaken, encompassing batch sorption trials, sorption kinetics analyses, sorption isotherm investigations, pesticide degradation studies, and soil column leaching assessments. In the kinetic experiments, the sorption rates of two pesticides on various soils were examined, while the isotherm experiments delved into the equilibrium sorption behaviours. Varied temperature and pH conditions were applied in sorption experiments to discern their impacts. Degradation experiments were conducted to ascertain the pesticides' half-life in the soil environment. This information was subsequently utilized to assess the leaching potential of the pesticides in the examined soils. As part of a strategy to control pesticide mobility, cotton stalk biochar was synthesized and applied to the soil, aiming to enhance the sorption capacity of the soils under investigation.

The utilization of cotton stem-derived biochar as a soil amendment represents a potentially cost-effective and environmentally friendly solution for pesticide management.

1.8 Organization of the Thesis

The present thesis is organized into nine chapters, each comprehensively explained through sections and sub-sections containing visible results and cited references. A brief outline of each chapter is given below:

Chapter 1 provides a concise introduction to pesticides and their classifications, including both the global and Indian contexts of pesticide production and consumption. It also discusses current pesticide practices in the Telangana region, highlights the associated problems of pesticide application in agricultural land, and explains the motivation for the study.

Chapter 2 presents a detailed discussion on the factors influencing the fate and behaviour of pesticides in soils. It examines the mobility of pesticides in soils and the potential contamination of groundwater and surface water resources. Additionally, the chapter explores the use of organic amendments, with a particular focus on biochar, to improve pesticide sorption in soils and reduce their mobility.

Chapter 3 describes the materials used in the study, including pesticides and soils. It details the methods of sample collection and characterization. The methodology for conducting sorption-desorption, column leaching, and pesticide degradation studies is thoroughly explained. Methods for HPLC analysis of pesticide residues, as well as the synthesis and characterization of biochar and hydrochar, are also discussed.

Chapter 4 discusses about the experimental output of sorption desorption study of Imidacloprid in various soils. The influence of temperature and pH on sorption behaviour of Imidacloprid is also discussed in this chapter.

Chapter 5 covers the sorption desorption behaviour of herbicide Atrazine in various agricultural soils of Telangana state. It also discusses the impacts of pH and temperature on the sorption behaviour of Atrazine.

Chapter 6 presents the experimental output of pesticide degradation study and soil column leaching study. It includes the calculation of the Groundwater Ubiquity Score based on the obtained results.

Chapter 7 focuses on the synthesis of various biochars and hydrochars from cotton stalk. It discusses the physical, elemental, structural, and thermogravimetric characterization of these synthesized products.

Chapter 8 examines the influence of the organic amendments on the sorption behaviour of pesticides in soils. It includes sorption-desorption, degradation, and soils column leaching studies in biochar amended soils to assess their efficacy in retaining pesticides in soils and mitigating possible groundwater contamination.

In **Chapter 9**, the entire study is summarized by highlighting the key findings and outcomes obtained from each of the aforementioned investigations. It also includes future scope of the study.

Chapter 2

Literature Review

2.1 Introduction

The fate of pesticides, in terms of their movement from soil to surface water, groundwater, or the surrounding environment, is determined by a complex interplay of environmental processes (Fig. 2.1). These processes encompass sorption/desorption phenomena, transportation mechanisms, and degradation processes (Worrall et al., 2001; Yang and Sheng, 2003a).

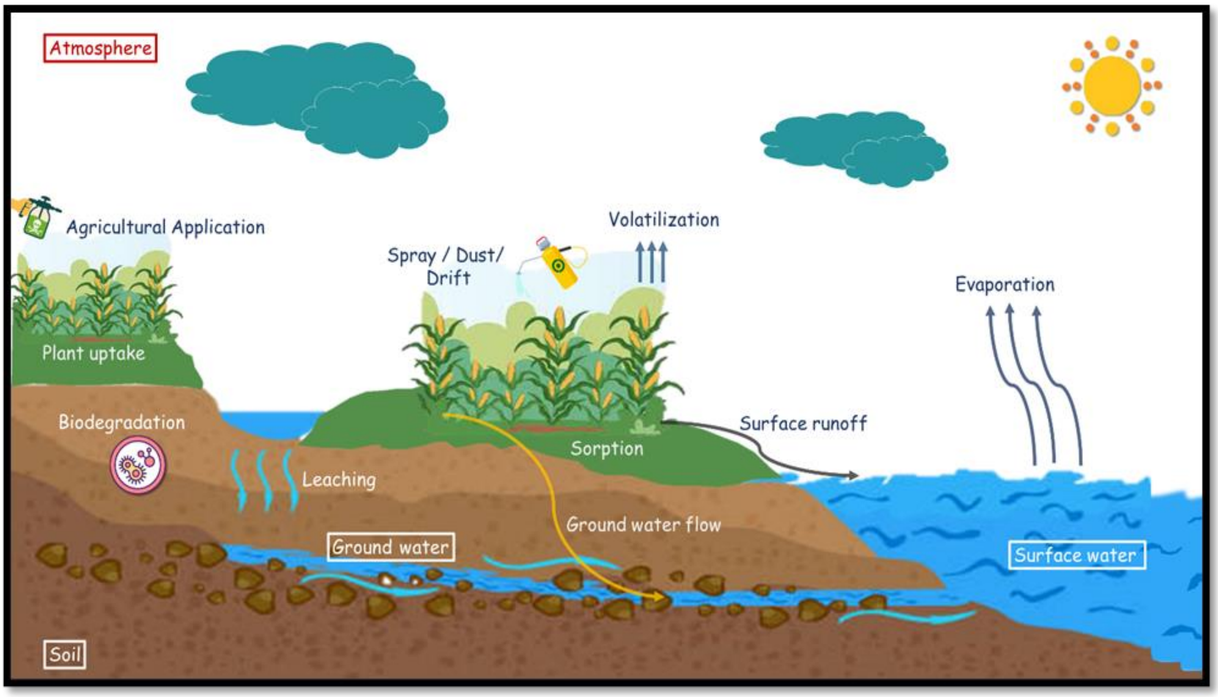

Fig. 2. 1 Fate of pesticides in the environment

The extent to which these processes occur, and which process predominates, depends on the attributes of the soil, the pesticide, and the surrounding environment. A comprehensive investigation specific to each case is necessary to understand these dynamics. Amongst these mechanisms, sorption is a fundamental process that initiates as soon as pesticides enter the soil. This process alters the way pesticides are bound and their accessibility, thereby influencing the extent of other actions such as transportation, bioaccumulation, and the ecological consequences on organisms (Khan, 1978; Yavari et al., 2015).

Factors such as the quality and quantity of soil organic matter (SOM), clay content, soil minerals, temperature, and pH play pivotal roles in controlling pesticide fate in the soil (Vryzas et al., 2007; Wauchope et al., 2002). Leaching through the soil matrix, surface runoff, and plant uptake of pesticide molecules are typically minimized by the formation of various bonds with the soil. Organic matter is one of the most significant soil characteristics governing the mobility of pesticides. Organic components present in the soil can adsorb pesticides. SOM exhibits a higher CEC compared to clays and tends to form complexes with organic molecules such as pesticides, often resulting in their immobilization. Pesticide adsorption improves with higher soil organic matter content.

2.2 Properties of Soil that Affect the Fate of Pesticides in Soil

2.2.1 Soil Organic Matter

The amount of organic matter (OM) in the soil significantly affects how effectively pesticides adhere to soil particles. Pesticides may become less mobile and accessible in soil due to their ability to bind firmly to OM.

The OM component plays a pivotal role in determining the extent of adsorption for most pesticides in natural soils, as emphasized by Bollag et al. (1992). This is due to the ability of OM to attract the positive charge of pesticide molecules and the negative charge of OM itself. Various instances have demonstrated that OM content significantly impacts the sorption of pesticide molecules within soil profiles (Parolo et al., 2017; Rojas et al., 2013). Prior research has established that the adsorption of non-ionic pesticides by soil in an aqueous environment is primarily governed by the concentration of OM within the soil (Chiou et al., 1983). Several organic molecules, including cellulose, lignin, proteins, and humus, make up organic matter. These organic compounds work together to create a complex and heterogeneous matrix that offers a variety of sorption sites for pesticides (Bollag et al., 1992).

The charge developed on the active sorption sites of soil organic matter's governs pesticide adsorption due to the ionization of carboxylic groups on its surface. The rate of pesticide application is directly proportional to the OM content of the soil. If the soils in a certain area have varied OM content, then the pesticide application rate should be selected based on the overall soil sorption capacity. This indicates that the risk of pesticide leaching is higher in soils with lower OM, which may lead to groundwater contamination (Fernandez et al., 1988). Soils with OM> 5% significantly impact pesticide adsorption, and the quality of the organic matter also plays a vital role (Bekbölet et al., 1999). Senesi et al. (2001) documented increased pesticide adsorption in soils amended with OM. The authors concluded that soils amended with sewage sludge exhibited higher sorption for herbicides such as alachlor, imazethapyr, and rimsulfuron. They attributed this enhanced adsorption to mechanisms like hydrogen bonding, charge transfer, and ionic bonds (Senesi et al., 2001).

Soil organic matter can be divided into humic and non-humic components. Non-humic compounds, including proteins, amino acids, lipids, waxes, carbohydrates, and low molecular weight organic acids, are chemically distinct and have a comparably short lifespan in soil due to microbial degradation. In contrast, humic material exhibits greater stability and constitutes the predominant portion of OM in most soils. The correlation between increased soil OM and elevated K_d values is well-documented (Williams et al., 2006). Humic substances form the major part of soil organic matter and are more stable than other constituents. In the context of pesticides, humic substances display greater chemical reactivity compared to non-humic substance (Farenhorst, 2006). Humic acids encompass a diverse array of reactive functional groups, including hydroxyl, carboxylic acids, amines, phenols, amides, carbonyl, esters, and alkoxy groups. Additionally, soil contains hydrophilic and hydrophobic groups, which significantly influence interactions between organic pesticides and soil-based organic substances (Zhang et al., 2010). The ratio of humic substance to total organic matter plays a significant role in pesticide adsorption and desorption. As this ratio increases, the binding capacity of the soil also increases (Krishna and Philip, 2008). Non-humic substances in soil have a shorter lifespan because they are more susceptible to microbial attack, making them less stable than humic substances. Lee and Farmer, (1989) reported a strong association between the herbicide napropamide and humic (humic and fulvic acid) substances present in soils.

Organic Matter in the soil can exist in either solid or dissolved forms. Solid organic matter plays a significant role in adsorbing pesticides (Huang and Lee, 2001). An increase in the amount of solid organic matter (SOM) generally results in higher pesticide adsorption. However, the presence of dissolved organic matter (DOM) disrupts pesticide movement, increasing the likelihood of pesticide leaching and groundwater contamination. This occurs because DOM prevents pesticides from binding to SOM (Álvarez-Martín et al., 2016; Marín-Benito et al., 2013). The impact of DOM on pesticide sorption can vary depending on the specific type and functional groups of the pesticide molecule. For instance, the sorption of Atrazine increases with higher levels of soil-dissolved organic matter, whereas, the herbicide 2,4-D and chlorpyrifos show an opposite effect (Ben-Hur et al., 2003; Li et al., 2005). A study by Lee and Farmer, (1989) examined the interaction between DOM and napropamide for sorption sites on clay, findings that DOM hindered the sorption of napropamide onto the clay surface. The extent of this competition depends on the origin and concentration of the DOM. Research by Flores-Céspedes et al. (2002) indicated that DOM could reduce the sorption of neonicotinoid (specifically Imidacloprid) on soil surfaces, potentially increasing Imidacloprid leaching and contributing to groundwater pollution. However, a study by Sadegh-Zadeh et al. (2011) found that napropamide used on sandy soils did not interact with DOM derived from chicken dung (CD) and palm oil mill effluent (POME), and DOM did not affect the soil's ability to bind napropamide. The effects of DOM on soil sorption of pesticides have produced conflicting results. Multiple factors contribute to this variability, including differences in soil characteristics, pesticide properties, and the diverse attributes of DOM from various sources (Briceño et al., 2007).

2.2.2 Soil Inorganic Constituents

Inorganic soil constituents, particularly soil clay particles, play a significant role in the sorption-desorption processes of insecticides (Baskaran et al., 1996). Sorption occurs due to the electrostatic attraction between the positive charges on pesticides, such as ammonium or quaternary ammonium ions, and the negative charges on mineral surfaces like clay minerals. Various types of clay and oxide minerals, including montmorillonite, kaolinite, or iron oxides, offer different surfaces for pesticide sorption, resulting in variations in sorption capacity and pesticide preference. Pesticides can bind to soil minerals forming aggregates that trap them within the soil matrix and provide additional sorption sites (Sarkar et al., 2020).

Clay particles are typically negatively charged and possess a larger surface area (Sarkar et al., 2018). Consequently, soils with higher clay content tend to adsorb more pesticides and exhibit a greater adsorption rate compared to coarse-textured or sandy soils. The larger surface area of clay particles provides more sorption sites, enhancing the soil's capacity to sorb pesticides. The sorption-desorption behaviour of pesticides is directly related to the soil's clay content. For instance, the desorption of the herbicide acetochlor was significantly lower (84%) in soil with high clay content (23.6%) compared to soil with low clay content (3.44%), where desorption reached 94% (Đurović-Pejčev et al., 2009). Wang and Keller, (2009) investigated Atrazine's sorption-desorption behaviour in four soils with different fractions of sand, clay, and silt. The study revealed that clay content was the most important factor influencing herbicide sorption. Likewise, the sorption of the herbicide metolachlor is positively affected by specific minerals and clay content in the soil (Kodešová et al., 2011). The presence of clay interlayers and surfaces enriched with various monovalent and divalent ions, such as Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}, plays a significant role in insecticide sorption. K^+ saturated clay minerals exhibit good sorption characteristics for pesticides compared to other exchangeable cations due to their weak hydration energy. Weissmahr et al. (1999) investigated the sorption of 4-nitrotoluene in soils rich in K^+ and Ca^{2+}, finding that increasing K^+ clay fraction enhanced adsorption. Rodríguez-Liébana et al. (2016) studied the sorption of the metalaxyl herbicide in soils from southern Spain, which had different mineral compositions, high calcium content, specific granulometry, and low-medium cation exchange capacity, concluding that adsorption was high due to electrostatic attraction. Furthermore, clay granulometry was identified as an important factor for the sorption of metalaxyl. Soils rich in smectite clay content exhibited high sorption of the herbicide imazethapyr (Oufqir et al., 2017), with adsorption strongly influenced by higher smectite content, cation exchange capability, and soil organic matter content.

The amount of clay, oxides, and hydroxides in soil significantly affects the sorption of agrochemicals. According to Spark and Swift, (2002), increasing the clay content in soil prolongs the retention time of pesticides, thereby reducing their movement and lowering the risks of leaching and surface runoff. The hydrophilicity of clay minerals' surfaces is attributed to the existence of -OH groups and exchangeable cations (Chaplain et al., 2011). Pesticides adsorption typically occurs on the exterior surfaces of clay particles rather than within the interlamellar regions. As the specific surface area of clay increases, so does the adsorption of pesticides. The small particle size, large surface area, and negatively charged surfaces of clay minerals are crucial for adsorbing organic pesticides (Undabeytia et al., 2020).

Pesticide solubility and mobility in soil are influenced by soil minerals and inorganic concentrations, impacting pesticide dispersion and sorption capability. Certain minerals, such as calcium carbonate or gypsum, can increase the solubility of pesticides by raising the soil pH, while other minerals can decrease solubility (Arias-Estévez et al., 2008). Variations in sorption properties may occur depending on the distribution of minerals and inorganic compounds throughout the soil matrix (Rasool et al., 2022).

In conclusion, inorganic content and soil minerals play a critical role in soil pesticide sorption. Inorganic substances can impact the solubility and mobility of pesticides in soil, affect their stability and persistence, and contribute to their sorption and degradation qualities. Understanding the function of soil minerals and inorganic content in pesticide sorption is crucial for predicting their fate and movement in the environment and creating efficient management plans (Sarkar et al., 2020).

2.2.3 Impact of pH

The sorption of pesticides is also influenced by soil pH. Generally, lower soil pH levels are associated with increased adsorption of pesticides. Nevertheless, this phenomenon has mainly been documented through artificially induced pH alterations and, on rare occasions, through the utilization of diverse soil samples. For instance, Bajeer et al. (2012) and Boivin et al. (2005) reported that higher soil pH results in diminished adsorption of Imidacloprid. At lower pH levels, pesticides with a positive charge tend to be more firmly adsorbed to negatively charged soil particles.

Several studies have documented the effect of pH on pesticide sorption-desorption, which is precisely influenced by the composition of soil and the characteristics of the pesticide. Soil colloids, mainly comprising organic matter, iron oxides, and alumina, play a crucial role in influencing the pH-dependent charge, which in turn affects the electrostatic interactions or ligand exchange responsible for pesticide sorption. The relationship between soil organic matter, pH, and the adsorption of nonionic herbicides like metalaxyl and penconazol has been investigated by Gondar et al. (2013). They found that the partitioning of pesticides between the solid phase and soil solution was negligible at $pH > 5$, whereas at a lower pH range, the percentage sorbed to the solid phase increased. This phenomenon can be rationalized by considering the impact of pH on the ionization process of carboxylic groups present in soil organic matter and its hydrophilic characteristics. An investigation into pesticide sorption on volcanic soil in relation to pH revealed that the highest quantities of adsorbed fluroxypyr, triclopyr, picloram, and clopyralid were 75.2%, 69.7%, 40.5%, and 11.7% respectively, occurring at a pH of 4.0 (Palma et al., 2015). Soil pH affects the electrical charge of OM and soil oxides, along with the sorption of pesticides (Kah and Brown, 2006). Pesticides with acidic properties act as sources of protons, undergoing dissociation into anions under elevated pH conditions. Conversely, pesticides with basic characteristics transform into cations when exposed to low pH levels, resulting in enhanced adsorption (Kah and Brown, 2006).

These findings suggest that both the soil's pH and the pesticide's properties play a crucial role in dictating pesticides accessibility and leaching through the soil. Consequently, the soil's pH indirectly impacts environmental conditions by altering the processes of pesticide sorption, desorption, and leaching after their application to the soil.

2.2.4 Impact of Temperature

Another factor that may affect the sorption of pesticides is temperature. For the majority of organic substances, equilibrium sorption typically decreases with rising temperature (Hulscher and Cornelissen, 1996). As the temperature increases, the soil’s ability to adsorb pesticides decreases. This is because higher temperatures can increase the mobility of water and the rate of organic matter decomposition in soil, leading to reduced pesticide adsorption capacity. Additionally, the solubility of pesticides in water can increase at higher temperatures, making more pesticides available for leaching or runoff, thus raising the risk of contamination of groundwater and surface water. However, the specific effects of temperature on pesticide sorption can depend on the properties of the pesticide and the soil. Some pesticides may be more susceptible to temperature changes than others, and different types of soil may have different sorption capacities. Studies conducted on the sorption-desorption patterns of Imidacloprid across six different soils at temperatures of 20 °C, 30 °C, and 40 °C revealed that greater sorption capacity was evident at lower temperatures (Broznić and Milin, 2012a). Conversely, Banerjee et al. (2008) proposed that the adsorption of Thiamethoxam could potentially rise with increasing temperature. This is due to the notion that at lower temperatures, the accessibility of adsorption sites might be limited, or they may not be adequately activated to effectively adsorb the substance. In conclusion, it is crucial to take into account the potential influence of temperature when evaluating the fate and movement of pesticides within the soil, as well as their potential environmental ramifications.

2.2.5 Soil Moisture

It has been demonstrated that soil water content or the level of soil water saturation affects the adsorption of pesticides. with increased soil moisture, pesticides may become more soluble and less adsorbent to soil particles.

Depending on the structure of the pesticide and the characteristics of the site, various pesticides compete differently with water for adsorption sites. Some insecticides do not have much success competing with water for these sites. Generally speaking, adsorption rises when water content falls, most likely as a result of additional sites opening up as the soil dries out (Tudi et al., 2021).

2.3 Properties of Pesticides that Influence the Soil Sorption

Pesticides, as agricultural chemicals, exhibit diverse physicochemical characteristics that influence their interactions with soil surfaces. The sorption behaviour of pesticides is influenced by various factors, including their chemical structure, polarity, hydrophobicity, solubility, molecular weight, and functional groups (Rasool et al., 2022).

The molecular structure and size of pesticides significantly influence their sorption behaviour in soils. Larger, more complex molecules tend to have more surface area and functional groups, which can interact with soil components, leading to stronger sorption (Sarkar et al., 2020). Complex molecular structures may also hinder the pesticide's mobility, causing them to be retained in the soil for longer periods. For example, Imidacloprid, a relatively large molecule with several functional groups, may engage in various interactions with soil particles, enhancing its sorption. In contrast, smaller and less complex molecules, like atrazine, have fewer interaction sites and may experience weaker sorption, making them more mobile in the soil environment. The three-dimensional shape and functional group arrangement can further affect how well a pesticide fits into the micropores and active sites on soil surfaces. In soils with a high content of clay or organic matter, the size and structure of pesticide molecules can determine how easily they are immobilized or degraded. Therefore, molecular structure and size are crucial factors that govern the persistence and transport of pesticides in agricultural soils.

The polarity of a pesticide, along with the functional groups present on its molecule, determines the strength and type of interactions with soil particles. Polar pesticides are more likely to engage in ionic and hydrogen bonding with soil minerals and organic matter, leading to stronger sorption. Functional groups, such as carbonyl, carboxylic, ester, amide, and phenol, can undergo ionization or polarization, affecting their sorption behaviour. The adjacent electronegativity or electro-positivity of these functional groups further modulates their ionization and polarization properties (Javanbakht et al., 2013). For instance, atrazine contains nitrogen atoms capable of forming hydrogen bonds with soil organic matter, though its overall polarity is relatively low, which limits its sorption potential. In contrast, Imidacloprid contains a nitroguanidine moiety, which can interact with soil components through both hydrogen bonding and van der Waals forces, potentially increasing its sorption capacity (Cox et al., 1998). The presence of specific functional groups that can interact with soil organic matter or clay minerals determines not only how strongly the pesticide binds to the soil but also how easily it can be degraded by soil microorganisms.

Hydrophobicity, often expressed as the octanol-water partition coefficient (K_{OW}), is a key determinant of a pesticide's affinity for soil organic matter. Pesticides with higher K_{OW} values are more hydrophobic, meaning they prefer to partition into organic phases rather than aqueous ones. This property is critical because soil organic matter is highly hydrophobic, and pesticides with similar hydrophobicity will sorb more strongly to it. Hydrophobic pesticides are less likely to dissolve in water, making them less mobile and more likely to remain bound in the soil. For instance, a pesticide with a high K_{OW}, such as DDT, exhibits strong sorption to soil organic matter, significantly reducing its leaching potential. In contrast, pesticides with low K_{OW} values, such as atrazine, are more hydrophilic and tend to remain dissolved in the soil solution, increasing their mobility and likelihood of leaching into groundwater.

The ionization state of pesticides also impacts their sorption behaviour. Pesticides can exist in either an ionized or non-ionized form, depending on their chemical composition and soil pH. Non-ionized pesticides tend to exhibit stronger binding to soil particles, while ionized pesticides are more soluble in water. The pH-dependent ionization of pesticides results in varied sorption behaviour, with basic pesticides forming cations at low pH, acidic pesticides becoming anions at high pH, and non-ionic pesticides undergoing temporary polarization on charged surfaces (Kah and Brown, 2006).

Water solubility is another fundamental property influencing pesticide sorption. Pesticides with low solubility in water tend to sorb more strongly to soil particles, especially to organic matter, while highly water-soluble pesticides remain in the soil solution and are more prone to leaching. This is because low-solubility pesticides do not dissolve easily in soil water, leading them to interact more with soil particles. For example, Imidacloprid, which has moderate water solubility, shows intermediate sorption behaviour, while highly soluble pesticides such as atrazine are more likely to be transported through the soil with water, making them susceptible to leaching.

Understanding the interplay between these physicochemical properties and the sorption behaviour of pesticides is essential for predicting their fate and transport in soil environments. By investigating variables such as chemical structure, polarity, hydrophobicity, solubility, molecular weight, functional groups, and ionization state, valuable insights into the sorption mechanisms of pesticides can be gained, enabling informed decisions regarding their application and environmental impact.

2.4 Influence of Organic Amendments on Sorption of Pesticides in Soil

In contemporary agriculture, utilizing organic residues as soil amendments is a widely adopted and prevalent practice. This approach is experiencing an upward trend in numerous European countries and the United States. Organic amendments are substances applied to soil to enhance its structure, nutritional content, and ability to retain water. Examples of widely used organic amendments include compost, manure, and agricultural leftovers.

In addition to enhancing soil quality, preserving soil health, and increasing soil productivity, applying organic residues as soil supplements provides environmental advantages over placing organic waste in landfills (Medina et al., 2012). Organic soil amendments that are high in nutrients and contain growth substrates impact microbial diversity and composition, increasing the number of ecological niches and promoting various biotic interactions, such as organism-to-organism competition (Gómez-Sagasti et al., 2018).

Soil amendments from tree bark, rice husk, dead leaves, sludge, organic manure, fruit peel, and biochar are efficient in retaining pesticides in the soil and can help prevent the leaching of organic contaminants into groundwater (Hamid et al., 2022; Singh et al., 2018). Organic amendments can increase the sorption and degradation of organic contaminants by enhancing soil organic matter, microbial activity, and nutrient availability. They can also reduce soil acidity and increase soil aggregation, improving soil structure and water retention. SOM plays a pivotal role in influencing the sorption and attraction of hydrophobic pesticides within the soil. The utilization of organic amendments leads to the enhancement of soil organic content (Gilani et al., 2016). Organic amendments also help retain pesticides in soil, preventing them from leaching into groundwater. The addition of organic waste to soil significantly impacts the immobilization of pesticides (Gilani et al., 2016). This can also alter the degradation, persistence, or mobility, as well as the biological and physicochemical properties of pesticides. Organic amendments may decrease the movement of pesticides through the soil profile, a crucial factor in mitigating pesticide contamination of groundwater (Marín-Benito et al., 2013).

Being an eco-friendly and cost-effective substance, biochar has gained significant attention. Biochar is a fine-grained, porous material with a high surface area that is prepared by pyrolysis of various organic remains, such as agricultural residue, animal waste, wood and municipal waste. Biochar derived from organic residues has emerged as a highly prevalent organic material utilized for both adsorption and soil amendment purposes, aimed at managing the movement and durability of pesticides within the soil ecosystem. Due to its effective adsorption capabilities, biochar is regarded as a promising substance for altering soil properties (Khorram et al., 2016b). The capacity of biochar to adsorb pesticides holds significant importance, impacting not only processes such as chemical transport, leaching, and bioavailability within the soil but also the uptake and utilization of pesticides by plants (Khorram et al., 2016b).

Numerous studies have documented the changes in pesticide behaviour in biochar amended soil (Table 2.1). Reports indicate that the presence of biochar in soil significantly reduces the levels of carbofuran and chlorpyrifos compared to soil without biochar (Yu et al., 2009). The adsorption of fipronil and chlorpyrifos by Allium tuberosum was reduced by 48% and 19%, respectively, when 1% cotton straw biochar was added (Yang et al., 2010). Additionally, biochar made from rice and wheat straw showed 2500 times more adsorption capacity for diuron pesticides compared to unamended soil (Yang and Sheng, 2003b). Spokas et al. (2009) stated that soil mixed with 5% sawdust biochar improved the sorption of acetochlor and Atrazine in sandy loam soil. Cabrera et al. (2014) studied the effect of different biochars on the adsorption-desorption of pentazocine, aminocyclopyrachlor, and pyraclostrobin in silt loam soil. The research revealed that soil enriched with wood biochar exhibited substantial sorption of aminocyclopyrachlor and bentazone, while macadamia nutshell biochar-amended soil displayed comparatively lower sorption of these substances. After incorporating pine chip biochar into the soil, Delwiche et al. (2014) observed a significant decrease in the leaching of the herbicide Atrazine, attributed to the presence of more macropores in pine chip biochar. Tang et al. (2013) investigated the impact of bamboo biochar on pesticides leaching losses from soil and found that bamboo biochar reduced pesticide leaching in soil by 60%. Biochar's sorption capacity for various pesticides varies based on its physicochemical properties, such as pore structure, Specific surface area, and the functional groups present (Cabrera et al., 2014). Typically, biochar contains a high amount of graphene crystalline sheets and amorphous aromatic compounds. Main heteroatoms such as oxygen, nitrogen, sulfur, and phosphorus can be integrated into these aromatic rings, making the surface of biochar highly reactive (Abdul et al., 2017).

The capacity of biochar to adsorb organic pollutants is influenced by factors such as the source of the feedstock, the production conditions of the biochar, and the specific types of organic pollutants present in the polluted soils (Downie et al., 2012; Wu et al., 2012). As a result, these factors can potentially influence other processes, including the availability of contaminants.

Biochar has a strong sorption affinity for pesticides due to its greater surface area, higher negative surface charge, and increased charge density (Zhang et al., 2010). The sorption capacity of biochar depends on attributes such as its surface area, pore volume, ash content, and the presence of functional groups (Yavari et al., 2015). Understanding how each production factor influences these biochar attributes is crucial for creating biochar that efficiently eliminates pesticides. For instance, achieving biochar with elevated sorption capacity and strong affinity involves prolonging the pyrolysis duration. Such biochar displays heightened carbon content, reduced nitrogen and oxygen content, an elevated C/N ratio, and increased O/C and H/C ratios. Additionally, it exhibits larger pore volumes, higher pH levels, and superior pesticide-adsorbing capabilities (Thomas et al., 2020). Furthermore, biochar contains a high amount of organic carbon, which might provide a hydrophobic environment that facilitates the sorption of pesticides. This hydrophobic environment can also facilitate the creation of micelle-like structures, which can entrap and immobilize pesticide molecules.

Biochar can change how pesticides behave in soil (Khorram et al., 2016a; Kumari et al., 2016). The impact of biochar on the effectiveness of herbicides such as clomazone (CMZ) and bispyribac sodium (BYP) was examined by Gámiz et al. (2017). They assessed the sorption, persistence, and leaching of bispyribac sodium and clomazone (CMZ) in soil amended with biochar. In soil modified with biochar generated at 700 °C, sorption of CMZ and BYP was greater.

The study conducted by Cabrera et al. (2014) investigated how various types of biochar affect the sorption of the herbicides aminocyclopyrachlor and bentazone, along with the fungicide pyraclostrobin, in silt loam soil. Their findings demonstrated that soils modified with biochar made from wood pellets virtually entirely adsorbed the pesticides aminocyclopyrachlor and bentazone.

Table 2. 1 Influence of biochar as an organic amendment for improvement of sorption capacity of soil

Feedstock	Pyrolysis Temperature (˚C)	Rate of application	Pesticide	Influence on Adsorption	Reference
Wood Pellets	500˚C	2%	Fluometuron	K_d increased 17 times	Cabrera et al. (2011)
Wood Pellets	500 ˚C	2%	MCPA	K_d increased 45 times	Cabrera et al. (2011)
Beech wood	550 ˚C	1.5%	Methyl-desphenyl-chloridazon	K_f increased 3.24 times	Dechene et al. (2014)
Red gum wood / Eucalyptus spp.	450 ˚C	0.5%	Acetamiprid	K_f increased by 2.1 times	Yu et al. (2011)
Red gum wood / Eucalyptus spp.	450 ˚C	1%	Pyrimethanil	K_f increased by 10.7 times	Yu et al. (2011)
Red gum wood / Eucalyptus spp.	850 ˚C	1%	Pyrimethanil	K_f increased by 62.7 times	Yu et al. (2010)
Composted Alperujo	550 ˚C	2%	Tricyclazole	K_f increased by 4.5 times	García-Jaramillo et al. (2014)
Cassava wastes	750 ˚C	1%	Atrazine	K_f increased by 28 times	Deng et al. (2017)
Pinus radiata wood	350 ˚C	0.5%	Phenanthrene	K_f increased by 51 times	Zhang et al. (2010)
Pinus radiata wood	700 ˚C	0.5%	Phenanthrene	K_f increased by 723 times	Zhang et al. (2010)
Sawdust	700 ˚C	1%	Terbuthylazine	K_f increased by 49.8 times	Wang et al. (2010)
Mixture of seed coat, chaff and wheat residues	500 ˚C	1%	Imidacloprid	K_d increased by 2 times	Larsbo et al. (2013)
Wheat straw	300 ˚C	1%	MCPA	K_f increased by 2.53 times	Tatarková et al. (2013)
Rice hull	600 ˚C	1%	Fomesafen	K_f increased by 7.8 times	Khorram et al. (2016)
Oak wood	550 ˚C	2%	Mesotrione	K_d increased by 2.8 times	Gámiz et al. (2019)
Wheat straw	400 ˚C	0.5%	Pyrazosulfuron-ethyl	K_f increased by 3.86 times	Manna and Singh (2015)
Wheat straw	600 ˚C	0.5%	Pyrazosulfuron-ethyl	K_f increased by 31.9 times	Manna and Singh (2015)
Rice straw	400 ˚C	0.5%	Pyrazosulfuron-ethyl	K_f increased by 5.68 times	Manna and Singh (2015)
Rice straw	600 ˚C	0.5%	Pyrazosulfuron-ethyl	K_f increased by 50 times	Manna and Singh (2015)

K_f: Freundlich sorption coefficient, K_d: partition coefficient

Biochar sorption primarily occurs through two distinct mechanisms: surface adsorption and partitioning (Chen et al., 2008). The presence of functional groups on the biochar surface can lead to the formation of stable chemical bonds with ions or organic compounds, resulting in surface adsorption. The physicochemical characteristics of the biochar's surface, as well as its structure, can change based on the pyrolysis temperatures employed during its production.

Biochar qualities (such as surface area, porous structure, and aromaticity), pesticide characteristics (such as molecular dimensions, and hydrophobicity), soil characteristics, and environmental conditions all play a role in the pesticide sorption of biochar (Qiu et al., 2009). Polar chemicals can adhere firmly to biochar due to interactions between electron donors and receptors. However, the chances of adsorption are diminished for large-sized pesticides with complex molecular structures, as they face challenges in accessing the intricate porous framework within the biochar. Biochar's sorption capacity for hydrophobic pesticides enhances as the aromaticity of the biochar increases, owing to the abundance of aliphatic double bonds and the diversity in aromatization structures. Furthermore, the interaction between biochar and the clay minerals present in the soil plays a significant role in influencing the sorption-desorption processes. Several aspects of biochar affect its capacity to absorb pesticides from soil (Figure 2.2). Among the most crucial characteristics are Surface area, Porosity, Functional groups on the surface of biochar, Temperature of pyrolysis & Residence time, and Type of feedstock (Abbas et al., 2018).

Surface area: The high surface area of biochar offers more active sorption sites, resulting in increased pesticide sorption. A greater surface area provides more binding sites for the adsorption of pesticides (Abbas et al., 2018).

Porosity: The porosity of biochar is crucial in determining surface area and other physical characteristics. Increased surface area due to high porosity can naturally result in greater pesticide sorption. Pore structure may develop in biochar during the pyrolysis of biomass due to water loss in the dehydration process, volatilization of organic matter, fracture, and collapse (Bagreev et al., 2001).

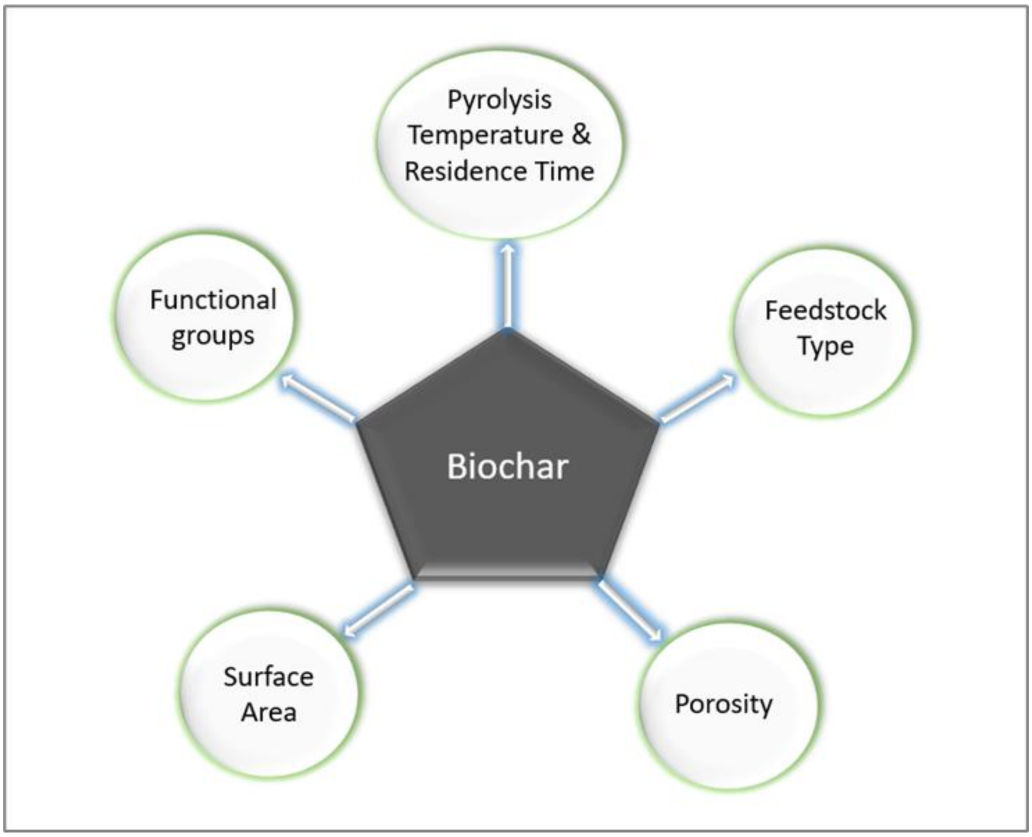

Fig. 2. 2 Factors influencing retention of pesticides in biochar

Functional groups on the surface of biochar: These groups can form strong chemical interactions with pesticide molecules, immobilizing them on the surface of biochar. Functional compounds like hydroxyl, carboxyl, and phenolic groups can improve pesticide sorption by adding more binding sites for each pesticide. The sorption capacity of biochar depends on the presence of surface functional groups such as carboxylic (-COOH), hydroxyl (-OH), lactonic, amide, and amine groups (Antón-Herrero et al., 2018). Generally, the number of functional groups present on the surface of biochar is greatly influenced by the pyrolysis temperature and the source material (Chen et al., 2015). Elevated temperatures commonly lead to reductions in the H/C, O/C, and N/C ratios, indicating a decrease in the presence of functional groups on biochar. Conversely, there is an increasing trend observed in surface area, porosity, and pH (Liu et al., 2017).

It's important to highlight that the quantity of functional groups on the biochar surface diminishes as the pyrolysis temperature rises (Khalid et al., 2020). Generally, changes in pyrolysis temperature result in diverse effects on sorption efficiency. Biochar produced at higher temperatures tends to have more active sites, yet the reduction in functional groups could lead to a decrease in pesticide sorption capacity (Liu et al., 2018). Hence, a comprehensive understanding is essential to ensure the production and application of biochar with the desired attributes in a well-balanced manner for soil enhancement.

Temperature of pyrolysis and residence time: The temperature at which biochar is produced significantly affects its ability to bind pesticides. Several findings indicated that as the pyrolysis temperature rises, there is an increase in both the SSA and the volume of macropores. Chen et al. (2014) investigated the impact of temperature on biochar properties and found that increasing the temperature from 600 ^{o}C to 900 ^{o}C increased the pore volume and surface area of biochar from 0.056 to 0.099 cm^3/g and 25.4 to 67.6 m^2/g, respectively. According to Yu et al. (2019), the pyrolysis residence time aids in increasing SSA and the O/C and H/C ratios (Khalid et al., 2020). Zhang et al. (2011) reported that raising the pyrolysis temperature (100-600 ^{o}C) enhances the carbon content of maize straw biochar (47.46 to 84.29 percent) while lowering the concentrations of H and O (6.23 to 2.60 percent and 45.95 to 11.95 percent, respectively). Consequently, elevated pyrolysis temperatures lead to a reduction in the O/C and H/C ratios within biochars, indicating the dehydration and removal of oxygen from the feedstock (Ahmad et al., 2014).

Type of feedstock: Biochar made from different feedstocks exhibits varied physicochemical properties such as pore size, surface area, and functional groups, all of which affect pesticide removal. Additionally, biochar prepared from the same material can show different properties based on the manufacturing technologies used (Lima et al., 2010). The type of feedstock used to produce biochar can influence its chemical reactivity, thereby affecting its ability to bind pesticides. Certain feedstocks are more suitable for creating biochar that efficiently sorbs pesticides. For instance, Cabrera et al. (2014) examined the effects of several kinds of biochar on the sorption-desorption patterns of pesticides. Studies have shown that the amount of aromatic carbon on the biochar surface is significantly influenced by the lignin content of the feedstock, which plays a crucial role in the pollutant adsorption process (Bornemann et al., 2007). The key explanation for this variation is the lignin concentration of the various biochar feedstocks. Generally, rice straw has lignin contents that ranging from 5 to 24 percent (Binod et al., 2010), compared to bamboo's 37 percent (Deshpande et al., 2000).

2.5 Groundwater Contamination due to Pesticides

The European Union Drinking Water Directive has set the maximum permissible limits for individual pesticides at 0.1 µg/L and for the total amount of pesticides in water at 0.5 µg/L (Chaza et al., 2018). More hazardous compounds such as aldrin, dieldrin, heptachlor, and heptachlor epoxide have a stricter limit of 0.03 µg/L. The Bureau of Indian Standards (BIS) has also established maximum limits for various pesticides, ranging from 0.03 µg/L to 190 µg/L (BIS, 2010).

Pesticide contamination in groundwater is well-documented globally. In Kanpur city, Uttar Pradesh, residues of organochlorine and organophosphate pesticides have been found in groundwater samples (Sankararamakrishnan et al., 2005). Groundwater samples collected from bore wells near agricultural and industrial areas revealed the presence of pesticides such as γ-HCH (0.30–0.471 µg/L), malathion (0.12–2.61 µg/L), and α-HCH (0.189 µg/L) in agricultural areas. In industrial areas, δ-HCH (1.272 µg/L), γ-HCH (0.15–0.92 µg/L), malathion (0.86–16.24 µg/L), and dieldrin (29.84 µg/L) were detected.

In the Kasargod district of Kerala, an alarming concentration of the insecticide endosulfan (58 µg/L) was documented in a dug well sample (Akhil and Sujatha, 2012). Additionally, high levels of aldrin, dieldrin, endrin, and heptachlor were found in groundwater samples from this region. The groundwater in the Thirvallur district of Tamil Nadu is also highly contaminated with organochlorine pesticides. Borewell samples revealed high concentrations of endosulfan (15.9 µg/L), DDT (14.3 µg/L), and HCH (9.8 µg/L), all exceeding permissible limits (Jayashree and Vasudevan, 2007).

A recent study by (Kurakalva and Aradhi, 2022) in the Swarnamukhi river basin area of Andhra Pradesh analyzed surface and groundwater samples using the Solid Phase Extraction process and gas chromatography-mass spectrometry. The maximum concentration of Hexachlorocyclohexane (HCH) detected was 2.97 µg/L in surface water and 2.15 µg/L in groundwater. DDT concentrations reached up to 2 µg/L in surface water and 1.54 µg/L in groundwater. Over 60% of the groundwater samples exceeded the maximum permissible limit set by the WHO.

Duttagupta et al. (2020) investigated the extent of persistent organic pollutants (PoPs) pollution in the Gangetic River basin of West Bengal, India. This study is among the first to document the widespread presence of pesticides in the water of the Ganges River and West Bengal's groundwater basin. Insecticide malathion and herbicide Atrazine were found at concentrations up to 46 times higher than WHO limits. The report indicates that approximately 20 million people in this area are potentially exposed to pesticide contamination in drinking water.

2.6 Summary of the Literature

The following observations could be made from the literature review:

- Pesticide behaviour in soil is location-specific, influenced by factors such as soil organic matter (SOM), clay content, and soil type, which control the sorption and desorption behaviour of pesticides.
- Sorption increases with higher SOM content. However, the sorption coefficient cannot be fully explained by the fraction of organic carbon alone, as SOM quality also plays a significant role.
- The nature of organic matter (OM) varies between soils from different regions due to differences in origin, age, environmental conditions, and cultural practices.
- Sorption and desorption of pesticides are influenced by soil temperature and pH.
- Traces of pesticides found in groundwater highlight the urgent need to monitor pollution levels to prevent environmental and health catastrophes.
- Soil amended with biochar can alter pesticide leaching by increasing sorption and decreasing desorption.
- Biochar reduces the mobility of organic and inorganic pollutants due to its large pore structure (micro and mesoporous), rich surface functional groups (e.g., carbonyl, hydroxyl, phenolic hydroxyl, and carboxyl), large specific surface area (SSA), and high cation exchange capacity (CEC).
- Adsorption capacity is greater for materials with a higher surface area and larger pore size. Surface area, pore volume, and average pore size increase with residence time and pyrolytic temperature.
- Incorporating biochar into the soil can decrease plant uptake of pesticides.

2.7 Research Gaps

- Imidacloprid and Atrazine are among the most commonly used pesticides in India. However, there have been few studies on their sorption and leaching behaviour in Indian soils. Therefore, thorough investigations into their leachability and fate in soil and groundwater are necessary.

- Most research on Indian soils has focused on the alluvial soils of northern India (Delhi, Punjab, Haryana). However, studies on black cotton soil, which covers approximately 30% of Indian soil, are sparse.
- There is limited research on the impact of pH and temperature on the sorption and desorption of pesticides in black cotton soil. Thus, assessing the effects of pH and temperature on the sorption, desorption, and leaching potential of pesticides in the black soils of the Telangana region is essential.
- Investigations into cotton stalk biochar have primarily focused on plant uptake of pesticides. However, studies on the effectiveness of its sorption, desorption, and leachability behaviour are minimal.

Chapter 3

Materials and Methods

3.1 Introduction

This chapter delves into the materials and methodologies employed for conducting in-depth experimental studies, aligned with the objectives outlined in the scope of the work. It begins by elucidating the specifics of the pesticides utilized in the study. Comprehensive information is provided on the soil samples used in the experimental procedures, including details on sample location points, collection procedures, sample preparation, and characterization procedures. The chapter then shifts focus to the methodologies employed for studying soil and pesticide interactions, along with various behavioural studies and the corresponding experimental setups. Additionally, the chapter outlines the procedures for pesticide extraction and cleanup for analysis.

A pivotal aspect of this research involves the generation of biochar and hydrochar from cotton stalks, with in-depth discussions on the specific procedures employed for their synthesis. Furthermore, the chapter concentrates on the thorough characterization of the synthesized materials, addressing crucial physicochemical properties and elemental composition. The application of diverse characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Thermogravimetric analysis (TGA), is meticulously explained.

3.2 Pesticides

Two pesticides, one insecticide, and one herbicide were selected for the study.

3.2.1 Imidacloprid

Imidacloprid is an insecticide that belongs to the neonicotinoid group. It was introduced in the early 1990s, and since then, it has become one of the most widely used insecticides worldwide. Currently, it is registered in more than 120 countries and is very effective in controlling various types of soil insects, termites, and a wide range of sucking and chewing insects. Analytical standard Imidacloprid at a purity of 99.9% was provided by Sigma-Aldrich (Germany). Figure 3.1 and Table 3.1 show the structure and properties of Imidacloprid, respectively.

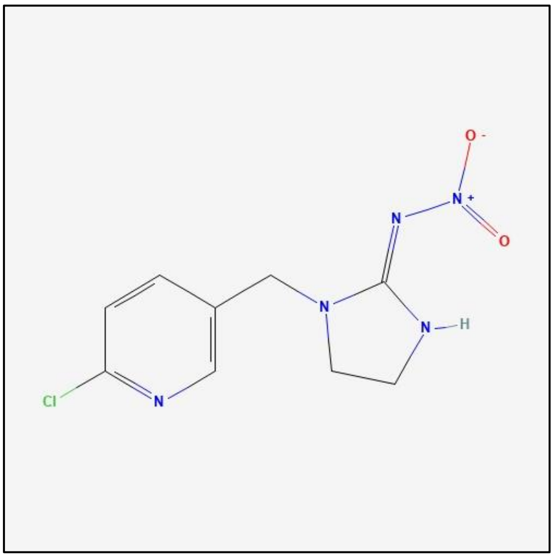

Fig. 3. 1 Chemical structure of Imidacloprid

An Imidacloprid stock solution of 1000 ppm was prepared by dissolving 25 mg of Imidacloprid in 25 ml of acetonitrile solvent. The acetonitrile used was of HPLC grade, and all other chemicals were analytical grade. Insecticide solutions of different concentrations were prepared in 0.01M $CaCl_2$ solution and all the prepared solutions were stored at a temperature below 0˚C.

Table 3. 1 Properties of Imidacloprid

IUPAC Name	[1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin- 2-ylideneamine
Pesticide Group	Neonicotinoids
Molecular Formula	$C_9H_{10}ClN_5O_2$
Molecular Weight	255.66
Solubility in water	0.61 g/L at 20˚C
Log K_{ow}	0.57
Vapor pressure	4×10^{-7} mPa
Toxicity class	II

3.2.2 Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is a very popular herbicide, primarily used to manage grassy and broadleaf weeds in both agricultural and non-agricultural fields. In the United States, it was first introduced in 1952 and registered for commercial use in 1958. Atrazine ranks as the second most widely used pesticide globally, with 7 to 9 million kilograms used annually. It belongs to the class of chemicals called triazines and is categorized as a selective herbicide because it targets specific plants without harming others. Atrazine of analytical standard with a purity of 99.9 percent was supplied by Sigma-Aldrich (India). The chemical structure of Atrazine is shown in Figure 3.2, and its characteristics are presented in Table 3.2. To prepare a 1000 ppm stock solution, 25 mg of Atrazine was dissolved in 25 ml of methanol. All chemicals were of analytical grade, and the methanol was HPLC grade. All the herbicide solutions were stored at temperature below 0˚C after being prepared in a 0.01M $CaCl_2$ solution.

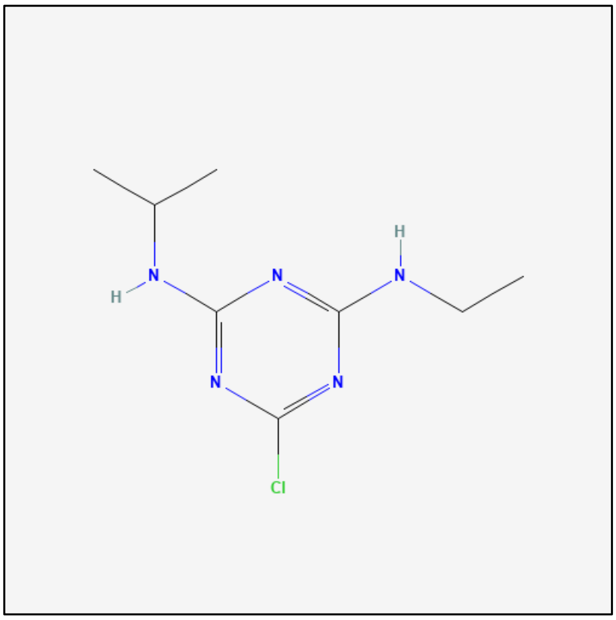

Fig. 3. 2 Chemical structure of Atrazine

Table 3. 2 Properties of Atrazine

IUPAC Name	6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine
Pesticide Group	Triazine
Molecular Formula	$C_8H_{14}ClN_5$
Molecular Weight	215.68
Solubility in water	33 mg/L at 25˚C
Log K_{ow}	2.61
Vapor pressure	2.89×10^{-7} mm Hg at 25˚C
Toxicity class	III

3.3 Soils

The soils were collected from various region of Telangana State, India. A total of three samples of black cotton soil and one sample of red soil were collected for the present study. Black cotton soil, also known as regur soil, typically covers around 25% of the total land area and has a high clay content. These soils develop on calcareous clay parent materials and contain a high calcium carbonate content. They are typically rich and fertile, containing ample nutrients that make them well-suited for either cultivating crops or serving as grazing land. Moreover, their dark coloration contributes to these soils' excellent water-holding capacity, enabling them to absorb more moisture compared to other soil types in Telangana. Red soils, on the other hand, are predominant in this region, accounting for around 48% of the total land area. Red soils predominantly originate from crystalline granite and metamorphic rocks like gneiss and schists, primarily dating back to the Archean period.

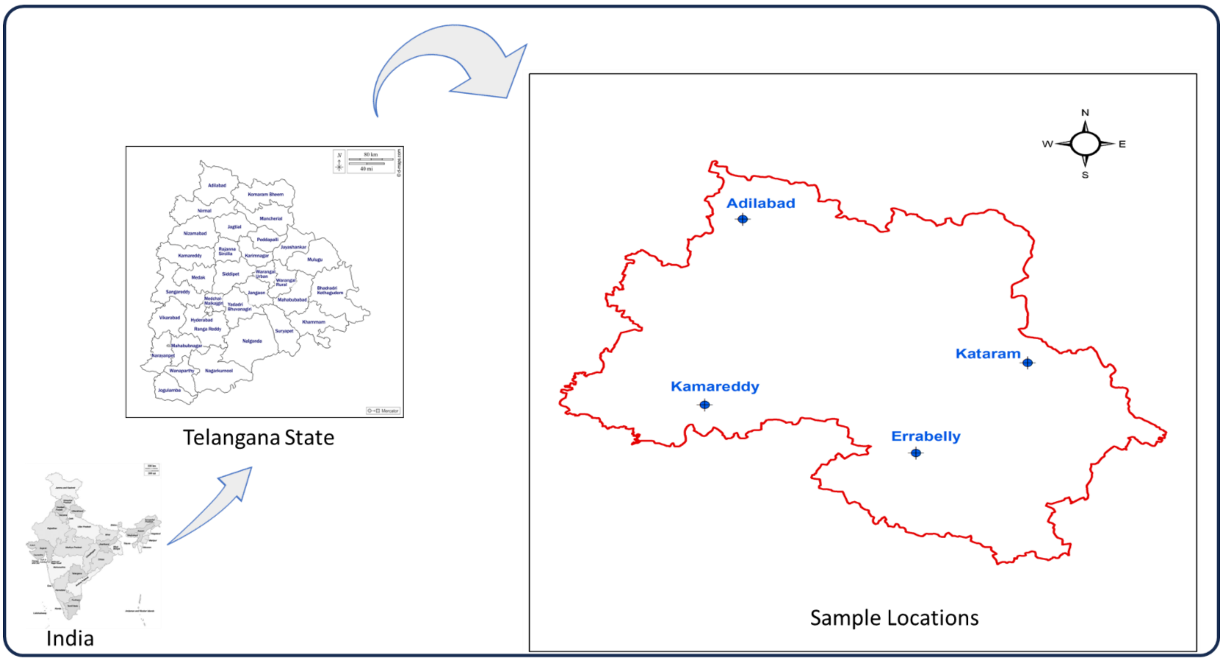

Fig. 3. 3 Soil sample location points

Three black cotton soil samples were collected from Kataram (18˚36’52” N, 79˚56’31” E), Adilabad (18˚29’19” N, 78˚29’54” E), and Kamareddy (18˚20’36” N, 78˚16’14” E) and one red soil sample was collected from a nearby village named Errabelly (18° 1' 54.12"N, 79° 21' 46.0938"E). Figure 3.3 depicts the locations of the sample collection points. Soil samples were collected preferably from the top layer at a depth of 0-20cm with the help of core cutter. The soil samples were gathered in collaboration with local farmers, and sampling locations were selected in areas with no recorded history of pesticide application in the previous year. Following collection, roots, leaves, and other undesirable elements were meticulously removed from the soil samples. Subsequently, the soils underwent air-drying at room temperature and were sieved using a 2 mm sieve. The samples were then stored for further use.

3.4 Characterization of Soils

Soil characterization study was conducted based on various experimental methods as discussed below.

3.4.1 Determination of Soil pH

Soil pH was measured by an electronic method in soil suspensions with a soil to water ratio of 1:2.5 (w/v) as per the guidelines of IS 2720 (part-26).

3.4.2 Determination of Cation Exchange Capacity (CEC) and Specific Surface Area (SSA)

The cation exchange capacity (CEC) of soil was determined using methylene blue adsorption test as discussed by Yukselen and Kaya (2008). The following equation was used for the calculation of CEC.

$$CEC = \frac{100}{W} \times V \times N \qquad (3.1)$$

Where, W is the weight of soil sample in 'g', V is the volume of methylene blue titrant used in mL, and N is the normality of methylene blue solution.

Specific surface area (SSA) was determined by European standard spot test method by using methylene blue solution (Yukselen and Kaya, 2008) and it was calculated by using below equation:

$$SSA = \frac{1}{319.87} \times \frac{1}{200} \times 0.5N \times A_V \times A_{MB} \times \frac{1}{10} \qquad (3.2)$$

Where, N is the number of methylene blue increment added to the soil solution, A_V is the Avagadro's number (6.02×10^{23}/mol), and A_{MB} is the area covered by one methylene blue molecule.

3.4.3 Soil Organic Matter

The total organic content present in the soil was calculated by using Walkley-Black method.

3.4.4 Hydrometer Analysis

The clay content of the soil samples was determined using hydrometer test. The samples were washed through a 75 µm sieve. The finer fractions passing through the sieve were collected, oven dried and analyzed by sedimentation using hydrometer method (ASTM, D422-63) to get clay percentage.

3.5 Physico-chemical Properties of Soils

The physicochemical properties of four different agricultural soils, namely Kataram (BC-1), Adilabad (BC-2), Kamareddy (BC-3), and red soil (RS), exhibit notable variations as shown in Table 3.3. The soil pH ranges from slightly acidic to slightly alkaline, with BC-1 and red soil being closer to neutral at 7.54 and 6.71, respectively, while BC-2 and BC-3 exhibit higher alkalinity with pH values of 8.59 and 7.97, respectively. Organic carbon content also varies, with red soil having the highest at 0.58%, indicating better organic matter content compared to the black cotton soils. Cation exchange capacity (CEC) is significantly higher in BC-2 and BC-3 soils, suggesting their greater ability to retain and exchange nutrients. Surface area (SSA) follows a similar trend, with BC-2 having the highest SSA, indicating greater surface activity. Particle size distribution shows that red soil has the highest percentage of sand particles, while the black cotton soils have higher proportions of clay. Overall, these variations in physicochemical properties highlight the diverse nature of soils found in this region of India.

Table 3. 3 Physico-chemical properties of air-dried soils

Soil	pH	Organic Carbon (%)	CEC (meq/100g)	SSA (m^2/g)	Dry Density (g/cm^3)	Moisture Content (%)	Particle Size		
							Sand (%)	Silt (%)	Clay (%)
Kataram (BC-1)	7.54	0.10	25.97	223.85	1.59	5.55	31	20	49
Adilabad (BC-2)	8.59	0.39	36.27	391.42	1.26	9.26	6	35	59
Kamareddy (BC-3)	7.97	0.26	36.97	363.23	1.28	8.98	18	23	59
Errabelly (RS)	6.71	0.58	15.09	55.04	1.63	4.87	51	13	36

3.6 Sorption Desorption Experiment

3.6.1 Kinetics Study

In order to investigate sorption and desorption characteristics, a series of experiments were conducted using the batch equilibrium approach, adhering to the guidelines set forth by the Organization for Economic Co-operation and Development (OECD). To maintain consistent ionic strength, a 0.01M $CaCl_2$ solution was used as the aqueous phase.

To ascertain the equilibration time, the kinetics of Imidacloprid and Atrazine were analysed across various soils, using a soil-to-solution ratio of 1:5 (w/v) and a pesticide concentration of 5 µg/mL. Each experimental run involved introducing a 5 g soil sample into 50 mL glass centrifuge tubes, followed by adding 25 mL of the pesticide solution. The tubes were agitated at 200 rpm for varying durations: 0.25, 0.5, 1, 2, 4, 6, 8, 16, 24 and 48 hours using an orbital shaker. To ensure reliability, the experiment was repeated three times, with an additional control group (lacking soil) in each iteration. After centrifuging the soil suspension at 6000 rpm for 15 minutes, the resulting supernatant was analysed using High-Performance Liquid Chromatography (HPLC). This analytical technique was employed to quantify and assess the concentration of pesticide in the solution, providing valuable insights into the sorption and desorption behaviour of the pesticide within the tested soils.

3.6.2 Sorption Desorption Study

The sorption behaviour of the target pesticides in soils was systematically investigated through batch equilibrium experiments conducted under various conditions. In order to create a range of concentrations, pesticide solutions spanning 0.5, 1, 2.5, 5, 10, and 20 µg/mL were meticulously prepared using a 0.01M $CaCl_2$ aqueous solution.

The experimental setup involved introducing 5 g of soil into a 50 mL centrifuge tube, followed by adding of 25 mL of the pesticide solution. This mixture underwent rigorous agitation for a predetermined duration at 200 rpm, facilitated by an orbital shaker. Subsequently, the soil slurry was subjected to centrifugation for 15 minutes at 6000 rpm, resulting in the separation of the solid and liquid phases.

To ensure clarity and precision in subsequent analyses, the supernatant was carefully pipetted out and refined through filtration using a 0.22-micron PVDF syringe filter. This meticulous preparation preceded the High-Performance Liquid Chromatography (HPLC) examination, which aimed to provide detailed insights into the pesticide concentration within the solution. By exploring these experimental conditions at different temperatures and concentrations, a comprehensive understanding of the sorption characteristics of pesticide in diverse soil matrices was pursued. Equation (3.3) was used to calculate the amount of Imidacloprid that was sorbed by the soil.

$$Q_e = \frac{(C_o - C_e) \times V}{m} \tag{3.3}$$

Where, Q_e is the quantity of pesticide sorbed at equilibrium (μg g^{-1}), C_o is the initial concentration of pesticide (μg mL^{-1}), C_e is the equilibrium concentration (μg mL^{-1}), V is the volume of pesticide solution (mL), m is the mass of soil (g).

The distribution coefficient (K_d) of pesticides between the solution and the solid state was determined by relating pesticide solubility on sorbent (Q_e, μg/g) to pesticide concentration in solution (C_e, μg/mL) using Equation (3.4):

$$K_d = \frac{Q_e}{C_e} \tag{3.4}$$

The organic carbon partition coefficient of the soil (K_{OC}) was computed by normalizing the adsorption constant with the total organic carbon content (TOC, %) of soil using Equation (3.5):

$$K_{OC} = {(K_d \times 100)}\big/{TOC(\%)} \tag{3.5}$$

Sorption experiments were immediately followed by desorption studies. Pipetting was used to remove supernatant, which was then replaced by the same amount of 0.01M calcium chloride. After shaking the samples in an orbital shaker for 24 hours at 200 rpm, the suspensions were centrifuged for 15 minutes at 6000 rpm. Following that, the supernatant was filtered and passed through an HPLC. To determine the quantity of pesticide adsorbed in the soil, Equation (3.6) was used:

$$Q_e^{des} = Q_e - (C_e^{des} \times V/m) \tag{3.6}$$

Where, Q_e^{des} is the amount of pesticide retained in soil (μg/g), and C_e^{des} is the equilibrium desorption concentration (μg/mL).

3.6.3 Sorption Kinetics and Isotherm Models

The present investigation involved the utilization of various kinetic models, including the Lagergren pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and the Weber and Morris intraparticle diffusion model (IPD), to evaluate the sorption kinetics of pesticide on the examined soils. The subsequent mathematical expressions were employed in accordance with the research of Lima et al. (2015):

PFO model	$Q_t = Q_e[1 - e^{(-k_1 t)}]$	(3.7)
PSO model	$\mathrm{Q}_t = \dfrac{k_2 . Q_e^2 . t}{1 + Q_e . k_2 . t}$	(3.8)
Elovich model	$Q_t = \dfrac{1}{\beta}\ln(\alpha\beta) + \dfrac{1}{\beta}\ln(t)$	(3.9)
IPD model	$Q_t = k_{int} t^{0.5} + c$	(3.10)

Where, Q_t and Q_e indicates quantity of pesticide adsorbed onto the soil at time 't (min) and at equilibrium (μg/g), respectively. The rate constants for the PFO and PSO kinetics models are denoted as k_1 (min^{-1}) and k_2 [g/ (μg min)], respectively. The Elovich model involves the initial sorption and desorption rate constants, represented by α [μg/ (g min)] and β (g/μg). The IPD model is characterized by the constant k_{int} [μg/ (g $\mathrm{min}^{0.5}$)], and 'c' represents the intercept of the IPD model.

The sorption data for pesticide was assessed using the linear forms of the Langmuir, Freundlich, and Temkin isotherm models.

Langmuir Isotherm Model:

The Langmuir model is relevant when pesticide molecules adhere to the soil surface in a monolayer and the surface has a certain number of identical sites for adsorptive attachment. The Langmuir isotherm equation is given as:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L C_e} \qquad (3.11)$$

In this framework, C_e (mg/L) denotes the equilibrium concentration, Q_e (µg/g) signifies the adsorbed amount of pesticide at equilibrium, Q_m (µg/g) represents the Langmuir adsorption capacity, K_L stands for the Langmuir adsorption constant (mL/g).

Freundlich Isotherm Model:

Unlike Langmuir isotherm, Freundlich isotherm is applied to multilayer sorption and is associated with non-ideal and reversible adsorption. This theory is frequently applied to explain the sorption of inorganic or organic compounds on heterogeneous surfaces. The Freundlich isotherm equation is given by:

$$\log (Q_e) = logK_f + ({}^{1}/_{n})\log (C_e) \tag{3.12}$$

Where, K_f is Freundlich constant and is a measure of the degree of adsorption and n is adsorption intensity.

Temkin Isotherm Model:

The Temkin isotherm depicts the sorption process on a heterogeneous surface. This model is based on the assumption that adsorption energy decreases linearly with surface coverage due to interactions between the adsorbent and the adsorbate. Temkin's isotherm is given as:

$$Q_e = \frac{RT}{b}\ln (AC_e) \tag{3.13}$$

R stands for the universal gas constant, A and b are constants, and T indicates the temperature (K).

3.6.4 Influence of pH

To examine the impact of pH on pesticide sorption in the studied soils, the soil solutions were modified to varying pH values of 3, 6, and 9. The pH was regulated using Hydrochloric acid (HCl) and Potassium hydroxide (KOH). The sorption study was conducted on all soils using pesticide concentration of 5 µg mL^{-1}, employing the same procedure as outlined in section 3.5.2.

3.6.5 Influence of Temperature

To investigate the influence of temperature on the sorption behaviour of the target pesticides, a total of three temperature regime were chosen: 273 K, 300 K, and 313 K. The experiments were conducted in a temperature controlled orbital shaker.

3.7 Soil Column Leaching

The leaching behaviour of pesticides was investigated following the guidelines outlined by OECD (2002), utilizing packed soil columns. The experiment employed a polyvinyl chloride (PVC) pipe with a length of 370 mm and an internal diameter of 42 mm. Initially, the columns were longitudinally halved and subsequently reassembled using adhesive to facilitate easy separation upon completion of the leaching cycle.

In the column, soil was incrementally added in approximately 50 g portions, with each addition being compacted to achieve uniform density. The columns were then packed to correspond with the respective bulk densities of the soils. The lower section of the column was filled with glass fibre (Figure 3.4) to minimize soil loss and facilitate the smooth passage of leaching water.

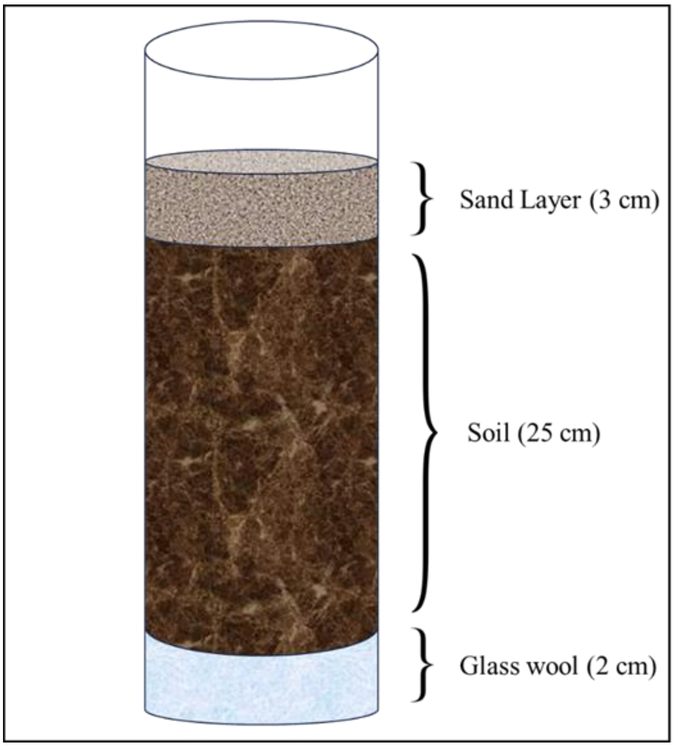

Fig. 3. 4 Distribution of different components in a column

The PVC columns were positioned in a Buchner funnel equipped with a Whatman glass filter. Figure 3.5 illustrates the detailed configuration of the experimental setup. Leaching was carried out using 0.01M $CaCl_2$ until saturation, allowing natural drainage. Subsequently, 500 µg of pesticides were applied to the top of the column and covered with a 3 cm layer of acid wash sand. This sand layer served the dual purpose of ensuring the even distribution of the $CaCl_2$ solution and preserving the integrity of the topsoil. A total of 500 mL of $CaCl_2$ solution passed through the column, maintaining a fixed head of 5 cm throughout the study, with natural drainage permitted.

Leachate was collected in a conical flask positioned at the base and stored in a freezer at 0 ˚C. After leaching, the columns were left undisturbed for a day to allow for complete drainage. Subsequently, the columns were opened, and the soil column was divided into five sections, each measuring 5 cm. The pesticides residues present in the soils then extracted by using QuEChERs method as explained in section 3.9.

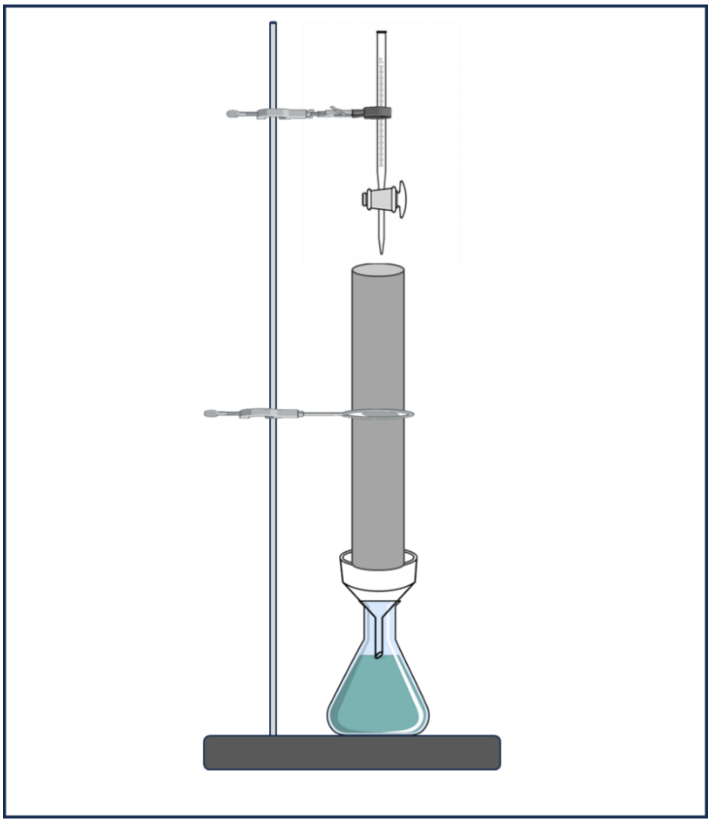

Fig. 3. 5 Experimental setup of Soil Column study

3.8 Pesticide Degradation Study

The pesticide degradation study on various soils were carried out as per the guidelines described by OECD (2002). The collected soil samples were air dried in the laboratory, plant parts and other unwanted things were removed before grinding, and the soil was sieved through a 2 mm size sieve. 10 g of soil samples were placed into a centrifuge tube and spiked with pesticide.

The intended initial spiking concentration was 10 µg of pesticides per gram of oven dried soil. The mixture was thoroughly blended to ensure uniform distribution of the pesticide. The tubes were stored in darkness while maintaining a consistent moisture level equivalent to 40% of their field capacity. The incubator was set to a constant temperature of 25±2 ˚C for the entire duration of the experiment. To prevent anaerobic conditions, the caps of the centrifuge tubes were deliberately kept loose. Moisture levels in each tube were monitored weekly throughout the study, and any lost moisture was replenished with deionized water using a dropper. At specified intervals, samples were gathered and promptly placed in a freezer set to 0 ˚C. They remained in the freezer until additional processing for extractions was conducted. The extraction of pesticides from soil samples were conducted by using QuEChERs method as mentioned in section 3.9.

The rate of degradation and half-life ($T_{1/2}$) of pesticides were calculated using the following equations:

$$\frac{C_t}{C_0} = e^{-k_R t} \tag{3.14}$$

Where C_t is the residual amount of pesticide in soil (µg/g), C_0 is the initial concentration of pesticide applied (µg/g), t is time (days), and k_R is degradation rate constant (day^{-1}). The half-life (days) of the pesticides was calculated as follows:

$$T_{1/2} = \frac{ln2}{k_R} \tag{3.15}$$

3.9 Sample Extraction and Cleanup

3.9.1 Extraction of Pesticide from Soil

To extract pesticide residue from soil, a 10 g soil sample was carefully measured and placed into a 50 mL tube. Subsequently, 20 mL of an acetonitrile/methanol solvent mixture was added to the tube, and the contents were thoroughly mixed using a shaker for approximately 3 minutes. Following this, 1±0.1 g of sodium chloride (NaCl) and 4±0.1 g of magnesium sulfate ($MgSO_4$) was introduced, and the mixture was gently shaken for 1 minute.

The tubes were then subjected to centrifugation at 3300 rpm for 5 minutes. To isolate the organic layer, 10 mL of the resultant solution was carefully transferred into a 15 mL centrifuge tube containing 1.5 g $MgSO_4$ and 0.25 g of primary secondary amine (PSA), which were mixed gently. Subsequently, the tubes underwent sonication for 1 minute to eliminate air bubbles, followed by centrifugation at 3300 rpm for 10 minutes.

Approximately 1 mL of the extracted solution was transferred into vials for subsequent analysis using High-Performance Liquid Chromatography (HPLC).

3.9.2 Extraction of Pesticide from Water

To extract the pesticide, 750 mL of a water sample was accurately measured and placed into a beaker. Following this, 150 g of sodium chloride was added to the water, and the mixture was vigorously shaken until complete dissolution of NaCl was achieved. The resulting solution was then carefully transferred to a separatory funnel.

In the separatory funnel, 100 mL of Dichloromethane (DCM) was added, and the contents were vigorously shaken for 1 minute, with pressure being released intermittently. Subsequently, the separatory funnel was positioned on a stand for approximately 5 minutes, allowing the organic and aqueous layers to separate. The organic phase was then selectively collected into a conical flask.

This extraction procedure was repeated three times, with 50 mL of DCM being added to the original sample each time. After gathering all the organic layers, 20 g of sodium sulfate (Na_2SO_4) was introduced into the conical flask and thoroughly mixed. The resulting mixture underwent concentration to approximately 3-4 mL using a rotary evaporator and was subsequently transferred into a test tube.

The DCM solvent was evaporated in a turbo evaporator, and the final volume was adjusted using acetonitrile/methanol. Following this, the samples were filtered through a 0.22 µm syringe filter and transferred into HPLC vials for further analysis.

3.10 Synthesis of Cotton Stalk Biochar and Hydrochar

3.10.1 Sample Collection

Raw cotton stalks (RC) were collected from a cotton field near Kondaparthy village (17.911365˚N, 79.551252˚E), Telangana state, India. The collected samples were first cut into small pieces, approximately 2 cm in size, and then rinsed with deionized water to remove dirt and other impurities. Following this, the material was subjected to a 24-hour treatment in a hot air oven at 105˚C to eliminate moisture content. Subsequently, the dried samples were pulverized, sieved through a 475-micron sieve, and stored in a desiccator for future use.

3.10.2 Synthesis of Biochar

The pyrolysis experiments of RC were carried out in a muffle furnace. A ceramic crucible with a lid containing 100 g of cotton stalk powder underwent pyrolysis at various temperatures (300 ˚C, 500 ˚C and 700 ˚C) for 4 hours under a limited oxygen environment. The heating rate was maintained approximately 10 ˚C per minute. After the pyrolysis process, the biochar sample was allowed to cool within the furnace until it reached room temperature. The collected biochar samples were labelled as CBC-300, CBC-500 and CBC-700, respectively.

3.10.3 Synthesis of Hydrochar

Hydrothermal Carbonization (HTC) of cotton stalk was conducted using a Teflon reactor situated within the confines of a stainless-steel enclosure. 30 g of RC were blended with 300 mL of deionized water (solid: liquid, 1:10, w/v) in the reactor, and the mixture was subjected to various temperatures (180 ˚C, 210 ˚C and 240 ˚C) for 4 hours under autogenous pressure in a muffle furnace. Following the reaction, the HTC reactor was left inside the furnace until it reached room temperature. The char was then separated with the help of vacuum filtration. The obtained hydrochar was washed multiple times with deionized water and subsequently placed in a hot air oven at 105 ˚C for 24 hours to remove all the moisture contained within it.

3.11 Characterization of Biochar and Hydrochar Samples

3.11.1 Proximate Analysis

The analysis of essential parameters, including moisture, volatile matter, ash content, and fixed carbon, encompasses various methods. The ASTM D1762 standard method was used to determine the moisture content, volatile matter, ash content present in various biochar and hydrochar samples. To determine moisture content, the sample is heated at 105 °C, and the weight loss is measured thereafter. Volatile matter (VM) is assessed by gauging weight loss during the combustion of approximately 1 g of the sample in a crucible at 900 °C. The same method is employed to determine ash content at 750 °C. The calculation of fixed carbon (FC) involves subtracting the percentage values of moisture content, volatile matter, and ash from 100, as described in Equation (3.16) below.

$$FC = 100\% - VM - ash \tag{3.16}$$

3.11.2 Ultimate Analysis

The elemental analyzer was employed to conduct both ultimate and basic elemental characterization on various biochar and hydrochar samples. This specialized analytical instrument is utilized to ascertain the elemental composition of a given sample, accurately determining the presence and quantities of various elements, including carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O). The analysis was conducted in a UNICUBE model elemental analyzer provided by Elementar, Germany. The CHNS(O) analyzer operates on the principle of the “Dumas method”, wherein the sample undergoes rapid and complete oxidation through “flash combustion”. The resulting combustion products are then separated by a chromatographic column and identified by the thermal conductivity detector (TCD). Argon gas was used as a carrier gas for the analysis.

3.11.3 Fourier Transform Infrared Spectroscopy

The determination of surface functional groups present in the samples through FT-IR was carried out utilizing a Bruker Alpha II apparatus. Spectral ranges spanning from 500 to 4000 cm^{-1} were recorded for each sample, employing a resolution of 2 cm^{-1} and the KBr pellets technique. The preparation of solid samples utilized the widely adopted KBr pressed-disc technique. Approximately 2 mg of the sample was blended with KBr powder to create KBr pellets, and the pressed-disc technique was employed for the preparation of pellets.

3.11.4 X-Ray Diffraction (XRD)

The crystallographic structures of biochars and hydrochars underwent a thorough examination using PAN analytical X-ray Diffraction. This comprehensive analysis involved the utilization of CuKα radiation with specific parameters set at 45 kV and 30 mA. The scattering angle (2θ) ranged from 10 to 70˚, with a meticulous step size of 0.001. The Xcelerator ultra-fast detector played a pivotal role in capturing and enhancing the precision of the diffraction data throughout the investigation process.

3.11.5 Thermogravimetry Analysis

Thermogravimetric experiments were performed on biochar and hydrochar samples using a Netzch STA 2500 thermogravimetric analyzer. The investigation targeted the exploration of combustion behaviour across a temperature spectrum of 30 to 850 ˚C, maintaining a heating rate of 30 ˚C/min. During the analysis, an inert atmosphere was maintained by the constant flow of argon gas at a rate of 60 mL/min. The TG/DTG curves were used to determine the ignition temperature (T_i) and burnout temperature (T_f). T_i represents the temperature at which the char initiates combustion, while T_f is the temperature at which the rate of weight loss decreases to 1% per minute. These values were computed using the tangent line method, as explained by Xu et al. (2021). The comprehensive combustion index (CCI) was determined by Equation (3.17):

$$\mathrm{CCI} = \frac{(DTG_{mean})\times(DTG_{\max})}{(T_i^2)\times(T_f)} \tag{3.17}$$

The comprehensive stability index (R_w) and ignition index (D_i) of biochar and hydrochar samples were calculated based on the following equations.

$$D_i = \frac{DTG_{\max}}{(T_i \times T_m)} \tag{3.18}$$

$$R_w = 8.5875 \times 10^7 \times \frac{DTG_{\mathrm{mean}}}{(T_i \times T_m)} \tag{3.19}$$

Where, DTG_{mean} and DTG_{max} are mean and max weight loss rates (%/min), and T_i, T_f, T_m are ignition temperature (˚C), burnout temperature (˚C) and maximum weight loss temperature (˚C), respectively.

3.12 High Performance Liquid Chromatography (HPLC) Instrumentation

The samples were analyzed using a Shimadzu-manufactured High-Performance Liquid Chromatography (HPLC) instrument, specifically the LC-20AD model. This HPLC system comprised a Degassing unit (DGU-20A5R), a Prominence Autosampler (SIL-20AHT), and a Photodiode Array Detector (SPD-M20A). The analytical process involved employing a C-18 column (250 mm × 4.6 mm, 5 µm particle size) as the stationary phase, following a method derived from a previous study (Leiva et al., 2015; Yue et al., 2017) with minor adjustments.

3.12.1 HPLC Analysis for Imidacloprid

A mobile phase containing water and acetonitrile at a ratio of 60:40 (%, v/v) was employed for isocratic elution, and a flow rate of 0.4 mL/min was used for the separation of Imidacloprid. The supernatant collected from the sorption desorption experiment was filtered through a 0.22 µm syringe filter. During HPLC analysis, 20 µL of the sample was injected by the autosampler and detected at 254 nm. The mobile phase was sonicated and filtered using a 0.22 µm filter before use. Integration of peak areas was used to quantify the pesticide present in the sample. The quantities of pesticides in the fortification samples were calculated by analysing the detector readings for the target chemical in the samples and comparing them with those acquired from the calibration curve. The peak retention time for Imidacloprid was observed at 10.09 min (Fig 3.6). The recovery efficiency of Imidacloprid in soil was found to be 95 ± 3.2 %. The linearity was good as indicated by the regression coefficient (R^2) value of 0.9998 (Fig 3.7).

3.12.2 HPLC Analysis for Atrazine

The HPLC analysis method used was adopted from Yue et al. (2017) after a few modifications. Methanol (HPLC grade) and Millipore water in a ratio of 70:30 (%, v/v) were used as the mobile phase, and a flow rate of 0.4 mL/min was maintained during the analysis. The column temperature was 35 ˚C, and the injection volume was 20 µL. The peaks were detected at a wavelength of 229 nm. The peak retention time for Atrazine was observed at 22.13 min (Figure 3.8). The linearity was good as indicated by the regression coefficient (R^2) value of 0.9999 (Figure 3.9).

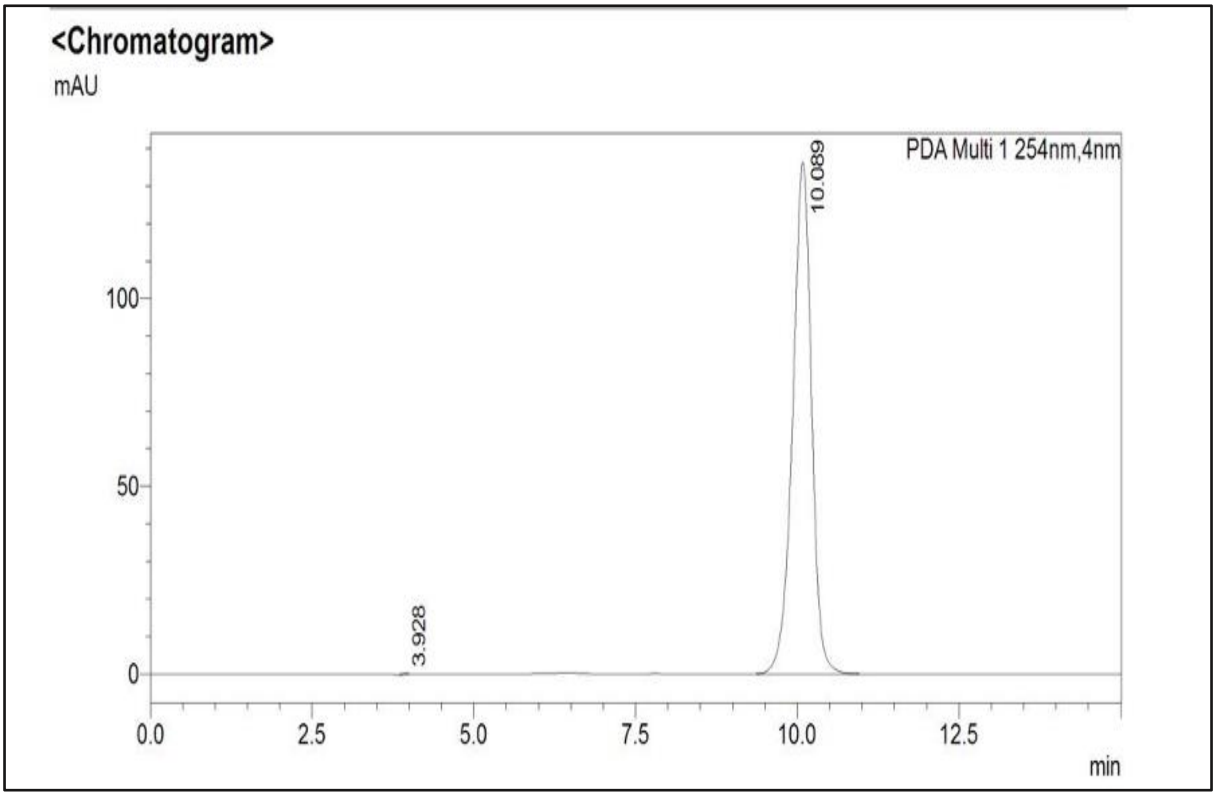

Fig. 3. 6 Chromatogram obtained for Imidacloprid

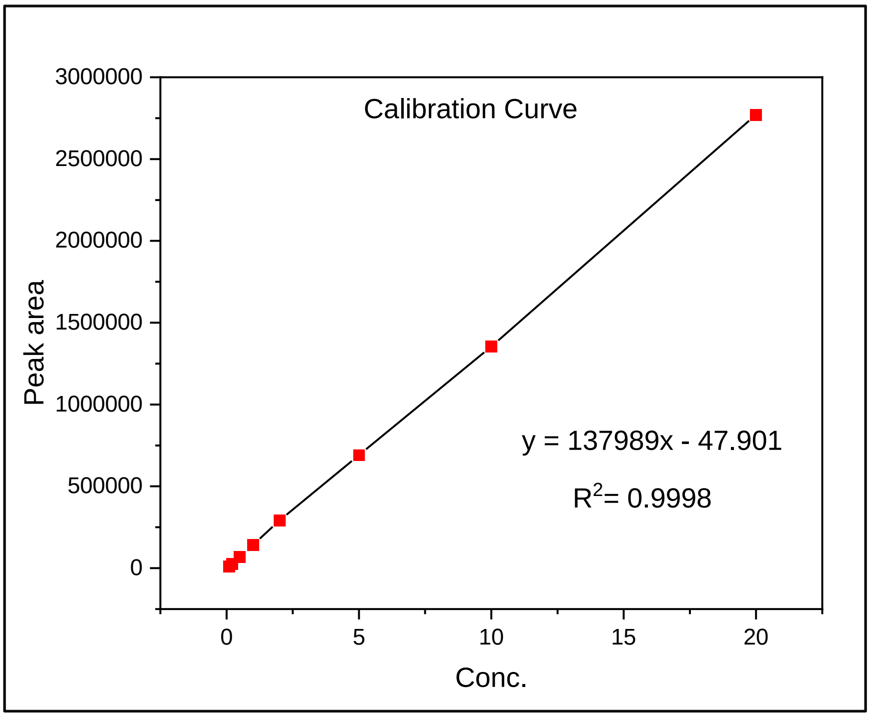

Fig. 3. 7 Calibration curve of Imidacloprid

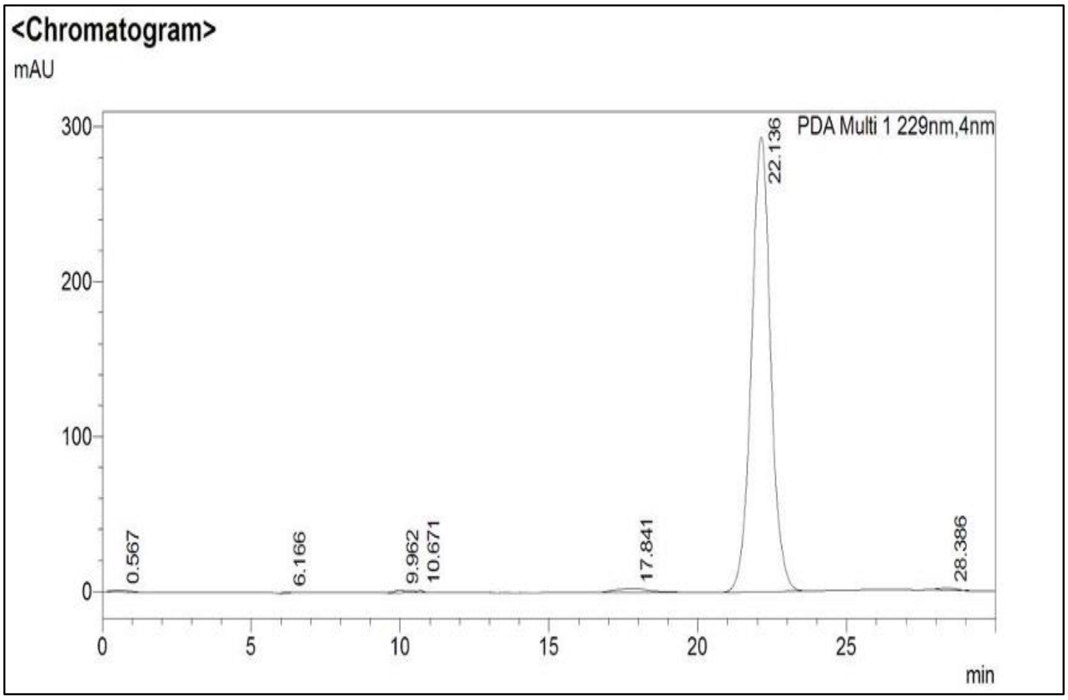

Fig. 3. 8 Chromatogram obtained for Atrazine

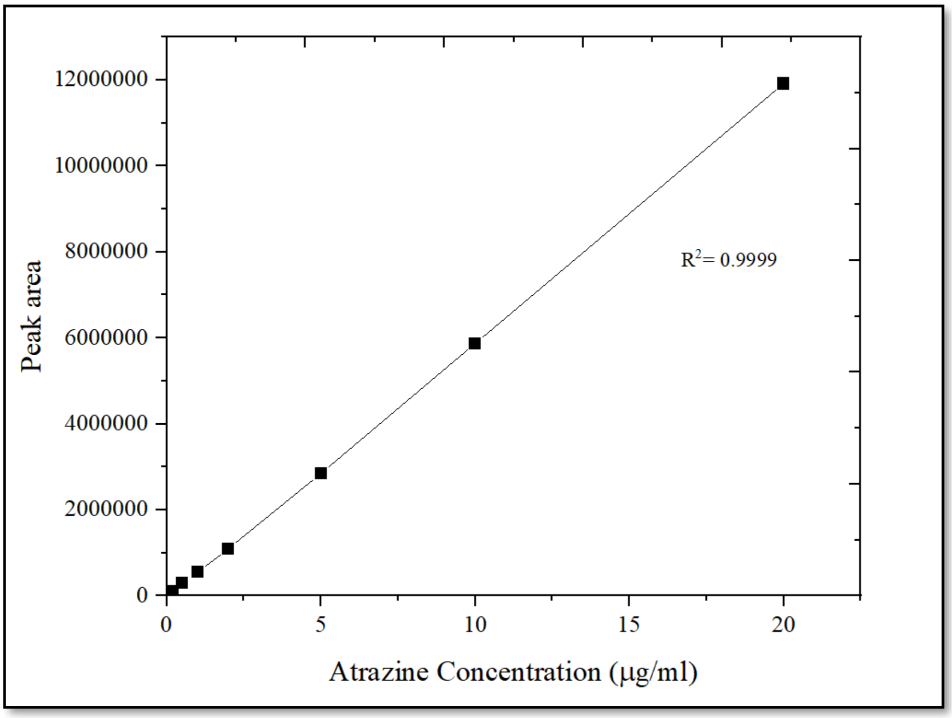

Fig. 3. 9 Calibration curve of Atrazine

Chapter 4

Imidacloprid Sorption-Desorption in Various Agricultural Soils

4.1 Introduction

As of January 2023, 330 pesticides were registered for agricultural use in India, with Imidacloprid among them. Imidacloprid, classified as an insecticide within the neonicotinoid group, was introduced in the early 1990s and quickly became one of the most widely utilized insecticides globally. Currently registered in over 120 countries, it is highly effective in controlling various soil insects, termites, and a broad spectrum of sucking and chewing insects. However, Imidacloprid is classified as moderately toxic, and exposure to it can lead to various health issues.

Human exposure to imidacloprid primarily occurs through agricultural activities, including handling and applying the insecticide, as well as through the consumption of contaminated food and water. The acute effects of exposure can include symptoms such as nausea, dizziness, headaches, and respiratory difficulties. Long-term or chronic exposure raises significant concerns due to potential to cause severe health complications. Prolonged exposure to imidacloprid may adversely affect the nervous system, leading to cognitive impairments, memory loss, and other neurological symptoms. Studies have indicated that neonicotinoids, including imidacloprid, can disrupt the normal functioning of the nervous systems by interfering with neurotransmitter signalling. Given these potential health impacts, it is crucial to evaluate and manage the use of imidacloprid in agricultural practices.

In the state of Telangana, situated on the Deccan plateau in Southern India, Imidacloprid is extensively employed, particularly in areas with black cotton soil, a predominant soil type covering approximately 30% of India's landmass. Its application is widespread, especially in cotton and paddy crops. In cotton cultivation, it acts as a neurotoxin targeting pests such as aphids, thrips, and whiteflies, while in paddy fields, it aids in the control of leaf hoppers.

Several studies have investigated the sorption and desorption characteristics of neonicotinoids, including Imidacloprid, in various soil types and environmental conditions to assess the potential risk of leaching into groundwater. However, research on the sorption behaviour of Imidacloprid specifically in black cotton soil from Southern India remains limited, despite its prevalence in the region. Additionally, there is a dearth of studies exploring the influence of temperature on soil sorption activity. Hence, the objective of the present study is to examine the behaviour of Imidacloprid in black cotton soils and red soil of Southern India, aiming to assess the potential risks associated with groundwater contamination.

4.2 Sorption of Imidacloprid in Various Soils

4.2.1 Kinetic Study

The kinetics of Imidacloprid sorption on specific Southern Indian soils were studied to determine how long it would take to reach sorption equilibrium. The sorption kinetics of Imidacloprid were investigated at a concentration of 5 µg/mL. The sorption kinetics of Imidacloprid were observed to be two-stage (Fig. 4.1). The first stage was rapid sorption, in which almost 90% of the Imidacloprid (of its capacity) was adsorbed into the soil within 3 hours. The second stage was the slow adsorption stage, and equilibrium was reached after 16 hours. The surface phenomenon known as "quick initial sorption" of Imidacloprid occurs when empty spaces in soil particles fill up quickly in the early stages and exhibit linear variation. Later, Imidacloprid molecules slowly migrate and diffuse through the soil (Gao et al., 1998). A similar pattern was observed in many different soil types all over the world (Bajeer et al., 2012; Broznić and Milin, 2012b).

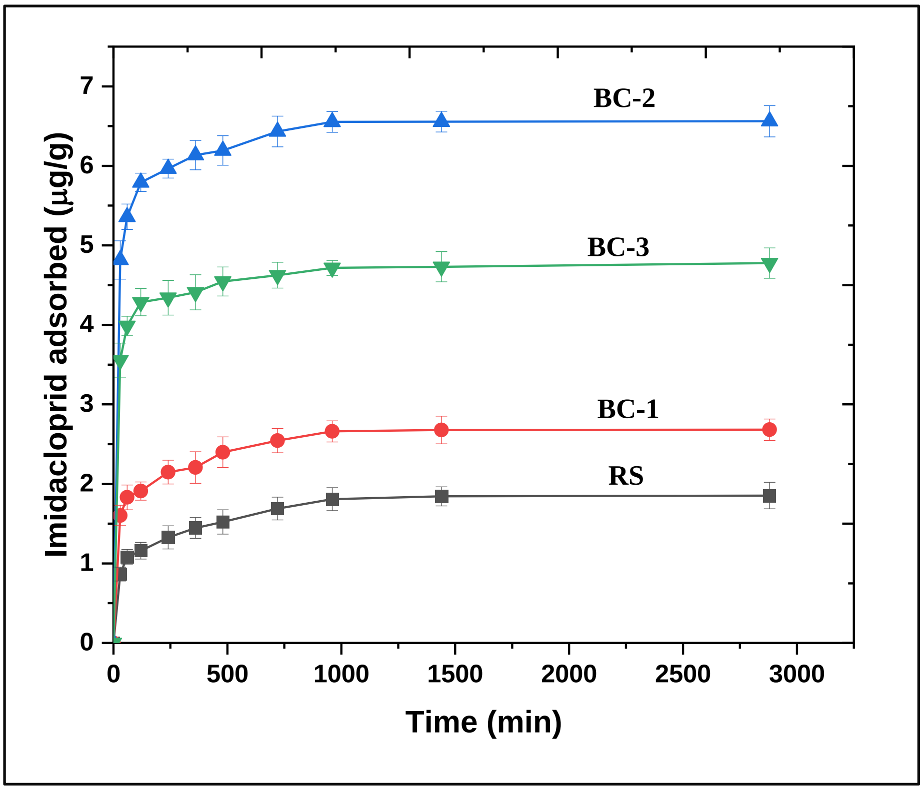

Fig. 4. 1 Sorption kinetics of Imidacloprid

To determine the mechanism of adsorption, different sorption kinetics models, as mentioned in section 3.6.3, were used. Both linear and non-linear approaches were adopted to check the suitability of the models applied. The suitability of the model was chosen based on the R^2 value obtained from the calculations. The kinetics equation with the highest R^2 value and the observed versus anticipated adsorption value was chosen as the best model for describing the sorption kinetics of Imidacloprid. The Lagergren PFO rate constant was calculated using Equation (3.7). The values of k_1 and Q_e were calculated from the slope and intercept of $ln(Q_e - Q_t)$ vs t plot.

Figure 4.2 represents various plots of the kinetics of Imidacloprid in different soils. The kinetic model parameters of Imidacloprid sorption in various soils are documented in Table 4.1 and 4.2. The PSO model showed the best fit with experimental findings compared to other models in both linearized and non-linearized forms. This demonstrates that the amount of pesticide present in the solution has a lower impact on the sorption rate than the amount of sorption (Salman et al., 2011). It also demonstrated that chemisorption controlled the sorption of Imidacloprid on soil, as ion exchange and covalent interaction were found to be the agents responsible for the process

(Boshir et al., 2017). Pore diffusion was not the rate-controlling step, as evidenced by the failure of the intraparticle diffusion model plot to pass through the origin (Cheung et al., 2007).

Table 4. 1 Kinetic model parameters of Imidacloprid in different soils (linear plot)

Model	**Parameters**	**BC-1 Soil**	**BC-2 Soil**	**BC-3 Soil**	**Red Soil**
Pseudo First Order	$EXP\ Q_e$	2.68	6.56	4.77	1.85
	$CAL\ Q_e$	1.61	2.29	1.17	1.27
	k_1	0.0001	0.0002	0.0009	0.0001
	R^2	0.968	0.924	0.939	0.977
Pseudo Second Order	$EXP\ Q_e$	2.68	6.56	4.77	1.85
	$CAL\ Q_e$	2.727	6.609	4.796	1.89
	k_2	0.134	0.009	0.01	0.008
	R^2	0.997	0.999	0.999	0.993
Elovich	α	130	78846	21709	13.95
	β	3.436	2.278	3.911	3.895
	R^2	0.977	0.959	0.915	0.981
Intraparticle diffusion	k_{int}	0.055	0.116	0.419	0.004
	c	1.028	3.326	2.864	0.546
	R^2	0.702	0.506	0.385	0.818

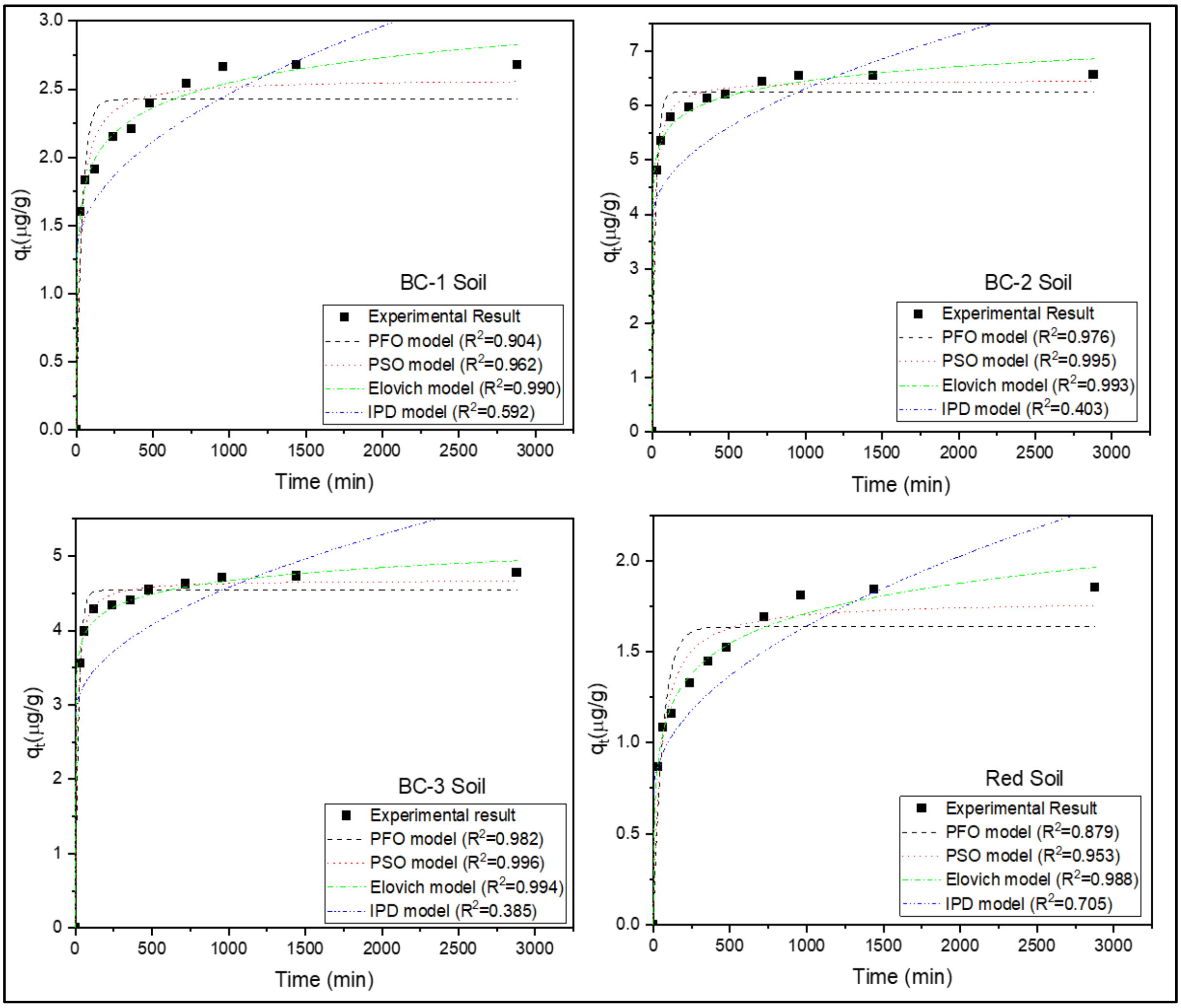

Fig. 4. 2 Kinetics model plot of Imidacloprid on various soils

4.4.2 Sorption Isotherm Study

Sorption isotherm studies were carried out at three temperatures: 273 K, 300 K, and 313 K, for an equilibrium time of 16 hours. The experiment was conducted for six different concentrations: 0.5, 1, 2.5, 5, 10, and 20 µg/mL. Three different isotherm models, namely, Langmuir, Freundlich, and Temkin, were applied to the experimental data to describe the Imidacloprid sorption process onto the soils. The results (Table 4.3) revealed that Freundlich isotherm model fitted better to the experimental data compared to the other models.

Table 4. 2 Kinetic model parameters of Imidacloprid in different soils (non-linear plot)

Model	Parameters	BC-1 Soil	BC-2 Soil	BC-3 Soil	Red Soil
Pseudo First Order	$EXP\ Q_e$	2.68	6.56	4.77	1.85
	$CAL\ Q_e$	2.42	6.25	4.53	1.64
	k_1	0.02	0.04	0.04	0.02
	R^2	0.904	0.976	0.982	0.879
Pseudo Second Order	$EXP\ Q_e$	2.68	6.56	4.77	1.85
	$CAL\ Q_e$	2.58	6.47	4.68	1.78
	k_2	0.01	0.01	0.02	0.01
	R^2	0.962	0.995	0.996	0.953
Elovich	α	3.486	6458	21714	0.309
	β	3.764	2.579	3.91	4.188
	R^2	0.990	0.993	0.994	0.988
Intraparticle diffusion	k_{int}	0.038	0.076	0.054	0.029
	c	1.268	3.88	2.864	0.714
	R^2	0.592	0.403	0.385	0.705

The shape of the sorption isotherms is useful because it provides information about the possible sorption mechanisms. Based on the initial slope, Giles et al. (1960) divided the adsorption isotherm shape into four categories: S, L, H, and C. The initial slope (1/n) measures the rate of change in the adsorption site and evaluates pesticide sorption intensity and concentration-dependent behaviour (Rani and Sud, 2014; Yadav and Singh, 2021). The 1/n value for most of the soils at different temperatures was found to be <1, indicating nonlinear sorption and following an L-shaped sorption isotherm. As the concentration of the aqueous phase of the sorbate in the solution increases, the sorption of molecules decreases, resulting in L-shaped isotherms. This is the distinguishing feature of an L-shaped isotherm (Piwowarczyk and Holden, 2012). Additionally, it indicates that the adsorption process began at high-energy sites and subsequently proceeded down to lower-energy sites as it progressed. Similar findings have been reported for Triazole fungicide in soils from Northern India (Singh, 2005a). As shown in Figure 4.3, the sorption of Imidacloprid decreased with an increase in temperature for each of the four soils studied. The fact that the K_f value decreases with increasing temperature further demonstrates that temperature has a significant impact on the sorption process. For example, when the temperature increases from 273 K to 313 K, the K_f value of BC-2 soil falls from 3.1 to 2.15.

Table 4. 3 Imidacloprid sorption isotherm parameters for various soils

Soil	**Temperature**	**Langmuir**			**Freundlich**			**Temkin**			**K_d**	**K_{oc}**
		Q_m	K_L	R^2	K_f	1/n	R^2	RT/b	A	R^2		
BC-1	273K	14.66	0.10	0.998	1.23	0.842	0.994	3.25	1.66	0.810	1.08	1103
	300K	7.63	0.11	0.984	0.71	0.89	0.982	2.28	1.48	0.842	0.65	667
	313K	4.55	0.15	0.966	0.54	0.86	0.973	2.28	1.50	0.841	0.48	499
BC-2	273K	26.04	0.15	0.994	3.10	0.874	0.998	7.19	2.11	0.803	2.87	736
	300K	10.98	0.32	0.961	2.32	0.806	0.988	5.16	2.00	0.778	2.05	527
	313K	9.17	0.37	0.959	2.15	0.776	0.989	5.16	1.89	0.790	1.87	481
BC-3	273K	30.40	0.08	0.994	2.05	0.969	0.994	6.89	1.65	0.742	2.01	764
	300K	12.48	0.11	0.982	1.14	0.94	0.995	4.04	1.47	0.769	1.08	413
	313K	5.60	0.16	0.954	0.68	0.96	0.975	4.04	1.34	0.674	0.67	255
RS	273K	10.35	0.12	0.981	0.99	1.143	0.976	2.88	1.51	0.740	0.87	151
	300K	2.77	0.32	0.798	0.57	0.903	0.959	2.14	1.31	0.750	0.53	92
	313K	0.86	0.66	0.423	0.27	0.93	0.850	2.14	1.17	0.664	0.29	51

The unit of Q_m (µg/g), K_L (mL μg^{-1}), K_f [$\mu g\ g^{-1}(\mu g\ mL^{-1})^{-1/n}$]

The highest K_f value was observed in BC-2 soil, followed by BC-3, BC-1, and red soil. A similar trend was noted for the K_d values. This indicates that BC-2 soil has a higher affinity for Imidacloprid compared to the other soils. The clay content of the soil could be responsible for the variations observed. Although BC-2 and BC-3 soils have similar clay proportions, they exhibited different affinities because BC-3 contains more sand and less organic carbon than BC-2. At the temperatures studied, a statistically significant relationship was found between K_f values and a variety of soil parameters, including organic matter (OM), pH, CEC value, SSA, and silt and clay content. According to the statistical analysis, clay content is positively correlated (r>0.9) with K_f value, indicating that it is responsible for the adsorption of Imidacloprid to the soil. Soil organic matter has a poor correlation with K_f value. This could be because the amount present is very low, and OM is only known to have a significant effect when it is present in large quantities (ElShafei et al., 2009). Despite having higher organic carbon present (0.57 %), red soil had a lower affinity for Imidacloprid than other soils. This could be due to the fact that red soil contains lower clay content than other soils. CEC and SSA of soil also had a strong positive (r>0.99) correlation with K_f value.

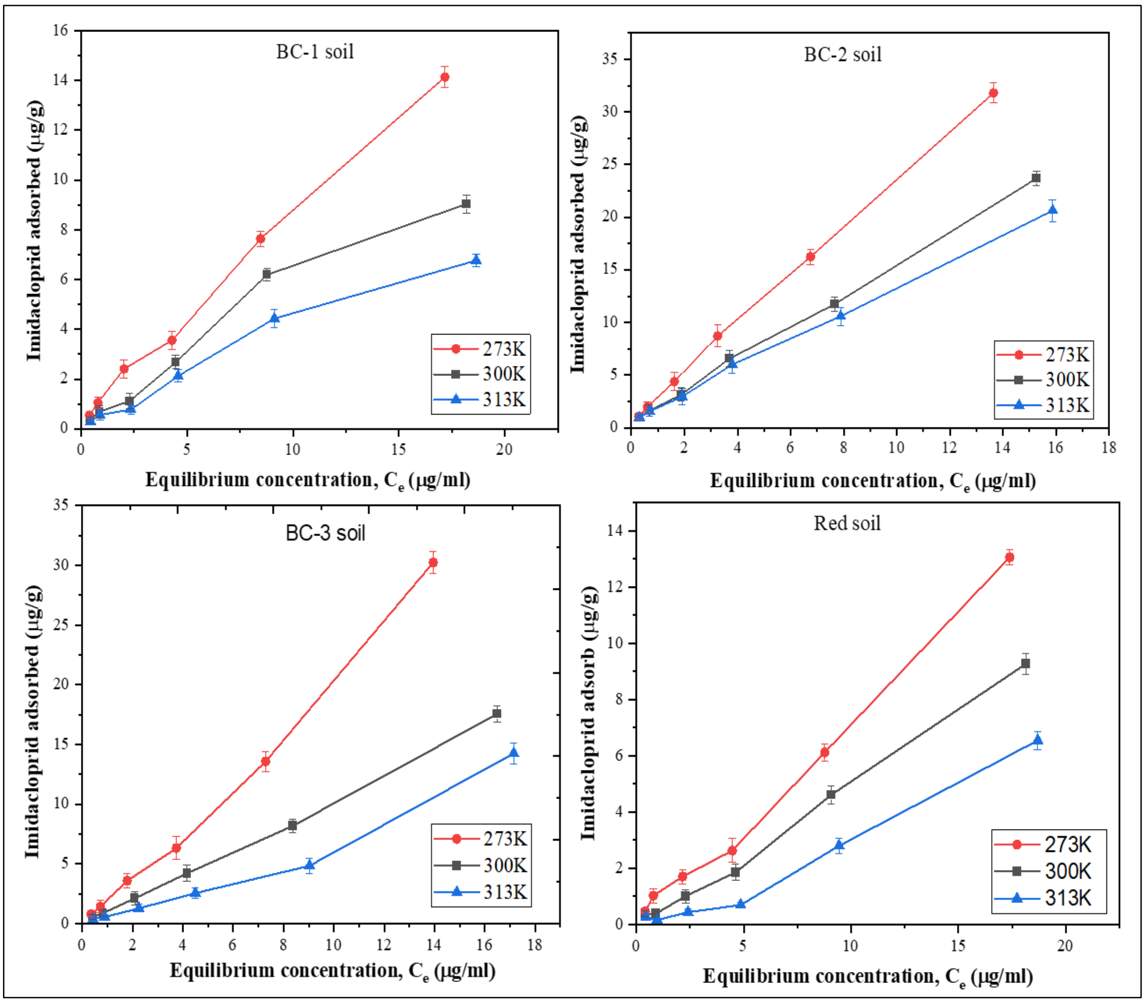

Fig. 4. 3 Imidacloprid sorption isotherm plots on various soils

Because pesticides in soil are prone to leaching, another method for determining their mobility in the soil is to examine its adsorption capacity. In order to evaluate the mobility of the soil in terms of leaching, the following criteria for Freundlich constant might be applied (Rotich et al., 2004):

K_f Value	Mobility
$K_f<2$	Highly Mobile
$2<K_f<5$	Mobile
$K_f>5$	Immobile

As a result, Imidacloprid was thought to be extremely mobile in terms of leaching in all the soils studied, with the exception of BC-2 soil, where it falls into the mobile category in all temperatures. Interestingly, at room temperature, Imidacloprid was considered mobile in BC-3 soil, whereas at 273 K, it was considered highly mobile in terms of leaching.

4.2.3 Influence of pH

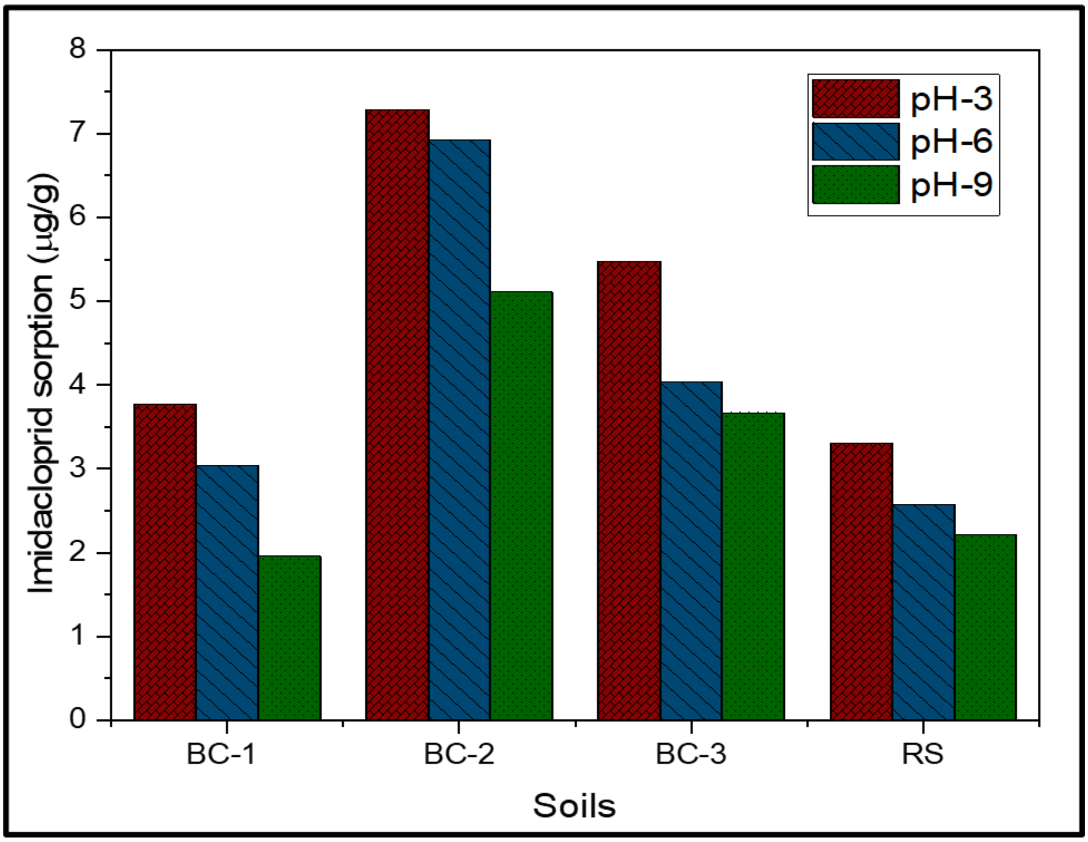

Fig. 4. 4 Influence of pH on sorption of Imidacloprid in soils

The pH level of the soil mixture plays a pivotal role in how pesticides interact during sorption processes, affecting the charge, shape, and surface properties of the adsorbents. This study aims to evaluate the impact of pH on sorption by analyzing soil samples at three distinct pH levels: 3, 6, and 9. The results, illustrated in Figure 4.4, demonstrate a decrease in the quantity of Imidacloprid adsorbed as soil pH increases. Lower pH levels create more favourable conditions for Imidacloprid sorption onto soils. This observed trend can be attributed to the chemical behaviour of Imidacloprid, which undergoes transformations based on the pH of its surroundings due to its weak alkaline properties and a pKa value of 1.56. Near its pKa, Imidacloprid exists in a mixture of cationic and non-ionized forms. Being a weakly alkaline pesticide, Imidacloprid exhibits higher affinity for soil at lower pH levels (Jing et al., 2020). As soil pH increases, the cationic state of Imidacloprid progressively diminishes, reducing protonation. Since ionic adsorption is a primary mechanism for Imidacloprid sorption, its capacity decreases with rising pH. Moreover, elevated pH levels can facilitate the hydrolysis of functional groups on soil surfaces, reducing the number of sorption sites for Imidacloprid. Consequently, higher pH conditions lead to decreased Imidacloprid sorption onto soil. Similar trends have also been observed by Ping et al. (2010).

4.2.4 Thermodynamic Analysis of Sorption

Table 4. 4 Thermodynamic parameters of Imidacloprid sorption on investigated soils

Soil	**Temperature (K)**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol/K)**
BC-1	273	-0.175	-13.84	-49.99
	300	1.074		
	313	1.862		
BC-2	273	-2393	-7.72	-19.56
	300	-1790		
	313	-1637		
BC-3	273	-747.42	-11.74	-39.86
	300	-191.9		
	313	-1038		
RS	273	-316.08	-18.24	-67.53
	300	1583		
	313	3221		

Thermodynamic parameters were calculated for the better understanding of mechanism involved in the sorption process. Values of various thermodynamic parameters were represented in Table 4.4. Pesticide molecules and soil are attracted to one another by Van der Waals force when ΔH˚ value is between 4 and 8 kJ/mol. H-bonds are responsible for sorption, when ΔH˚ value ranges between 8 to 40 kJ/mol (Broznić and Milin, 2012b). Chemisorption is often linked with ΔH˚ values greater than 40 kJ/mol. Since the ΔH˚ value of Imidacloprid sorption in the four soils was less than 40 kJ/mol, it is reasonable to assume that physisorption was responsible for Imidacloprid sorption in the soils investigated (Yue et al., 2017). The ΔH˚ value for the present study was found to be negative for all soils, indicating that the sorption process was exothermic and spontaneous in nature. The ΔH˚ values in three soils ranged from -8.485 to -12.803 kJ/mol, implying that H-bonding is the mechanism responsible for Imidacloprid sorption. The relatively low negative entropy change (ΔS˚) value indicated that there was lower randomness on the soil/solution interface during adsorption. Thermodynamic parameters (ΔH˚ and ΔS˚) for Imidacloprid reported in soils from Croatian coastal region showed a similar trend (Broznić and Milin, 2012b).

4.2.5 Desorption Study

Desorption measurements are necessary in addition to sorption studies, which assess the amount of pesticide retained by the soil, because they may reveal interactions between the pesticide and various types of soils. A desorption study was performed on all soils and it was discovered that red soil has a higher tendency to release Imidacloprid than other soils (Table 4.5). Red soil had around 33% desorption, whereas BC-2 and BC-3 soils had 26.6% and 26.16% desorption, respectively. This could be because red soil contains more sand content than black cotton soil.

In most cases, Imidacloprid's desorption ($K_{f,des}$) values were higher than sorption (K_f) values, indicating that the pesticide was difficult to release after it had been adsorbed. The sorption and desorption isotherm slopes were used to calculate the hysteresis coefficient (H) (Equation 4.1):

$$H = \frac{\frac{1}{n_{des}}}{\frac{1}{n_{sorp}}} \qquad (4.1)$$

Hysteresis is a phenomenon that occurs when desorption is significantly impeded or delayed compared to sorption. A positive hysteresis is shown when H-value is less than 1, indicating that the adsorption rate is greater than the desorption rate. For all the soils, the H-value ranged from 1.01 to 1.35. An H-value greater than 1 in any soil indicates negative hysteresis, and

Imidacloprid desorption was favoured (Yue et al., 2017). Some researchers have interpreted this phenomena of sorption and desorption hysteresis as a consequence of: i) irreversible binding between insecticide and clay minerals or organic matter, and ii) entrapment of adsorbed insecticide molecules into microporous and mesoporous structures within the organic carbon and the mineral structures of soil aggregates (Bhandari et al., 1996; Carroll et al., 1994; Weber Jr et al., 1998).

Table 4. 5 Freundlich desorption parameters and desorption percentage of Imidacloprid

Soil	**$K_{f,des}$**	**$1/n_{des}$**	**R^2**	**%Desorption**
BC-1	11.07	1.113	0.985	30.02
BC-2	9.97	0.885	0.976	26.60
BC-3	9.72	0.988	0.996	26.15
RS	0.63	0.913	0.975	33.04

4.3 Summary

The findings of the study are listed below:

- The sorption kinetics of Imidacloprid occur in two stages. The initial stage involved rapid sorption, with nearly 90% of Imidacloprid reaching adsorption capacity within 3 hours. The subsequent stage is characterized by slow adsorption, reaching equilibrium after 16 hours. This phenomenon, known as "quick initial sorption", is attributed to the rapid filling of empty spaces in soil particles during the early stages, followed by the slower migration and diffusion of Imidacloprid molecules through the soil.
- Various sorption kinetics models, including the Lagergren pseudo-first-order kinetic model (PFO), pseudo-second-order kinetic model (PSO), Elovich kinetic model, and Weber and Morris intraparticle diffusion model (IPD), are employed to analyze the experimental data. The PSO model demonstrated the best fit to the experimental data compared to the other models.
- Analysis of isotherm models indicated that the Freundlich isotherm model provided the best fit compared to the Langmuir or Temkin isotherm models. Among the soil samples, BC-2 soil exhibited the highest Freundlich coefficient value (K_f), followed by BC-3,

BC-1, and red soil. A strong positive correlation (r>0.9) is observed between clay content and the K_f value, indicating that clay content significantly influences Imidacloprid adsorption to the soil. Interestingly, despite having a higher organic carbon content (0.57%), red soil showed a lower affinity for Imidacloprid compared to other soils, possibly due to the relatively low quantity of organic carbon present.

- Lower temperature provides more favourable sorption conditions for Imidacloprid in all investigated soils. The pH study revealed that Imidacloprid sorption capacity decreases with an increase in soil pH.
- Sorption thermodynamics calculations revealed that ΔH° values ranged from -8 to -40 kJ/mol, suggesting that hydrogen bonding primary drives Imidacloprid sorption.
- A desorption study conducted on all soils showed that red soil (RS) exhibited a greater propensity to release Imidacloprid compared to other soils. Red soil demonstrated approximately 33% desorption, whereas BC-2, BC-3, and BC-1 soils exhibited desorption rates of 26.6%, 26.16%, and 30%, respectively. This difference may be attributed to the higher sand content present in red soil compared to black cotton soils.
- Imidacloprid is found to be highly mobile in terms of leaching in all soils except BC-2, which is categorized as mobile at both temperatures. The low adsorption of Imidacloprid to soils renders groundwater and surface water vulnerable to contamination.

Chapter 5

Atrazine Sorption-Desorption in Various Agricultural Soils

5.1 Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is a very popular herbicide, primarily used to manage grassy and broadleaf weeds in agricultural and non-agricultural fields. In the United States, it was first introduced in 1952 and registered for commercial use in 1958 (Yue et al., 2017). It ranks as the second most widely used pesticide globally, with 7 to 9 million kilograms being used annually (Singh et al., 2018). It falls under the class of chemicals called triazines and is categorized as a selective herbicide because it targets specific plants without harming others. This selectivity makes it a useful tool for farmers who aim to protect their crops from weeds without damaging the crops. Due to its extensive use, prolonged half-life in soil, and high mobility in soil, Atrazine is often found in surface water and groundwater at levels that significantly exceed regulatory standards. Atrazine has been detected in groundwater in various regions across the globe (Gawel et al., 2020; Pérez-Indoval et al., 2022; Wang et al., 2022). A recent study conducted in the Gangetic River basin of eastern India found that the Atrazine concentration exceeded the permissible limit in almost all samples, making around 20 million residents of that area vulnerable to Atrazine contamination (Duttagupta et al., 2020). According to Lasserre et al. (2009), Atrazine can act as an endocrine disruptor and affects multiple bodily systems, including the endocrine, central nervous, and immune systems. As a result, there has been considerable interest among researchers in the way Atrazine interacts with soil, especially in terms of its behaviour and fate.

Atrazine is one of the most popular herbicides in this region, as it aids in the management of pre-emergence weeds in crops such as maize, soybeans and sugarcane. Studies have demonstrated that Atrazine adsorption in soil varies significantly depending on the environment. Few studies have been carried out in the northern and eastern parts of India (Ghosh and Singh, 2013; Khan et al., 2023; Yadav and Singh, 2021). However, the behaviour of Atrazine in black cotton soils and red soil under investigation is not well documented and needs further exploration. Furthermore, very limited studies have focused on how soil's sorption behaviour concerning Atrazine is affected by factors such as temperature and pH. This chapter explored the behaviour of Atrazine in three black cotton soils of different characteristics and one red soil at three different temperatures, with the purpose of assessing the potential dangers related to the contamination of groundwater.

5.2 Sorption of Atrazine in Various Soils

5.2.1 Kinetic Study

The kinetics of sorption plays a critical role in determining how quickly and effectively solutes are adsorbed, making them a crucial factor in understanding the movement and alteration of Atrazine in soil settings (Yu et al., 2020). Sorption kinetics can be utilized to assess how the length of contact affects the capacity of Atrazine to adsorb in four different soil samples. Figure 5.1 depicts the sorption kinetics of Atrazine herbicide in different soils of southern India. The Atrazine sorption process was comparable in all types of soil and exhibited two distinct phases: initial rapid sorption, subsequent slow sorption, and eventually reaching a state of equilibrium sorption (Fig. 5.1). In the rapid sorption stage, almost 90% of the Atrazine equilibrium sorption amount was adsorbed within the first 6 hours. This could be due to the hydrogen bonds and chemical bonds between the herbicide molecules and soil minerals (Sun et al., 2019; Yu et al., 2020). As the contact time increases, the sorption rate decreases and reaches equilibrium after 24 hours. This occurrence could be attributed to the fact that a high initial concentration of Atrazine leads to an increase in the frequency of molecular collisions. This, in turn, enables the Atrazine molecules in a dissolved state to quickly adhere to the soil particle surface. On the other hand, when the initial concentration of Atrazine is low, the frequency of molecular collisions decreases, which results in a slower rate of sorption (Yu et al., 2020). Atrazine's quick initial sorption can also be attributed to its distribution in soil organic matter (OM) and on mineral surfaces (Wauchope et al., 2002), while delayed sorption may be caused by Atrazine being transported through soil micropores or strongly cross-linked OM areas as a result of the concentration gradient (Cheng et al., 2012; Ren et al., 2018).

The kinetics parameters for all soils were calculated by both linear and nonlinear fitting of the kinetics data of Atrazine to various models, including PFO, PSO, Elovich, and IPD. Figure 5.2 represents various plots of kinetic models of Atrazine. Based on the greatest R^2 value derived from the best-fit kinetics equation, the most suitable model to represent the sorption kinetics of

Atrazine was chosen. Additionally, assessment was conducted to compare the observed ($Q_{e, EXP}$) and predicted ($Q_{e, CAL}$) sorption values (Table 5.1, Table 5.2). Out of the four kinetics models, the PSO model showed the highest R^2 value for Atrazine sorption in all soils (Table 5.1). Also, the PSO model showed a similar level of Atrazine sorption between the predicted ($Q_{e, CAL}$) and observed ($Q_{e, EXP}$) amounts. This indicates that the rate of sorption is more influenced by the quantity of sorption sites than the quantity of Atrazine present in the solution (Salman et al., 2011).

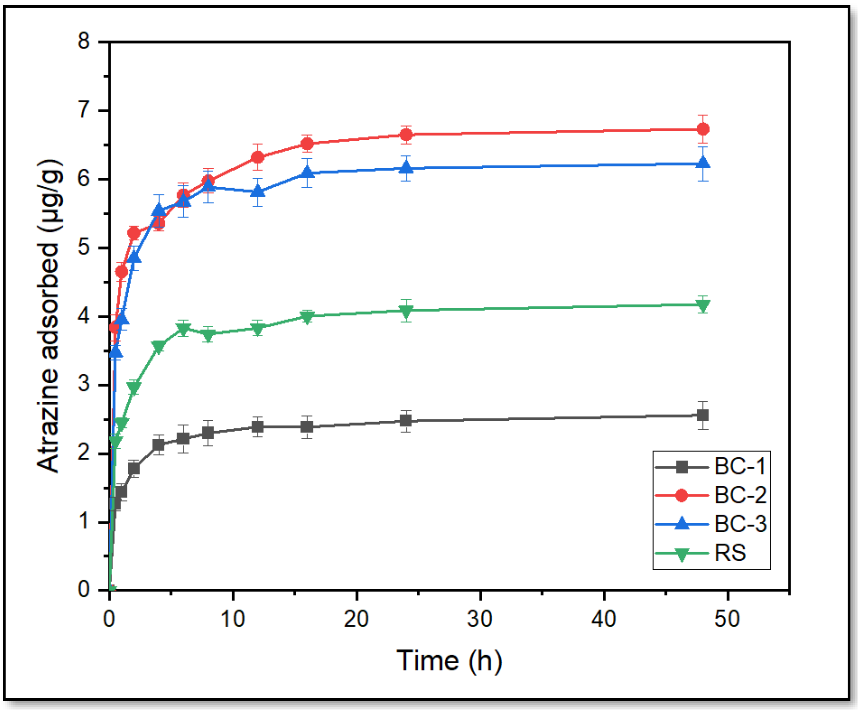

Fig. 5. 1 Sorption kinetics of Atrazine

5.2.2 Sorption Isotherm Study

The present study aimed to acquire a deeper understanding of the interaction between Atrazine and soil, and to quantify the sorption of Atrazine by four different soils. To achieve this, quantitative sorption isotherms were developed. The transfer of Atrazine from the liquid to the solid phase was examined using these isotherms. The sorption isotherm of Atrazine in four soils were studied at three distinct temperatures (273 K, 300 K and 313 K) (Fig. 5.3).

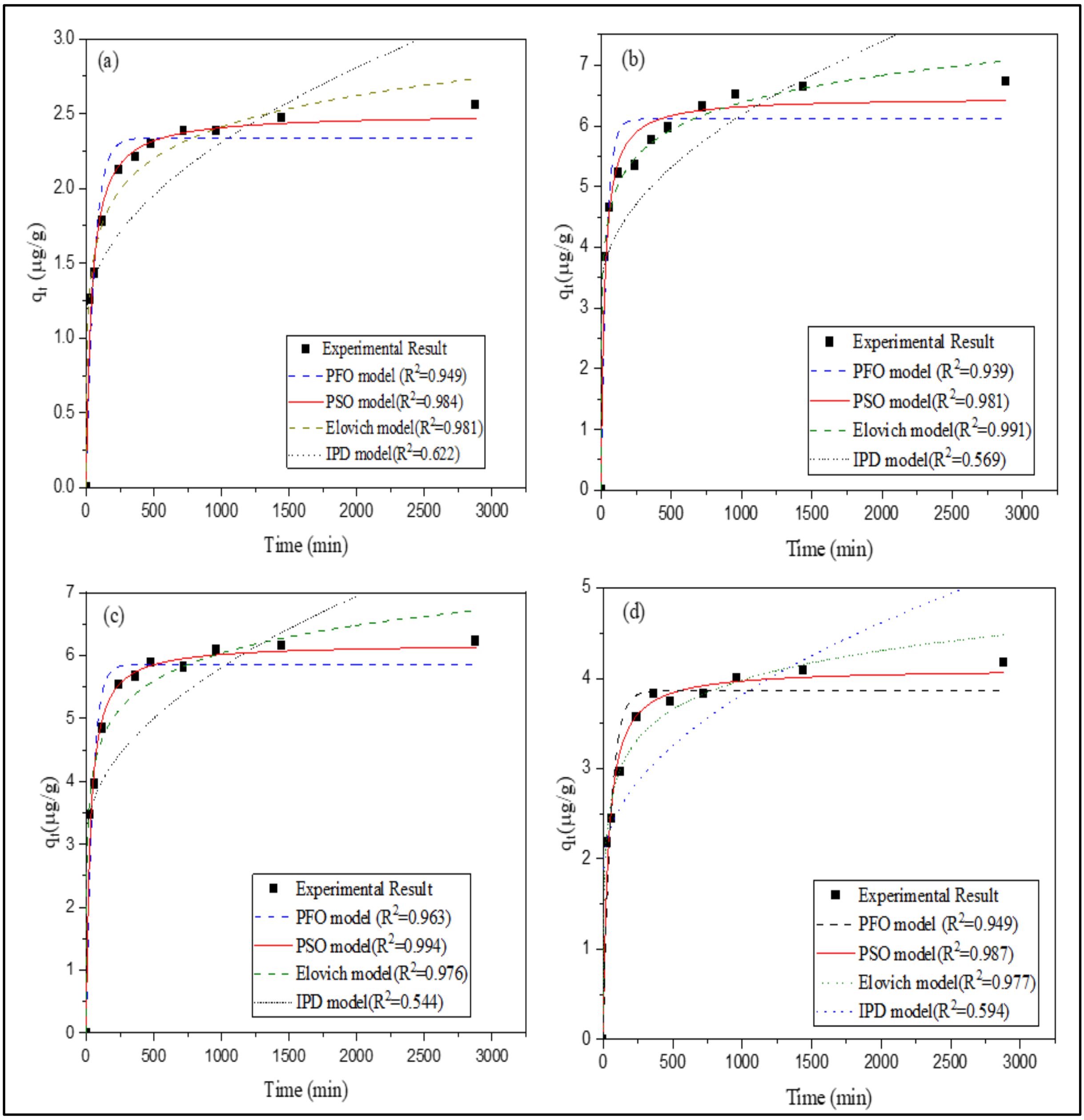

Fig. 5. 2 Kinetics model plots of Atrazine on various soils (a) BC-1 soil, (b) BC-2 soil, (c) BC-3 soil, (d) Red soil

The sorption pattern exhibited a similar trend across all soils, where an increase in herbicide concentration resulted in a gradual increase in sorption; however, the sorbed concentrations varied. This might be due to the dissimilarity in the soils' physical and chemical properties (Kodešová et al., 2011; Sita, 2001). Three sorption isotherm models were utilized to fit the adsorption data, and the corresponding sorption parameters were calculated (Table 5.3). The Temkin model showed a poor fit to the experimental results, with R^2 values ranging between 0.711- 0.869 in all investigated soils. Langmuir fitting is often connected with monolayer sorption of adsorbent to the soils. The Freundlich isotherm model displayed the most accurate correspondence with the experimental data. Thus, the Freundlich model may provide a more compelling explanation for the sorption data at all temperature conditions.

Table 5. 1 Kinetic model parameters of Atrazine in different soils (linear plots).

Model	Parameters	BC-1 Soil	BC-2 Soil	BC-3 Soil	Red Soil
Pseudo First Order	$EXP\ Q_e$	2.56	6.73	6.22	4.17
	$CAL\ Q_e$	1.09	2.03	2.35	1.73
	k_1	0.05	0.06	0.07	0.06
	R^2	0.834	0.929	0.872	0.852
Pseudo Second Order	$EXP\ Q_e$	2.56	6.73	6.22	4.17
	$CAL\ Q_e$	2.51	6.80	6.23	4.14
	k_2	0.16	0.21	0.35	0.43
	R^2	0.998	0.999	0.993	0.998
Elovich	α	2.99	1.55	1.39	1.91
	β	32.79	766.09	235.13	76.05
	R^2	0.974	0.905	0.938	0.947
Intraparticle diffusion	k_{int}	0.422	0.719	0.995	0.683
	c	0.875	3.24	2.48	1.51
	R^2	0.726	0.569	0.661	0.704

The unit of EXP Q_e ($\mu g\ g^{-1}$), CAL Q_e ($\mu g\ g^{-1}$), k_1(min^{-1}), k_2($g\ \mu g^{-1} min^{-1}$),α ($\mu g\ g^{-1} min^{-1}$), β ($g\ \mu g^{-1}$). k_{int} [$\mu g\ (g\ min^{0.5})^{-1}$]

The slope of the sorption isotherm plots can provide insights into the mechanism involved in the interaction of Atrazine with the soils. Giles et al. (1960) introduced a classification system for the shape of isotherms, categorizing them into four types: S, L, H, and C. These categories are determined by the initial slope (1/n) of the isotherm, which is a crucial parameter that reflects the rate of change in the availableness of sorption sites. The initial slope (1/n) value for all the investigated soils was found to be greater than 1, indicating that the sorption isotherm is an S-type isotherm. S-shaped isotherms are frequently observed when agrochemicals are adsorbed by soils with minimal organic matter content. This particular isotherm category suggests a weak attraction between herbicides and soil at low concentration levels due to significant competition with the water component. However, as the pesticide concentration in the aqueous phase rises, the adsorption onto the soil becomes increasingly favourable (Vagi et al., 2010). Kumari et al. (2020) also found similar findings for flucetosulfuron in soils from northern and eastern India.

Table 5. 2 Kinetic model parameters of Atrazine in different soils (non-linear plots).

Model	**Parameters**	**BC-1 Soil**	**BC-2 Soil**	**BC-3 Soil**	**Red Soil**
Pseudo First Order	$EXP\ Q_e$	2.56	6.73	6.22	4.17
	$CAL\ Q_e$	2.34	6.11	5.85	3.85
	k_1	0.02	0.03	0.02	0.02
	R^2	0.949	0.939	0.963	0.949
Pseudo Second Order	$EXP\ Q_e$	2.56	6.73	6.22	4.17
	$CAL\ Q_e$	2.50	6.47	6.19	4.10
	k_2	0.10	0.01	0.01	0.01
	R^2	0.984	0.981	0.994	0.987
Elovich	α	0.86	12.76	8.37	2.19
	β	3.29	1.54	1.57	2.12
	R^2	0.981	0.991	0.976	0.977
Intraparticle diffusion	k_{int}	0.04	0.09	0.08	0.06
	c	1.10	3.24	3.06	1.89
	R^2	0.622	0.569	0.544	0.594

The unit of EXP Q_e (μg g^{-1}), CAL Q_e (μg g^{-1}), k_1(min^{-1}), k_2(g $μg^{-1}min^{-1}$),α (μg $g^{-1}min^{-1}$), β (g $μg^{-1}$). k_{int} [μg (g $min^{0.5}$)$^{-1}$]

The results presented in Figure 5.3 demonstrate that the sorption of Atrazine declined in all four soil samples as the temperature increased. The observed decrease in the K_d value with rising temperature provides additional evidence supporting the significant impact of temperature on the sorption process (Table 5.3). For instance, the K_d value for BC-2 soil was determined to be 2.25 at 273 K. However, when the temperature rose to 300 K, the K_d value fell to 1.44, and at 313 K, it further dropped to 1.09. As the temperature increases, the solubility of Atrazine in solution increases, leading to a decrease in its adsorption in the investigated soils. Moreover, the rise in temperature can potentially modify the characteristics of humic substances found in the soil, influencing their attraction to minerals and the available surface area, consequently impacting the adsorption process of Atrazine (Broznić and Milin, 2012a).

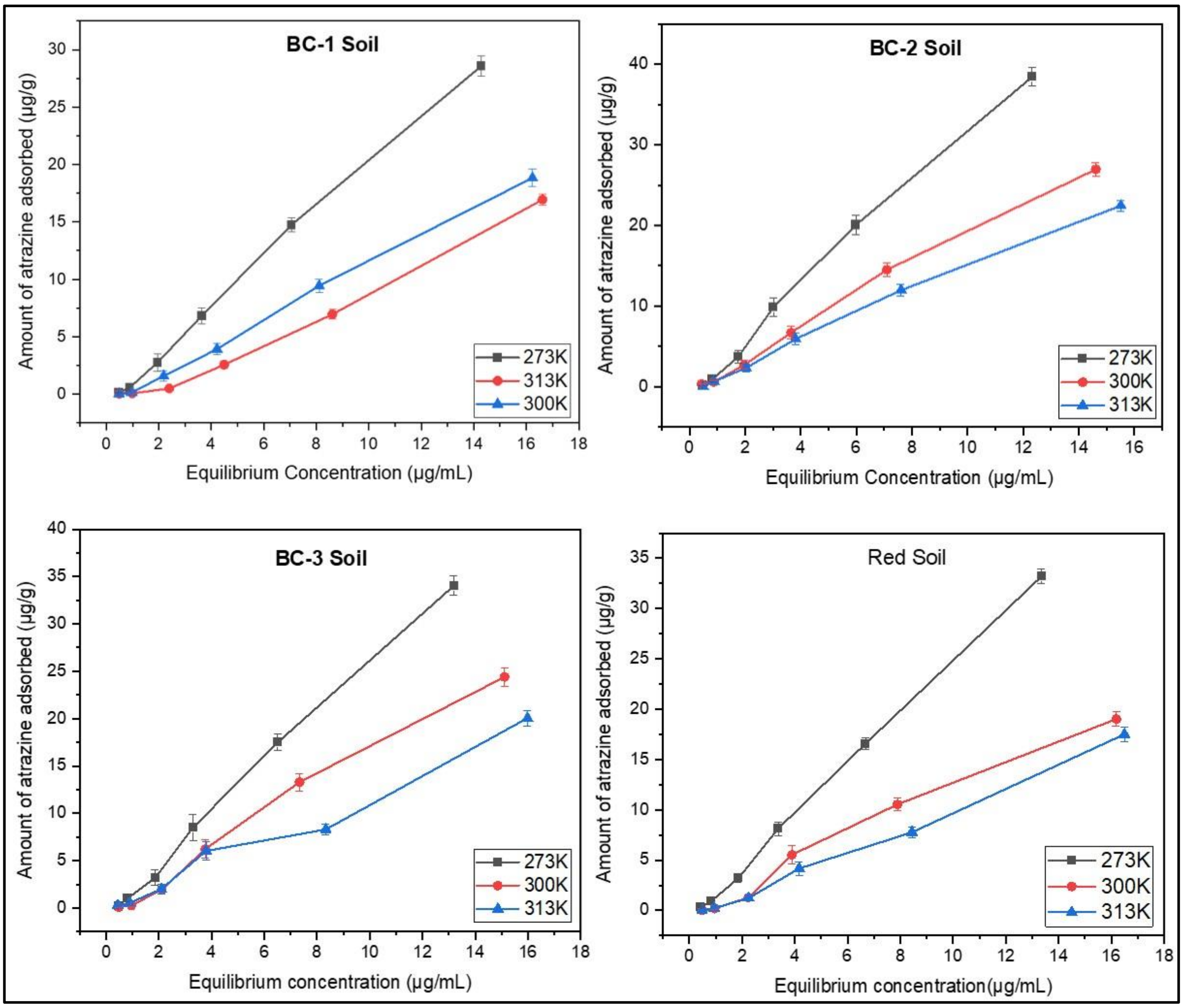

Fig. 5. 3 Atrazine sorption isotherm plots on investigated soils at various temperatures

The highest adsorption capacity for Atrazine herbicide was recorded for BC-2 soil, followed by BC-3, RS and BC-1 soils. The linear adsorption coefficient (K_d) value followed the same order. The partition coefficient (K_d) is commonly used to evaluate the potential groundwater contamination risk by measuring the distribution between the solid soil phase and the aqueous phase. The highest K_d value was reported for BC-2 soil (2.25) and the lowest for BC-1 soil (0.44) at a temperature of 273 K. This indicates that BC-2 soil had a higher sorption capacity for Atrazine compared to the others, likely due to its higher clay content. Despite having less clay content than BC-1 soil, red soil showed a much higher sorption capacity. The higher organic content in red soil may explain its increased sorption capacity compared to than BC-1 soil. Since the binding nature of Atrazine was found to be very poor in all the soil samples collected from various parts of southern India, Atrazine may have the potential to leach into groundwater. Another criterion applied by many researchers to assess whether a particular pesticide is mobile in soil is its K_f value. If the measured K_f value is less than 2, the pesticide is categorized as highly mobile. If the value falls between 2 and 5, it is considered mobile, and if the K_f value is greater than 5, it is deemed immobile (Rotich et al., 2004). The K_f values for all the investigated soil samples were below 2, indicating that Atrazine is highly mobile and prone to leaching.

Table 5. 3 Atrazine sorption isotherm parameters for various soils

Soil	**Temperature**	**Langmuir**			**Freundlich**			**Temkin**			**K_d**	**K_{oc}**
		Q_m	**K_L**	**R^2**	**K_f**	**1/n**	**R^2**	**RT/b**	**A**	**R^2**		
BC-1	273K	1.08	0.25	0.914	0.64	1.58	0.971	7.89	1.19	0.833	1.38	1408
	300K	0.32	0.22	0.941	0.19	1.83	0.965	5.01	1.06	0.802	0.69	713
	313K	0.15	0.21	0.951	0.17	1.79	0.991	4.23	1.04	0.711	0.44	458
BC-2	273K	1.87	0.27	0.912	1.18	1.54	0.969	25.56	1.13	0.854	2.25	577
	300K	9.69	0.08	0.977	1.02	1.29	0.985	16.59	1.12	0.828	1.44	371
	313K	0.31	0.29	0.786	0.90	1.66	0.905	14.09	1.08	0.853	1.09	281
BC-3	273K	2.07	0.25	0.898	1.02	1.29	0.974	21.70	1.12	0.836	1.89	719
	300K	0.87	0.21	0.969	0.35	1.72	0.968	6.84	1.13	0.829	1.08	411
	313K	8.72	0.07	0.991	0.79	1.19	0.978	11.34	1.118	0.79	1.01	387
RS	273K	4.42	0.17	0.979	1.24	1.35	0.991	8.93	1.32	0.821	1.83	318
	300K	0.18	0.26	0.868	1.23	1.34	0.941	5.01	1.13	0.869	0.77	134
	313K	0.62	0.20	0.946	0.27	1.61	0.982	10.59	1.03	0.775	0.66	115

The unit of Q_m (µg/g), K_L (mL μg^{-1}), K_f [$\mu g\ g^{-1}(\mu g\ mL^{-1})^{-1/n}$]

5.2.3 Influence of pH

The pH level of the soil mixture plays a crucial role in determining how pesticides behave during sorption. It can alter the adsorbent's charge, shape, and surface properties. This study aimed to assess the influence of pH on sorption by examining soil samples at three distinct pH levels: 3, 6, and 9. The findings, depicted in Figure 5.4, indicate that the quantity of Atrazine adsorbed decreases as the soil's pH value increases.

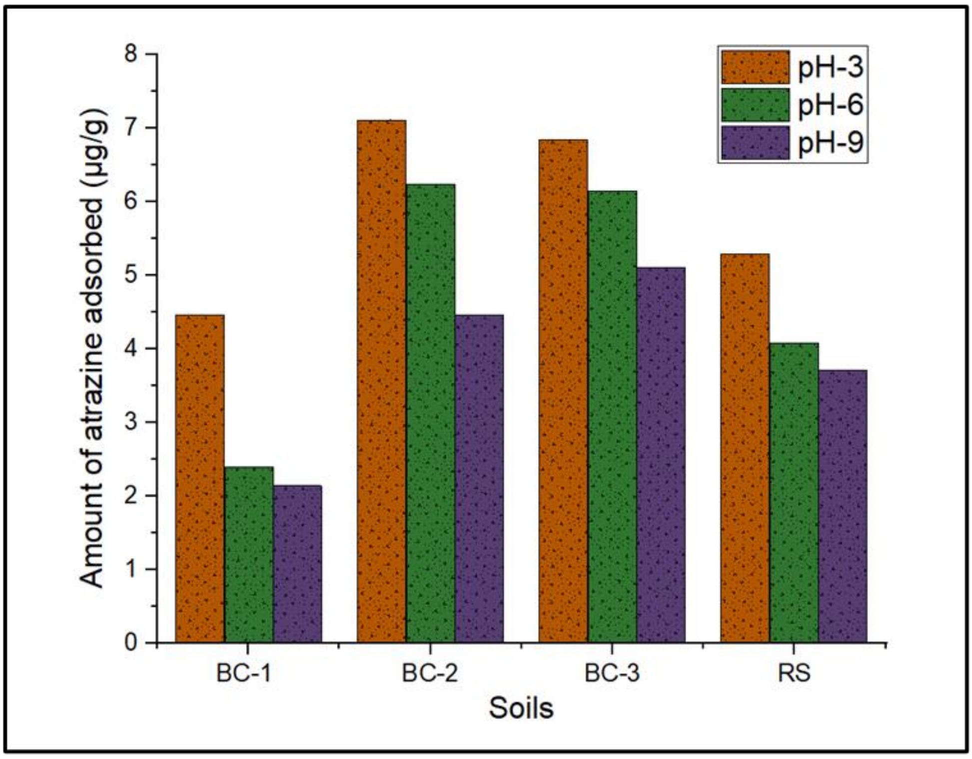

Fig. 5. 4 Influence of pH on sorption of Atrazine in various soils

The lower pH provides more favourable conditions for Atrazine sorption on soils. This observed pattern can be attributed to the fact that Atrazine, a herbicide with weak alkaline properties and a pKa value of 1.68, undergoes chemical transformations in response to the pH of its environment. When the pH approaches the pKa, Atrazine exists in a mixture of cationic and non-ionized forms. As the pH decreases, there is an increase in protonation and ion exchange processes. Consequently, the dominant mechanism for Atrazine adsorption onto the soil is primarily through ion exchange (Lima et al., 2010; Taha et al., 2014). As Atrazine is a weakly alkaline pesticide, the lower the pH of the soil, the higher the affinity of Atrazine for the soil (Jing et al., 2020). With the increase in the pH value, the cationic condition of the Atrazine in the soil solution progressively diminishes, leading to a gradual decrease in protonation. Since ionic adsorption is one of the primary mechanisms for Atrazine sorption, the sorption capacity of Atrazine in soil diminishes as the pH increases. Furthermore, the elevated pH value can promote the hydrolysis of different functional groups found on the surface of the soil. The number of Atrazine adsorption sites is reduced as a result of hydrolysis process. Consequently, elevated pH conditions result in a decrease in the sorption of Atrazine onto the soil. A similar trend was also documented by other researchers (Abate and Masini, 2005; Jing et al., 2020; Yue et al., 2017).

5.2.4 Thermodynamic Analysis of Sorption

Thermodynamic parameters play a crucial role in elucidating the energy fluctuations that occur during the adsorption process**.** To gain a deeper understanding of the sorption of Atrazine into different types of soil, a thermodynamic assessment was conducted at varying temperatures: 273 K, 300 K, and 313 K. Table 5.4 presents the values of different parameters involved in the thermodynamic analysis. A negative ΔG° value indicates that Atrazine adsorption to soil is considered spontaneous in most situations, except in BC-1 and RS at elevated temperatures. When the ΔH° value falls within the range of 4 to 8 kJ/mol, the attraction between pesticide molecules and soil occurs through Van der Waals forces. On the other hand, sorption is primarily facilitated by hydrogen bonds when the ΔH° value ranges from 8 to 40 kJ/mol. Chemisorption, which involves stronger chemical bonds, is typically associated with ΔH° values exceeding 40 kJ/mol (Alkan et al., 2004). Hence, based on the findings of this study, it appears that the adsorption of Atrazine occurs through physical sorption. The enthalpy change (ΔH°) for the investigated soils ranged from -11.67 kJ/mol to -19.79 kJ/mol, indicating that hydrogen bonding is responsible for the sorption mechanism between Atrazine and soils. Additionally, the negative ΔH° value suggests that the transfer of solid phase Atrazine from the aqueous phase to the soil occurs through an exothermic process. The entropy change (ΔS°) value recorded relatively low for all the investigated soils indicates that there was lower randomness at the soil/solution interface during adsorption. Similarly, low ΔH° and ΔS° values were also reported for Atrazine in soils from northeast China and the Yangzi River basin (Sun et al., 2019; Yu et al., 2020).

5.2.5 Desorption Study

When analyzing sorption studies to determine the quantity of pesticide adsorbed by the soil, it is crucial to also assess the desorption process. This is important because it can reveal potential interactions between the agrochemical and the soil. The highest desorption was reported for BC-1 soil, with 56.73% of adsorbed Atrazine molecules released to the aqueous phase after the desorption experiment (Table 5.5). Red soil also showed significant desorption, with 44.74% of herbicides desorbed. This may be due to the relatively higher quantity of sand present in both soils. BC-2 soil recorded the lowest desorption value at 28.74%, followed by BC-3 soil at 35.28%.

Table 5. 4 Thermodynamic parameters of Atrazine sorption on soils

Soil	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
BC-1	273	-0.731	-19.79	-69.64
	300	0.926		
	313	2.136		
BC-2	273	-1.841	-12.58	-39.23
	300	-0.901		
	313	-0.224		
BC-3	273	-1.445	-11.67	-37.64
	300	-0.192		
	313	-0.026		
RS	273	-1.372	-18.79	-64.03
	300	0.652		
	313	1.081		

Table 5. 5 Freundlich desorption parameters and desorption percentage of Atrazine

Soil	$K_{f,des}$	$1/n_{des}$	R^2	%Desorption
BC-1	2.57	1.34	0.995	56.73
BC-2	10.25	1.13	0.949	28.74
BC-3	8.08	1.23	0.942	35.28
RS	5.37	1.19	0.903	44.74

The hysteresis effect is commonly used to explain desorption investigations. Hysteresis is a phenomenon that is characterized by a noticeable hindrance or delay in the desorption process compared to the sorption process. Hysteresis during desorption is primarily attributed to the existence of diverse adsorbing sites in soils characterized by varying energies and heterogeneous properties. The presence of hysteresis indicates that the process of pesticide sorption is only partially reversible and is influenced by the unique properties of the pesticide and the physicochemical properties of the soil. Hysteresis is typically absent when the hysteresis index value is close to 1, indicating that the desorption process proceeds at a rate comparable to that of sorption. Conversely, when the hysteresis index value is less than 1, it indicates that desorption happens at a slower pace than sorption, leading to the occurrence of hysteresis. All soils showed positive hysteresis, with H-value ranging from 0.73 to 0.89. Positive hysteresis has also been reported for Atrazine in several other soil samples (Boivin et al., 2005; D. L. D. Lima et al., 2010).

5.3 Summary

The conclusions drawn from the results are summarized as follows:

- The kinetic study reveals that the adsorption process of Atrazine is comparable in all types of soil and exhibited two distinct phases: initial rapid adsorption, followed by slow adsorption, eventually reaching equilibrium. During the rapid sorption stage, nearly 90% of the equilibrium adsorption amount of Atrazine is adsorbed within the first 6 hours. This phenomenon may be attributed to the formation of hydrogen bonds and chemical bonds between the herbicide molecules and soil minerals. As the contact time increases, the sorption rate decreases and reaches equilibrium after 24 hours.
- Among the four kinetics models considered, the PSO model exhibited the highest R^2 value for Atrazine sorption in all soils. This suggests that the rate of sorption is primarily influenced by the quantity of sorption sites rather than the concentration of Atrazine in the solution.
- The findings reveal a decline in the sorption of Atrazine across all four soil samples with increasing temperature. The observed decrease in the K_d value as temperature rises provides further evidence of temperature's significant impact on the sorption process. For instance, in BC-2 soil, the K_d value is determined to be 2.25 at 273 K. However, as the temperature increased to 300 K, the K_d value decreased to 1.44, and further dropped to 1.09 at 313 K. This trend indicates that as temperature increases, the solubility of Atrazine in solution also increases, resulting in reduced adsorption in the studied soils. Furthermore, the elevation in temperature may potentially alter the characteristics of humic substances present in the soil, affecting their affinity to minerals and the available surface area, thereby influencing the adsorption process of Atrazine.
- This study aimed to assess the influence of pH on sorption by examining soil samples at three distinct pH levels: 3, 6, and 9. The findings indicate that the quantity of Atrazine

adsorbed decreases as the soil's pH value increases. Lower pH provides more favourable conditions for Atrazine sorption on soils.

- Based on the findings of the thermodynamic study, it appears that the adsorption of Atrazine occurs through physical sorption. The enthalpy change (ΔH°) for the investigated soils ranged from -11.67 kJ/mol to -19.79 kJ/mol, indicating that hydrogen bonding is responsible for the sorption mechanism between Atrazine and soils. Additionally, the negative ΔH° value suggests that the transfer of solid phase Atrazine from the aqueous phase to the soil occurs through an exothermic process.
- The highest desorption is reported for BC-1 soil, in which 56.73% of adsorbed Atrazine molecules are released to the aqueous phase after the desorption experiment. Red soil also shows significant desorption, with 44.74% of herbicides desorbed. This might be because both soils have a relatively higher quantity of sand present in them. BC-2 soil recorded the lowest desorption value at 28.74%, followed by BC-3 soil at 35.28%.

Chapter 6

Soil Column Leaching and Degradation Study

6.1 Introduction

Chapters 4 and 5 provided an in-depth analysis of the sorption capacities of Imidacloprid and Atrazine in various soils. The findings from these chapters indicated that both pesticides possess a significant potential to leach through the soil matrix, posing a risk of groundwater contamination. However, while sorption capacity is a crucial factor in determining the mobility and retention of pesticides in soil, it alone does not present a complete picture of their environmental impact.

To thoroughly understand the behaviour and fate of pesticides in soil environments, it is imperative to consider additional factors such as pesticide degradation and leaching potential. Degradation refers to the breakdown of pesticides into simpler substances, which affects their persistence and toxicity in the environment. Leaching potential, on the other hand, assesses how readily a pesticide can move through the soil profile and reach groundwater.

This chapter aims to address these additional aspects by focusing on the leaching behaviour of Imidacloprid and Atrazine using soil column experiments. These experiments simulate natural conditions to provide insights into how these pesticides migrate through the soil. Alongside leaching studies, the chapter also examines the degradation patterns of these pesticides in the same soils. This dual approach of studying both leaching and degradation will help elucidate the extent to which these pesticides can persist in the environment and their potential to contaminate water resources.

By integrating data on sorption capacity, degradation rates, and leaching potential, this chapter seeks to present a comprehensive evaluation of the environmental risks posed by Imidacloprid and Atrazine. The combined results will offer a clearer understanding of the likelihood and extent of groundwater and surface water contamination by these pesticides. This holistic assessment is crucial for developing effective management strategies and regulatory policies to mitigate the adverse impacts of pesticide use on environmental and human health.

6.2 Soil Column Leaching Study

The downward movement of pesticides was studied using a PVC column with a length of 370 mm and an internal diameter of 42 mm. These columns were packed to match the bulk densities of the respective soils. After fully saturating the columns with a 0.01M $CaCl_2$ solution, a total of 500 µg of pesticides was applied to the top of each column. The pore volume of the columns ranged from 151 mL to 182 mL. To conduct the experiment, 500 mL of $CaCl_2$ solution (approximately three pore volumes) was passed through each column, maintaining a fixed head of 5 cm throughout the study, while allowing for natural drainage. Figure 6.1 illustrates the experimental setup of the leaching study, with leachate collected in a conical flask positioned at the bottom of each column. After the leaching process, the columns were left undisturbed for one day to ensure complete drainage. The columns were then opened (as shown in Figure 6.2), and the soil columns were sectioned into five segments, each measuring 5 cm.

Fig. 6. 1 Experimental setup of Column Leaching Test

Fig. 6. 2 Longitudinally halved column after the completion of leaching test

Figure 6.3 illustrates the distribution of Imidacloprid across various segments of the soil column and in the leachate. Out of the 500 µg of Imidacloprid applied, approximately 88-90% was recovered from the soil column and leachate. The unrecovered portion could be due to several factors, including losses during the experimental procedure, sample processing errors, or transformation of the pesticide into other compounds. The data indicates that Imidacloprid was present in the leachate for BC-1 soil and red soil, suggesting higher mobility of Imidacloprid in these soil types. Conversely, in BC-2 and BC-3 soils, no traces of Imidacloprid were detected in the leachate, implying limited mobility. The detailed analysis of the leachate and soil column fractions revealed that the majority of Imidacloprid was retained within the soil. The highest concentration was found in the first segment (0-5 cm) of the column, with progressively lower amounts in the subsequent segments. This pattern is evident in Figure 6.3, which shows that Imidacloprid penetrated all sections of the soil column, reaching the deepest segment. This indicates a high degree of mobility for Imidacloprid in the studied soils.

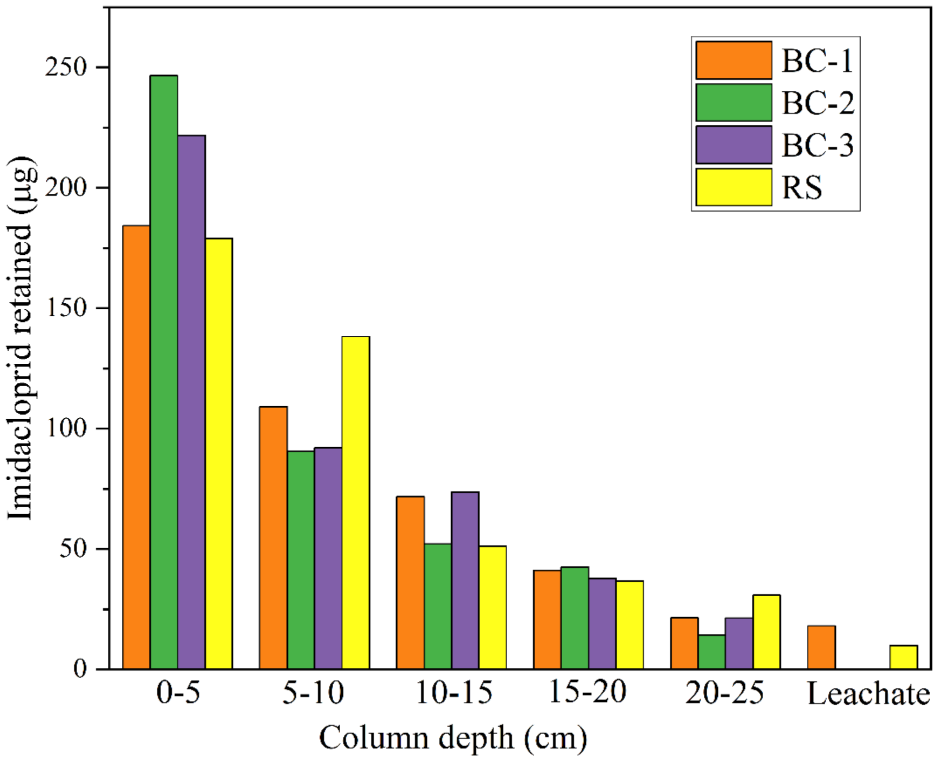

Fig. 6. 3 Distribution of Imidacloprid in various soil columns

A similar pattern was observed for Atrazine, as illustrated in Figure 6.4. Traces of Atrazine were found in the leachate samples for all soil types except BC-2 soil. Like Imidacloprid, Atrazine was primarily found in the first segment of the soil column, with diminishing concentrations in the lower segments. The presence of Atrazine throughout the soil column underscores its high mobility, posing a significant concern for groundwater contamination.

The detection of these pesticides in the deeper sections of the soil matrix is particularly troubling. Deeper soil layers typically lack microorganisms essential for pesticide degradation, leading to increased chemical persistence (Larsen et al., 2000; Rodríguez-Cruz et al., 2006). This persistence means that both Imidacloprid and Atrazine can remain in the soil for extended periods, increasing the likelihood of their transportation with irrigation or rainwater and potentially contaminating groundwater supplies.

The high mobility and persistence of these pesticides underscore the need for careful management and monitoring. Their ability to move through the soil and reach deeper layers highlights the potential risks to environmental and human health, particularly concerning groundwater contamination.

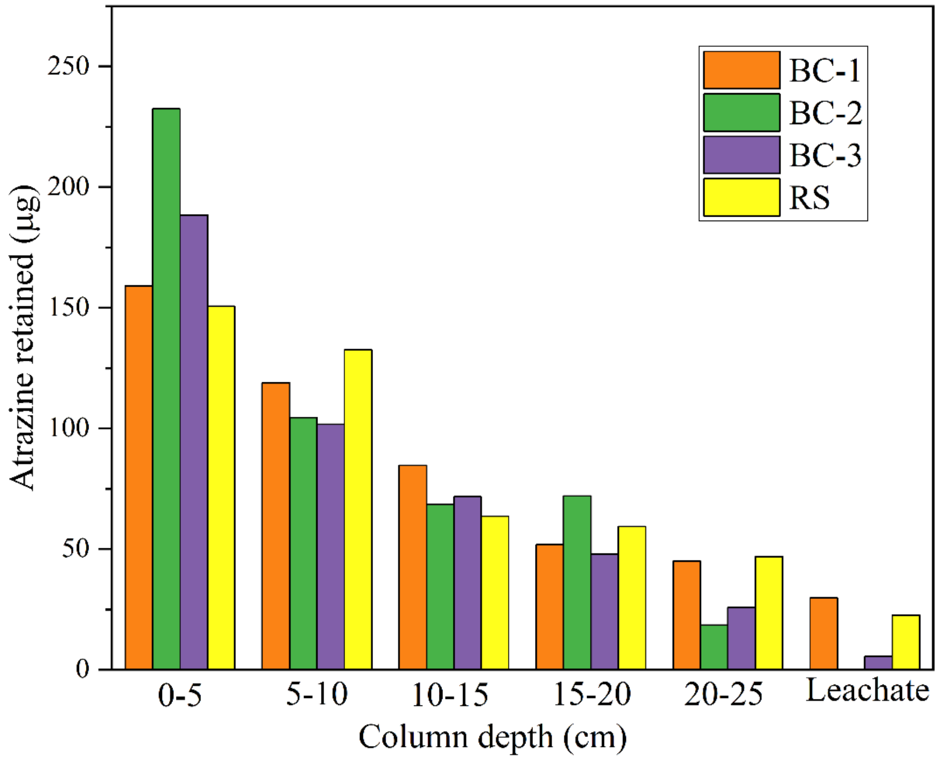

Fig. 6. 4 Distribution of Atrazine in various soil columns

6.3 Pesticide Degradation Study

6.3.1 Degradation of Imidacloprid in Various Soils

The study on pesticide degradation followed OECD guidelines to assess its persistence in various soils. The aim of this study was to determine the duration of Imidacloprid's activity in different soil environments. Degradation kinetics were established by plotting pesticide residue concentrations against time, enabling researchers to observe the rate at which the pesticide breaks down in different soil types.

Figure 6.5 illustrates the degradation patterns of Imidacloprid across the various soils examined in the study. The results indicated that the degradation kinetics of Imidacloprid followed first-order kinetics, where the rate of degradation is directly proportional to the pesticide concentration. The correlation coefficients (R^2 values) for these kinetics ranged from 0.958 to 0.989, indicating a strong fit to the first-order kinetic model in all the soils tested.

Among the soils, BC-2 exhibited the highest degradation rate for Imidacloprid, with a rate constant of 0.0045 day^{-1} (Table 6.1). This suggests that Imidacloprid breaks down more rapidly in BC-2 soil compared to other soils. In contrast, BC-1 soil showed the lowest degradation rate, indicating that Imidacloprid persists longer in this type of soil.

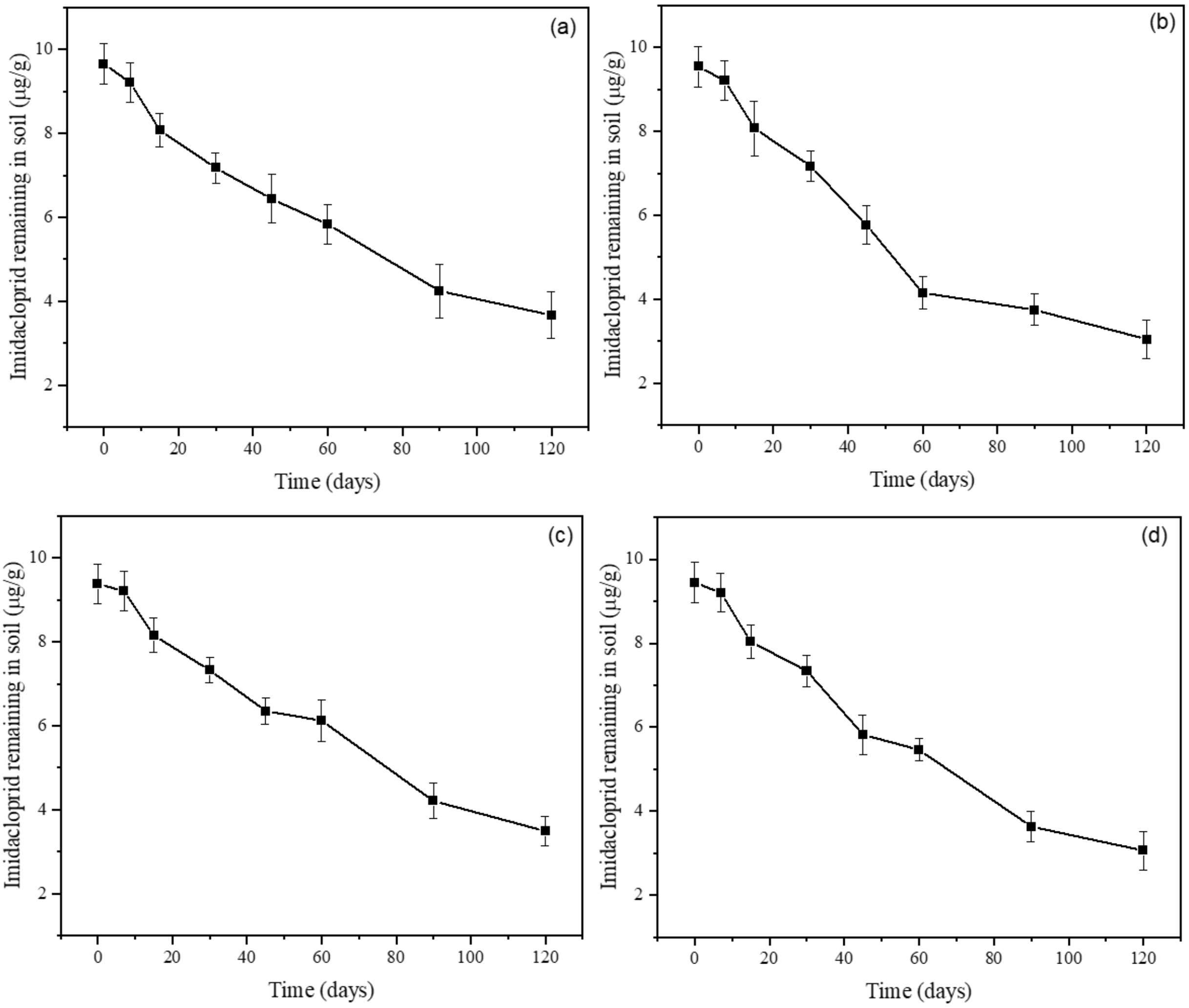

Fig. 6. 5 Degradation of Imidacloprid in (a) BC-1, (b) BC-2, (c) BC-3, and (d) Red soil

The differences in degradation rates among the soils can be attributed to several factors. One significant factor is the presence and activity of specific bacteria that facilitate the breakdown of pesticides. These bacterial populations vary between soils, leading to different degradation rates. Additionally, the organic content of the soil plays a crucial role in pesticide degradation. Soils with higher organic content, such as BC-2 and red soil, tend to support more robust bacterial activity, which can enhance the degradation process (Li et al., 2023). On the other hand, BC-1 soil have the lowest organic content, which may limit bacterial activity and result in slower degradation of Imidacloprid.

The persistence of a pesticide is generally expressed in terms of half-life ($T_{1/2}$). The half-life of Imidacloprid was calculated from the degradation rate constant as mentioned by Sharma and Singh, (2014). The lowest half-life value was reported for BC-2 soil (67 days), followed by red soil (70 days), BC-3 soil (79 days), and BC-1 soil (83 days). Sarkar et al. (2001) has reported the half-life of Imidacloprid in Lateritic soils of the Eastern part of India, ranging from 27.8 to 47.8 days. Another study on soils from the Western Indian state of Gujarat reported half-life values ranging from 42 to 50 days (Samnani et al., 2013).

6.3.2 Degradation of Atrazine in Various Soils

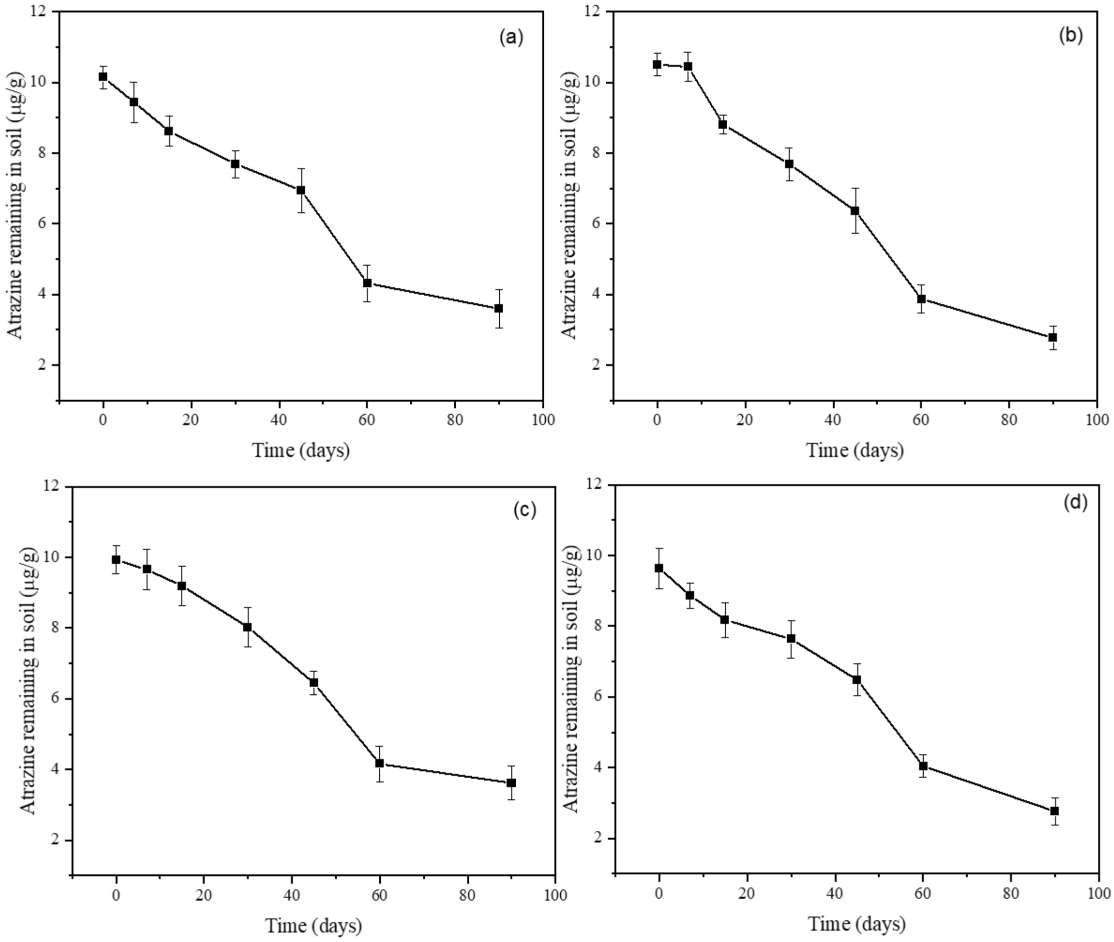

Fig. 6. 6 Degradation of Atrazine in (a) BC-1, (b) BC-2, (c) BC-3, and (d) Red soil

Figure 6.6 illustrates the degradation of the herbicide Atrazine in all the investigated soils. Table 6.2 shows that the degradation rate of Atrazine is higher compared to Imidacloprid in all soils. The half-life of Atrazine ranged from 44 to 57 days in the investigated soils, with the lowest value recorded for BC-2 soil (44 days) and the highest for BC-1 soil (57 days). Satisha et al. (2003) reported a half-life for Atrazine in Karnataka soils ranging from 28 to 37 days.

Imidacloprid was observed to be more persistent in the investigated soils compared to Atrazine, as indicated by its longer half-life. This higher persistence is likely due to Imidacloprid's complex chemical structure, which includes a chlorinated pyridine ring and a nitroguanidine moiety, making it more resistant to microbial degradation. In contrast, Atrazine has a simpler triazine structure that is more amenable to microbial degradation. Various soil bacteria, such as those from the genera Pseudomonas and Rhodococcus, possess specific enzymes (e.g., Atrazine chlorohydrolase and hydrolase enzymes) that can effectively degrade Atrazine by cleaving its bonds and using it as a carbon and nitrogen source. This enzymatic activity results in faster and more efficient microbial degradation of Atrazine in soils.

Table 6. 1 Degradation rate and half-life of Imidacloprid in various soils

Soil	**k_R (day^{-1})**	**R^2**	**$T_{1/2}$ (days)**
BC-1	0.0036	0.989	83
BC-2	0.0045	0.958	67
BC-3	0.0038	0.989	79
Red soil	0.0043	0.988	70

Table 6. 2 Degradation rate and half-life of Atrazine in various soils

Soil	**k_R (day^{-1})**	**R^2**	**$T_{1/2}$ (days)**
BC-1	0.012	0.949	57
BC-2	0.015	0.969	44
BC-3	0.012	0.944	55
Red soil	0.014	0.952	49

6.4 Groundwater Ubiquity Score (GUS) Calculation

The determination of a pesticide's potential to leach into groundwater is crucial for assessing its environmental impact. To achieve this, scientists utilize the Groundwater Ubiquity Score (GUS), a metric derived from the observed half-life value. This value serves as a key indicator of a pesticide's likelihood to leach into groundwater. To calculate the GUS value, the log K_{oc} (soil organic carbon partition coefficient) and $T_{1/2}$ (half-life) values of pesticides in various soils are considered. These parameters provide insights into the adsorption and degradation characteristics of pesticides within soil matrices. Based on established criteria, pesticides are categorized as leachers if their GUS value exceeds 2.8, non-leachers if it falls below 1.8, and potential leachers if it ranges between 1.8 and 2.8. The analysis of GUS values, as illustrated in Figure 6.7, offers valuable insights into the leaching potential of specific pesticides, such as Imidacloprid and Atrazine, across diverse soil types. In black cotton soils, the GUS values for Imidacloprid ranged from 2.25 to 2.62, while in red soil, it was reported as 3.72. For Atrazine, GUS values ranged from 2.01 to 2.41 in black cotton soils, and in red soil, it was 3.16. Notably, in red soil, both Imidacloprid and Atrazine exhibited pronounced leaching propensity, with a recorded GUS value of 3.72 and 3.16, respectively. These findings underscore the heightened risk of groundwater contamination posed by these pesticides within red soil environments.

Table 6. 3 The calculated GUS values for both pesticides in various soils

Soil	**Imidacloprid**				**Atrazine**			
	Log K_{oc}	$T_{1/2}$	**log** $T_{1/2}$	**GUS**	**Log K_{oc}**	$T_{1/2}$	**log** $T_{1/2}$	**GUS**
BC-1	2.824	83	1.919	2.257	2.853	57	1.756	2.014
BC-2	2.722	66	1.820	2.326	2.569	44	1.643	2.351
BC-3	2.616	79	1.898	2.626	2.614	55	1.740	2.412
RS	1.968	68	1.833	3.723	2.127	49	1.690	3.166

Conversely, GUS values falling within the range of 1.8 to 2.8 for other soil types suggest a moderate potential for leaching, albeit to a lesser extent. This indicates that while Imidacloprid and Atrazine may still pose some risk of groundwater contamination in these soils, the degree of leaching is not as significant as observed in red soil.

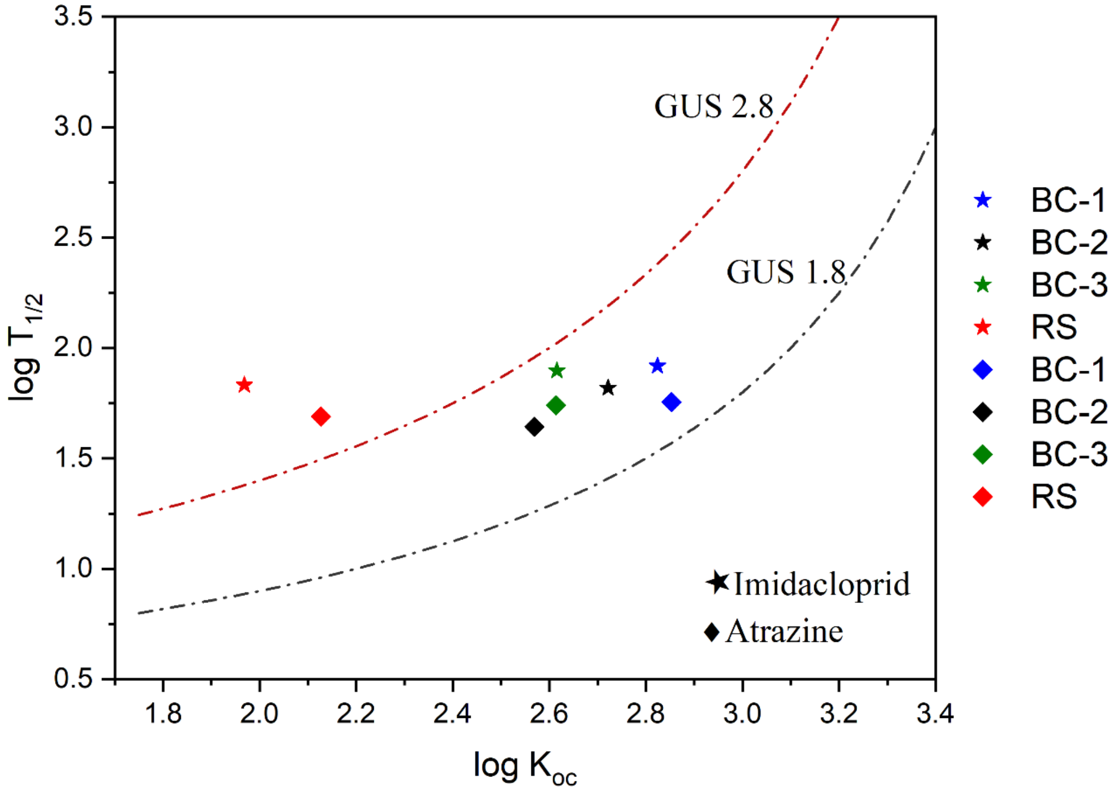

Fig. 6. 7 GUS values of Imidacloprid and Atrazine in various soils

6.5 Summary

- The study reported that the half-life of Imidacloprid ranged from 67 to 83 days in the investigated soils, while the half-life of Atrazine ranged from 44 to 57 days. The degradation of pesticides in soils is attributed to the presence of specific bacteria, which varies between soils, resulting in differing degradation rates.
- Imidacloprid exhibited greater persistence in the investigated soils compared to Atrazine. The degradation rate of Atrazine is reported to be higher than that of Imidacloprid in all investigated soils.
- The GUS values for Imidacloprid ranged from 2.25 to 2.62 in black cotton soils, while in red soil, it is reported as 3.72. For Atrazine, GUS values ranged from 2.01 to 2.41 in black cotton soils, and in red soil, it is 3.16. GUS values falling between 1.8 and 2.8 in

all black cotton soils suggest that both pesticides fall into the potentially mobile category. However, in red soil, where the values exceeded 2.8 for both pesticides, they are considered highly mobile.

- The results of the soil column leaching study corroborated these findings, as both Imidacloprid and Atrazine are detected in the leachate sample and migrated to the deeper sections of the column.
- The presence of pesticides in the deeper layer of the soil matrix could make the pesticides more persistent due to the absence of microorganisms, ultimately leading to groundwater contamination.

Chapter 7

Cotton Stalk Biochar and Hydrochar Synthesis and Characterization

7.1 Introduction

India, with its agrarian focus, stands as one of the world's leading cotton producers, and cotton stalks represent a plentiful source of non-food biomass. Despite being often considered as farm waste with limited economic value that does not directly compete with food or animal feed, cotton stalks prove to be valuable resources, provided cotton production remains unaffected. Cotton cultivation yields a staggering 50 million tonnes of biomass waste residues annually (Hamawand et al., 2016). Unfortunately, the majority of cotton stalks are either burned or discarded, actions that result in the loss of valuable biomass material, environmental contamination, and contribute to global warming concerns. This chapter discusses the synthesis and characterization of various biochar and hydrochar from raw cotton stalks. These materials were subsequently amended into soils to assess their efficacy in enhancing pesticide sorption and mitigating their mobility, as presented in chapter 8.

7.2 Characterization of Biochar and Hydrochar

7.2.1 Mass Yield, Proximate analysis, and Energy Properties of Biochar and Hydrochar

Table 7.1 provides a detailed representation of various key parameters (proximate analysis, mass yield, energy yield, energy density and high heating value) related to raw cotton stalk and the products derived through synthesized pyrolysis and hydrothermal carbonization. Notably, cotton hydrochars (CTH) exhibited a higher mass yield (M_Y) compared to cotton biochars (CBC) produced at varying temperatures. In both processes, elevated temperatures resulted in a reduction of the mass yield. The hydrochar prepared at 180 ˚C (CTH-180) achieved the highest mass yield. Conversely, for biochar, the M_Y dropped from 51.82% to

31.84% with increasing temperature. This decline can be ascribed to the thermal decomposition of hemicellulose, cellulose, and lignin at elevated temperatures, as observed by Gao et al. (2021). A similar trend was observed in the hydrothermal carbonization process, with the yield decreasing from 66.89% to 53.2% with increased temperature. The temperature elevation triggers the liberation of volatile substances, accelerating dehydration and elimination reactions, ultimately leading to a diminished yield, as discussed by Periyavaram et al. (2022).

Table 7. 1 Physico-chemical properties of biochar and hydrochar derived from cotton stalk

Sample	M_Y (%)	Proximate Analysis (wt %, d.b.)			Fuel ratio	HHV_c (MJ/kg)	HHV_m (MJ/kg)	E_D	E_Y (%)
		VM	Ash	FC[a]					
RC	-	79.48	5.77	14.75	0.19	15.29	15.62	-	-
CBC-300	51.82	68.43	13.09	18.48	0.27	22.71	20.89	1.34	69.30
CBC-500	38.95	34.29	14.87	50.84	1.48	24.41	23.67	1.52	59.02
CBC-700	31.84	23.57	17.73	58.7	2.49	29.12	29.83	1.91	60.81
CTH-180	66.89	70.55	6.12	23.33	0.33	18.50	19.97	1.28	85.52
CTH-210	59.66	61.72	7.59	30.69	0.50	21.56	22.74	1.46	86.85
CTH-240	53.2	52.98	7.92	39.1	0.74	24.15	25.88	1.66	88.14

[a] FC= 100%-VM-ash.
HHV_m: Measured high heating value.
HHV_c: Calculated high heating value.

On a dry basis, raw cotton stalk (RC) exhibited the maximum volatile matter (VM) at 79.48%, the minimum ash content at 5.77%, and the least fixed carbon (FC) at 14.75%. In contrast, biochar produced at 700 ˚C (CBC-700) displayed the lowest VM at 23.57%, the highest FC at 58.7%, and the highest ash content at 17.73%. The VM of the synthesized biochar decreased from 68.43% to 23.57% with an increase in temperature from 300 ˚C to 700 ˚C. Higher pyrolysis temperatures resulted in biochar with increased ash content, primarily attributed to the accumulation of cations and salts during the carbonization process. The FC content also improved across all cases as the process temperature increased. The biochar produced at 300 °C experienced incomplete carbonization, resulting in a decreased FC content, a characteristic that can be linked to the sample's lesser degree of carbonization. The carbonization process encompasses two primary reactions: the predominant depolymerization reaction during the initial carbonization stage and the prevailing polycondensation reaction at elevated carbonization temperatures. The decline in biochar M_Y at elevated temperatures can be a result of the transformation of VM into carbon black via polycondensation reactions, as discussed by Al Afif et al. (2020). In the hydrothermal carbonization (HTC) process, proximate analysis data indicates a significant decrease in VM from 70.55% to 52.98% and an increase in FC content from 23.33% to 39.1%. These changes are attributed to dehydration and decarboxylation in the HTC process, which release H_2O and CO_2.

As presented in Table 7.1, the high heating value (HHV) of biochar derived from cotton stalk increased progressively with temperatures ranging from 300 ˚C to 700 ˚C, reaching its peak at CBC-700 with a value of 29.83 MJ/kg. In comparison, the HHV value of raw cotton stalk was recorded at 15.62 MJ/kg. The escalation in pyrolysis temperature corresponds to an augmented release of volatile matter and a higher concentration of fixed carbon, resulting in an enhanced degree of carbonization. Consequently, the biochar exhibits elevated carbon content while experiencing a sharp reduction in oxygen content. These cumulative changes result in a sustained increase in the HHVs of the biochar, as discussed by He et al. (2018). The HHV of synthesized hydrochars similarly increased from 19.97 MJ/kg to 25.88 MJ/kg with a rise in process temperature from 180 ˚C to 240 ˚C, surpassing that of raw cotton stalk (15.62 MJ/kg). The augmentation of fixed carbon content in hydrochar is a contributing factor to the elevation of HHV. Energy densification (E_D) also exhibits an upward trend with increasing temperature in both processes. For biochars, the E_D values range from 1.34 to 1.91, while for hydrochar, the range is from 1.28 to 1.66. The increased energy densification with rising temperature can be ascribed to enhanced devolatilization and dehydration reactions during thermal and hydrothermal treatments. The maximum E_D was observed for biochar prepared at CBC-700 (1.91). The intricate relationship between mass yield, energy densification, and energy yield signifies that changes in mass yield or energy densification can have a notable impact on energy yield. Elevating the pyrolysis temperature from 300 ˚C to 700 ˚C results in an increase in energy densification (from 1.34 to 1.91). Surprisingly, a reduction in mass yield leads to decline in energy yield, from 69.30% to 60.81%. In contrast, for hydrochar, both the energy yield and energy densification exhibit an upward trend with increasing process temperature (Table 7.1).

7.2.2 Elemental Analysis

Table 7.2 displays the findings of the elemental analysis of biochar and hydrochar samples. The carbon content in the char samples exhibited an increasing trend with rising temperature. The highest carbon content, reaching 77.65%, was detected at a pyrolytic process temperature of 700 ˚C (CBC-700), while the lowest, at 40.44%, was found in the raw cotton stalk (RC). The carbon percentage in biochar products increased from 58.77% to 77.65% as the temperature increased, coinciding with a decline in hydrogen and oxygen content from 4.02% to 2.09% and 21.80% to 0.65%, respectively. The reduction in hydrogen and oxygen is ascribed to deoxygenation and dehydration reaction occurring at elevated temperatures, as discussed by Al Afif et al. (2020). Similarly, in HTC, carbon content rose from 48.73% to 62.9% as the temperature increased (180 ˚C to 240 ˚C). Molar ratios of H/C and O/C markedly decreased with increasing process temperature in both cases. The H/C value for raw cotton was reported at 1.54, reducing to 0.32 for biochar synthesized at 700 ˚C and 0.78 for hydrochar synthesized at 240 ˚C. The O/C value also changed from 0.87 (for RC) to 0.01 (CBC-700) and 0.29 (CTH-240). The decreasing H/C and O/C molar ratios signify a progressive augmentation in the degree of carbonization and aromaticity, as emphasized by Al Afif et al. (2020). The observed variations in H/C and O/C ratios suggest that certain important mechanisms, such as decarboxylation, dehydrogenative polymerization, and the decomposition of lignocellulosic biomass, played a significant role in reducing these values. This reduction process resulted in the generation of condensable fractions, including alcohols and acids, alongside non-condensable fractions such as CO_2 and CO (Chen et al., 2019; Cheng et al., 2021).

Table 7. 2 Elemental composition of cotton stalk, biochar and hydrochar

Sample	Ultimate Analysis (wt %, d.b.)					H/C	O/C
	C	H	N	S	O[a]		
RC	40.44	5.20	1.69	0.21	46.69	1.54	0.87
CBC-300	58.77	4.02	2.1	0.22	21.80	0.82	0.28
CBC-500	65.86	2.76	1.65	0.21	14.66	0.50	0.17
CBC-700	77.65	2.09	1.71	0.17	0.65	0.32	0.01
CTH-180	48.73	4.86	0.49	0.08	39.72	1.20	0.61
CTH 210	56.25	4.48	0.64	0.11	30.93	0.96	0.41
CTH 240	62.9	4.11	0.86	0.16	24.05	0.78	0.29

[a] %O= 100- (%C+ %H+ %N+ %ash).

The Van Krevelen diagram in Figure 7.1 illustrates that the H/C and O/C molar ratios of the biochar and hydrochar samples indicate their suitability with appropriateness increasing at higher process temperatures. Careful selection of char samples, particularly those generated at specific pyrolysis temperatures, suggests that a temperature of 700 °C yields the highest quality char for fuel. This is attributed to its superior carbonization, and the molar ratios of H/C and O/C indicate its potential as a viable substitute for coal.

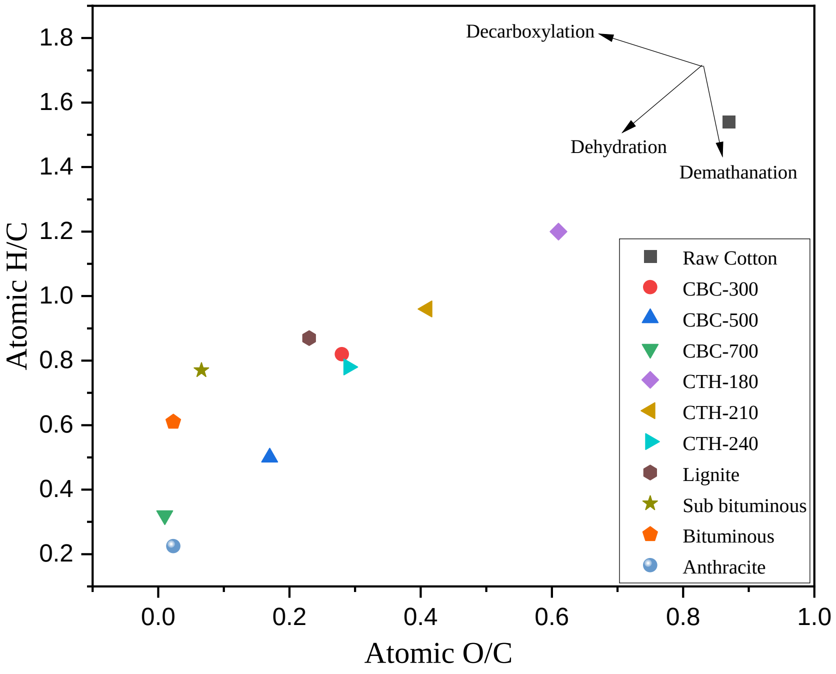

Fig. 7. 1 Van Krevelen diagram

7.2.3 Structural Properties

Figures 7.2 depict the FTIR spectral bands of raw cotton stalk, hydrochar, and biochar synthesized at different temperatures, confirming the presence of diverse functional groups in each sample. The observed variations across spectral ranges illustrate the significant impact of both pyrolysis and hydrothermal carbonization processes on the functional groups within raw cotton stalk. The peaks identified at 3450 cm^{-1} and 3390 cm^{-1} in all synthesized biochar and hydrochar samples signify the existence of hydroxyl (-OH) functional groups (Liu et al., 2019). For biochar, the peak intensity diminishes with higher pyrolysis temperatures, indicating the loss of hydroxyl groups at elevated temperatures (Yuan et al., 2011). The spike detected at 2920 cm^{-1} signifies the presence of aliphatic carbon (specifically methyl and methylene) and aromatic carbon in all analyzed samples (Wang et al., 2018; Zhang et al., 2021). The intensity of peaks between 1620 cm^{-1} and 1450 cm^{-1} is notably higher in the hydrochar and biochar bands compared to the raw cotton stalk band. This higher intensity is attributed to hydrothermal carbonization and pyrolysis reactions at elevated temperatures, leading to the transformation of single aromatic compounds into polyaromatic compounds. The spectral peak at 1318 cm^{-1} in the hydrochar is associated with primary and secondary aromatic amines, while the biochar sample displays a reduction in peaks at 1050 cm^{-1}, indicating a decrease in hemicellulose content (Wang et al., 2018).

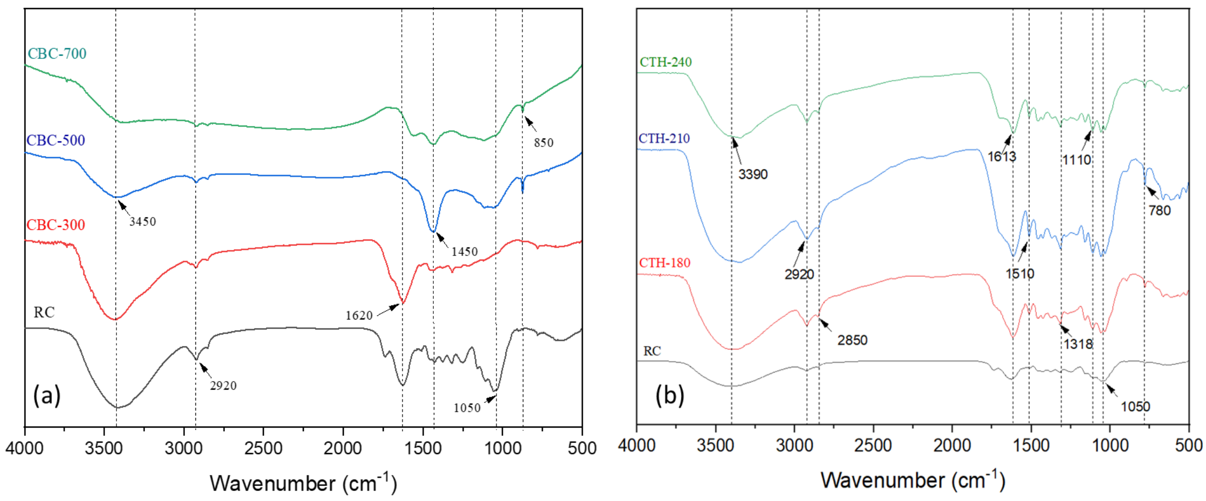

Fig. 7. 2 FTIR plots of (a)Biochar and (b) Hydrochars

Figure 7.3 display the X-ray diffraction (XRD) spectrum of biochar and hydrochar within the 10-70° range. In the instances of raw cotton, all hydrochars, and CBC-300, a peak around 15° is observed, corresponding to the crystalline cellulose structure diffraction, potentially stemming from incomplete carbonization (Ercan et al., 2023; Xiao et al., 2014). With rising temperature, particularly in the cases of CBC-500 and CBC-700, the peak becomes less apparent, indicating cellulose conversion (Kim et al., 2011). The broad peak around 22-23° suggests the existence of graphite planes in the samples (Wang et al., 2018). XRD analyses reveal that higher temperatures result in an increased number of minor peaks in both biochars and hydrochars, implying the presence of various minerals. Additionally, the heightened sharpness of the peaks at elevated temperatures signifies increased crystallinity of the material. In the case of biochars, minerals such as Calcite ($CaCO_3$), Sylvite (KCl), and Whewellite ($CaC_2H_4.H_2O$) dominate, while hydrochars exhibit a prevalence of Whewellite, MgP_2O_{10}, and $C_7NO_2H_4$.

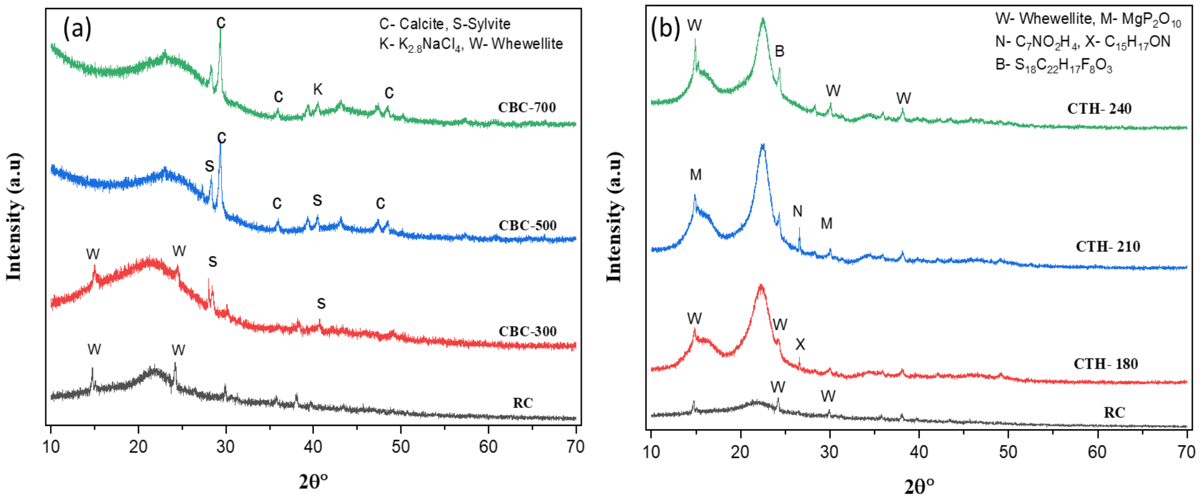

Fig. 7. 3 XRD plots of (a)Biochar and (b) Hydrochars

7.2.4 Analysis of Thermal and Combustion Properties

Thermogravimetry analysis (TGA) was conducted to explore the behaviour of cotton stalk, hydrochar, and biochar over a temperature range of 30 °C to 850 °C. The corresponding TGA and DTG plots are presented in Figure 7.4. From the TGA plot of hydrochar produced from cotton stalk at different operating temperatures (180/210/240 °C), it can be observed that they exhibit similar thermal behaviour up to 400 °C. However, there is a greater mass loss in the later stages for the sample produced at 240 °C. This can be ascribed to increased carbon densification, as evidenced in the proximate and elemental analysis.

There are dissimilarities in the thermal behaviour of biochar and hydrochar, as observed in the TGA analysis. Biochar is thermally stable compared to hydrochar, which is more combustible. Biochar exhibits greater thermal stability than cotton stalk, and this stability increases with the rise in pyrolysis temperature from 300° C to 700° C. The percentage mass loss decreases from about 45% and 25%, which can be ascribed to greater carbon densification due to increased devolatilization reactions, as seen in proximate analysis (Sun et al., 2014; Zhong et al., 2022).

The DTG_{mean} represents the average thermal degradation of the sample per minute for each degree rise in temperature, and the values are given in Table 7.3. It can be observed that the DTG_{mean} values for raw cotton, CTH-180 and CTH-210 are provided. Furthermore, the combustion of CTH-240 is relatively stable, as it has a lower DTG_{mean} than raw cotton. Biochar exhibits better combustion stability than raw cotton and the synthesized hydrochars. As the pyrolysis temperature increases, the DTG_{mean} reduces drastically, indicating a better combustion reaction due to the loss of volatile matter (Yang et al., 2018).

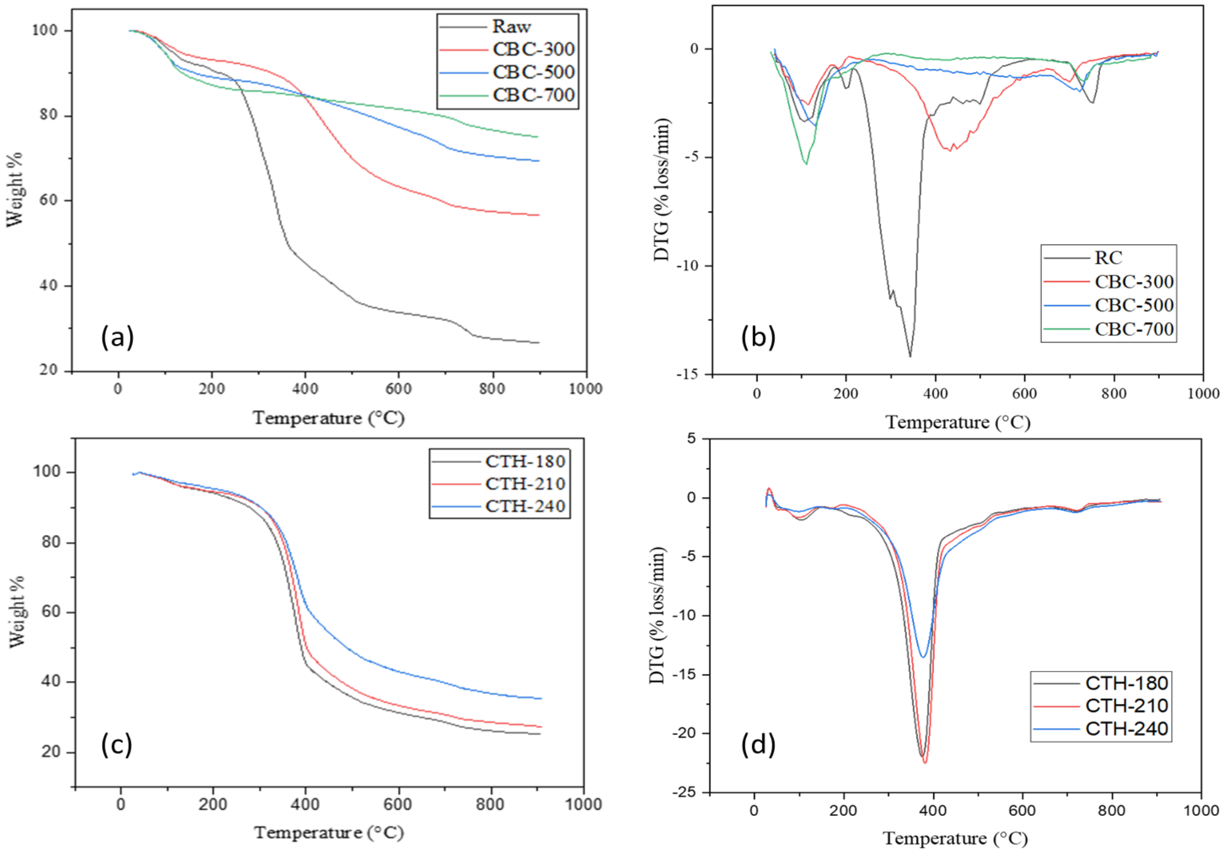

Fig. 7. 4 TGA and DTG plots of biochar and hydrochar.

The ignition temperature of hydrochar is higher than that of raw cotton, which can be attributed to devolatilization reactions occurring during HTC. Similarly, for biochar, the ignition temperature exceeds that of raw cotton, attributed to the reduction in volatile matter during the pyrolysis reaction. Furthermore, the ignition temperature of biochar is higher than that of hydrochar, a result of more severe operating conditions than HTC, leading to greater volatile matter loss during pyrolysis (Chen et al., 2021). The active degradation window, which is the difference between the final burnout temperature and the ignition temperature, is around 300 °C for hydrochar, similar to that of raw cotton stalk. Despite the rise in the ignition temperature for biochar, there is a significant increase in the degradation window, indicating better combustion properties.

The combustion reaction, as indicated in earlier studies (Periyavaram et al., 2022), is presumed to adhere to first-order kinetics, and the corresponding kinetic parameters are derived using the slope-intercept method. Considering the high coefficient of determination (R^2) value depicted in Figure 7.5, it is justifiable to infer that there is a strong correlation between the first-order kinetics and the TGA data. There is a considerable decrease in the activation energy (Table 7.4) for the synthesized biochars and hydrochars compared to that of raw cotton. As the pyrolysis temperature rises from 300 °C to 700 °C, the activation energy for the synthesized biochars is reduced from 24.1 KJ/mol to 3.21 KJ/mol, which can be attributed to carbon densification during pyrolysis; however, no such trend is observed in the case of hydrochars.

Table 7. 3 Combustion properties of cotton stalk, biochar and hydrochar

Sample	T_i (˚C)	T_f (˚C)	M_f (%)	DTG_1 (%/min)	T_1 (˚C)	DTG_{mean} (%/min)
Raw cotton	236.08	535.5	26.65	14.19	343.08	2.57
CBC-300	335.9	710.12	56.66	4.7	432.9	1.51
CBC-500	343.1	745.08	69.49	1.97	722.65	1.06
CBC-700	345.0	748.27	75.01	1.47	731.5	0.85
CTH-180	318.19	585.03	25.35	21.98	375.34	2.56
CTH-210	329.70	596.60	27.49	22.50	378.93	2.50
CTH-240	323.77	623.59	35.51	13.49	379.77	2.21

T_i: ignition temperature.
T_f: burnout temperature.
M_f: residual mass.
DTG_1: weight loss rates according to the first peaks.
T_1: temperature at the first peak.
DTG_{mean}: average weight loss rate.

A lower pre-exponential factor is an indicator of a stable combustion reaction, and this factor is lower for both synthesized biochars and hydrochars compared to cotton waste, making them efficient fuels. The decrease in CCI for hydrochars and biochars can be ascribed to the loss of volatile matter during the hydrothermal carbonization and pyrolysis, respectively, indicating a more stable flame and combustion (Chen et al., 2021; He et al., 2013).

Table 7. 4 Combustion kinetic parameters of cotton stalk and synthesized biochar and hydrochar

Sample	CCI×10^{-7} (min^{-2} $°C^{-3}$)	R_w×10^3	D_i×10^{-5}	E_a (kJ/mol)	A (min^{-1})	R^2
Raw cotton	12.2	2.72	17.5	43.78	393.44	0.999
CBC-300	0.88	0.89	3.23	24.11	0.0678	0.989
CBC-500	0.24	0.36	0.79	19.24	0.0191	0.985
CBC-700	0.14	0.29	0.58	3.21	0.0004	0.967
CTH-180	9.49	1.84	18.4	40.98	336.13	0.947
CTH-210	8.67	1.71	18	42.93	426.92	0.936
CTH-240	4.56	1.54	10.9	35.49	79.12	0.957

7.3 Sorption of Imidacloprid in Soils Amended with Organic Amendments

A preliminary study was carried out to investigate the efficacy of various types of char as soil amendments in enhancing the sorption capacity of Imidacloprid. The study was conducted on BC-1 soil with an initial Imidacloprid concentration of 10 µg/mL. The experiment involved incorporating synthesized biochar and hydrochar samples into the soils at different ratios to evaluate their sorption capacities. Analysis, as illustrated in Figure 7.6, elucidated the influence of different organic amendments, highlighting minimal impact from the addition of cotton hydrochar (CTH) on sorption capacity. Specifically, the addition of 6% (w/w) cotton hydrochar to the soils was assessed. Hydrochar produced at 240 °C (CTH-240) exhibited superior Imidacloprid sorption compared to samples produced at 210 °C (CTH-210) and 180 °C (CTH-180). However, Imidacloprid sorption was notably lower compared to soils amended with biochar. Furthermore, biochar produced at 300 °C demonstrated reduced sorption compared to that produced at 500 °C. Notably, the highest sorption was observed with CBC-700 amendment to the soil. Additionally, Figure 7.6 revealed that a 1% addition of CBC-700 exhibited greater sorption than a 6% addition of CBC-500. The elevated temperature during biochar production

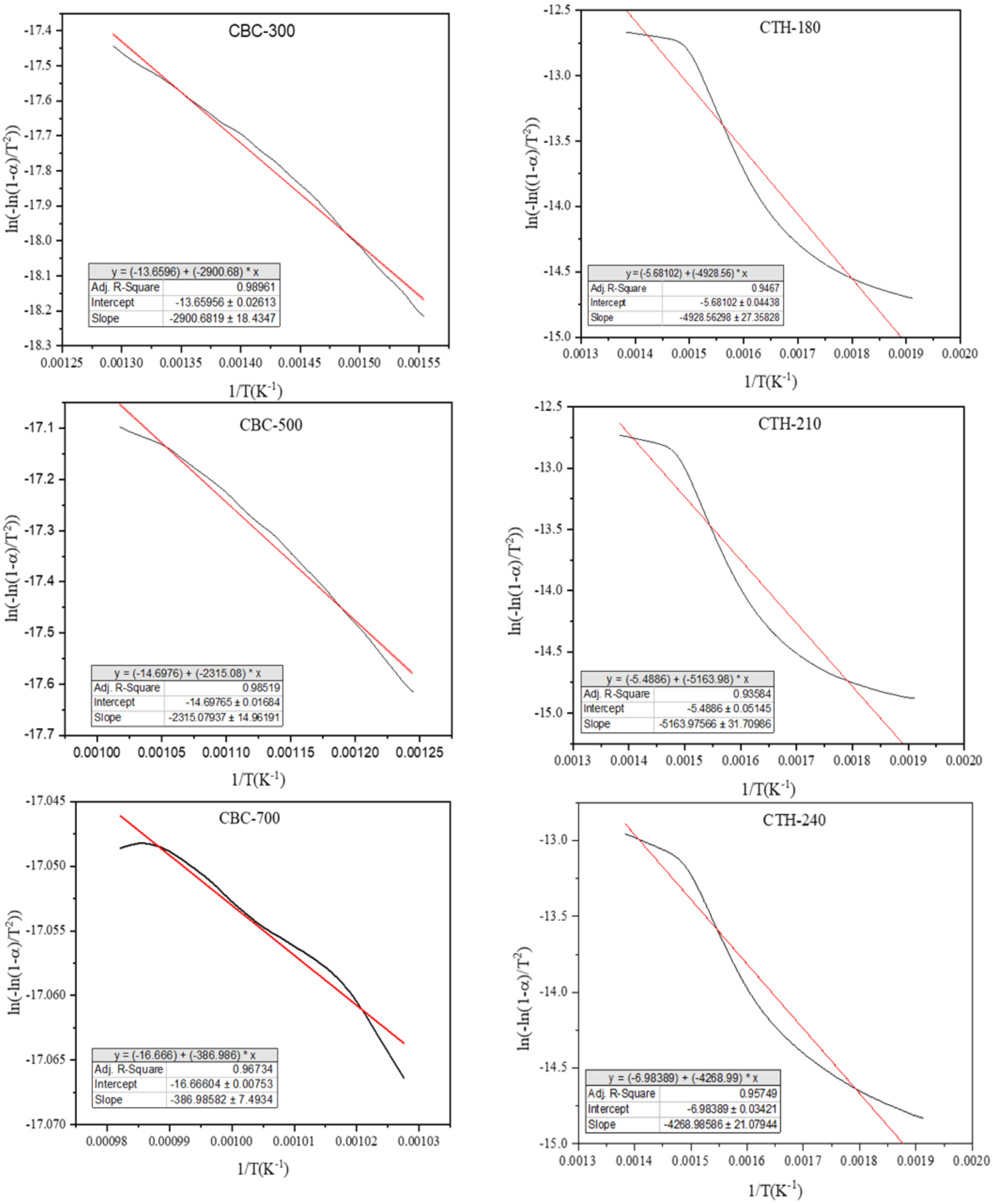

Fig. 7. 5 ln[(-ln(1-α^2)/T^2)] vs 1/T plot of different biochars and hydrochars

enhances the carbon percentage, surface area, and pore volume of the biochar, facilitating the retention of pesticide molecules on its surface. Consequently, further soil amendment studies were conducted using CBC produced at 700 °C.

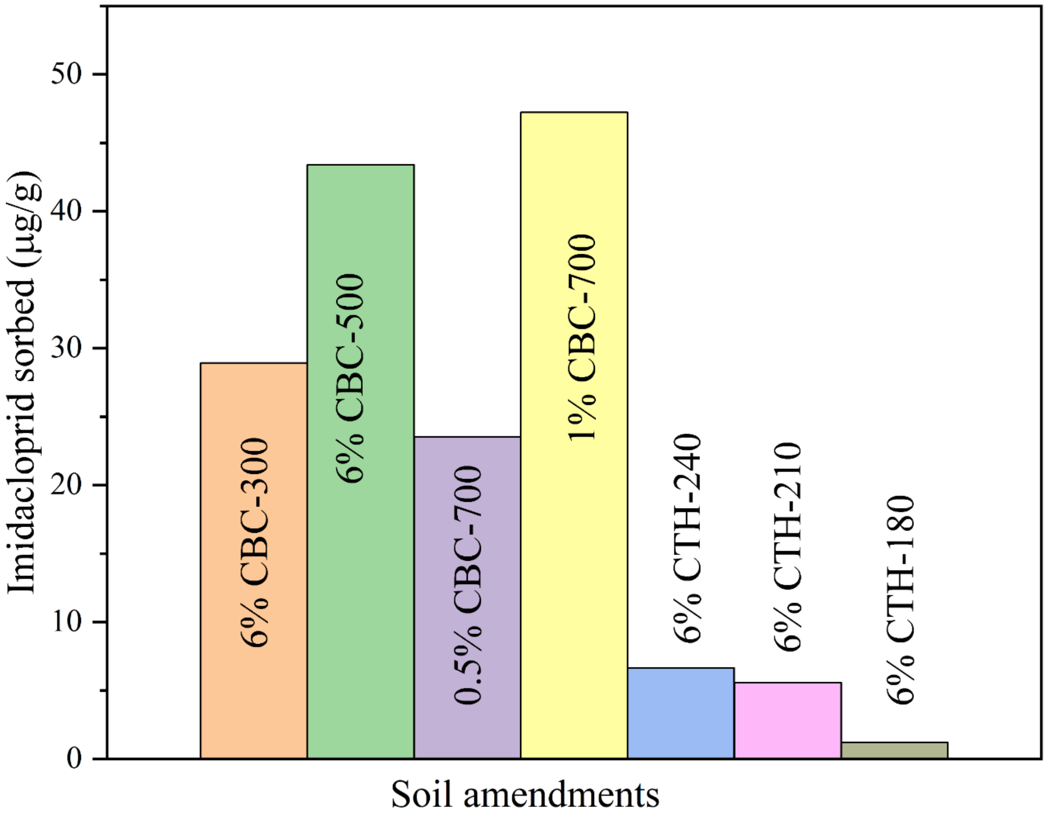

Fig. 7. 6 Influence of various organic amendments on sorption of Imidacloprid in BC-1 soil

7.4 Summary

- Higher mass yield and energy yield are observed in the hydrothermal carbonization (HTC) process compared to pyrolysis.
- Biochars exhibited higher percentages of fixed carbon (FC) and lower percentages of volatile matter (VM) compared to hydrochars.
- Elemental analysis revealed that higher carbon content developed at higher temperatures in both processes, with pyrolysis being more effective for higher carbonization.
- The higher heating value (HHV) is recorded as 29.83 MJ/kg for CBC-700 biochar and 25.88 MJ/kg for CTH-240 hydrochar. Energy densification is higher for biochar samples compared to hydrochars, but the energy yield is higher for hydrochars due to lower mass yield of biochar.

- The Van Krevelen diagram indicated that fuel substitute suitability increased with temperature in both pyrolysis and HTC processes.
- Combustion parameters showed thermal stability in the order of biochar > hydrochar > raw cotton. Combustion kinetic analysis revealed that biochars and hydrochars have lower activation energy (E) and pre-exponential factor (A) than raw cotton, indicating better combustion properties.
- The sorption study indicated that soils amended with cotton hydrochar (CTH) exhibited minimal affinity towards Imidacloprid, rendering it unsuitable for soil amendment purposes. Results from biochar amendments demonstrated that biochar produced at higher temperatures enhanced the sorption capacity of the soil, with biochar produced at 700 °C yielded superior results in terms of sorption capacity.

Chapter 8

Behaviour of Pesticides on Biochar Amended Soils

8.1 Introduction

Chapters 4 and 5 delve into the sorption capacity of pesticides in the soils of the Telangana regions. The results clearly indicate that both pesticides exhibit a notably low affinity for the soils under investigation, rendering this area susceptible to surface water and groundwater contamination by pesticides. The current chapter shifts focus towards examining the behaviour of pesticides in soils amended with cotton stalk biochar (CBC), aiming to assess the efficacy of CBC amendment in enhancing pesticide sorption and mitigating their mobility.

8.2 Sorption Kinetics of Pesticides on Biochar Amended Soils

The assessment of sorption kinetics plays a pivotal role in understanding the dynamics of pesticides within soil environments. In this study, sorption kinetics were examined across four distinct soil samples, for both Imidacloprid and Atrazine, with 0.5% and 1% biochar, at an initial concentration of 5 µg/mL. The results revealed that biochar amended soils demonstrated quicker equilibrium times compared to unamended soils. For Imidacloprid, equilibrium reached within the initial 6 hours in soils amended with 1% CBC, while with 0.5% CBC amendment, equilibrium occurred after approximately 8 hours. For Atrazine, equilibrium reached after 16 hours in amended soils, while in unamended soils it reached after 24 hours. This rapid equilibrium attainment in biochar amended soils suggests that the porous characteristics of biochar facilitate the swift adsorption of pesticide molecules within its structure. These findings provide insights into the temporal aspects of pesticide sorption and highlight the potential influence of biochar amendments on sorption kinetics.

To evaluate the sorption mechanisms of pesticides in biochar-amended soil, the sorption kinetic data were analyzed using non-linearized versions of the PFO, PSO, Elovich, and IPD models. Figure 8.1 and 8.2 depicts the plots corresponding to the kinetics models of Imidacloprid and Atrazine in all biochar amended soils. The model with the highest R^2 value, along with the observed (Q_e, EXP) versus anticipated (Q_e, CAL) adsorption values, was selected as the optimal model for characterizing the sorption kinetics. Among the considered models, the PSO model exhibited the highest R^2 value for pesticide sorption across all soils (Table 8.1 and 8.2). Furthermore, the PSO model demonstrated a good agreement between the predicted and observed amounts of pesticide sorption. In various sorption studies, the PSO model has shown a tendency to describe organic contaminant sorption kinetics effectively (Broznić and Milin, 2012a; Jing et al., 2020). This model suggests the occurrence of chemisorption, involving the formation of covalent and hydrogen bonds between the pesticide and the soil (Ho and McKay, 1999).

8.3 Sorption Equilibrium Study on Biochar Amended Soils

The primary objective of this study was to improve the comprehension of the relationship between pesticides and soil when combined with biochar. Furthermore, the study sought to measure the degree of pesticide adsorption in four distinct soil types following the application of biochar. To accomplish these objectives, a sorption equilibrium study was conducted, covering pesticide concentrations ranging from 0.5 µg/mL to 20 µg/mL. Soil amendments of 0.5% and 1% biochar (w/w) produced at 700 ˚C were utilized. Subsequently, quantitative sorption isotherms were established based on these parameters. The sorption patterns displayed a consistent trend across all scenarios, where an increase in pesticide concentration corresponded to a proportional increase in sorption. However, variations in sorbed concentrations were observed, likely due to differences in the physical and chemical characteristics of the respective soils (Kodešová et al., 2011; Sita, 2001). Figure 8.3 and 8.4 clearly show that the amount of pesticide adsorbed increased with the addition of biochar for both Imidacloprid and Atrazine.

The sorption process of Imidacloprid and Atrazine onto soils, with and without biochar amendment, was analyzed using three different isotherm models: Langmuir, Freundlich, and Temkin. The R^2 values derived from the Temkin isotherm model (Table 8.3 and 8.4) ranged from 0.723 to 0.852 for soils amended with 0.5% CBC, and from 0.711 to 0.879 for soils amended with 1% CBC for Imidacloprid. In the case of Atrazine, the values ranged from 0.793 to 0.922 in soils amended with 0.5% CBC and from 0.823 to 0.953 in soils amended with 1% CBC. Conversely, the Freundlich isotherm model demonstrated superior fitting compared to the

Langmuir and Temkin isotherm models, providing a more comprehensive understanding of the sorption data.

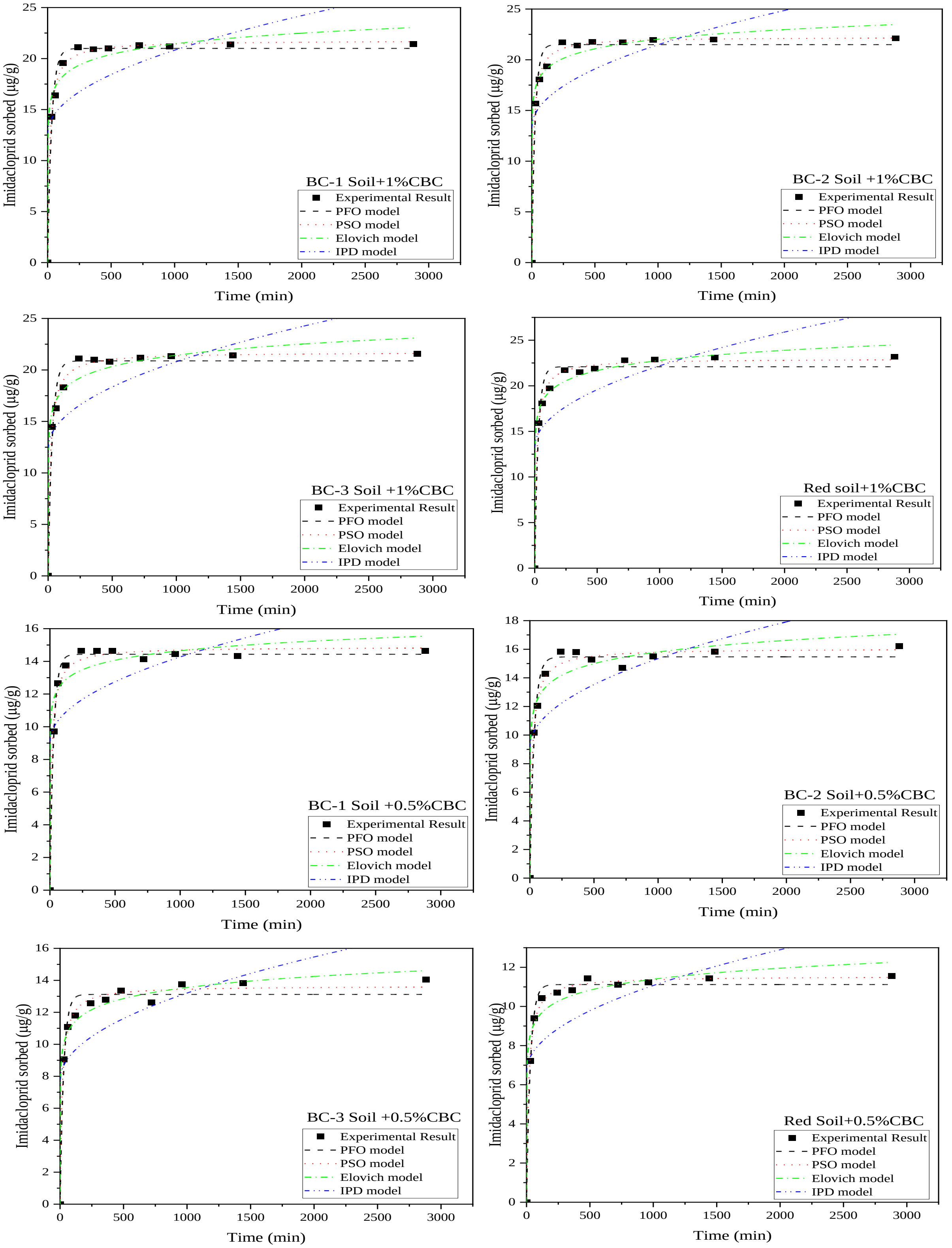

Fig. 8. 1 Sorption kinetics model plots of Imidacloprid in biochar amended soils

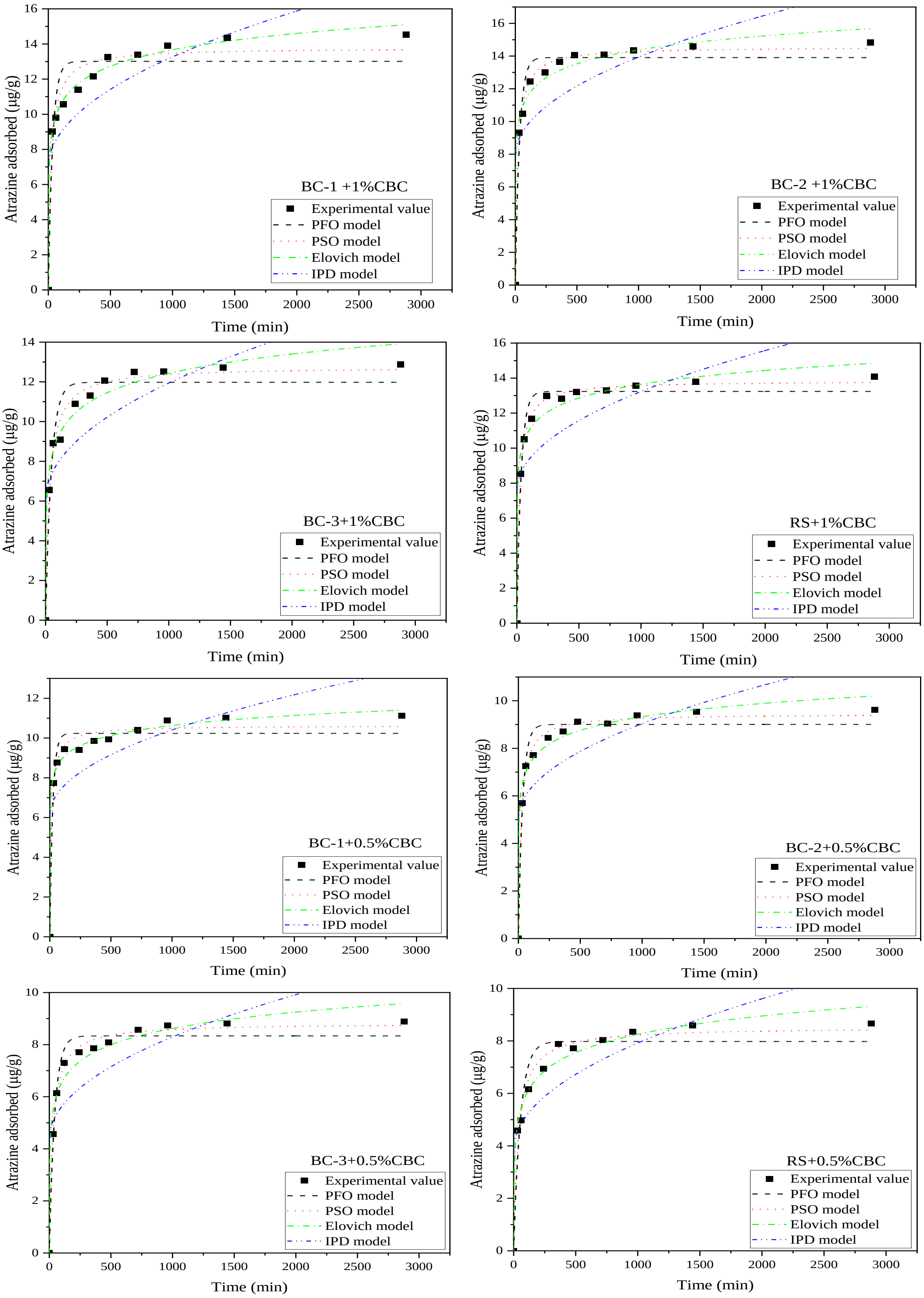

Fig. 8. 2 Sorption kinetics model plots of Atrazine in biochar amended soils

Table 8. 1 Kinetic model parameters of Imidacloprid in various amended soils

		Pseudo First Order model				**Pseudo Second Order model**				**Elovich model**			**Intraparticle diffusion model**		
		$EXP\ Q_e$	$CAL\ Q_e$	k_1	R^2	$EXP\ Q_e$	$CAL\ Q_e$	k_2	R^2	α	β	R^2	k_{int}	c	R^2
Amended with 1% CBC	BC-1	21.44	20.99	0.03	0.986	21.44	21.77	0.003	0.996	2386	0.66	0.966	0.25	12.65	0.399
	BC-2	22.13	21.49	0.04	0.982	22.13	22.24	0.003	0.997	14460	0.73	0.980	0.26	13.32	0.385
	BC-3	21.57	20.88	0.03	0.974	21.57	21.72	0.002	0.994	1198	0.63	0.973	0.26	12.41	0.424
	RS	23.17	22.09	0.04	0.973	23.17	22.96	0.003	0.996	2281	0.62	0.987	0.28	13.25	0.433
Amended with 0.5 % CBC	BC-1	14.65	14.13	0.04	0.996	14.65	14.88	0.01	0.991	31930	1.19	0.955	0.16	9.07	0.344
	BC-2	16.23	15.46	0.03	0.982	16.23	16.06	0.01	0.989	842	0.85	0.959	0.19	9.15	0.419
	BC-3	14.06	13.12	0.04	0.974	14.06	13.65	0.01	0.992	785	1.01	0.984	0.17	7.76	0.451
	RS	11.55	11.12	0.03	0.991	11.55	11.54	0.01	0.996	1034	1.23	0.968	0.14	6.67	0.412

The unit of EXP Q_e (µg/g), CAL Q_e (µg/g), k_1(min^{-1}), k_2 [(g/ (µg min)], α [µg/ (g min)], β (g/µg). k_{int} [µg/ (g min$^{0.5}$)]

Table 8. 2 Kinetic model parameters of Atrazine in various amended soils

Sample		**Pseudo First Order model**				**Pseudo Second Order model**				**Elovich model**			**Intraparticle diffusion model**		
		$EXP\ Q_e$	$CAL\ Q_e$	k_1	R^2	$EXP\ Q_e$	$CAL\ Q_e$	k_2	R^2	α	β	R^2	k_{int}	c	R^2
Amended with 1% CBC	BC-1	14.53	13.01	0.03	0.908	14.53	13.77	0.003	0.964	33.92	0.74	0.994	0.199	6.95	0.577
	BC-2	14.82	13.91	0.03	0.967	14.82	14.56	0.003	0.994	153.59	0.81	0.985	0.191	7.89	0.486
	BC-3	12.87	11.97	0.02	0.945	12.87	12.75	0.002	0.986	9.88	0.71	0.977	0.185	6.07	0.574
	RS	14.07	13.23	0.03	0.979	14.07	13.83	0.004	0.997	191.31	0.88	0.980	0.178	7.57	0.471
Amended with 0.5% CBC	BC-1	11.12	10.23	0.04	0.960	11.12	10.62	0.007	0.983	1546.5	1.37	0.994	0.134	6.14	0.457
	BC-2	9.62	9.00	0.03	0.968	9.62	9.45	0.005	0.994	67.44	1.21	0.983	0.125	5.05	0.498
	BC-3	8.88	8.33	0.02	0.974	8.88	8.82	0.004	0.995	12.52	1.10	0.972	0.123	4.38	0.539
	RS	8.66	7.97	0.02	0.934	8.66	8.52	0.003	0.981	3.70	0.99	0.980	0.128	3.84	0.615

The unit of EXP Q_e (µg/g), CAL Q_e (µg/g), k_1(min^{-1}), k_2 [(g/ (µg min)], α [µg/ (g min)], β (g/µg). k_{int} [µg/ (g $min^{0.5}$)]

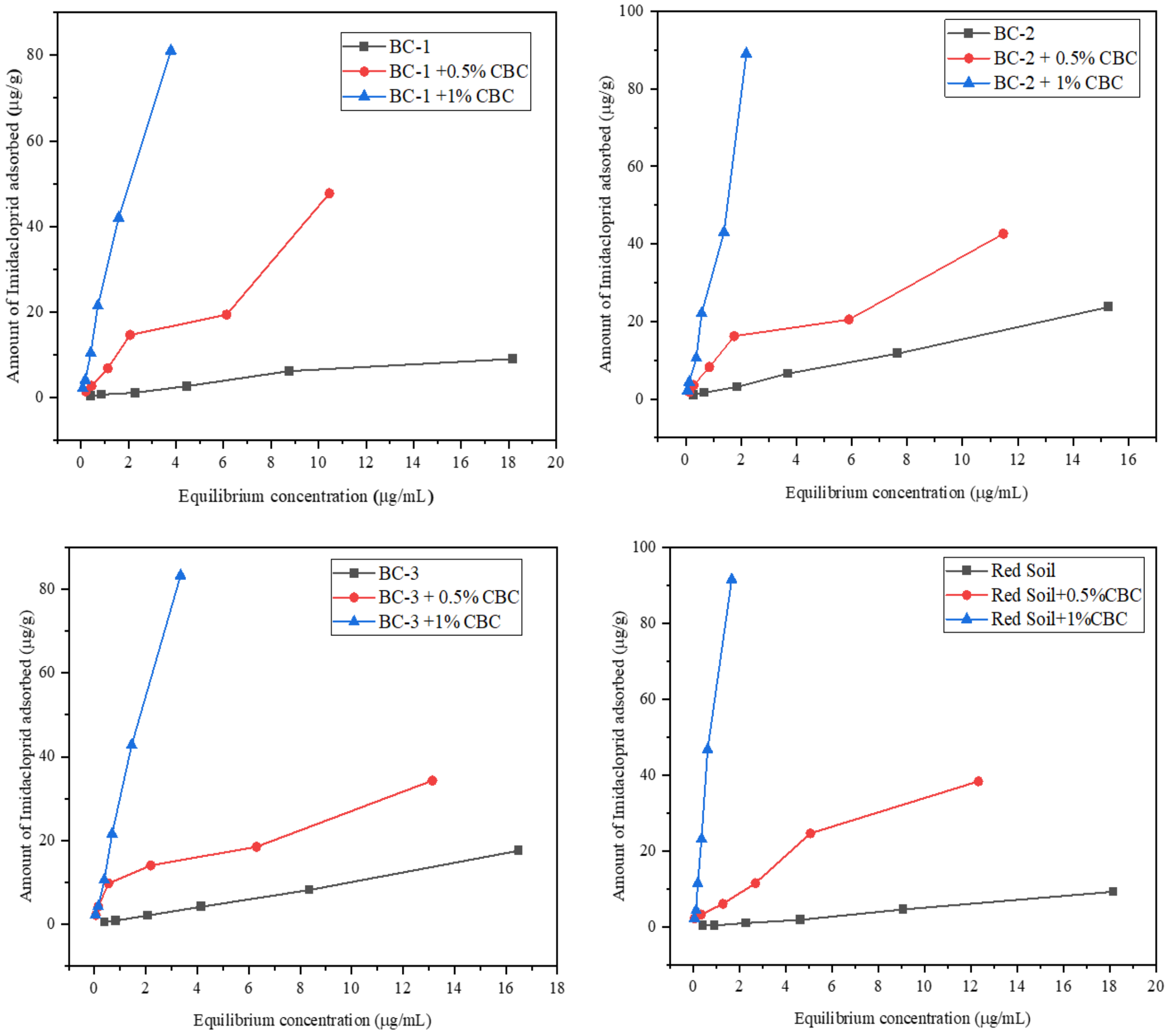

Fig. 8. 3 Sorption isotherm plots of Imidacloprid in various biochar amended and unamended soils

The 1/n value (slope) for the majority of cases in both 0.5% and 1% biochar amended soils was found to be less than 1, indicating nonlinear sorption and conforming to an L-shaped isotherm. As the concentration of the sorbate in the aqueous phase increases, there is a corresponding decrease in molecule sorption, resulting in the characteristic L-shaped isotherms. This feature defines an L-shaped isotherm (Piwowarczyk and Holden, 2012). Moreover, it indicates the commencement of the sorption process at high-energy sites, gradually shifting towards lower-energy sites as the process unfolds (Singh, 2005b).

The Freundlich constant (K_f) values for soils without biochar amendment were notably lower compared to those obtained for biochar amended soils for both Imidacloprid and Atrazine. A similar trend was also observed for the partition coefficient (K_d). In case of Imidacloprid sorption, the red soil exhibited the lowest K_d value (0.53), while the highest was observed for BC-2 soil (2.06) in the absence of biochar addition. The K_d value showed a significant improvement with the increase in the biochar doses applied to the soil. For instance, the K_d value for red soil alone was 0.53. However, with the addition of 0.5% CBC, it increased to 10.69, and with the further addition of 1% CBC, it reached 53.61. Similarly, the K_d value for Atrazine also improved following the addition of biochar to the soils.

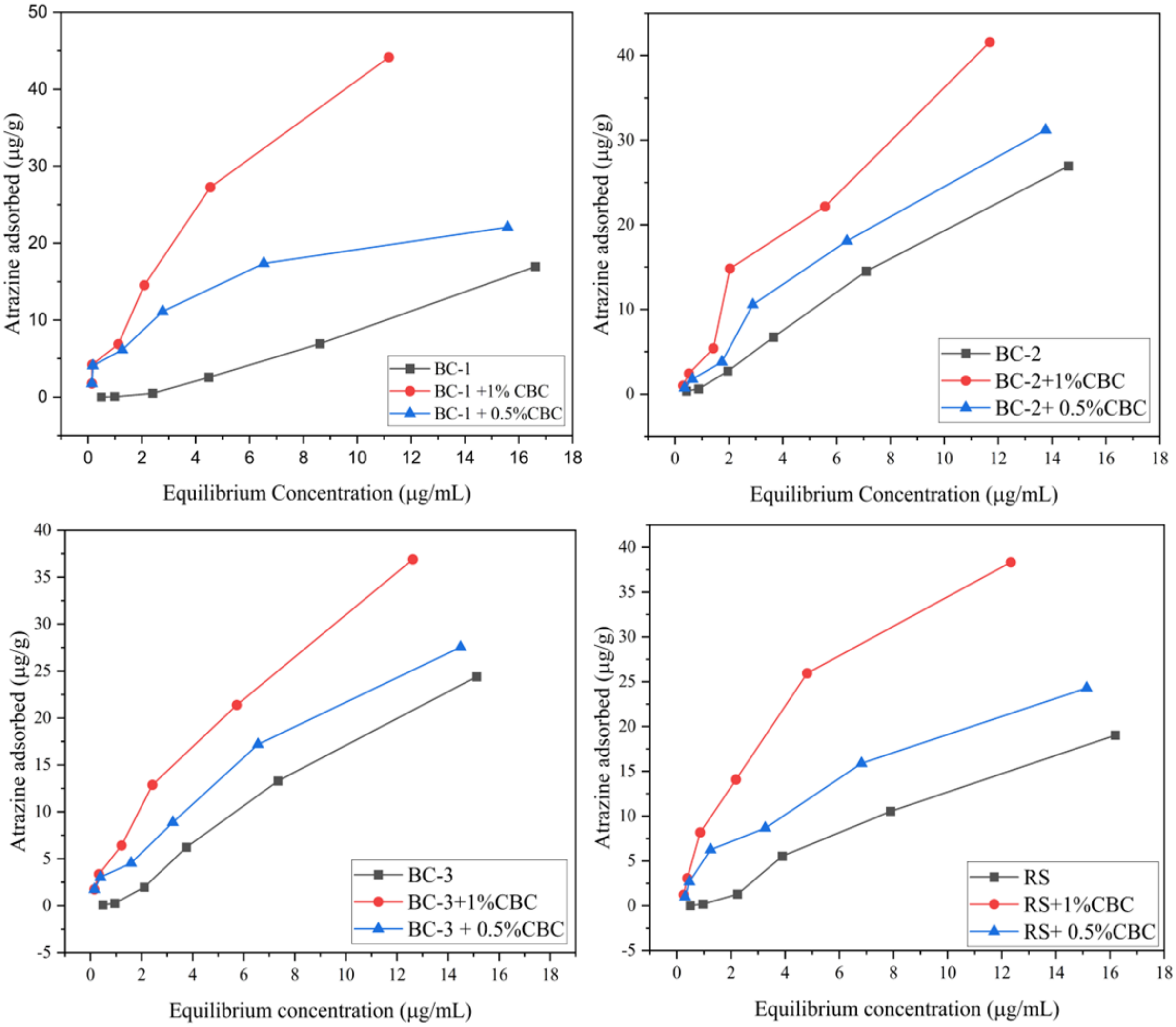

Fig. 8. 4 Sorption isotherm plots of Atrazine in various biochar amended and unamended soils

Table 8. 3 Sorption isotherm parameters of Imidacloprid in various biochar amended and unamended soils

Soil	**Condition**	**Langmuir**			**Freundlich**			**Temkin**			**K_d**	**K_{oc}**
		Q_m	**K_L**	**R^2**	**K_f**	**1/n**	**R^2**	**RT/b**	**A**	**R^2**		
BC-1 Soil	Unamended soil	7.63	0.11	0.984	0.71	0.89	0.982	2.28	1.48	0.842	0.65	667
	BC-1 +0.5% CBC	52.63	0.13	0.964	5.83	0.85	0.972	10.04	3.00	0.764	5.65	2135
	BC-1 +1% CBC	70.42	0.43	0.977	25.02	0.95	0.990	19.17	7.61	0.711	25.98	5249
BC-2 Soil	Unamended soil	10.97	0.32	0.961	2.31	0.81	0.988	5.16	2.01	0.778	2.06	527
	BC-2 +0.5% CBC	35.85	0.39	0.998	8.16	0.67	0.969	8.12	5.34	0.841	8.61	1782
	BC-2 +1% CBC	1428	0.02	0.927	34.89	1.03	0.991	49.12	2.60	0.752	34.23	4705
BC-3 Soil	Unamended soil	12.48	0.11	0.982	1.14	0.93	0.995	4.04	1.47	0.769	1.08	412
	BC-3 +0.5% CBC	18.14	2.44	0.983	9.82	0.46	0.970	5.04	16.07	0.852	16.34	3529
	BC-3 +1% CBC	27.39	2.08	0.936	28.29	0.86	0.984	17.26	11.01	0.839	32.92	6270
Red Soil	Unamended soil	2.77	0.32	0.798	0.57	0.90	0.959	2.14	1.32	0.750	0.53	91
	RS +0.5% CBC	9.85	4.63	0.761	7.69	0.55	0.927	6.30	7.62	0.723	10.69	1607
	RS +1% CBC	46.08	0.77	0.902	64.34	1.17	0.975	64.41	2.67	0.878	53.61	6109

The unit of Q_m (µg/g), K_L (mL µg^{-1}), K_f [µg g^{-1}(µg mL^{-1})$^{-1/n}$]

Table 8. 4 Sorption isotherm parameters of Atrazine in various biochar amended and unamended soils

Soil	Condition	Langmuir			Freundlich			Temkin			K_d	K_{oc}
		Q_m	K_L	R^2	K_f	1/n	R^2	RT/b	A	R^2		
BC-1 Soil	Unamended soil	0.32	0.22	0.941	0.19	1.83	0.965	5.01	1.06	0.802	0.69	713
	BC-1 +0.5% CBC	16.47	0.06	0.811	6.29	0.48	0.928	4.04	9.03	0.914	7.86	1588
	BC-1 +1% CBC	25	0.71	0.773	8.78	0.65	0.936	8.42	5.96	0.823	10.29	2079
BC-2 Soil	Unamended soil	9.69	0.08	0.977	1.02	1.29	0.985	16.59	1.12	0.828	1.44	371
	BC-2 +0.5% CBC	23.25	0.09	0.981	2.49	1.03	0.979	18.57	1.29	0.876	2.62	360
	BC-2 +1% CBC	38.46	0.11	0.991	5.01	0.93	0.963	23.14	1.52	0.902	5.02	690
BC-3 Soil	Unamended soil	0.87	0.21	0.969	0.35	1.72	0.968	6.84	1.13	0.829	1.08	411
	BC-3 +0.5% CBC	11.28	1.13	0.934	4.86	0.60	0.967	11.99	1.87	0.793	4.87	928
	BC-3 +1% CBC	21.45	0.58	0.987	6.53	0.68	0.994	16.85	1.91	0.846	6.53	1244
Red Soil	Unamended soil	0.18	0.26	0.868	1.23	1.34	0.941	5.01	1.13	0.869	0.77	134
	RS +0.5% CBC	100	0.03	0.911	3.71	0.74	0.943	5.52	2.98	0.922	3.43	442
	RS +1% CBC	44.84	0.13	0.956	6.38	0.83	0.951	9.29	3.46	0.953	6.32	813

The unit of Q_m (μg/g), K_L (mL μg^{-1}), K_f [μg g^{-1}(μg $mL^{-1})^{-1/n}$]

The BC-2 soil exhibited the highest K_f value among the unamended soils for both pesticides (Table 8.3 and 8.4). The observed variations in K_f values may be ascribed to differences in the clay percentage of the soils. Despite its greater TOC content (0.57%), red soil displayed a reduced affinity for both Imidacloprid and Atrazine compared to other soils. This discrepancy might be explained by the lower clay content present in red soil compared to the other soils. The introduction of 0.5% and 1% cotton biochar (CBC) to the soil has significantly enhanced the K_f values across all the examined soils. In the case of BC-1 soil, the unamended K_f value was 0.71 for Imidacloprid sorption. However, with the incorporation of 0.5% CBC, it notably increased to 5.83. Furthermore, the addition of 1% CBC resulted in a substantial elevation of the K_f value to 25.02. A similar pattern was observed in the other soils as well.

For Atrazine sorption, the lowest K_f value (0.19) was recorded for BC-1 soil in the unamended scenario. However, in soils amended with 0.5% CBC, it improved to 6.29, and further increased to 8.78 with a 1% CBC amendment. The improved sorption capacity is a direct outcome of the augmented surface area and additional sorption sites resulting from the addition of cotton stalk biochar (CBC) to the soil. Imidacloprid exhibited higher sorption in all conditions compared to Atrazine. This can be attributed to the relatively large and complex chemical structure of Imidacloprid. Imidacloprid contains polar functional groups such as nitro ($-NO_2$) and amine ($-NH_2$) groups, which enhance the interactions between Imidacloprid molecules and polar components of soil particles such as clay minerals, organic matter, and biochar. In contrast, Atrazine primarily contains a single triazine ring with chlorine substituents, which are less polar compared to the functional groups present in Imidacloprid. Therefore, Atrazine may exhibit weaker interactions with soil particles.

8.4 Pesticide Degradation and Leaching Potential on Biochar Amended Soils

The degradation kinetics of pesticides both in amended and unamended soils conformed to first order kinetics as R^2 value ranging from 0.958 to 0.989 for Imidacloprid and 0.931 to 0.969 for Atrazine. Among unamended soils, BC-2 soil exhibited the highest degradation rate for both Imidacloprid (0.0045 day^{-1}) and Atrazine (0.0156 day^{-1}), while BC-1 soil showed the lowest. The degradation of pesticides in soils is attributed to the presence of specific bacteria, which varies between soils, resulting in differing degradation rates. Soil organic content may also contribute to these differences, with BC-1 soil exhibiting the lowest organic content, while BC-

2 and red soil have relatively higher levels, potentially fostering increased soil bacterial activity (Li et al., 2023). This trend was similarly observed in biochar-amended soils, where the addition of biochar had minimal impact on degradation rates.

Table 8. 5 Degradation rate and half-life of Imidacloprid and Atrazine in various soils

Soils		**Imidacloprid**			**Atrazine**		
		k_R (day^{-1})	R^2	$T_{1/2}$ (days)	k_R (day^{-1})	R^2	$T_{1/2}$ (days)
Unamended soils	BC-1	0.0036	0.989	83	0.0122	0.949	57
	BC-2	0.0045	0.958	67	0.0156	0.969	44
	BC-3	0.0038	0.989	79	0.0124	0.944	56
	Red soil	0.0043	0.988	70	0.014	0.951	49
Biochar amended soils	BC-1	0.0034	0.989	88	0.0108	0.938	64
	BC-2	0.0042	0.959	71	0.0145	0.965	48
	BC-3	0.0035	0.985	86	0.0112	0.931	61
	Red soil	0.0041	0.983	73	0.0131	0.946	53

The calculated half-life ($T_{1/2}$) value of both pesticides in biochar amended and unamended soils were presented in Table 8.5. Imidacloprid's half-life in unamended soils ranged from 67 to 83 days, whereas for Atrazine the value was ranged from 44 to 57 days. The addition of biochar to the soil had a slight effect on pesticides half-life, with all cases showing a modest increase. In BC-1 soil, the half-life of Imidacloprid increased from 83 to 88 days, in BC-2 soil from 67 to 71 days, in BC-3 soil from 79 to 86 days, and in red soil from 70 to 73 days. For Atrazine these values increased from 57 to 64 days in BC-1 soil, 44 to 48 days in BC-2 soil, 56 to 61 days in BC-3 soil and from 49 to 53 days in red soil. The observed prolongation of pesticide half-life in biochar-amended soils can be attributed to the porous nature of biochar, which facilitates the adsorption of pesticides, thereby limiting its availability to soil microorganisms. However, the relatively small quantity of biochar added may explain the marginal nature of these changes, highlighting the importance of dosage considerations in soil amendment practices.

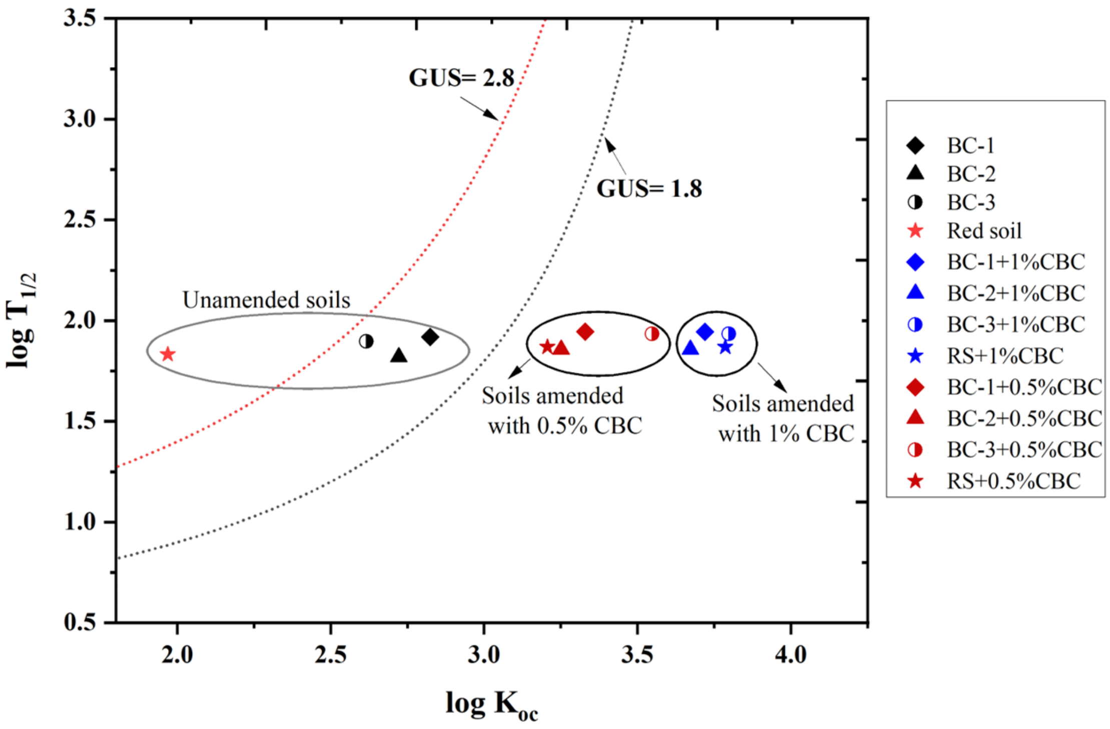

Fig. 8. 5 GUS values of Imidacloprid in various biochar amended and unamended soils

The observed half-life value was utilized for the calculation of Groundwater Ubiquity Score (GUS) to anticipate the potential of pesticides to leach into groundwater. According to the criteria, if the GUS value exceeds 2.8, the chemical is classified as a leacher; if it falls below 1.8, it is deemed a non-leacher; and if it ranges between 1.8 and 2.8, it is considered a potential leacher. The analysis of GUS values, as presented in Figure 8.5 and 8.6, sheds light on the leaching potential of Imidacloprid and Atrazine across various soil conditions. Notably, the highest GUS value recorded at 3.72 for Imidacloprid and 3.16 for Atrazine in red soil under unamended conditions signifies a pronounced leaching propensity within this specific soil type. Conversely, GUS values falling within the range of 1.8 and 2.8 for all other soils indicate the potential for Imidacloprid and Atrazine leaching, albeit to a lesser extent, as per the defined criteria.

An intriguing discovery unfolded when biochar was introduced into the soil matrix, shedding light on its potential benefits. Incorporated biochar led to a noticeable decrease in GUS values for both pesticides under examination. For instance, in soils treated with 0.5% CBC, the GUS values for Imidacloprid ranged from 0.87 to 1.48. However, with the addition of 1% CBC, this range decreased significantly to 0.39 to 0.60. A similar trend was observed for Atrazine, where the introduction of biochar led to a notable improvement in GUS values (as depicted in Figure

8.6). The GUS values for Atrazine in unamended soils ranged from 2.81 to 3.16. With the addition of 0.5% CBC, the GUS values decreased to a range of 1.44 to 2.36. Further reduction was observed with a 1% CBC amendment, resulting in GUS values ranging from 1.23 to 1.87. This observed phenomenon implies a substantial reduction in the mobility of both Imidacloprid and Atrazine within the soil samples under investigation. Consequently, the addition of biochar holds promise in mitigating the potential leaching of these pesticides, thereby enhancing environmental sustainability and minimizing the risks of groundwater contamination. This underscores the potential of biochar as a valuable tool in environmentally friendly agricultural practices.

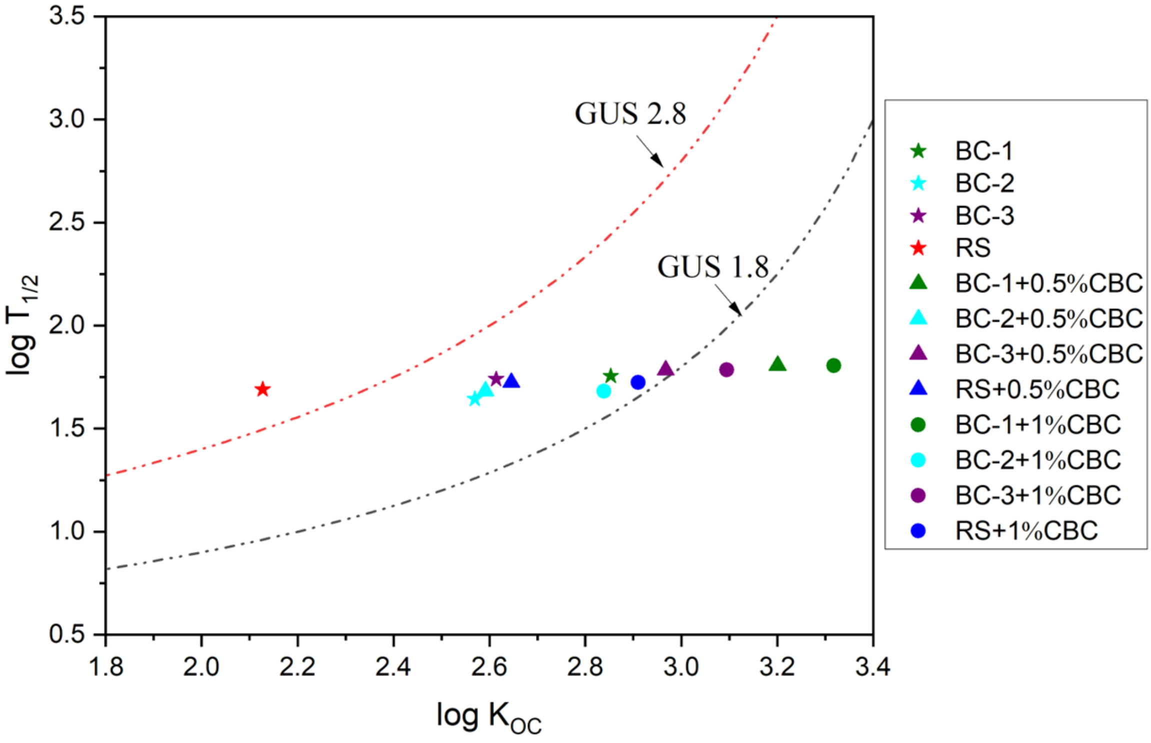

Fig. 8. 6 GUS values of Atrazine in various biochar amended and unamended soils

8.5 Soil Column Leaching Study of Pesticides on Biochar Amended Soils

In the soil column leaching study, both biochar-amended and unamended soils were analyzed to assess how Imidacloprid and Atrazine move through various soil compositions. The results of the study provided insights into the mobility of these pesticides and their potential to reach groundwater, which is a critical concern for environmental protection and water quality management.

The results depicted in Figure 8.7 revealed that Imidacloprid managed to permeate through all layers of the unamended soil. Additionally, its presence was detected in the leachate of BC-1 and red soil, indicating its ability to migrate through these soil types as well. This mobility suggests a significant potential for Imidacloprid to seep into groundwater reservoirs, posing a potential risk to water quality. The findings for Atrazine were similarly concerning. Atrazine was able to penetrate all segments of the soil column, moving through various soil types and compositions (Fig. 8.8). The pesticide was detected in the leachate of nearly all soil types tested, except for BC-2, where it still managed to reach the deepest layers of the soil profile. This result indicates that, like Imidacloprid, Atrazine is also highly mobile in the soil, and poses a substantial risk of leaching into groundwater reservoirs. The presence of these pesticides in deeper soil layers raises significant environmental concerns. Typically, these deeper sections lack the abundant microbial activity found nearer to the surface, which serves to degrade contaminants (Fierer et al., 2003; Hao et al., 2021). Consequently, the pesticides may persist for longer durations in these regions, potentially accumulating over time. Furthermore, their movement with rainwater or irrigation could facilitate their transportation towards groundwater sources, further exacerbating the risk of contamination. Such contamination could have far-reaching consequences, affecting ecosystems, human health, and agricultural productivity. Thus, these findings underscore the importance of implementing careful pesticide management practices to mitigate environmental risks and safeguard water resources.

The incorporation of biochar into the soil columns yielded promising results in the leaching study, effectively retained pesticides within the upper soil layers. Figure 8.7 illustrates Imidacloprid's retention primarily within the first two sections of the column across all soils, except for red soil, where it extended to the third section. Remarkably, Imidacloprid was not detected in the leachate samples. Similarly, Atrazine leaching studies yielded comparable outcomes, with herbicide molecules predominantly retained within the soil sections, and no detectable concentration in the leachate samples (Fig. 8.8). These findings suggest that biochar amendment possesses the capability to confine pesticides to the upper layer of the soil matrix, offering a sustainable solution for controlling pesticide leaching into groundwater.

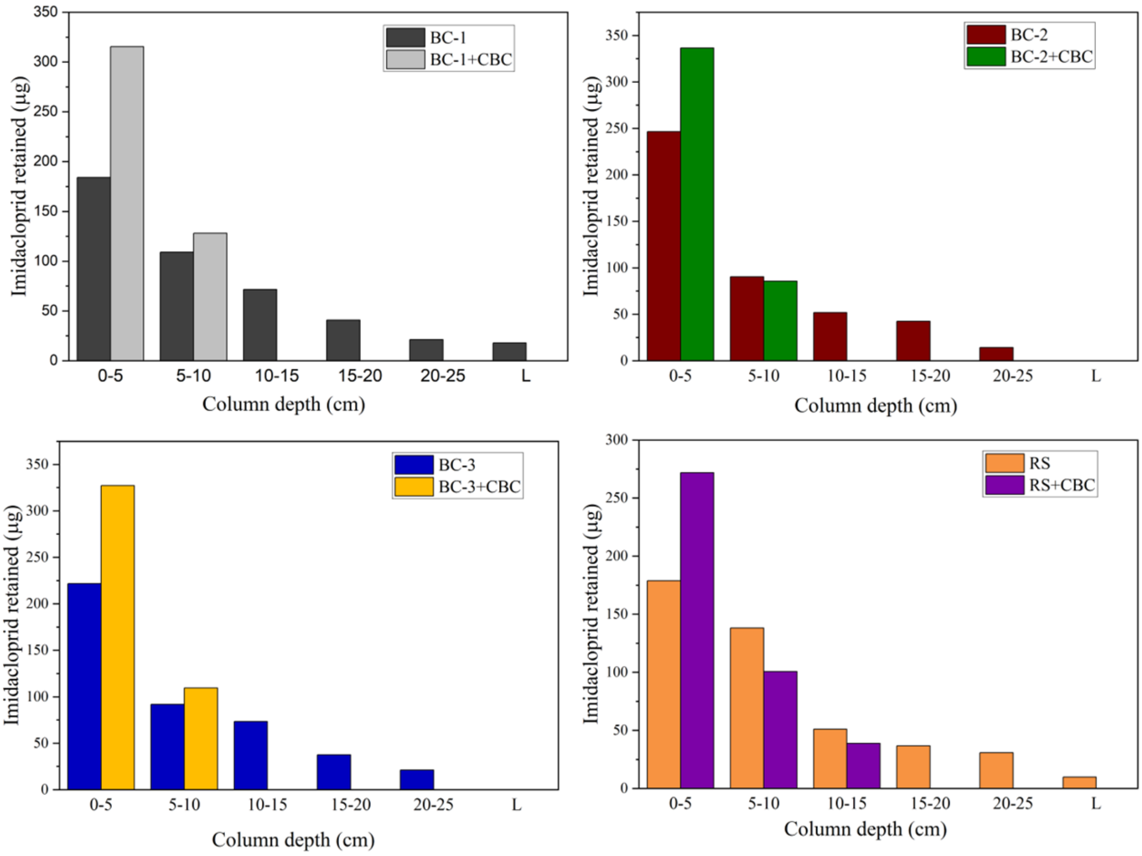

Fig. 8. 7 Soil column leaching of Imidacloprid in various amended and unamended soils

Biochar amendment improves pesticide retention in the soil layer primarily due to the unique surface area, pore size, and pore volume of biochar. Biochar's high surface area provides abundant active sites for pesticide adsorption, allowing it to trap more contaminants near the soil surface. Its porous structure, with a range of micro- and mesopores, enhances this retention by offering spaces that physically capture pesticide molecules. The pore volume and size distribution play a crucial role in accommodating both small and large pesticide molecules, effectively limiting their mobility. Additionally, biochar’s surface is rich in functional groups that interact with pesticides through various mechanisms such as hydrophobic interactions, hydrogen bonding, and π-π stacking. These interactions further strengthen the adsorption of pesticides onto biochar, preventing them from leaching into deeper soil layers and reducing the risk of groundwater contamination.

These findings suggest that biochar amendment can serve as an effective strategy to confine pesticides to the upper soil layers, which could be a sustainable solution for preventing pesticide leaching into groundwater.

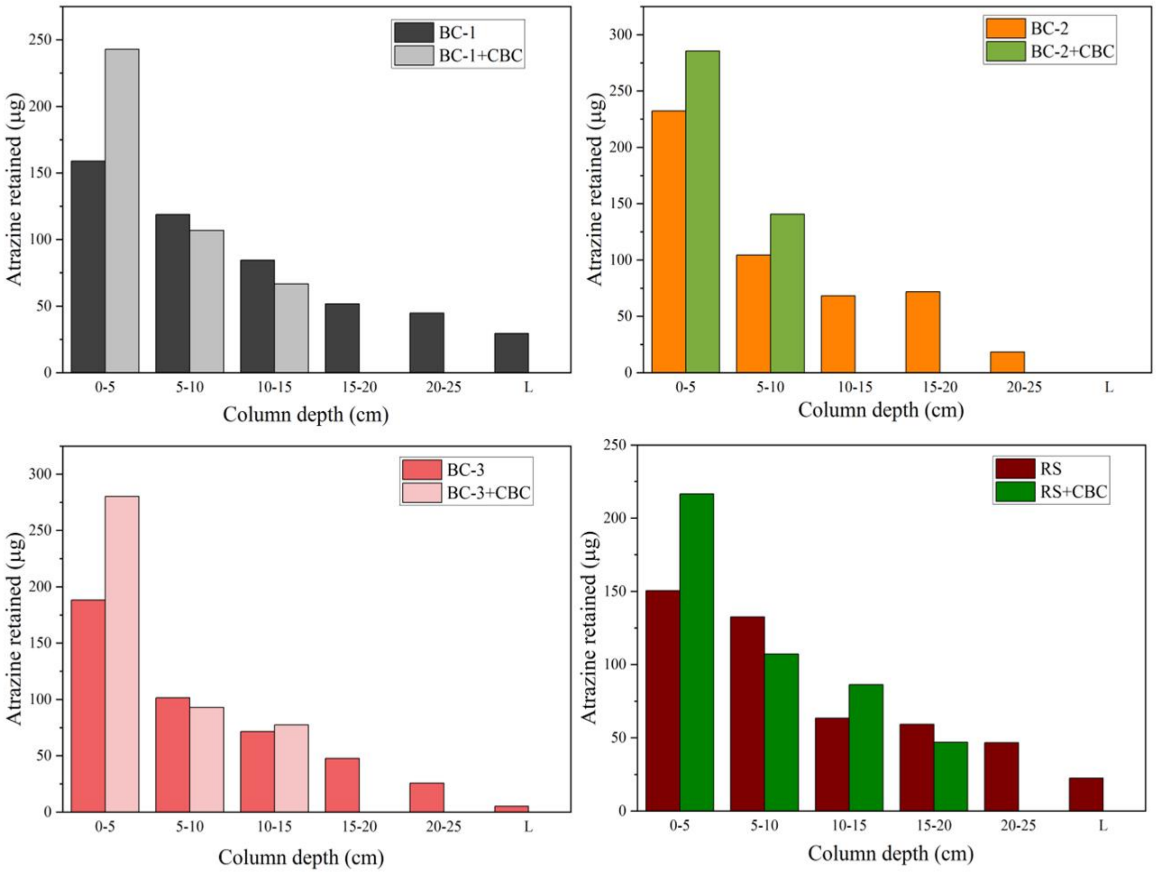

Fig. 8. 8 Soil column leaching of Atrazine in various amended and unamended soils

8.6 Summary

The summary of the findings is listed below:

- The introduction of 0.5% and 1% cotton stalk biochar (CBC) into the soil significantly enhanced the K_f values of Imidacloprid sorption across all the examined soils. In the case of BC-1 soil, the unamended K_f value was 0.71. However, with the incorporation of 0.5% CBC, it notably increased to 5.83. Furthermore, the addition of 1% CBC resulted in a substantial elevation of the K_f value to 25.02. A similar pattern was observed in the other soils as well. For BC-2 soil, the K_f value saw an increase from 2.31 to 8.16 and further to 34.89 after the addition of 0.5% and 1% CBC, respectively. In BC-3 soil, the K_f value experienced a rise from 1.14 to 9.82 and 28.29 with the corresponding additions of 0.5% and 1% CBC. Similarly, in the case of red soil, the K_f value escalated from 0.57 to 7.69 and 64.34 upon the introduction of 0.5% and 1% CBC.

The improved sorption capacity is a direct outcome of the augmented surface area and additional sorption sites resulting from the addition of CBC to the soil.

- Biochar amendment has also increased the sorption of Atrazine in soils, following the same trend as Imidacloprid. For example, the K_f for Atrazine in unamended BC-1 soil was 0.69. After addition of 0.5% CBC to the soil, the value increased to 7.86. Further it improved to 10.29 after addition of 1% CBC.
- The degradation kinetics of soils, both in amended and unamended conditions, conformed to first-order reactions. The addition of biochar to the soil had a slight effect on the half-life of Imidacloprid and Atrazine, with all cases showing a modest increase. In BC-1 soil, the half-life of Imidacloprid increased from 83 to 88 days, in BC-2 soil from 67 to 71 days, in BC-3 soil from 79 to 86 days, and in red soil from 70 to 73 days. The observed prolongation of pesticides half-life in biochar-amended soils can be attributed to the porous nature of biochar, which facilitates the adsorption of Imidacloprid, thereby limiting its availability to soil microorganisms. However, the relatively small quantity of biochar added may explain the marginal nature of these changes, highlighting the importance of dosage considerations in soil amendment practices.
- With the incorporation of biochar, GUS values notably declined, falling below the threshold of 1.8. Specifically, GUS values ranged from 0.87 to 1.48 in soils amended with 0.5% CBC. Furthermore, with the addition of 1% CBC, the range decreased to 0.39 to 0.60. The GUS values for Atrazine in unamended soils ranged from 2.81 to 3.16. These values were reduced to a range of 1.23 to 1.87 in soils amended with 1% CBC. This phenomenon suggests a significant reduction in the mobility of both pesticides within the investigated soils. Therefore, the addition of biochar demonstrates promise in mitigating the potential leaching of both Imidacloprid and Atrazine, thereby enhancing environmental sustainability and minimizing groundwater contamination risks.
- The soil column leaching study revealed that biochar amended soils can retain pesticides in the top layers of the soil matrix for both Imidacloprid and Atrazine.

Chapter 9

Conclusions and Recommendations

9.1 Introduction

Telangana, characterized by its agrarian nature, relies heavily on agricultural activities to drive its economy. Among the various crops cultivated in the region, cotton and paddy stand out as primary staples, positioning the state as one of the leading producers of cotton in India. However, the cultivation of these crops comes with challenges, particularly concerning pesticide usage. Cotton and paddy, being the predominant crops, account for approximately 70% of the total pesticide consumption in the country. The extensive use of pesticides poses environmental risks, particularly with respect to groundwater contamination. Understanding the behaviour of these chemicals in different soil types is crucial for mitigating such risks. Thus, this study delves into the behaviour of two commonly used pesticides, Imidacloprid and Atrazine, specifically in black cotton soils and red soils prevalent in the region. Sampling focused on areas predominantly cultivating cotton, with three samples of black cotton soil and one sample of red soil collected. Following OECD guidelines, laboratory experiments employing the batch equilibrium method were conducted to study the sorption of Imidacloprid and Atrazine in these soils. The experiments were carried out at varying temperatures (273 K, 300 K, and 313 K) to assess the influence of temperature on sorption behaviour. Additionally, experiments were conducted at different pH levels (3, 6, and 9) to evaluate the impact of pH on pesticide sorption. Furthermore, pesticide degradation studies were conducted to determine the half-life of Imidacloprid and Atrazine in the selected soils. The Groundwater Ubiquity Score (GUS), derived from sorption and half-life data, was utilized to gauge the leachability of these pesticides in the soils. Soil column leaching studies provided insights into the depth of pesticide penetration.

To explore potential mitigation strategies, experiments were repeated with the addition of 0.5% and 1% cotton stalk biochar (CBC) to assess its efficacy as a soil amendment. This aimed to enhance pesticide sorption capacity and reduce mobility within the soils. The findings of the study provide valuable insights into the behaviour of Imidacloprid and Atrazine in Telangana's soils and the efficacy of cotton stalk biochar as a potential soil amendment. The conclusions drawn from the present study are discussed in this chapter.

9.2 Conclusions

9.2.1 Major Conclusions

- The sorption capacity of both Imidacloprid and Atrazine was notably low in all three black cotton soils and the red soil. Clay content was identified as the primary factor influencing pesticide sorption, while soil organic matter showed a negative correlation with the sorption coefficient due to its limited availability in the soil.
- Imidacloprid exhibited a higher sorption capacity compared to Atrazine in all investigated soils. Moreover, temperature was found to significantly affect the sorption capacity for both Imidacloprid and Atrazine, with lower temperatures resulting in increased sorption.
- Imidacloprid's prolonged half-life compared to Atrazine indicates its greater persistence in all investigated soils. The calculated GUS value categorized both Atrazine and Imidacloprid as falling within the highly mobile to mobile category, highlighting the region’s vulnerability to groundwater contamination from pesticides.
- The study underscored the high susceptibility of groundwater in this specific area of the Telangana region to contamination, emphasizing the urgent need for proactive measures to prevent potential catastrophes.
- The incorporation of cotton stalk biochar into the soils emerged as a promising strategy to mitigate the leaching potential of both pesticides, offering a potential solution to reduce the environmental risks associated with pesticide use.

9.2.2 Minor Conclusions

- The sorption kinetic study showed that sorption equilibrium reached earlier in the case of Imidacloprid than Atrazine, and the Pseudo Second Order model best fit the kinetics data for both pesticides.
- The analysis showed that the Freundlich isotherm model was the best fit among the Langmuir and Temkin models. The BC-2 soil had the highest K_f value, with a strong positive correlation ($r>0.9$) between clay content and K_f, indicating that clay content had a significant influence on pesticide sorption. Despite having higher organic carbon

content (0.57%), the red soil exhibited lower pesticide affinity, likely due to the lower overall quantity of organic carbon.

- Both temperature and pH exert significant influences on pesticide sorption behaviour in the examined soils. As temperature rises, the sorption of Imidacloprid decreases, possibly due to increased solubility at higher temperatures. Additionally, lower pH levels create favourable conditions for sorption, as they facilitate the protonation of the solution, thereby increasing the cationic charge of the pesticide molecules.
- Sorption thermodynamics calculations revealed that ΔH° values ranged from -8 to -40 kJ/mol, suggesting that hydrogen bonding primary drives both Imidacloprid and Atrazine sorption.
- Imidacloprid exhibited more persistence in the investigated soils compared to Atrazine. The degradation rate of Atrazine was higher than that of Imidacloprid in all investigated soils.
- The GUS values for Imidacloprid ranged from 2.25 to 2.62 in black cotton soils, while in red soil, it was reported as 3.72. For Atrazine, GUS values ranged from 2.01 to 2.41 in black cotton soils, and in red soil, it was 3.16. GUS values falling between 1.8 and 2.8 in all black cotton soils suggest that both pesticides fall into the potentially mobile category. However, in red soil, where the values exceeded 2.8 for both pesticides, they are considered highly mobile.
- The results of the soil column leaching study corroborated the findings, as both Imidacloprid and Atrazine were detected in the leachate sample and migrated to the deeper sections of the column. The presence of pesticides in the deeper layers of the soil matrix could increase their persistence due to the absence of microorganisms, ultimately leading to groundwater contamination.
- The introduction of 0.5% and 1% cotton biochar (CBC) into the soil significantly enhanced the K_f values of Imidacloprid sorption across all the examined soils. The improved sorption capacity is a direct outcome of the augmented surface area and additional sorption sites resulting from the addition of cotton stalk biochar (CBC) to the soil.
- The addition of biochar to the soil had a slight effect on the half-life of Imidacloprid and Atrazine, with all cases showing a modest increase. The observed prolongation of pesticides half-life in biochar-amended soils can be attributed to the porous nature of biochar, which facilitates the adsorption of pesticides, thereby limiting their availability

to soil microorganisms. However, the relatively small quantity of biochar added may explain the marginal nature of these changes, highlighting the importance of dosage considerations in soil amendment practices.

- With the incorporation of biochar, GUS values notably declined, falling below the threshold of 1.8. Specifically, GUS values ranged from 0.87 to 1.48 in soils amended with 0.5% CBC. Furthermore, with the addition of 1% CBC, the range decreased to 0.39 to 0.60. A similar trend was observed for Atrazine, where the introduction of biochar led to a notable improvement in GUS values. This phenomenon suggests a significant reduction in the mobility of both the pesticides within the investigated soils. Therefore, the addition of biochar demonstrates promise in mitigating the potential leaching of both Imidacloprid and Atrazine, thereby enhancing environmental sustainability and minimizing the risks of groundwater contamination.
- The soil column leaching study revealed that biochar amended soil can retain pesticides, specifically both Imidacloprid and Atrazine, in the top layers of the soil matrix.

9.3 Limitations of the Study

- The studies were conducted under controlled laboratory conditions, which may not fully represent the complex and dynamic environment of soil in the field.
- Batch studies typically run for a limited time, usually hours to days, which may not capture long-term sorption desorption dynamics.
- The present studies typically focus on the parent compound of the pesticides, neglecting the potential effect of transformation products, which can also interact with soils and exhibit different sorption desorption behaviours.
- Soil column leaching experiments often involve disturbed columns, which may not accurately mimic the undisturbed soil structure and hydraulic properties found in the field. The disruption of soil structure during column preparation can affect water flow pathways, retention mechanisms, and ultimately, the leaching behaviour of pesticides.
- Extrapolating results from small-scale batch experiments to field-scale conditions can be challenging due to differences in scale, soil heterogeneity, and environmental factors.

9.4 Recommendation for Future Studies

- The present study focuses on only two of the widely used pesticides. The behaviour of other pesticides such as Acephate, Carbofuran, Chlorpyrifos, Monochrotophos, etc should also be explored for a better pesticide management plan.
- The current study was conducted on a laboratory scale. A real-time investigation study with a proper agricultural setup would give a better understanding.
- The application of biochar was limited to assessing the sorption, degradation, and leaching behaviour of pesticides in soils. However, a thorough study should also be conducted to evaluate the impact of biochar on crop yield in biochar-amended soils.
- An assessment of the current groundwater quality as well as surface water quality with respect to pesticides is necessary to investigate the current contamination situation.

List of Publications

Journals

1. Prasanta Majee, P Hari Prasad Reddy (2023) “Sorption desorption behaviour of Imidacloprid in agricultural soils of Deccan plateau of Southern India: kinetics and thermodynamic analysis”, *International Journal of Environmental Analytical Chemistry*, DOI: 10.1080/03067319.2023.2206964 (SCI)

2. Prasanta Majee, P Hari Prasad Reddy (2023) “Sorption behaviour of Atrazine on agricultural soils of different characteristics: equilibrium and kinetics studies”. *Clean Technology and Environmental Policy*, 25, 3407–3417. https://doi.org/10.1007/s10098-023-02600-5 (SCIE)

3. Prasanta Majee, Sudheekar Reddy, Lava Kumar Uppala, P Hari Prasad Reddy (2024) “Physicochemical and Energy Characteristics of Biochar and Hydrochar derived from Cotton Stalks: A Comparative Study”, *BioEnergy Research*. (Under Review)

4. Prasanta Majee, Shubham Giri, P Hari Prasad Reddy (2024) “Efficacy of Cotton Stalk Biochar on Sorption Behaviour and Leaching Potential of Imidacloprid in Agricultural Soils: A Comprehensive Study”, *Journal of Environmental Science and Health, Part B*. (Under Review)

5. Prasanta Majee, Shubham Giri, P Hari Prasad Reddy (2024), “Factors Influencing the Sorption Behavior of Pesticides in Soil: A Comprehensive Review”, *Journal of Environmental Chemical Engineering* (Under Review)

Conference

- Prasanta Majee, Shubham Giri, P Hari Prasad Reddy (2023) “Influence of cotton stalk biochar amendment on sorption behaviour of Imidacloprid in red soil”, *5th Euro-Mediterranean Conference for Environmental Integration*, 2nd -5th October 2023, Rende, Italy (SCOPUS)

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