AN INTEGRATED HERBICIDE REMEDIATION SYSTEM UTILIZING MODIFIED BIOCHAR FROM PALM KERNEL SHELLS AND WATER HYACINTH (*EICHHORNIA CRASSIPES*)

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by

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LIST OF SYMBOLS

%	Percentage
<	Less than
>	Greater than
±	Plus-minus
◦	Degree
°C	Degree Celsius
µm	Micrometre
1/n	The term heterogeneity factor
1/T	Inverse of temperature
A_T	Constant for Temkin isotherm
B_T	Heat of adsorption
C_0	Initial adsorbate concentration
C_e	Concentration of adsorbate at equilibrium
C_{in}	Initial concentration of herbicide before treatment
cm	Centimetre
C_{out}	Final concentration of herbicide after treatment
C_t	Concentration of adsorbate at time, t
FFW	Final fresh weight
g	Gram
h	Hour
IFW	Initial fresh weight
K	Kelvin
k_1	Adsorption rate constant for pseudo-first order kinetic model

k_2	Adsorption rate constant for pseudo-second order kinetic model
K_F	Adsorption or distribution coefficient for Freundlich isotherm
KJ	Kilojoules
K_L	Rate of adsorption for Langmuir isotherm
L	liter
$\ln K_L$	Logarithm of the equilibrium constant
M	Amount of adsorbent
mg	Milligrams
mg/L	milligrams per liter
mL	Milliliters
n	Total number of experiments required/data point
nm	Nanometre
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium
q_{max}	Adsorption capacity for Langmuir isotherm
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t
R	Represents the gas constant
R°C	stands for room temperature
R^2	Coefficient of determination
RGR	relative growth
R_L	Correlation coefficient
S_{BET}	BET surface area the total surface area of a material per unit of mass
t	Time
V	Solution volume
W1	Weight of the air-dried sample

W2	Weight of the sample after heating to 105°C
W3	Weight after heating to 950°C
W4	Weight of the residue after heating to 750°C
Wt%	Percentage weight
α	Alpha
β	Beta
ΔG°	Changes in standard free energy
ΔH°	Changes in standard enthalpy
ΔS°	Changes in standard entropy
Θ	Theta
λ	Wavelength
μL	Microliter

LIST OF ABBREVIATIONS

2,4-D	2,4-dichlorophenoxyacetic acid
AOP	Advanced oxidation process
ASTM	American Society for Testing and Materials
ATP	Adenosine triphosphate
BET	Brunauer-Emmett-Teller
CABI	Agriculture and Bioscience International
CW	Constructed wetland
E	Removal efficiency
ECs	Environmentally concerning compounds
ECs	Concerning compounds
EDA	Electron-donor acceptor
EDX	Electron-dispersive X-ray
Eq	Equation
EU	European Union
FTIR	Fourier Transform Infrared
FT-MIR	Fourier transform mid-infrared
FT-NIR	Pharmaceuticals. Fourier transform near-infrared
FWT	Floating wetland treatment
GDP	Gross domestic products
H_2O_2	Hydrogen peroxide
IBAMA	Brazilian Institute of the Environment
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide

MCPA	Malaysian CropLife and Public Health Association
MOA	Modes of action
NADPH	Nicotinamide adenine dinucleotide phosphate
PKS	Palm kernel shell
PKS-B	Biochar palm kernel shells activated solely by KOH
PKS-BM	Biochar modified with melamine derived from palm kernel shells
POPs	Persistent Organic Pollutants
PPKS	Powder palm kernel shells
PSII	Photosystem II
PZC	point of zero charge
rpm	Rotation per minute
SEM	Scanning electron microscopy
SOD	enzyme superoxide dismutase
TCE	Trichloroethylene
TEM	Transmission electron microscopy
TEs	Trace elements
TFCWs	Through-Flow Constructed Wetlands
TNT	Trinitrotoluene
TOPs	Typical organic pollutants
WFD	Water Framework Directive
WH	Water hyacinth
WHO	World Health Organization
XRD	X-ray diffraction

LIST OF APPENDICES

APPENDIX A	SOME INSTRUMENTATION USING IN LABORATORY EXPERIMENTS: (A) UV-VISIBLE SPECTROPHOTOMETER, (B) CONTROLLED SHAKER, (C) PH METER, (D) ANALYZER (NANO-ZS90, MALVERN, UK), (E) ANALYZER FOR X-RAY DIFFRACTOMETER, (F) SCANNING ELECTRON MICROSCOPE (SEM), and (G) TRANSMISSION ELECTRON MICROSCOPY (TEM).
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SISTEM PEMULIHAN RACUN RUMPAI BERSEPADU MENGGUNAKAN BIOARANG TERUBAH SUAI DARIPADA TEMPURUNG KELAPA SAWIT DAN KELADI BUNTING (*EICHHORNIA CRASSIPES*)

ABSTRAK

Pencemaran racun herba dalam persekitaran akuatik menimbulkan risiko yang ketara kepada alam sekitar dan kesihatan awam disebabkan oleh ketahanan, mobiliti, dan ketoksikan bahan kimia ini. Kaedah pemulihan tradisional selalunya kurang cekap, kurang mampan, ataupun kurang berkesan dari segi kos, menonjolkan perlunya pendekatan inovatif. Kajian ini berfokuskan kepada sintesis dan pencirian biochar yang diubahsuai dengan nitrogen yang dihasilkan daripada tempurung isirung sawit (PKS), menerokai prestasi penjerapannya untuk racun herba dan menilai peranannya dalam fitoremediasi yang dibantu oleh biochar. Bagi mencapai hal ini, satu sistem bersepadu yang menggunakan biochar yang diubah suai dengan melamin, digabung dengan tumbuhan akuatik *Eichhornia crassipes* (keladi bunting), telah dibangunkan untuk pemulihan tiga racun herba yang biasa digunakan: diuron, paraquat, dan 2,4-asid diklorofenoksi asetik (2,4-D) dalam larutan berair. Biochar yang diubah suai (PKS-BM) telah melalui pencirian menyeluruh, termasuklah analisis proksimat dan unsur, pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), analisis Brunauer-Emmett-Teller (BET), penilaian pengagihan saiz zarah, mikroskopi elektron imbasan (SEM), dan mikroskopi elektron transmisi (TEM). Analisis-analisis ini mengesahkan sifat penjerapan yang dipertingkatkan, dengan luas permukaan BET yang tinggi, struktur mesopori, dan kandungan nitrogen yang ketara disebabkan oleh doping melamin, yang mana prestasinya lebih baik berbanding serbuk tempurung isirung sawit (PPKS) dan biochar daripada tempurung isirung sawit yang diaktifkan hanya dengan KOH (PKS-B). Eksperimen penjerapan menunjukkan kecekapan penyingkiran yang tinggi untuk diuron, paraquat, dan 2,4-D, dengan kapasiti penjerapan maksimum masing-masing 675 mg/g, 454.55 mg/g, dan 990.10 mg/g. Kinetik penjerapan adalah berdasarkan model pseudo-urutan kedua dan Elovich, manakala model isoterm Langmuir menunjukkan penjerapan lapisan tunggal yang menggalakkan. Analisis termodinamik menunjukkan proses endotermik untuk penjerapan diuron dan paraquat, manakala penjerapan 2,4-D adalah bersifat eksotermik. Integrasi PKS-BM dengan keladi bunting dalam sistem fitoremediasi secara signifikan meningkatkan kadar penyingkiran racun herba ini, mencapai sehingga 99.7%-82.8% untuk paraquat, 99.4%-94.2% untuk diuron, dan 98.7%-90.3% untuk 2,4-D, pada kepekatan yang berbeza, melangkaui kecekapan hanya biochar atau fitoremediasi. Tambahan lagi, kehadiran biochar meningkatkan kesihatan tumbuhan dengan mengurangkan ketoksikan racun herba. Kajian ini menonjolkan kebaharuan menggabungkan biochar yang diubahsuai dengan nitrogen dengan fitoremediasi bagi membangunkan teknologi pemulihan air yang lebih berkesan dan mampan, menawarkan satu penyelesaian yang berpotensi bagi memerangi pencemaran racun herba dalam persekitaran akuatik.

AN INTEGRATED HERBICIDE REMEDIATION SYSTEM UTILIZING MODIFIED BIOCHAR FROM PALM KERNEL SHELLS AND WATER HYACINTH (*EICHHORNIA CRASSIPES*)

ABSTRACT

Herbicide contamination in aquatic environments poses significant environmental and public health risks due to the persistence, mobility, and toxicity of these chemicals. Traditional remediation methods often lack efficiency, sustainability, or cost-effectiveness, highlighting the need for innovative approaches. This study focuses on the synthesis and characterization of nitrogen-modified biochar derived from palm kernel shells (PKS), exploring its adsorption performance for herbicides and assessing its role in biochar-assisted phytoremediation.To achieve this, an integrated system utilizing biochar modified with melamine, in combination with the wetland plant *Eichhornia crassipes* (water hyacinth), was developed for the remediation of three commonly used herbicides: diuron, paraquat, and 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solutions. The modified biochar (PKS-BM) underwent comprehensive characterization, including proximate and elemental analysis, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) analysis, particle size distribution, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). These analyses confirmed enhanced adsorption properties, with a high BET surface area, a mesoporous structure, and significant nitrogen content due to melamine doping, outperforming powdered palm kernel shells (PPKS) and biochar activated solely by KOH (PKS-B). Adsorption experiments demonstrated high removal efficiencies for diuron, paraquat, and 2,4-D, with maximum adsorption capacities of 675 mg/g, 454.55

mg/g, and 990.10 mg/g, respectively. The adsorption kinetics followed the pseudo-second-order and Elovich models, while the Langmuir isotherm model indicated favorable monolayer adsorption. Thermodynamic analysis revealed an endothermic process for diuron and paraquat adsorption, whereas 2,4-D adsorption was exothermic. The integration of PKS-BM with water hyacinth in a phytoremediation system significantly improved herbicide removal rates, achieving 99.7%–82.8% for paraquat, 99.4%–94.2% for diuron, and 98.7%–90.3% for 2,4-D at varying concentrations, surpassing the efficiency of biochar or phytoremediation alone. Furthermore, biochar presence enhanced plant health by mitigating herbicide toxicity. This study highlights the novelty of combining nitrogen-modified biochar with phytoremediation to develop a more effective and sustainable water remediation technology, offering a promising solution to combat herbicide pollution in aquatic environments.

CHAPTER 1
INTRODUCTION

1.1 Background of the Study

The need to manage the regular release of hazardous chemicals into the environment, such as herbicides used in agriculture, is becoming increasingly pressing. There are several ways to remove pesticides from water, but adsorption on mesoporous biochar derived from palm kernel shells with doped melamine (as a nitrogen source) serves as a cost-effective alternative to commercial activated carbon for herbicide pollution treatment in water, laying the groundwork for a swift and efficient cleanup process. Additionally, when combined with phytoremediation in one system to alleviate stress on plants used in phytoremediation and reduce toxicity at high concentrations of herbicides, it enhances removal efficiency. This research delineates a robust methodology for the elimination of emerging pollutants, providing researchers with a platform to make pioneering advancements in this scientific field. The chapter presents the problem statement, research objectives, scope of the study, significance of the research, and organisational structure of the thesis.

1.1.1 Water Pollution

Using pesticides or herbicides in agriculture is a standard practice to boost yield and ensure an ample supply of high-quality, reasonably priced food for the expanding population. Like virtually all chemicals, these herbicides are mostly synthesized and may pose hazards to the environment and public health (Gupta, 2018).

The use of pesticides in agricultural systems is unavoidable. Every day, new pesticides with improved qualities for targeted application and reduced side effects are released. However, a significant portion of these chemicals does not reach the intended pests.

Up to 95% of herbicides and over 98% of insecticides may be lost due to environmental factors such as wind, water runoff, and atmospheric weathering processes (Rad et al., 2022). As a result, pesticides often contaminate soil, water, and air, leading to environmental pollution. Pesticides can move through the environment via various pathways, including surface runoff, spray drift, leaching, groundwater inflow, and subsurface drainage systems (Cosgrove et al., 2022; Ravier et al., 2005; Cosgrove et al., 2019; Gzyl et al., 2014). These transport mechanisms contribute to the contamination of lakes, oceans, and ground and surface waters, as shown in Figure 1.1. Additionally, interactions between these chemicals and environmental components may lead to the formation of harmful intermediates, exacerbating ecological risks. Uncontrolled pesticide use in agriculture can influence product quality and affect physiological processes in the human body, potentially leading to health issues such as toxicity, carcinogenicity, and mutagenicity (Abdollahdokht et al., 2021). Consequently, the pervasive use and uncontrolled dispersal of pesticides pose significant environmental and health risks by contaminating water resources and exposing humans to harmful chemicals.

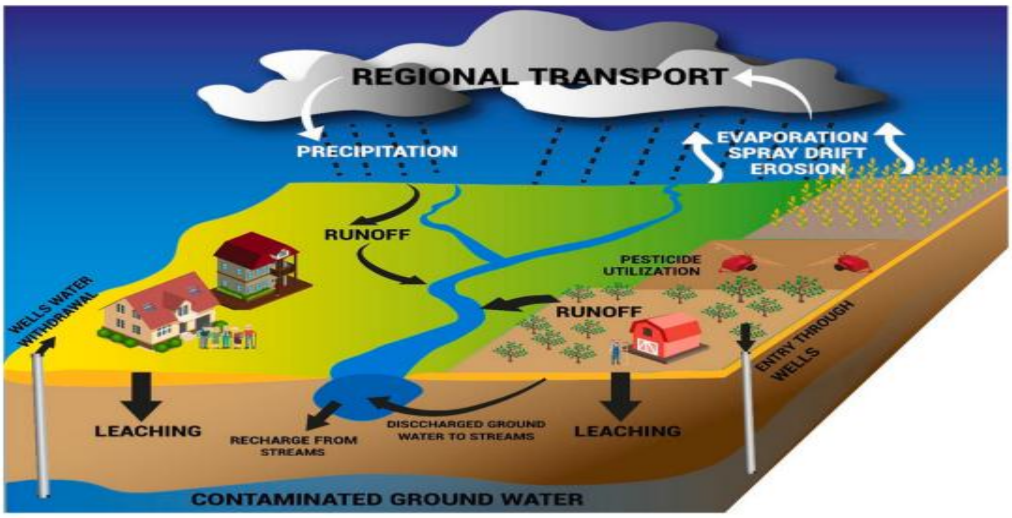

Figure 1.1 Pathways for herbicides and pesticides to enter surface and ground water. Reprinted from (Lunardi et al., 2022).

1.1.2 Herbicides in the Agriculture Sector

The global population is projected to reach 9–10 billion by 2050 (Rad et al., 2022), leading to an increased demand for additional food resources. The survival of the world hinges on sustainable agriculture, especially in the face of our rapidly growing population. Expanding agriculture into the remaining regions of wild vegetation is not conducive to maintaining the planet's biodiversity. It is crucial to sustain or even enhance crop yields on existing farmland, whether on larger farms or smallholder farms. Weed control often poses a significant challenge; mechanical control is either prohibitively expensive when done manually or frequently problematic with machinery. Biological control of weeds typically offers limited benefits (Abbas et al., 2018). As a result, the reliance on chemical herbicides has become widespread. The loss of grains, fruits, and vegetables to pests and illnesses would be as high as 78%, 54%, and 32%, respectively, if herbicides or pesticides were not used (Zhang et al., 2011). Because of this and the fact that pesticides are widely used in both agricultural and urban settings, they can travel to different surface water resources through some channels, such as surface runoff. Using herbicides in the wrong way is n't the sole concern; the contamination of groundwater due to regular pesticide application is now acknowledged as a broader issue requiring urgent attention. Beyond the risks to health and the environment, the leakage of pesticides from fields and their contamination of unintended areas like surface water and groundwater pose significant challenges (Lunardi et al., 2022). Addressing these challenges requires stricter regulations, the promotion of sustainable agricultural practices, and greater public awareness of the long-term consequences of pesticide misuse.

In 2005, the Malaysian CropLife and Public Health Association (MCPA) defined a pesticide as a biological or chemical product designed and applied to control agricultural pests, including insects, diseases, weeds, and other organisms such as nematodes, which can severely impact the quantity and quality of crops harvested for food, grain, and fiber. These herbicides are frequently applied in agriculture to increase the yield of targeted crops. They are commonly used in the management of landscape turf, such as lawns and golf courses. Herbicides can be classified as either selective or non-selective. The former is designed to eradicate particular plant species, such as grass-growing broadleaf weeds. The latter are frequently employed to eradicate all vegetation within the application area, which includes railway embankments and building sites (Tsai, 2020). Since the late 1960s, the primary and virtually only method for controlling weeds worldwide has been the application of herbicides. However, the constant application of the same herbicide or herbicides with a similar mode of action (MOA) has unavoidably caused resistant weed populations to arise (Shaner, 2014). Additionally, the pesticide industry has slowed down the development of novel herbicidal compounds, especially those with new MOAs, as a result of the widespread use of transgenic crops that are tolerant to herbicides over the past 20 years. The usage of a limited number of herbicides due to their rapid efficacy and ease of application has encouraged the emergence of resistant weeds, particularly in the United States, Australia, and South America. The issue also raises concern within the EU, as the widespread cultivation of conventionally bred herbicide-tolerant crops has resulted in the spread of instances of herbicide resistance. (Perotti et al., 2020). As a result, herbicide-resistant weeds are a global challenge, requiring integrated weed management strategies combining cultural, mechanical, biological, and chemical approaches for sustainable agriculture.

1.1.3 Herbicides

Herbicides are used to control unwanted plants in commercial woods, lawns, and controlled landscapes. Herbicides are occasionally sprayed directly onto surface water to suppress aquatic weeds. Due to their toxicity, carcinogenicity, and mutagenicity, they may manifest as contaminants in water sources and pose a risk to human health. In developed countries, there are stringent laws governing the amount of herbicides in drinking water (Parra-Arroyo et al., 2022). Therefore, continuous monitoring and advanced treatment are crucial to ensure compliance and protect public health from herbicide contamination.

Paraquat (1,1-dimethyl-4,4-bipyridyl dichloride), also known as methyl viologen, is synthesized in the form of a dichloride salt from pyridine. Paraquat is the most widely used synthetic herbicide globally due to its high solubility, cost-effectiveness, efficiency, and non-selective contact nature for weed management in crop fields (Hassaan and El Nemr, 2020). However, paraquat has emerged as a recognised source of contamination to water resources, posing risks to the ecosystem and environment at large due to leaching or runoff from agricultural areas, deposition from aerial applications, and careless discharge of industrial wastewater (Yang et al., 2023). The Ontario Ministry of Environment fixed the maximum level of paraquat in drinking water as 10 µg/L (Rajaram and Neelakantan, 2023). Hence, it is crucial to implement effective measures to regulate the use and discharge of paraquat.

Diuron is a commonly used phenyl urea herbicide, utilized to control annual weeds and broad-leaved plants. The herbicide acts by inhibiting the process of photosynthesis, which keeps the weeds under control. Diuron is also known by the names Direx and Karmex. Its chemical name is 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Rubio-Bellido et al., 2018). It is among the many agrochemicals currently in use and is extensively utilized as a herbicide for both pre-and post-emergence purposes. Its primary purpose is to effectively manage broad-leaved weeds in various agricultural environments, such as cotton fields, wheat fields, olive tree orchards, sugar cane plantations, and even urban areas (Tantarawongsa and Ketrot, 2020). As a result, diuron is increasingly emerging as a contaminant responsible for declining water quality. Diuron is often detected at concentrations exceeding the maximum allowable concentration of 1.8 μg/L set by the EU Water Framework Directive (Moisset et al., 2015). Therefore, the use and persistence of diuron raise concerns about its environmental and health impacts, requiring stricter regulations and alternative weed management

2,4-dichlorophenoxyacetic acid (2,4-D) is frequently used in the field of agriculture. It is applied to plantation crops such as sugar cane, rubber, oil palm, and cocoa to suppress a variety of broadleaf weeds. Due to its outstanding selectivity and inexpensive cost, 2,4-D is commonly chosen. It has been classified as moderately hazardous, with a maximum permitted content in drinking water of 0.1 mg/L (Orooji et al., 2022). However, 2,4-D is a contaminant that degrades slowly in the biodegradable state. The half-life of 2,4-D in water ranges from 15 to 300 days, depending on environmental parameters. As a result, it has been regularly found in water bodies throughout the world. Due to their toxicity and the products of their breakdown, herbicides pose a risk to public health by contaminating the environment (Islam et al., 2018). Because of its persistence and toxicity, 2,4-D presents environmental and health risks, necessitating stricter regulations and the development of sustainable alternatives.

1.1.4 Methods of Herbicide Removal

Continuously, the human population is rapidly growing and urbanizing. This can be a problem in securing water resources, as the habit of disposing of polluted pesticide-contaminated wastewater will progressively become more challenging (Sturve et al., 2016). Using the sub-drainages, the herbicide's contaminated wastewater is transported from farms or household gardens into the centralized stormwater drainages and runs down into streams and lakes/ponds. Advanced technologies are required to assist in the monitoring and lowering of emerging contaminants such as herbicide-contaminated wastewater (Foo and Hameed, 2010). Current herbicide removal methods include advanced oxidation, membrane filtration, and chemical precipitation. However, these techniques are often costly, complex, and ineffective against diverse chemical contaminants (Derylo-Marczewska et al., 2017; Sellaoui et al., 2023). Adsorption is one of the most often used techniques due to its large-scale application, efficiency, and capacity (Valdés-Rodríguez et al., 2022; Zhen et al., 2022). Biochar, sometimes known as activated carbon, is the most widely utilized adsorbent in adsorption procedures. The aggregation of solutes in solution onto the adsorbent surface is known as adsorption. There could be a physical or chemical interaction between the adsorbed species and the surface. Intermolecular attraction produces weak forces known as Van Der Waals forces that hold molecules to the carbon surface during the physical adsorption process. Thus, there is no chemical change in the carbon or the adsorbate. However, in a process called chemisorption, molecules interact chemically with the surface of carbon (or an impregnate on it) and are bound together by far more powerful chemical bonds. Additionally, floating wetlands, an entirely novel kind of technology called artificial floating islands, ecological floating beds, or floating wetland treatment (FWT) (Prajapati et al., 2017), are becoming more and more renowned globally. FWTs are an economical and environmentally beneficial way to clean up tainted wastewater (Samal et al., 2019). They consist of a floatable structure that contains the growing medium to allow plants to grow only on the water's surface. Emerging contaminants are removed by the plants' dense root systems that dangle into the water column (Mohd Nizam et al., 2020).

1.1.5 Modified Biochar

A variety of adsorbents can be modified into porous materials to remove emerging contaminants from water (Dai et al., 2019). One of these porous materials is biochar or activated carbon, which is produced from biomass wastes such as banana peels (Viena and Nizar, 2019) and durian peels (Musthapa et al., 2023). Further, the PKS as biomass waste is widely accessible in huge amounts throughout Southeast Asia, and its disposal has become a major environmental concern. Therefore, the conversion of these wastes into porous biochar for wastewater treatment is a feasible approach for environmental sustainability and economy. However, the production of porous activated carbon or biochar from waste biomass is often costly and complex. Moreover, standard biochar typically lacks the necessary surface functionality to effectively adsorb herbicides. To address this, biochar modification, particularly nitrogen doping, enhances adsorption capacity by introducing functional groups that increase pollutant binding sites. Recently, N-doped methods have gained attention for improving the surface chemistry and functional groups of activated carbon or biochar. Researchers have employed the following techniques: (1) combining activated carbon with ammonia (Liu et al., 2020), (2) direct carbonization of N-rich raw materials (Chang et al., 2018), or (3) co-carbonization of activated carbon precursors with N-rich raw materials (Wan et al., 2020). The presence of nitrogen-rich compositions in activated carbon or biochar enhances the competitive adsorption of emerging pollutants from water. Furthermore, nitrogen doping may promote the formation of π-electron-enriched sites on the surface of porous carbon, further increasing contaminant adsorption. It has been reported that nitrogen-rich activated carbon enhances the adsorption of emerging pollutants (Wang et al., 2017). Melamine, a prevalent organic micropollutant, is frequently used in industrial manufacturing for melamine formaldehyde resin, coatings, adhesives, and plastics (Dorieh et al., 2022). In 2017, WHO classified melamine as a 2B carcinogen; hence, safe disposal of melamine is crucial. Melamine, a triazine N-containing heterocyclic organic molecule, has a high nitrogen content and a low carbon-to-nitrogen ratio, making it a potential nitrogen source for the development of porous biochar enriched with functional groups. High-temperature pyrolysis can result in ring breaking and polycondensation of melamine, forming a quaternary nitrogen structure and assisting in fixing nitrogen in biochar derived from PKS, along with the development of functional surface groups (Yaumi et al., 2018). Consequently, the biochar produced through this method exhibits enhanced nitrogen retention and functional group development, making it more effective for applications such as water remediation.

1.1.6 Wetland Plants

Phytoremediation, also known as phytocorrection when applied by wetland plants, involves a range of methods and processes centered around harnessing the power of plant species and their associated microorganisms (Yadav et al., 2022). These techniques aim to eliminate, absorb, trap, or alter contaminants in soil or water (Oyuela Leguizamo et al., 2017). However, phytoremediation alone is often insufficient for complete pollutant removal due to its relatively slow rate, limited applicability to certain contaminants, and dependency on plant growth conditions (Rezania et al., 2015). Thus, complementary or enhanced remediation strategies are frequently required to achieve more effective decontamination. The effectiveness of phytoremediation hinges largely on the photosynthetic activity and growth rate of plants. Various aquatic macrophytes, including water hyacinth (Eichhornia sp.), duckweeds (Lemna sp., Spirodella sp.), small water fern (Azolla sp.), and water lettuce (Pistia sp.), have been employed to remove emerging pollutants from wastewater (Gupta et al., 2012; Okunowo and Ogunkanmi, 2010; Rai, 2008; Suhag et al., 2011). Water hyacinth, recognized as the globe's most invasive aquatic plant, exhibits rapid proliferation, offering promising potential for eliminating a significant portion of emerging pollutants. Among its seven species, the common water hyacinth (*Eichhornia crassipes*) stands out, belonging to the perennial free-floating aquatic plants in the Pontederiaceae family (Saha et al., 2017). According to the particular reaction that occurs during the removal of emerging pollutants by wetland plants, the role of wetland plants in pollutants removal can be divided into two categories: (1) direct roles, including plant uptake, translocation, and degradation, and (2) indirect roles including promotion of microbial and enzymatic activities through the secretion of exudates, and radial oxygen loss, the production of humic acids that increase adsorption sites, all of which enhance pollutants removal efficiency (Hu et al., 2021). Thus, while phytoremediation utilizes plants to clean polluted environments and offers a sustainable, nature-based solution for pollution control, its limitations necessitate the integration of other remediation techniques to achieve comprehensive and effective environmental restoration

1.2 Problem Statement

Over the past few years, environmental pollution has become a critical global concern due to the increasing presence of various contaminants in aquatic ecosystems (Ebele et al., 2017). Among these contaminants, herbicides represent a particularly urgent threat, with studies indicating that millions of tons of herbicides are applied worldwide annually, leading to significant contamination of water bodies (Tang et al., 2021). The persistence of herbicides in the environment has been linked to severe ecological and health risks, including carcinogenicity, endocrine disruption, and bioaccumulation in food chains. Despite regulatory measures, alarming levels of herbicides continue to be detected in surface and groundwater, posing a significant challenge to public health and environmental sustainability (Foong et al., 2022). The necessity to remove herbicides from water stems from their toxicological profile. Paraquat, for instance, is associated with oxidative stress-induced toxicity, leading to severe damage to vital organs such as the lungs, brain, liver, and kidneys. It has also been implicated in Parkinson's disease, with numerous fatalities reported due to accidental or intentional poisoning (Singh et al., 2021; Zheng et al., 2022). Diuron, classified by the Environmental Protection Agency as a probable human carcinogen, has been linked to bladder, kidney, and mammary gland cancer in animal studies (Cardona and Rudel, 2020). Similarly, 2,4-D has been shown to disrupt endocrine functions, induce reproductive abnormalities, and exhibit mutagenic properties (Rocha et al., 2023). Given these dangers, sustainable agricultural policies must prioritize the effective removal of herbicides from water systems to align with the United Nations Sustainable Development Goals (SDG 3: Good Health and Well-being, and SDG 6: Clean Water and Sanitation) (Foong et al., 2022; Koul et al., 2022).

Various methods have been employed for herbicide removal, including electrochemical processes, ozonation, coagulation, flocculation, membrane filtration, and adsorption (Sieliechi and Thue, 2015). However, most of these techniques suffer from drawbacks such as high costs, complexity, and unsuitability for large-scale applications. Among these methods, adsorption has been recognized as one of the most effective due to its cost-effectiveness, ease of operation, and ability to remove pollutants at different concentrations. Nonetheless, traditional adsorbents, such as commercial activated carbon, exhibit limitations in adsorption efficiency due to factors like limited surface area, pore size distribution constraints, and reduced selectivity for specific contaminants (Essandoh et al., 2017; Nguyen et al., 2023). Additionally, their performance can be hindered by slow adsorption kinetics, susceptibility to fouling, and difficulties in regeneration, all of which impact their long-term usability, cost-effectiveness, and scalability, particularly when dealing with high concentrations of herbicides (Hasanuzzaman et al., 2020). Phytoremediation has also been explored for herbicide removal, yet its effectiveness is often compromised by the very nature of herbicides, which are designed to be toxic to plants. Previous studies have investigated various wetland plants, such as *duckweed and Azolla*, but their limited biomass production and slower pollutant uptake rates hinder large-scale applications (Chander et al., 2018; De et al., 2016; Pattappan et al., 2023). Therefore, an innovative, integrated approach is required to enhance the removal efficiency and scalability of herbicide remediation strategies. This study proposes a novel hybrid system integrating nitrogen-doped biochar derived from palm kernel shells with the wetland plant water hyacinth (*Eichhornia crassipes*) for enhanced herbicide remediation. Unlike traditional biochar or commercial activated carbon, nitrogen-doped biochar exhibits superior physicochemical properties, including enhanced surface area, higher adsorption capacity, and improved chemical reactivity for removing herbicides (Yahayu et al., 2018). The nitrogen doping process increases the number of functional groups on the biochar surface, thereby improving its affinity for herbicide molecules and enhancing its overall removal efficiency. Water hyacinth, compared to other wetland plants such as *duckweed and Azolla*, presents distinct advantages for phytoremediation. It is characterized by its prolific growth, high biomass yield, rapid nutrient uptake, and remarkable ability to accumulate and degrade pollutants. Moreover, its widespread occurrence and status as an invasive species make it an ideal candidate for remediation purposes, transforming an environmental nuisance into a valuable resource (Ayanda et al., 2020). Large infestations of water hyacinth often obstruct waterways, disrupt ecosystems, and create breeding grounds for disease-carrying mosquitoes. Therefore, utilizing water hyacinth for herbicide remediation serves the dual purpose of environmental management and pollution control. Previous studies have largely focused on phytoremediation or biochar-based adsorption as separate strategies for pollutant removal. However, these methods, when used in isolation, exhibit limitations in terms of adsorption efficiency, scalability, and phytoremediation performance. For instance, conventional biochar alone may lack the specificity required for effective herbicide adsorption, while phytoremediation by wetland plants is often constrained by herbicide phytotoxicity and uptake efficiency (Tang et al., 2021).

To address these challenges, this study integrates nitrogen-doped biochar with water hyacinth to create a synergistic remediation system. The biochar component serves as an efficient adsorbent, reducing herbicide concentrations to levels that are less toxic to the plant. Simultaneously, water hyacinth contributes to further pollutant uptake and degradation, enhancing overall removal efficiency. This combined system not only increases the effectiveness of herbicide removal but also promotes a sustainable, cost-effective solution that leverages agricultural waste and invasive plant species for environmental remediation. By addressing the limitations of previous approaches and introducing a novel, scalable remediation system, this study contributes to advancing sustainable strategies for herbicide removal and aligns with global environmental sustainability goals.

1.3 Objectives of the Study

To prepare nitrogen-doped biochar from palm kernel shells to be used in the adsorption of herbicides in an aqueous solution and evaluate its ability to be used as an aid in phytoremediation for herbicide removal. However, to achieve this, the research has several specific objectives, including:

1. To evaluate the physiochemical properties of nitrogen-doped mesoporous biochar derived from palm kernel shells before and after adsorption

2. To determine the initial concentrations, biochar dosage, pH, temperature, and time at which the prepared modified biochar will adsorb herbicides from an aqueous solution

3. To study adsorption isotherms, kinetic modeling, thermodynamics, and mechanism adsorption for the herbicides onto prepared modified biochar

4. To assess the potential of the integrated system in the remediation of herbicide-contaminated water through a combination of adsorption on biochar and phytoremediation by wetland plants (*Eichhornia crassipes*) and compare it with phytoremediation alone

1.4 Novelty of the Study

The novelty of this study lies in the strategic integration of phytoremediation with melamine-modified biochar derived from waste palm kernel shells. Unlike conventional single-method remediation techniques, this approach uniquely couples the well-established phytoremediation capacity of water hyacinth with the advanced adsorption properties of engineered biochar. The synergistic action between the modified biochar and aquatic plants significantly enhances the removal efficiency of herbicide pollutants. The biochar not only serves as a pollutant adsorbent but also supports plant survival and mitigates the phytotoxic effects of herbicides, fostering a resilient remediation system. This innovative dual-system methodology offers a promising and sustainable platform for addressing emerging environmental pollutants, paving the way for future advancements in green remediation technologies.

1.5 Scope of the Study

This study investigates the potential of using palm kernel shell waste and the invasive weed *Eichhornia crassipes* to enhance water treatment efficiency through an integrated system. The research encompasses both batch adsorption experiments and an integrated phytoremediation-biochar system to evaluate herbicide removal from aqueous solutions. Herbicide adsorption by modified biochar was tested at concentrations ranging from 50 to 300 mg/L over a time frame of 15 to 420 minutes to determine removal efficiency. For the integrated system combining biochar and phytoremediation, herbicide concentrations ranged from 50 to 150 mg/L, with experiments running for 1 to 10 days to assess removal efficiency. Relative growth studies were conducted for 30 days, and the external influences on plant morphology were also monitored for 30 days. Adsorption experiments were conducted under controlled laboratory conditions to ensure reproducibility and reliability. Additionally, adsorption isotherms and kinetic modeling were applied to understand the adsorption mechanisms of modified biochar. The research also compares the effectiveness of nitrogen-doped biochar derived from palm kernel shells with raw palm kernel shell powder and biochar activated using KOH. Batch adsorption studies were performed to evaluate the adsorption capacity, while the effectiveness of biochar-assisted phytoremediation was assessed by monitoring the relative growth and uptake capacity of *Eichhornia crassipes* under different treatment conditions. Furthermore, this study assesses the potential for scaling up the integrated system for environmental applications. It also explores the feasibility of implementing this approach in large-scale water treatment settings, as well as its limitations when confined to laboratory conditions. Finally, the research examines sustainable methods for managing herbicide-laden wastewater using a combined approach of modified biochar and wetland plants, providing insights into its practical applications and environmental impact.

1.6 Significance of Research

The research presents an innovative approach to treating herbicide contamination and its impacts on ecosystems and human health. It emphasizes the urgent need for sustainable solutions to address environmental challenges. By incorporating wetland plants and modified biochar derived from palm kernel shells, the study presents a sustainable method for remediating herbicide pollution. This strategy not only helps restore ecosystems but also safeguards human health by reducing herbicide exposure. Additionally, the use of palm kernel shells for biochar production promotes waste reduction and resource utilization. Moreover, the study addresses the environmental issues caused by the invasive water hyacinth, providing a comprehensive approach to ecosystem restoration. Overall, the research contributes significantly to environmental science and sustainability by offering a holistic solution to herbicide remediation, emphasizing the importance of addressing various dimensions of the problem, from conservation to human health protection. Here are some key points highlighting the significance of this study:

I. Synthesis of nitrogen-doped biochar derived from palm kernel shells resulting in excellent physiochemical attributes.

II. Obtaining optimum pH, temperature, time, and dosage for modified biochar utilized for the adsorption of herbicides from contaminated water.

III. Understanding how herbicides interact with modified biochar by studying adsorption isotherms, kinetic modelling, thermodynamics, and mechanism adsorption can help in designing efficient and eco-friendly methods for removing these chemicals from the environment.

IV. Enhance phytoremediation efficiency under high herbicide concentrations by using melamine-modified biochar to enhance phytoremediation efficiency under high herbicide concentrations, opening avenues for further scientific advancements in this area.

1.7 Organization of Thesis

This thesis includes five chapters that cover the work done in addition to the appendices.

Chapter one (Introduction) offers a comprehensive view of water pollutants, particularly focusing on herbicides in the agricultural sector, types of herbicides, a simplified picture of methods of herbicide removal, modified biochar that is used in the adsorption process, and wetland plants that are used in phytoremediation, as well as the problem statement, objectives of the study, scope of the study, and significance of the research.

Chapter two (Literature Review) presents a review of the literature on herbicide removal, focusing on the adsorption technique, biochar, or activated carbons, as well as modified methods for the preparation of biochar or activated carbons and the optimization parameters in different conditions for the of removal herbicides. This also includes the characterization of biochar or activated carbon. The adsorption isotherms, kinetics, thermodynamics, and mechanism of adsorption for the herbicides onto biochar or activated carbons. Chapter two also focuses on phytoremediation techniques and wetland plants that are used in phytoremediation to remove emerging pollutants. The contribution of biochar to improving wetland systems' phytoremediation effectiveness.

Chapter three (Materials and Methods) addresses the experimental work done in this study. The materials and equipment, the experimental procedures that include collection of precursor palm kernel shells, preparation of nitrogenated mesoporous biochar as adsorbent, characterization, and experimental design for batch adsorption studies, kinetics studies, isotherm studies, and adsorption thermodynamics, as well as plant selection and preparation, and experimental setup of coupling biochar and phytoremediation.

Chapter Four presents the findings and discusses the results in detail. It provides a comprehensive characterization of PKS-BM, comparing its properties with those of PPKS and PKS-B. Adsorption studies were conducted to investigate variables such as initial herbicide concentrations, PKS-BM dosage, pH, temperature, and contact time for the removal of herbicides from aqueous solutions. Optimal conditions for herbicide removal using PKS-BM were also identified and compared to those of PPKS and PKS-B. Additionally, the chapter explores the kinetics, isotherms, thermodynamics, and adsorption mechanism of herbicides on the PKS-BM surface. An integrated system for remediating herbicide-contaminated water was examined, combining biochar adsorption with phytoremediation using wetland plants (*Eichhornia crassipes*) and comparing it to phytoremediation alone. This included an analysis of removal efficiencies for both biochar-assisted phytoremediation and standalone phytoremediation, as well as the mechanisms involved in biochar-assisted phytoremediation for herbicide removal. The results also assess plant growth, external influences, and morphological changes in the phytoremediation of herbicides.

Chapter five offers conclusions from each objective of the study in addition to recommendations for future studies.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction and Background

This chapter provides background information and an in-depth review of the effects of herbicide contamination in water. It covers the chemical classification of herbicides, with a focus on diuron, paraquat, and 2,4-D, as well as treatment technologies for herbicide removal, particularly adsorption and phytoremediation. The chapter also reviews the adsorption process using biochar or activated carbon, including the production of biochar or activated carbon from various precursor materials. Furthermore, the properties of biochar and activated carbon are explained, with detailed discussions on the influence of parameters in the adsorption process, as well as adsorption isotherms, kinetics, and thermodynamics in batch processes as reviewed in the literature. The section explores herbicide removal mechanisms based on biochar or activated carbon. Additionally, phytoremediation techniques are discussed, including the mechanisms of phytoremediation and the effectiveness of various wetland plant species in removing herbicides and other pollutants. Lastly, this section highlights the impact of biochar in enhancing the effectiveness of phytoremediation in wetland environments.

2.2 Typical Organic Pollutants (TOPs)

Anthropogenic activities have contributed to the release of waste products into the environment, many of which are hazardous and incompatible with sustainable practices. In the case of synthetic materials, their impacts can be significant even at very small concentrations and may accumulate over time, causing severe effects on biological ecosystems and the food chain (Ali et al., 2021). Pollution can be classified into four main categories based on human activities: transportation, energy, industry, and agriculture (Council et al., 2010). In other words, sectors like transportation, energy, industry, and agriculture have contributed to the emergence of a whole new class of pollutants. This shift is driven by significant global population growth and widespread industrialization across much of the world. Similarly, scientific advancements based on an understanding of the fundamental physical and chemical forces of nature have produced new goods and processes that have revolutionized society and significantly improved human health. However, these human activities can also contaminate water, making it less usable for both people and other living organisms.

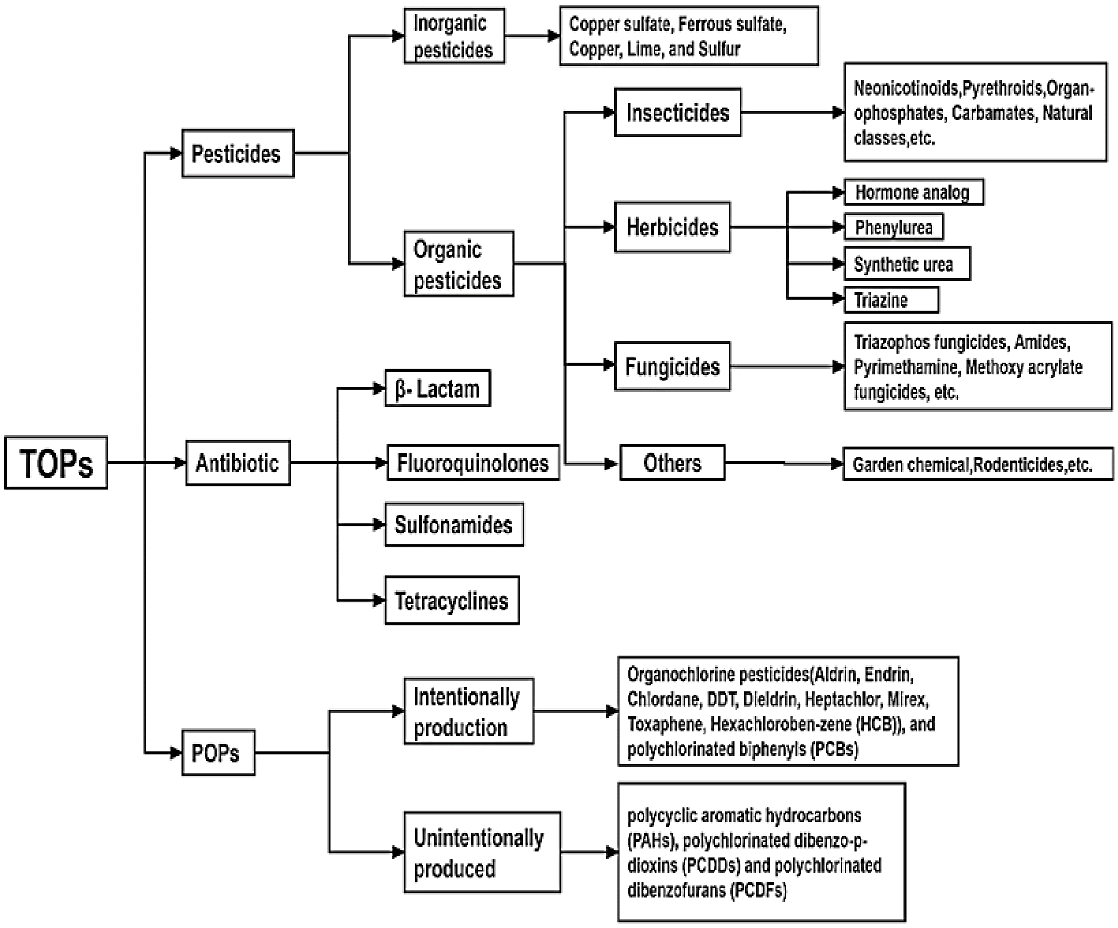

Figure 2.1 The classification of common organic pollutants present in the agricultural environment. Reprinted from (Hua et al., 2022).

This is known as water pollution. In recent years, persistent organic pollutants (POPs) have been discovered globally, even in regions where their usage has never been recorded (Hua et al., 2022). The 1998 Aarhus Protocol on POPs listed 16 specific substances, including 11 pesticides, 2 industrial chemicals, and 3 by-products (see Figure 2.1) (Chen et al., 2021). Different TOPs exhibit distinct transport behaviors in agroecosystems due to their diverse sources and application methods. This highlights how various organic pollutants move from the environment to crops, as well as the factors influencing this process, depending on their origins and methods of application. Typically, the dispersion or movement of TOPs is affected by processes such as photolysis, volatilization, plant absorption, and runoff or leaching, which are dictated by prevailing soil and environmental conditions as shown in Figure 2.2.

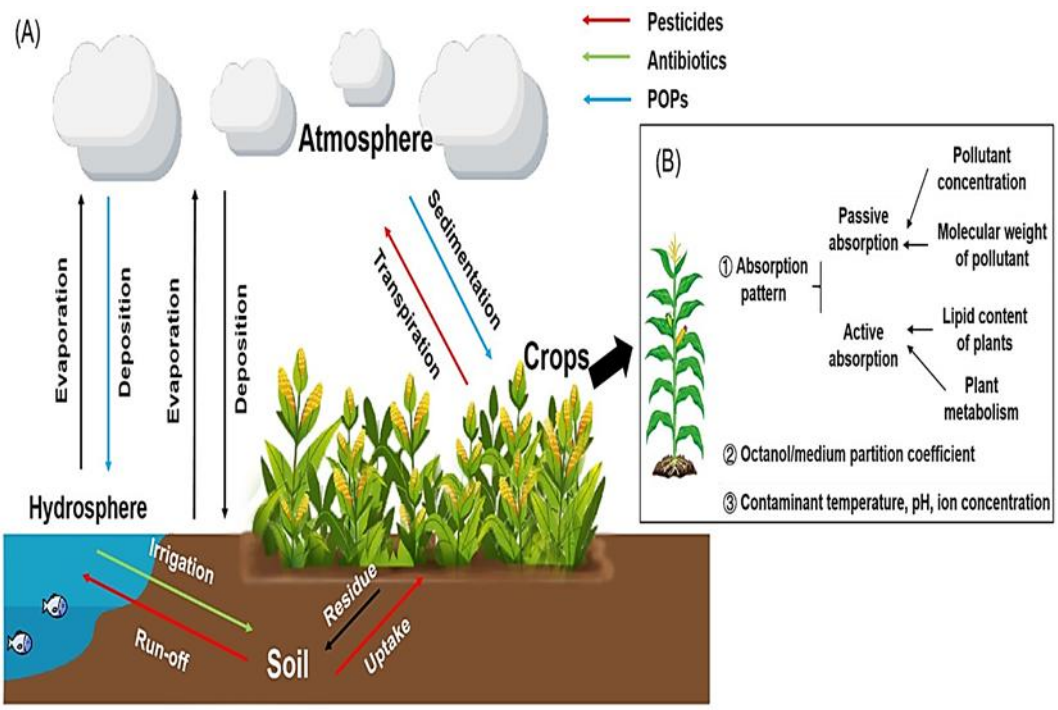

Figure 2.2 Illustrates the transport dynamics of organic chemical pollutants in different environments. (A) Depicts the transfer of these pollutants across atmospheric, water, and agricultural environments (B) Highlights factors affecting the movement of organic chemical pollutants in crops. Reprinted from (Hua et al., 2022).

Hazardous chemicals, pesticides, fertilizers, herbicides, and other pollutants can infiltrate our water supply system. If our water supply is polluted, it could be harmful to the health of people, animals, and plants unless it undergoes an expensive purifying process (Madhav et al., 2020).

Pesticide use in agriculture has been a major source of contamination in the environment. The use of pesticides is intended to suppress the growth of weeds, fungi, and insects that threaten human food supplies. Their application reduces food costs, boosts crop production, and helps prevent illnesses such as encephalitis and malaria (Clesceri and Clesceri, 2021). However, these dangerous chemicals are transported to the environments of non-target animals by crop spraying and irrigation runoff water. These substances accumulate in the tissues of these animals, and when ingested by humans, they strengthen the herbicides' effectiveness and cause health difficulties that, in rare cases, may be fatal. Recently, chemists have created naturally occurring insecticides that are safe for birds and animals but poisonous exclusively to certain targets (Zaller and Zaller, 2020). The most significant herbicide of the 21st century is arguably glyphosate, which is commonly known by its trade name Roundup. Glyphosate revolutionized agriculture due to its broad-spectrum effectiveness in killing weeds and its relatively low toxicity to humans and animals. However, it has also been the subject of controversy and debate regarding its environmental impact and potential health risks.

2.3 Herbicides

One of the pesticides that is most frequently used worldwide is herbicides. Herbicides are still thought to be the best way to keep weeds out of crops when they are used on cultivated land, but using them also exposes the environment to these chemicals (Vormeier et al., 2023; Zhang et al., 2024). Herbicides not only have the potential to enhance the nutritional quality and safety of food but also offer various other benefits that often escape public attention (Damalas and Eleftherohorinos, 2011). From an economic and practical standpoint, herbicides are invaluable tools for pest management, streamlining labor efforts, and boosting efficiency across various sectors of agricultural production (Rad et al., 2022). Among these herbicides are paraquat, diuron, and 2,4-dichlorophenoxyacetic acid (2,4-D).

Paraquat is classified as a group of bipyridinium herbicides, widely acclaimed for its outstanding performance in agricultural practices. Its ability to effectively eradicate weeds is particularly noteworthy, characterized by its potent weed control properties. Paraquat swiftly kills various weed species upon application by triggering bursts of reactive oxygen species. Its nonselective herbicidal activity allows for the suppression of a broad spectrum of weeds, making it highly adaptable across a variety of agricultural settings. Furthermore, paraquat stands out as one of the few resources capable of managing weeds that have developed resistance to glyphosate and glufosinate. These diverse advantages have firmly established paraquat as a preferred choice among herbicides in agriculture (Xia et al., 2024). The mechanism of paraquat molecules entering plants depends on when paraquat is taken up and transferred by plants from the outside environment to the chloroplasts by the plant's vascular system, where it primarily acts, which plays a crucial role in photosynthesis in plants (Corti et al., 2023). The transport of paraquat occurs through a process known as translocation, which involves the movement of paraquat from one part of the plant to another. Once paraquat reaches the chloroplasts, it becomes an essential component of the electron transport chain. Paraquat accepts electrons from photosystem II (PSII) and transfers them to the cytochrome B6F complex, where they are eventually used to produce ATP (Tomar et al., 2019). It has also been reported that paraquat plays a critical role in the