POROUS CARBONACEOUS MATERIALS FOR PESTICIDE REMOVAL FROM VARIOUS ENVIRONMENTAL MATRICES: A BRIEF OVERVIEW

Abstract

Pesticides are considered as an inevitable input in sustainable food production as they play a crucial role in the maximization of agricultural productivity. Despite their useful role in modern farming, the indiscriminate and widespread uses of pesticides possess a serious threat to the environment. Around 90% of the applied pesticides are lost in the different environmental compartments, either directly through intentional use (such as agronomic practices) or unintentionally (e.g. spray drift, leaching, surface runoff, etc.). For sustainable environmental pollution mitigation, it is necessary to alleviate the ecosystem from unwanted pesticide residues. Adsorption has been demonstrated as a productive, economically feasible, yet, facile method for removing organic contaminants from different matrices. One of the innovative technologies for eliminating a wide spectrum of pesticide molecules from soil and water is the use of low-cost adsorbents. Talking about such sorbents, porous carbonaceous materials such as graphene and graphene oxides, carbon nanofibers, carbon nanotubes, biochar, etc. possess unique physical and chemical properties, as well as diverse electrical and mechanical characteristics which render them useful for potential application in remediation processes. Enhanced contaminant removal efficiency can be achieved by the use of these materials owing to their high surface area, significant pore volume, diverse surface chemistry with immense modification potential, and high conductivity. Adsorption of pesticide molecules on porous carbon materials is a complex process that depends upon various factors including not only the physicochemical properties of the sorbents and the adsorbates but the overall solution chemistry is also involved in the phenomena, as

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well. Therefore, a spotlight in the form of this chapter has been shown upon the role of the physicochemical nature of porous carbonaceous materials, used as adsorbents of pesticide residues, the mechanistic perspectives and removal efficiencies from different environmental matrices have been summarized.

Keywords: Pesticides, pollution, adsorption, porous carbon, carbon nanotubes, biochar

I. INTRODUCTION

An increase in emerging pollutants in the environment is being caused by anthropogenic activities and industrial outputs [1]. Emerging pollutants are a worry for public health and despite extensive research being done on the subject worldwide, no definitive remedies have been proposed to date. Pharmaceuticals (hormones, antibiotics, etc.), cosmetics, synthetic colors, and pesticides are among the developing pollutants that are of the most concern in many parts of the world [2]. Pesticides are used in modern agriculture to raise productivity to a level that is commercially viable [3]. Depending on their intended application, pesticides can be divided into different groups such as insecticides, fungicides, herbicides, miticides, nematicides, bactericides, molluscicides, and rodenticides. Pesticides can be categorized into a number of groups based on their chemical identity, including organochlorines, organophosphorus, carbamates, synthetic pyrethroids, neonicotinoids, etc. Many pesticides are long-lasting and can contaminate areas far from their point of origin by traveling through the soil, water, and air. Ecosystems have been harmed by the infrequent use of pesticides, endangering fish, livestock, domestic animals, birds, and other wildlife [4].

Pesticides can get into the environment intentionally or accidentally by things like transportation mishaps, leaching or runoff from the disposal sites or leaks from industrial storage, etc. [5]. After pesticide application to crops, the applied pesticides may reach the soil through wind action or rain and irrigation water. They then infiltrate surface water and groundwater systems from the soil through runoff and infiltration mechanisms [6]. Moreover, a number of pesticides are pervasive substances that linger in soil and sediments due to their low bioavailability [7]. Pesticides may damage the ecosystem and biodiversity while being extremely hazardous to humans and capable of causing chronic disorders. For instance, long-term exposure to herbicides like atrazine may result in cancer, cardiovascular issues, retinal disorders, and muscle degeneration. Azoxystrobin, a broad-spectrum fungicide, is well known for being extremely hazardous to freshwater fish and estuaries [8].

The commercial interest in porous materials for their use in various fields, such as separation, catalysis, adsorption, energy storage, and conversion, as well as the scientific interest in the synthesis, treatment, and characterization have accelerated the research development in this sector in recent decades [9]. With the increase in global population, scientific and industrial advancements related to pesticides are dramatically worsening the pollution of several environmental matrices. A need-based decontamination method is therefore crucial. There have been a number of pesticide decontamination methods created so far, but the adsorption of pesticides onto porous materials is showing the most promise for removing pesticides from soil and water because of its low cost and simplicity of disposal when used on a wide scale. The diameter of the pores that make up porous materials can be used to classify them, according to the International Union of Pure and Applied Chemistry-USA (IUPAC). In contrast to mesoporous and macroporous materials, which have pore diameters that range from 2 to 50 nm and more than 50 nm, respectively, microporous materials have pores that are smaller than 2 nm in size [10]. Because of their huge specific surface area, diversity of functional groups, and structural variety (macro-, meso-, and micropores), porous carbonaceous materials are thought to be the most effective at removing pesticides. This chapter gives the reader a summary of the sorption and remediation properties of several porous carbonaceous adsorbents for the removal of pesticides from environmental matrices including soil and water. Additionally, the role of the

physicochemical properties of porous carbonaceous materials used as pesticide adsorbents has been highlighted in this chapter. The mechanistic perspectives and removal efficiencies from various environmental matrices have also been addressed.

II. POROUS CARBONACEOUS MATERIALS AND THEIR ROLE IN PESTICIDE REMOVAL FROM DIFFERENT ENVIRONMENTAL MATRICES

1. **Graphene and Graphene Oxides:** The most commonly used porous carbon adsorbents applied for pesticide removal from soil and water have been shown in Figure 1. In recent years, both the experimental and theoretical scientific communities have paid intense attention to graphene, a type of innovative and fascinating carbon substance. The "mother of all graphitic forms" of nano-carbon i.e graphene is one atom thick two-dimensional (2D) layers of sp2-bonded carbon [11]. It is the main ingredient in the majority of carbon-based nanomaterials, and it also possesses exceptional qualities like great mechanical, electrical, thermal, and optical capabilities as well as a very high specific surface area. They may be a strong contender for use as an adsorbent for the adsorption of compounds in the benzenoid form because their large delocalized electron system can generate a strong stacking interaction with the benzene ring.

The predecessor of graphene, graphene oxide (GO), is a 2D carbon sheet having functional groups that contain oxygen [12]. Due to the conductivity of GO, it can be mixed with polymers and other materials to create composites that have improved tensile strength, elasticity, and conductivity qualities. Due to its distinctive 2D structure, GO is seen as a strong candidate for use as an adsorbent. It has a large surface area and functional groups that are plentiful on the surface which is brought about by the oxidation of graphite. These properties make it a material with great potential for adsorption [13].
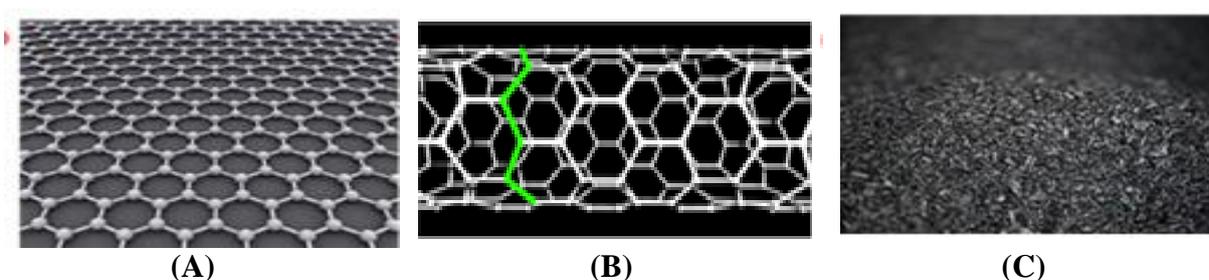

(A) **(B)** **(C)**

Figure 1: Commonly Used Porous Carbon Adsorbents (A): Graphene, (B) Zigzag Carbon Nanotube, (C) Biochar

- **Interaction mechanism with different contaminants:** The common interaction mechanisms of porous carbonaceous materials with pesticides have been shown in Figure 2. In the case of graphenes and graphene oxides, the weaker noncovalent bond creates the locus of pollution separation because it is primarily involved in adsorption after the mechanical separation of pollutants or their catalysis. Covalent bonds are primarily formed during the formation of composites in this case. The non-covalent bond breakdown is clear evidence that the pollutants must be able to be separated with the least amount of energy possible for mechanical separation and catalysis. The majority of the organic pollutants interact via noncovalent bonds, according to

research on the interactions between graphene and its contaminants. The analysis of the adsorption process with a view on thermodynamics and kinetics is facilitated by the study of interactions, which further establishes the types of interactions between the adsorbate and the adsorbent [14].
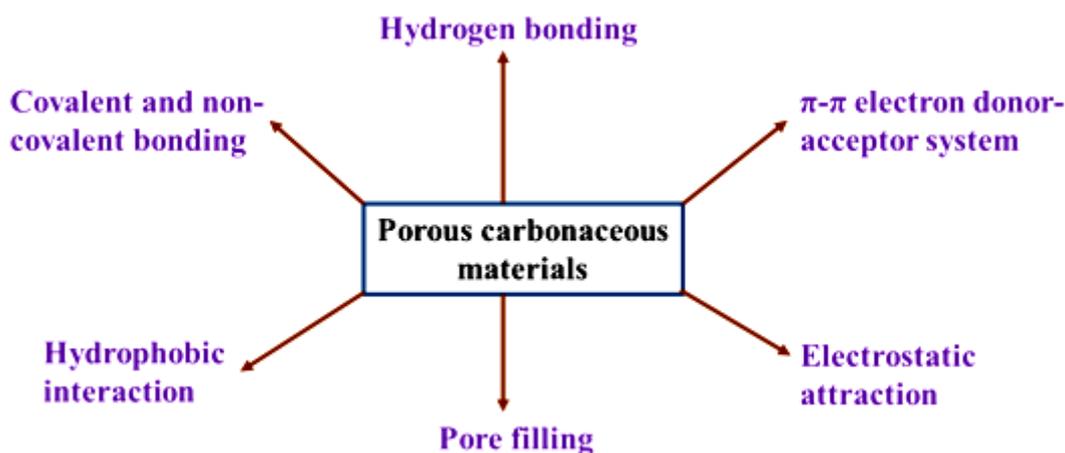

Figure 2: Common Interaction Mechanisms of Porous Carbonaceous Materials with Pesticides

- **Effect on removal of pesticides from various environmental matrices:** The effect of the most commonly used porous carbonaceous materials on the removal of pesticides from different environmental matrices has been depicted in Table 1. Graphene-based nanocomposite materials are nowadays being used as an extracting reagent in analytical studies of pesticide samples in various matrices. Recently, a graphene-based magnetic nanocomposite material has been developed and used as an adsorbent of five carbamate pesticides namely isoprocarb, pirimicarb, carbofuran, metolcarb, and diethofencarb from water samples prior to detection by using high performance liquid chromatography-diode array detector [15]. The developed nanocomposites exhibited high adsorption capacity of the test analytes.

Table 1: Effect of Commonly Used Porous Carbonaceous Materials on Removal of Pesticides

Type of porous carbonaceous material	Pesticide removed	Matrix	Reference
Graphene and graphene oxide (GO)s			
Cellulose/ graphene oxide composites	Organophosphorus pesticides	Water	[13]
GO functionalized by iron oxide magnetic nanoparticles	Glyphosate	Water	[16]
Carbon nanotubes (CNTs)			
Single-walled CNTs	Dicamba	Aqueous solution	[17]
Multi-walled CNTs	Malathion	Water	[18]
Multi-walled CNTs	Organophosphorus pesticides	Soil and water	[19]

Biochar			
Wood chips biochar	Carbofuran and Chlorpyrifos	Soil and plant	[20]
Grass biochar	Fluidone	Water	[21]
Wood biochar	Isoproturon	Soil	[22]
Rice straw biochar	Oxamyl	Water	[23]
Rice straw biochar (H$_3$PO$_4$ treated)	Diazinon	Water	[23]

A graphene oxide-based adsorbent was developed by functionalization of GO by iron oxide magnetic nanoparticles (α-γ-Fe$_2$O$_3$) using an ultrasonication process. The prepared material was successfully used for glyphosate removal from water. The equilibrium adsorption time for glyphosate was found to be 2 h and the maximum removal percentage (92%) was achieved at 15 ℃. The maximum adsorption capacity of the developed material was 46.8 mg g^{-1} [16]. A schematic representation of the application of graphene-based materials in the decontamination of wastewater has been explained in Figure 3.
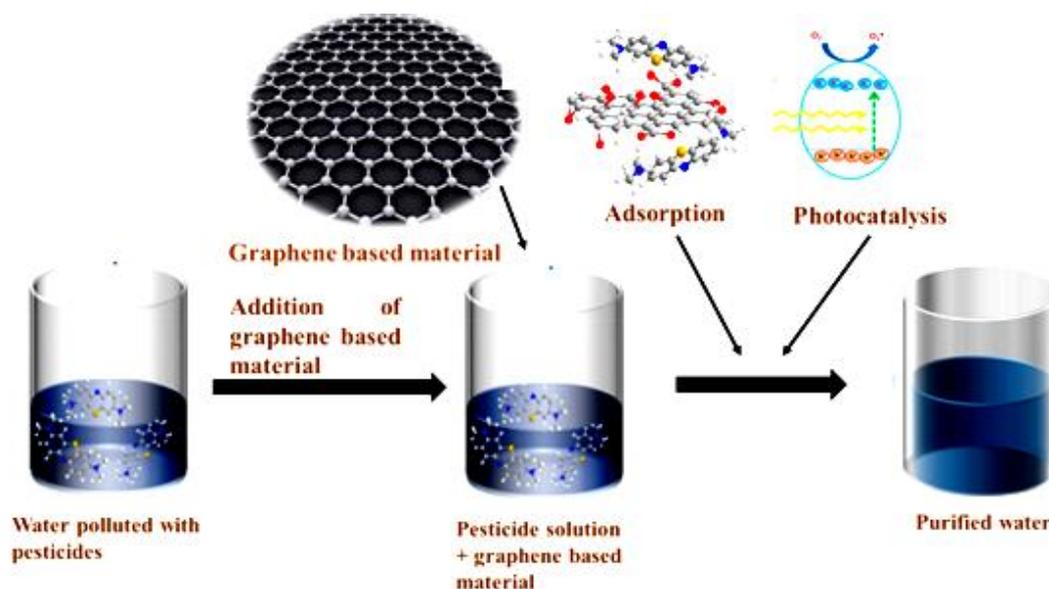

Figure 3: Schematic Representation of Application of Graphene-Based Materials in Decontamination of Waste Water (Modified From Ref. [14])

An activated carbon material was developed from sieve-like cellulose/ graphene oxide composites. In this study, corn straw was utilized for the development of the composite material. The developed composite was tested for the removal of several organophosphorus pesticides from water. The adsorption capacity of the developed composite was found to be superior over the commonly employed sorbents such as multiwall carbon nanotube, activated carbon, graphitized carbon black, C18, and primary secondary amine. The maximum adsorption capacity of the prepared composite was found to be 152.5 mg g^{-1} for chlorpyrifos. Moreover, the adsorption efficiency was > 80% after eight times of recycling, suggesting it as a potent candidate for the removal of organophosphorus pesticides [13].

Another Fe_3O_4/reduced graphene oxide (Fe_3O_4/rGO) nanocomposite had been developed for the adsorption of harmful pesticides from an aqueous medium. The test pesticides for this study were atrazine, ametryn, simeton, simazine, and prometryn [24]. Efficient adsorption (93.61%) of the test pesticides was achieved due to electrostatic, and hydrophobic interactions of the Fe_3O_4/rGO nanocomposite towards the heterocyclic conjugation of the test pesticides. Moreover, the developed adsorbent showed easy and rapid separation from the aqueous matrix using the external magnet for reuse. The adsorption efficiency was 88.66% even up to seven cycles.

Another magnetic graphene oxide-based nanocomposite was developed and utilized as an adsorbent for the extraction of organophosphorus (OP) pesticide residues (profenofos, malathion, isocarbophos, chlorpyrifos, fenamiphos) from environmental water samples by using magnetic solid phase extraction techniques [25]. For the development of the nanocomposite, Fe_3O_4 was coated with SiO_2 first and bonded thereafter with graphene oxide under the catalytic activity of the hydrazine hydrate. Thus, the adsorbent material GO-based magnetic composites serve as a potent candidate for the removal of pesticides from environmental matrices, presenting low cost, superior adsorption capacity, and magnetic properties that facilitate easy separation of the adsorbent material from the test matrix.

In another study, graphene quantum dots were prepared by using the microwave-assisted hydrothermal route and evaluated for removal capacities of oxamyl from aqueous solutions using batch adsorption experiments [26]. The results revealed increase in oxamyl removal with the increase in oxamyl concentration for all the test contact times.

The photocatalytic activity of a home-made titanium dioxide (TiO_2) and graphene oxide (GO) based composite (GO-TiO_2) had been evaluated in the photodegradation of a pesticide mixture of diuron, isoproturon, alachlor, and atrazine under UV–VIS in ultrapure and natural water matrices [27]. These four pesticides have been considered as priority pollutants by the European Union. Natural water resulted in decreased photodegradation of the test pollutants when only a bare TiO_2 photocatalyst was used. However, the photodegradation efficiency of the GO-TiO_2 composite was less affected by the variations in water matrices, with high initial pesticide photodegradation rates.

2. **Carbon nanotubes:** The development of novel adsorbent material with high sorption capacity and removal efficiency is of utmost importance from the soil and water remediation perspective. Carbon nanotubes have currently emerged as a promising candidate in this domain due to their large specific surface area and tuneable physicochemical properties. In addition to that, the small, hollow, and layered structure of carbon nanotubes (CNTs) makes them an efficient adsorbent for the elimination of different organic and inorganic micropollutants from soil and wastewater [28].

Laser vaporization and arc methodology were employed initially to synthesize CNTs. However, due to the high cost of these fabrication technologies, metal catalysts (Ni, Fe, Co, etc.) were further used as a synthesizing technology to scale up the production of carbon nanotubes. However, structures of CNTs obtained through the catalysis process are not as prominent as the structures of CNTs generated by the arc laser technique. Therefore, the chemical vapor deposition technique (CVD) is widely used at

the commercial and laboratory level where the vapor of desired carbon precursor is deposited on the surface of a suitable metal catalyst [29]. In general, carbon nanotubes are derivatized from graphite and composed of many sheets (graphene sheets) in which sp2 hybridized carbon atoms are arranged at the corner of the hexagon in the honeycomb crystal lattice. Based on the structural walls, these graphene sheets can be rolled into a cylindrical form to give rise to multi-walled, double-walled, and single-walled CNTs. While single-walled CNTs (SWCNTs) are made of a single-layer graphene sheet, multi-walled CNTs (MWCNTs) are produced by staking two or more concentric SWCNTs into a tubular form [30]. The outer diameter of SWCNTs is in the range of several nm to 0.4 nm, but the length of CNTs is in the micrometer range (Length: Diameter is about > 1000) [31]. In MWCNTs, the interlayer distance is around 0.33 nm, roughly the same as the spacing between graphene layers in graphite [32]. SWCNTs are classified into (i) armchair patterns, (ii) chiral structures, (iii) zigzag patterns, and (iv) helical patterns, whereas MWCNTs can be categorized into two main groups, i.e., (i) Russian doll model and (ii) parchments like structure.

Structural analysis of CNTs revealed that they exhibit some unique physical characteristics like lower electrical resistivity, higher thermal conductivity, and higher mechanical strength, bringing about a widespread application in the remediation of soil and wastewater. Due to the high chemical stability, large specific surface area, interstitial pore spaces between the graphene sheets, and hollow interiors of tubes, CNTs are also considered a potential candidate for the degradation of different emerging pollutants [33]. Functional modification of the surface and structure of CNTs during their fabrication through activation or catalysis improves their sorption capacity significantly. Generally, covalent and non-covalent functionalization does the transformation. In the covalent approach, the oxidation of CNTs by acid introduced hydroxyl or carboxylic groups [34], whereas the end functionalization of CNT introduces carbonyl, carboxyl, and hydroxyl groups [35]. The amino group does the surface modification of CNTs and makes them an efficient organophosphorus pesticide adsorbent [36]. The non-covalent approach allows for the attachment of various biochemically active molecules to the CNTs by non-covalent sidewall mechanisms such as π-π stacking, van der Waals forces, hydrophobic contacts, and H-bonding. However, non-covalent modification is preferred more over covalent functionalization because it retains the structural properties of pure CNTs. Moreover, structural and surface transformation improve the performance of CNTs.

- **Interaction mechanism with different contaminants:** The efficiency of pesticide removal by using CNTs from various matrices depends on the sorption potential of the CNTs, which in turn depends on the physicochemical characteristics of the carbon nanotube and the polarity of the pesticide molecules. The pesticide adsorption mechanism on CNTs is a complex phenomenon. It could be physisorption, chemisorption, interaction with the specific functional groups, intraparticle diffusion, or combining these different interaction mechanisms [37]. Adsorption of pesticides on CNTs completed in two steps. Pesticide molecules diffuse from the mass into the mesopore region in the first step and then interact with the CNT surface and pore in the second step. Thus, small-size compounds are adsorbed on the micro and mesopores of the interlayer matrix of the CNTs, while the sorption sites on the surface of CNTs serve for the adsorption of larger species [38]. Therefore considering all

these facts, it can be stated that the pesticide adsorption mechanism on CNTs depends on the type and nature of CNT and pesticide molecules.

- **π -π Interaction mechanism:** Carbon atoms of CNTs contain π electrons and they can form π -π bond quickly with the unshared π electron of pesticide molecule. However, the strength of the π -π bond depends upon the differences in hydrophobicity between the adsorbent surface and pesticide molecule and the functional groups present on the aromatic ring of the pesticide molecule. Adsorption of carbamazepine on Carbon dot-and magnetite-modified magnetic carbon nanotubes (CMNTs) was investigated by Deng et al. [39]. The result suggested that π -π electron donor-acceptor (EDA) interaction mechanism is highly responsible for removing carbamazepine through CMNTs. Pan et al., 2008 studied the sorption mechanism of 17R-ethinyl estradiol (EE2) and bisphenol A on SWCNT and found that the dominant adsorption mechanism was π -π coupling. A similar finding has also been reported for other endocrine-disrupting compounds by Jung et al. [40].

- **H-bonding mechanism:** The oxygen-containing functional groups present on the surface of SWCNTs and MWCNTs form H-bond with -OH, -NH$_2$, -NH containing pesticide molecules, consequently resulting in adsorption of such compounds on the surface of CNTs and subsequent removal from different matrices [41]. Removal of diuron and dichlobenil from wastewater is carried out through adsorption on MWCNTs, and H-bonding is found to be the prime sorption mechanism [42]. Sun et al. [43] studied the adsorption behavior of diuron, fluridone, and norflurazon on SWCNT and three MWCNTs. They discovered that H-bonding, Hydrophobic interaction, and oxygen-containing functional groups of CNTs were dominant sorption mechanisms. However, the metal ions on the inside of the pesticide molecules may combine with functional groups containing oxygen, interfering with the removal of the pesticide [44, 45].

- **Electrostatic interaction mechanism:** The surface of CNTs has both positive and negative charges, which generate electrostatic forces at a zero-point charge. Similarly, due to the differences in pH in the various matrix, pesticide molecules can be protonated or deprotonated, making them charged species. Electrostatic interactions cause adsorption as a result of these electrostatic forces on the surface of pesticide molecules and CNTs. However, the strength of these interactions depends on the functional group's potential to be protonated or deprotonated [46]. Electrostatic interaction is the dominant sorption mechanism for the removal of ibuprofen [47]. The available literature is little evidence of pesticide sorption on CNTs through electrostatic interaction; however, this kind of interaction mechanism is widely investigated for pharmaceuticals and personal care products (PCPs).

- **Hydrophobic interaction mechanism:** By using different composites of CNTs, hydrophobic pesticides can also be removed from various matrices. Hydrophobic interaction is playing a significant role in such interactions. The highest sorption was achieved at zero net point charge of CNTs. In a study by X. Yu et al. [48], the dominant adsorption mechanism for the elimination of sulphonamides was found to be hydrophobic interactions.

- **Effect on removal of pesticides from various environmental matrices:** Pesticides are the primary source of groundwater contamination. Extensive use of pesticides in agricultural practice causes a severe problem to living organisms directly or indirectly. So, proper remediation measures need to be taken to alleviate the ecosystem from unwanted pesticide residues. Therefore, in this part of the chapter, attempts have been made to briefly highlight significant studies on removing various pesticides from environmental matrices using different CNTs and composites based on CNTs.

    De Martino et al. [49] compared the sorption potential of SWCNT, three MWCNTs, and nanoscale metal oxides on the removal of MCPA (4-chloro-2-methylphenoxyacetic acid) from wastewater. This experiment showed that SWCNT has the highest sorption capacity, followed by MWCNTs and nanoscale metal oxides. SWCNT and MWCNTs can remove the herbicide from wastewater on two sorption cycles. In comparison, nano metal oxides need four sorption cycles to remove MCPA from the same wastewater completely. Porous carbonaceous nature, hollow layered structure, and high surface area could be the possible reason for the higher efficiency of CNTs than nanoscale metal oxides. Higher desorption of MCPA from SWCNT also explained the potential reuse capability of SWCNT for many sorption cycles.

    Dehghani et al. [18] performed the batch experiment to determine the adsorption capacity of MWCNT to remove organophosphorus pesticide malathion from water. The findings of this study pointed out that the adsorption efficiency of the process depends on the initial concentration of the pesticide, pH of the solution, temperature, quantity of adsorbent and contact time. Statistical analysis and three-factor response modeling (RSM) proved that MWCNT efficiently removes malathion from water under optimized conditions.

    Al-Shaalan et al. [50] prepared low-cost MWCNTs for the effective removal of diuron pesticide from an aqueous solution. Under optimized conditions, 90% removal of diuron has been achieved. Sorption kinetics followed the pseudo-first-order kinetics, and sorption of diuron conformed to the Freundlich, Langmuir, and Temkin isotherm. Moreover, negative values of enthalpy suggested that sorption was endothermic.

    Dehghani et al. [51] showed that nano adsorbents like MWCNTs could completely remove Diazinon pesticide (100%) from aqueous solution under specified conditions (initial concentration of the pesticide 0.3 mg L^{-1}, the concentration of nano-adsorbent was 0.1 g L^{-1} at pH 4 and 7 and contact time 15 min). The high surface area and the layered and hollow structure of CNTs could be the reason for the efficient removal of the pesticide from water samples.

    Youssef et al. [52] prepared cross-linked nanocomposite films of poly (vinyl alcohol) (PVA) incorporated with functionalized multiwall carbon nanotubes (f-MWCNTs) at different concentrations. The result suggested that pesticide removal efficiency from wastewater increases with an increase in f-MWCNTs concentration.

Ali et al. [53] prepared inexpensive and efficient MWCNTs (10–40 nm particle sizes and 9.0 $m^2 g^{-1}$ surface area) to effectively remove fenuron pesticide from water samples. Under optimized conditions (@100 μg L^{-1} concentration, 60 min contact time, 2.0 g L^{-1} dose, pH 7, and 25 °C), 90% removal of fenuron has been achieved. Sorption kinetics followed the pseudo-first-order kinetics, and sorption data well fitted to the Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich isotherm models. Moreover, negative values of enthalpy suggested that sorption was spontaneous and endothermic.

3. **Biochar:** Biochar is considered as a potential adsorbent for the removal of various contaminants from several environmental matrices due to their low cost, higher abundance, and superior sorptive capacities [54]. It is a stable organic carbon compound produced by heating the biomass to 300-1000 °C under anaerobic conditions [55]. Biochar can be classified into two categories i.e activated and non-activated biochar. Activated biochar is those whose properties have been modified by physical, chemical, and biological means. Non-activated biochar is without any modification but has been used as a precursor for activated carbon production [56]. Various processes such as slow and fast pyrolysis and gasification are used for the development of activated or non-activated biochar. The various physicochemical properties of the biochar developed from these processes vary depending upon several factors such as feedstock material, activation technique, process conditions, etc. The physicochemical properties of activated and non-activated biochars produced from various thermochemical processes are shown in Figure 4.
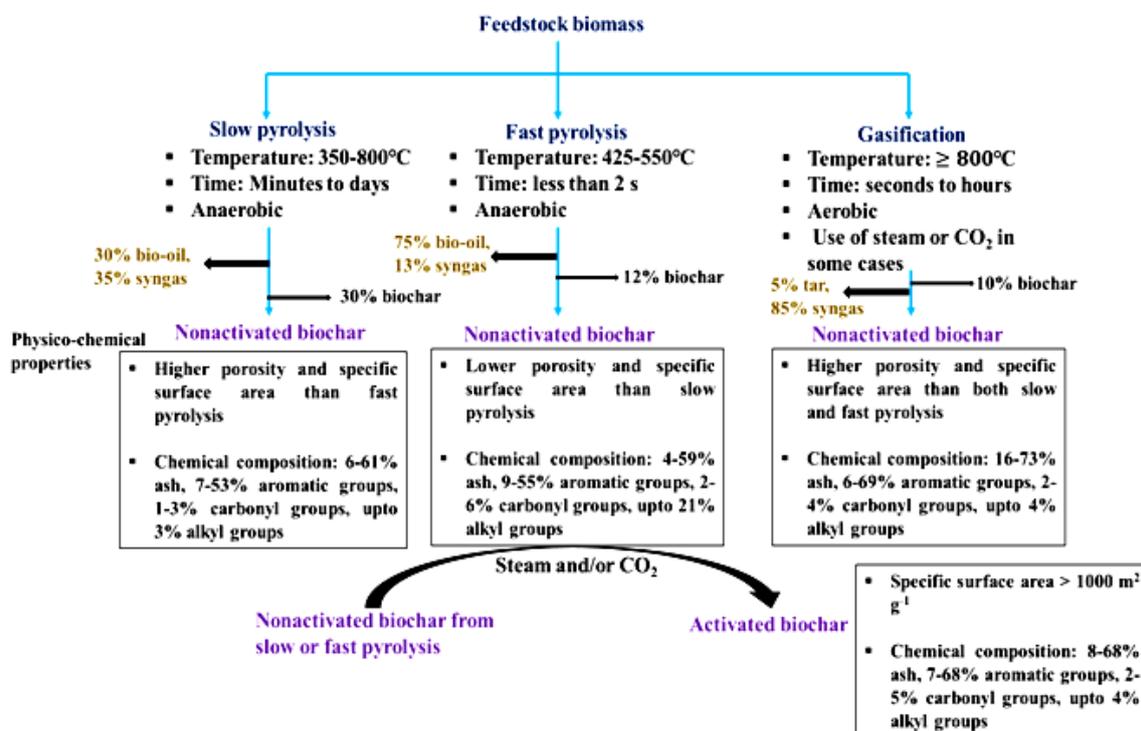

Figure 4: Physico-Chemical Properties of Activated and Non-Activated Biochars Produced from Various Thermochemical Processes (Modified from Ref. [57])

- **Interaction mechanism with different contaminants:** The pyrolysis temperatures, raw materials used, and any post-production processing all play a significant role in determining the high surface area and cation exchange capacity of biochar. As the main method for reducing pollutant mobility in contaminated soils, a high surface area is crucial for the sorption of both organic and inorganic pollutants on biochar [58]. Numerous beneficial immobilization characteristics of biochar, including its microporous structure, active surface functional groups, high pH, and CEC, allow chemical alterations of contaminants [59].

  Higher temperature-produced biochar often has high pH, CEC, and surface areas. On the other hand, biochar made at low temperatures has more active sites and stable carbon-oxygen complexes. Biochar removes pesticides through adsorption, reduction, oxidation, and immobilization. The matrix of biochar has macro, micro, and nanoporous structures that may help reduce contaminants into less transportable species [60]. Due to the strong affinities of biochar for pollutants and the capacity to transfer electrons to adsorbed reactants, the microscopic graphene moieties in biochar may act as both adsorption and redox reaction sites [61]. Furthermore, compared to pesticides in solution, adsorbed pesticides are less accessible for microbial degradation, which is why biochar amendments have been proven to inhibit pesticide degradation in soils [62].

- **Effect on removal of pesticides from various environmental matrices:** Several pieces of research have been conducted to study the effect of biochar as a potent adsorbent of pesticides from soil and water. A schematic representation of the effect of biochar on pesticides in case of soil matrix has been shown in Figure 5. Zhang et al. [63] developed maize straw-based biochar prepared at different temperatures (300, 500, and 700 °C) to evaluate the adsorption effect on thiacloprid (THI). The study revealed that adsorption of THI on prepared biochars was likely through pore-filling, hydrophobic interaction, and p-p interaction. Another group of scientists evaluated the efficacy of swine manure-based biochar on imidacloprid adsorption. Pour filling was found to be the principal adsorption mechanism in this study [64].
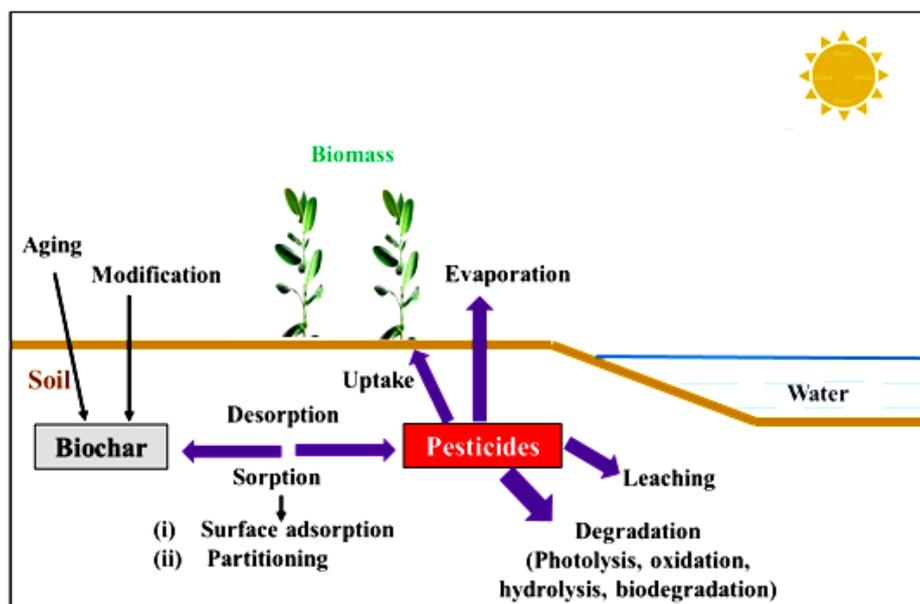
Figure 5: Effect of Biochar on Pesticide Behaviour in Soil Matrix (Modified from Ref. [65])

Different agri-waste-based biochar has also the potential to decontaminate the pesticide and/or their metabolites mainly by adsorption [66, 67]. Recently, sugarcane bagasse has been used to develop potent magnetic biochar to adsorb imidacloprid, a neonicotinoid group of insecticide [68]. The research has demonstrated the spontaneous, endothermic, and randomly increasing rate of test insecticide adsorption on the prepared biochar involving both chemisorption and physisorption. The major mechanisms for the adsorption included pour filling, π-π conjugation, and complexation of oxygen-containing functional groups.

The effect of biochars on the removal of pesticides from aqueous solutions is not comprehensive, and limited literature can be referenced in this context [69]. In a study by Klasson et al. [70], almond shell-activated biochars were used to adsorb dibromochloropropane (DBCP), a soil fumigant, from well waters. The maximum adsorption capacity of the developed matrix was found to be 102 mg g^{-1}.

4. Other porous carbon materials

- **Hierarchical porous carbon:** Hierarchical porous carbon (HPC) materials have been gaining attention over the last two decades for various applications [71]. HPC can be developed from various carbon precursor materials such as polyacrylonitrile [72], chitosan [73], polystyrene [74], etc. by chemical activation method and templating with other materials. HPC has various unique structural features for several application areas, such as unique pore surface chemistry, high porosity, surface area, and electrical conductivity [75]. These unique properties of HPC have enabled them to be used as potent adsorbents of various pesticides.

- **Activated carbon:** The term activated carbon is typically used to describe highly porous carbonaceous materials. It is the conventionally used adsorbent due to its large surface area ranging from 500 to 3000 m^2 g^{-1}, low cost, good charge-holding capacity,

and ability to generate a variety of functional groups, which may be responsible for the efficient removal of a number of contaminants from aqueous or gaseous media [76]. There are several types of activated carbon for use in a variety of applications, including activated carbon fabric, activated carbon powder, active carbon granules, and extruded activated carbon. Activated carbon is typically made in two steps. To create a carbon surface, raw materials must first undergo carbonization. Following this, the resultant material is activated through chemical oxidation or heat treatment to further improve its surface properties. The adsorption study of three pesticides onto activated carbon developed from chemical and thermal treatment of waste rubber tires revealed the removal of around 93.3%, 87.4%, and 74.1% of methoxychlor, atrazine, and methyl parathion respectively [77]. In a comparative evaluation of the adsorption of two herbicides, 2, 4-dichlorophenoxyacetic acid (2, 4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA), on chemically prepared activated carbon from polymer waste (Polyethyleneterephthalate (PET) and Polyacrylonitrile (PAN), the activated carbon obtained with KOH was found to have better adsorption of the test pesticides due to its higher microporosity and specific surface area than that obtained with K_2CO_3 [78].

- **Metal-Organic frameworks (MOFs) derived porous carbon:** Porous carbonaceous materials can be prepared by using metal-organic frameworks (MOFs) using the facile pyrolysis method. The MOF skeleton can be transformed into porous carbon with homogeneous heteroatom ornamentation [79]. The MOF-derived porous carbon can also be served as a unique adsorbent having size selectivity. The first MOF-derived porous carbonaceous material had been developed with MOF-5, showing high hydrogen uptake capacitance. Thereafter, several MOF-derived carbon materials have been prepared to have diverse applications in pollutant removal, energy storage, catalysis, etc. [80].

A multifunctional porous carbonaceous material based on β-cyclodextrin metal-organic framework MOF (β-CD MOF) was developed by C. Liu et al. [81] to serve as a rich potassium source and potential adsorbent of pesticides from wastewater. The batch adsorption study expressed the potential of the developed porous material in the removal of four amide herbicides from the water matrix. The developed porous carbon material revealed an effective contribution to rice seedling growth culture in herbicide-contaminated water in pot experiments. In a study by Elhussein et al. [82], CeO_2 nanofibers were prepared by using the calcination technique from $Ce(1,3,5-BTC)(H_2O)_6$ metalorganic frameworks (MOFs) and its application on adsorption of 2,4-D, a widely used herbicide, from the water was investigated. The maximum adsorption capacity was found to be 84.29 mg g^{-1} at 318 K temperature.

Another magnetic copper-based MOF (M-MOF) was developed for the removal of neonicotinoid insecticides from an aqueous matrix [83]. The adsorption models expressed that equilibrium data for all the test insecticides except fitted in Freundlich bimolecular layer adsorption and thiacloprid showed Langmuir monolayer adsorption. The developed hybrid adsorbent MOF may serve as a promising tool for the rapid removal of neonicotinoid insecticides from environmental water samples.

- **Carbon nanofibers:** Carbon nanofibers having 50–200 nm average diameters can be made using two techniques, vapor deposition growth, and electro spinning. For the synthesis of CNFs, the electrospinning technology has more extensive applicability. In this case, polymer nanofibers are typically used to produce the precursors of CNFs. Several polymers, including lignin, polybenzimidazole, polyvinyl alcohol, polyacrylonitrile, and polyvinyl alcohol can be used to serve the purpose.

  A lot of research has been done on the mechanical and thermal transport phenomena of CNF composites, which have good thermal, electrical conductivity, and mechanical properties. The successful polymer synthesis of nanofibers that had been thermally treated up to 1000 ^{0}C to carbonize them under varied ambient conditions and temperatures has already been demonstrated to produce CNFs. As a result, the carbonization technique typically results in a volume and weight shift, which reduces the diameter of these nanofibers. Due to their functional groups, high surface area, and electron transfer ability, which provide the conditions for their consideration as potent adsorbents, activated carbon nanofibers are used to remove various contaminants from different matrices with high efficiency [76]. Strong catalytic activity towards the breakdown and mineralization of dichlorvos, an organophosphate insecticide, has been demonstrated by copper dispersed-CNFs supported by phenolic carbon beads under mild reaction conditions (Temperature: 200 ^{0}C, Pressure: 25 bar). In that study, within 3 hours of reaction time, 150 ppm of original DDVP concentration has been found to be almost completely degraded [84]. In another study, the destructive adsorption of an insecticide, diazinon has been documented by using porous sites of the activated carbon nanofibers containing Al_2O_3 and MgO nanoparticles [85].

III. CONCLUSION

A brief overview of different porous carbonaceous materials for removing pesticides from various environmental matrices is described in this chapter. It is crucial to consider all the relevant factors when selecting the best material for pesticide removal, including pH, matrix type, temperature, amount of soil and water, cost of the investment, the solubility of the pollutants, etc. Therefore, before beginning a full-scale remediation treatment, laboratory scale optimization is paramount. Moreover, correlating the physicochemical properties of the pesticide with its environmental fate, including its molecular weight, solubility, partition coefficient, reactivity with free radicals, etc., is essential to design the best remediation alternative material for effective pesticide removal. The chosen material should also be appropriate for the environmental conditions of the application region and depend on the readily available resources to boost the cost-effectiveness of the remediation strategy.

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