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Innovative Biosorbents from Agro-Waste: Advancing Sustainable Solutions for Heavy Metal, Dye, and Organic Pollutant Removal

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ABSTRACT

Ensuring clean water and safe food remains a global challenge due to the rising contamination of natural resources by heavy metals, dyes, and organic pollutants. This review highlights innovative, low-cost, and eco-friendly biosorbents derived from agricultural waste, presenting a comprehensive overview of their application in wastewater treatment. Unlike conventional reviews, this study categorizes a wide range of agro-waste materials including fruit peels, shells, husks, and plant residues according to their sorption properties and pollutant specificity. Notably, biosorbents such as activated carbon from rice husk, coconut shells, and banana peels demonstrated high adsorption capacities (up to 744.39 mg/g for dyes and 480.9 mg/g for heavy metals) under optimized conditions. The review further provides an in-depth analysis of chemical, thermal, and magnetic modifications that significantly enhance adsorption performance and selectivity. A key contribution of this work is the original economic analysis of these biosorbents, revealing their cost-effectiveness (as low as 0.49 €/kg) and practical scalability compared to commercial activated carbon. By integrating recent advancements, environmental implications, and regeneration potential, this review offers a valuable roadmap for researchers and practitioners aiming to implement sustainable, circular economy-based solutions in water purification systems.

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1. Introduction

The release of harmful substances into the environment, or pollution, continues to be a major issue that affects both human health and ecosystems [1]. When dangerous materials like waste, chemicals, and pollutants contaminate natural water bodies like rivers, lakes, and oceans, it is specifically referred to as water pollution and can have serious negative effects on the environment and human health [2, 3]. The urgent need for robust environmental conservation and management strategies is underscored by the grave threats posed by water pollution [4, 5].

Water pollution emerges from a complex interplay of natural processes and human-induced activities. Agricultural runoff, carrying fertilizers and pesticides, infiltrates water sources, precipitating nutrient imbalances and hazardous algal blooms [6, 7]. Industrial discharges introduce toxins and heavy metals, significantly compromising water quality [8]. Improper waste disposal methods and inadequate sewage treatment introduce pathogens, perpetuating contamination [9]. Urbanization exacerbates pollution through stormwater runoff, transporting pollutants from roads and construction sites [10, 11]. Oil spills and transportation activities release hydrocarbons into water bodies [12]. Additionally, deforestation and erosion contribute to elevated sediment levels, causing turbidity and disrupting aquatic habitats [13]. Climate change further exacerbates pollution by altering precipitation patterns and water temperatures [14, 15].

Effectively addressing water pollution necessitates comprehensive strategies that encompass these multifaceted sources, maintaining vital aquatic ecosystems and guaranteeing present and future generations have access to clean water [7, 16, 17]. The persistent increase in greenhouse gases from anthropogenic activities underscores the urgency for sustainable waste management strategies. Beyond water pollutants, agricultural waste-derived materials like biomass and biochar also hold promise for addressing broader environmental challenges, including CO2 capture, due to their cost-effectiveness, abundance, and versatile adsorption properties. While this review focuses on their application in wastewater treatment (e.g., heavy metal and dye removal), the principles of activation techniques and cyclic adsorption processes (e.g., PSA, TSA) discussed herein may inspire future cross-disciplinary applications in gas-phase pollutant mitigation [18].

Various methods serve in wastewater treatment to extract contaminants before discharge. While biological methods use microorganisms to break down organic matter, physical processes like screening and sedimentation remove large particles [19, 20]. Chemical approaches encompass coagulation, flocculation, and disinfection to eliminate impurities [21, 22]. Water quality is further improved by cutting-edge methods like membrane filtration, solar photo-oxidation, and activated carbon adsorption [23-25]. Their combination in treatment plants ensures comprehensive purification, ensuring environmental sustainability and public health protection [26, 27].

Adopting the most suitable wastewater treatment technique hinges on factors like existing pollutants, wastewater volume, compliance with environmental standards, and treatment objectives [9]. Each method boasts unique strengths. Biological processes effectively degrade organic matter, fitting for municipal wastewater treatment [28, 29]. Chemical methods like coagulation and disinfection are crucial for specific pollutant and pathogen removal [30]. Selected organic and inorganic pollutants and microorganisms can be effectively eliminated using advanced techniques [30]. The Fig. (**1**) illustrates a sketch outlining various techniques for treating industrial waste. The figure likely highlights methods such as physical, chemical, and biological processes, including filtration, sedimentation, chemical neutralization, and bioremediation. These techniques aim to reduce pollutants, recycle materials, and minimize environmental impact. The visual representation helps convey the complexity and diversity of waste treatment strategies employed in industrial settings to ensure sustainable and eco-friendly practices.

In practice, combining methods leverages their individual merits and addresses a broader contaminant spectrum [31]. This integrated approach ensures compliance with stringent water quality standards and comprehensive purification. Method selection or integration is site-specific, influenced by economic viability, technical capacities, and environmental considerations [32]. Because of its potential to manage waste and water pollution, the use of agricultural byproducts as adsorbents for wastewater treatment has attracted attention [33].

Materials like crop husks, shells, and stalks, typically regarded as waste, possess high surface area and porosity, making them excellent candidates for adsorption-based water treatment [34, 35].

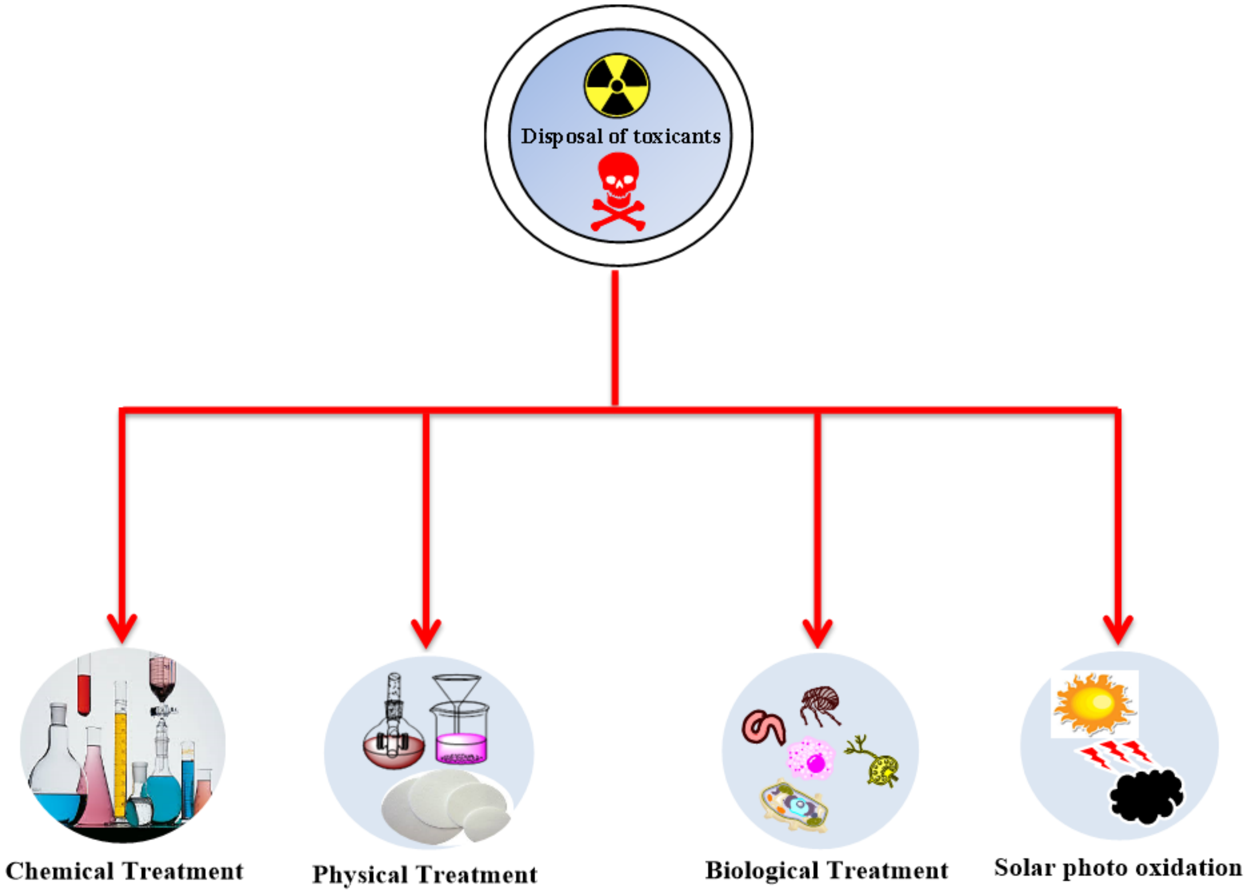

Figure 1: Flow sheet diagram of different methods for the disposal of toxicants.

Adsorption involves pollutants adhering to the adsorbent material's surface [36]. The porous nature of agricultural wastes provides a wealth of binding sites, which efficiently eliminate pollutants that endanger human health and the environment, such as organic compounds, heavy metals, and dyes [37-39]. Notably, employing agricultural byproducts as adsorbents is environmentally friendly, repurposing waste to assist in wastewater treatment and mitigating environmental impact [40]. It also presents a cost-effective solution, as these byproducts are often available at minimal or no cost [41]. However, challenges in adsorbent preparation, scalability, and regeneration persist. Research endeavors aim to enhance adsorption capacity, stability, and reusability of these materials.

The motivation for this study stems from the urgent need to develop sustainable, low-cost solutions for wastewater treatment amid growing environmental pollution from heavy metals, dyes, and organic contaminants. Conventional methods are often costly and environmentally taxing. In literature, several recent review papers discussing the adsorption efficiency of heavy metals and dyes using bio-based materials. However, this review presents several distinct contributions that differentiate it from the existing literature. Our review, in contrast to earlier research, concentrates on a thorough classification of biosorbents made exclusively from agricultural waste, including components like stone fruits, husks, shells, and fruit and vegetable peels. This targeted classification allows for a more detailed analysis of each material's adsorption properties and its suitability for different types of pollutants, offering a perspective that has not been extensively covered in earlier works. Furthermore, an important gap in the literature that this review addresses is the lack of economic analysis. While many studies explore the adsorption capabilities of bio-based materials, they often overlook the financial feasibility and scalability of these biosorbents for real-world wastewater treatment. Our review fills this gap by incorporating a thorough examination of the economic aspects, evaluating cost-effectiveness, resource availability, and potential for large-scale implementation, which is crucial for practical applications but underexplored in current research. Additionally, this review highlights the dual benefits of using agricultural waste, not only as an eco-friendly alternative for removing pollutants from water systems but also as a sustainable solution for waste management. This focus on the environmental impact and the promotion of a circular economy sets this work apart from other reviews that mainly emphasize pollutant removal without considering the broader sustainability implications. Lastly, our review emphasizes the need for further research on integrating these biosorbents into existing water treatment infrastructures and assessing their performance in real-world conditions, an area that remains underexplored in the literature. Researchers and practitioners looking for sustainable wastewater treatment solutions will find this review to be a useful resource as it fills in these particular gaps and provides fresh perspectives on the scalable and practical application of biosorbents derived from agricultural waste.

2. Water Pollution Caused by Heavy Metals

The existence of heavy metal pollutants in water arises from a variety of origins, encompassing industrial actions such as mining, smelting, and manufacturing [42]. Agricultural runoff, improper waste disposal, and corroded pipes also contribute [43]. Natural sources, such as geological formations, can release metals into water [44]. Contamination of water by heavy metals poses severe health and environmental risks. These hazardous substances, which include lead, mercury, and cadmium, seep into water sources as a result of improper waste disposal and industrial discharges [45]. Ingestion can lead to various health issues, making effective water quality management crucial for human and ecosystem well-being. Heavy metal exposure leads to severe health issues in humans, including lead-caused cognitive impairment, mercury-induced neurological damage, and cadmium-related kidney dysfunction [46-48]. Aquatic life suffers from metal accumulation, causing impaired growth, reproductive problems, and ecosystem disruption [49, 50]. Controlling metal release and minimizing exposure is imperative for both human health and aquatic biodiversity. Vigilance and control measures are vital to prevent widespread pollution and safeguard water quality.

3. Contamination of Water by Dyes

Aquatic life and human health are significantly impacted when dyes contaminate water. The presence of dyes, especially synthetic ones, in water bodies can have a negative impact on aquatic ecosystems, wildlife health, and human health because they are extremely toxic to both [51]. Hazardous dyes that have detrimental effects on aquatic life, human health, and the environment are found in the waste discharges from industries that use dyes. Because they are carcinogenic, dyes, particularly those containing organic contaminants, are bad for people and aquatic life [52]. Water quality is seriously threatened by organic contaminants, such as dyes, because of their acute toxicity and carcinogenic qualities [53]. Due to their poisonous nature and complex molecular structures, most dyes released into natural water are difficult for biodegradation. The presence of dyes in aquatic ecosystems has detrimental impacts on marine organisms and human well-being, primarily due to their harmful and potentially mutagenic consequences [54]. A large amount of dye consumption is made up of synthetic azo dyes, which, if discharged into water sources untreated, may reduce aquatic oxygen and interfere with photosynthetic processes. Additionally, azo dyes have the ability to bioaccumulate in people, which can have detrimental effects on neurological and respiratory health [55]. The global issue of environmental degradation due to harmful dyes in water is a matter of significant concern. Various sectors, like paper, leather, textiles, pigments, and more, release substantial quantities of noxious dyes into the surroundings, leading to water pollution. The proliferation of this pollution has become a prominent challenge for society in the 21st century, as the presence of harmful and non-biodegradable dye waste gives rise to a range of health issues in human populations [56]. Therefore, in order to address biological, ecological, and environmental issues, it is imperative that carcinogenic dyes be removed from industrial wastewater. Fig. (**2**) depicts the contamination of freshwater by heavy metals and dyes from various industrial and anthropogenic sources. The figure likely illustrates pollutants entering water bodies through discharges from factories, agricultural runoff, or urban waste, highlighting pathways like rivers or groundwater. It emphasizes the harmful impact of these contaminants on ecosystems and human health. The visual serves as a concise representation of pollution sources and their widespread effects on freshwater resources.

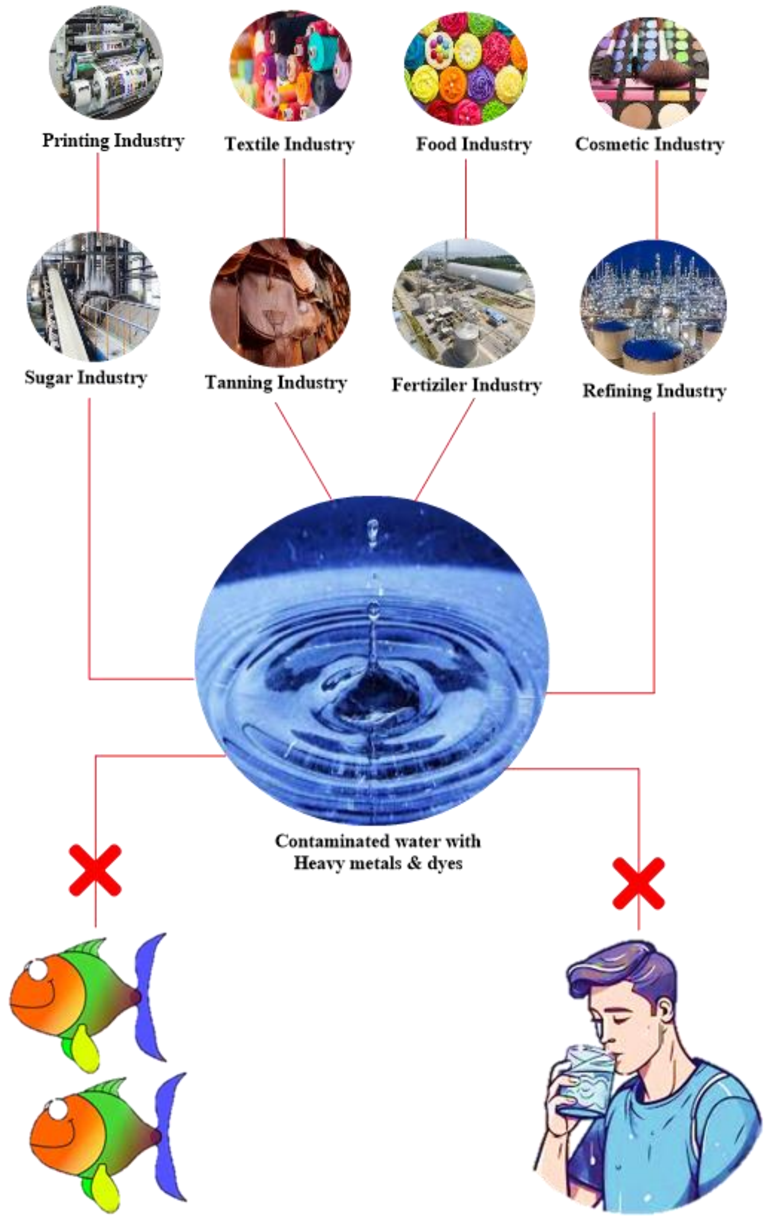

Figure 2: Mixing of heavy metals and dyes from different industrial sources. This contaminated water is unfit from drinking purpose and for aquatic life as well.

4. Turning Trash into Treasure: Agricultural Residue as Biosorption Materials

An economical and environmentally friendly substitute for water treatment procedures is the use of agricultural waste as adsorbents to remove heavy metals. Using agricultural waste as adsorbents promotes waste-to-wealth initiatives in addition to aiding in the removal of heavy metals. One specific heavy metal that has been extensively studied for removal using agricultural waste adsorbents is manganese. Adsorption has surfaced as a pragmatic and effective technique for eliminating manganese, with considerable focus directed towards agricultural waste adsorbents due to their economical nature and impressive efficacy [57]. The adsorption process depends heavily on the physicochemical characteristics of adsorbents made from bio-agricultural waste, including surface area, porosity, surface functional groups, pore distribution, and cation exchange capacity. In order to remove heavy metals from wastewater, date pits both raw and burned have been used extensively as adsorbents for agricultural waste. The high adsorption capacity and short adsorption time of date pit-based adsorbents have demonstrated encouraging results. Other agricultural wastes have also been investigated as possible adsorbents for the removal of different pollutants, including date palm biomass [58].

A variety of dyes, pesticides, herbicides, and other organic pollutants have been investigated for removal using agricultural waste adsorbents in addition to heavy metals. Comparative research has been done using both synthetic and actual textile dyeing effluents, and these unconventional, inexpensive adsorbents have demonstrated promise in the adsorption of dyes [59]. Agricultural waste can be altered chemically or physically, or it can be used directly. Fig. (**3**) illustrates the process of converting eggshells into a functional adsorbent for toxic metal removal. The figure likely depicts key steps such as eggshell collection, cleaning, processing (e.g., crushing or calcination), and application in wastewater treatment. It highlights the eggshell's porous structure and high calcium content, which enable efficient adsorption of heavy metals. This eco-friendly approach repurposes waste material into a sustainable solution for mitigating water pollution.

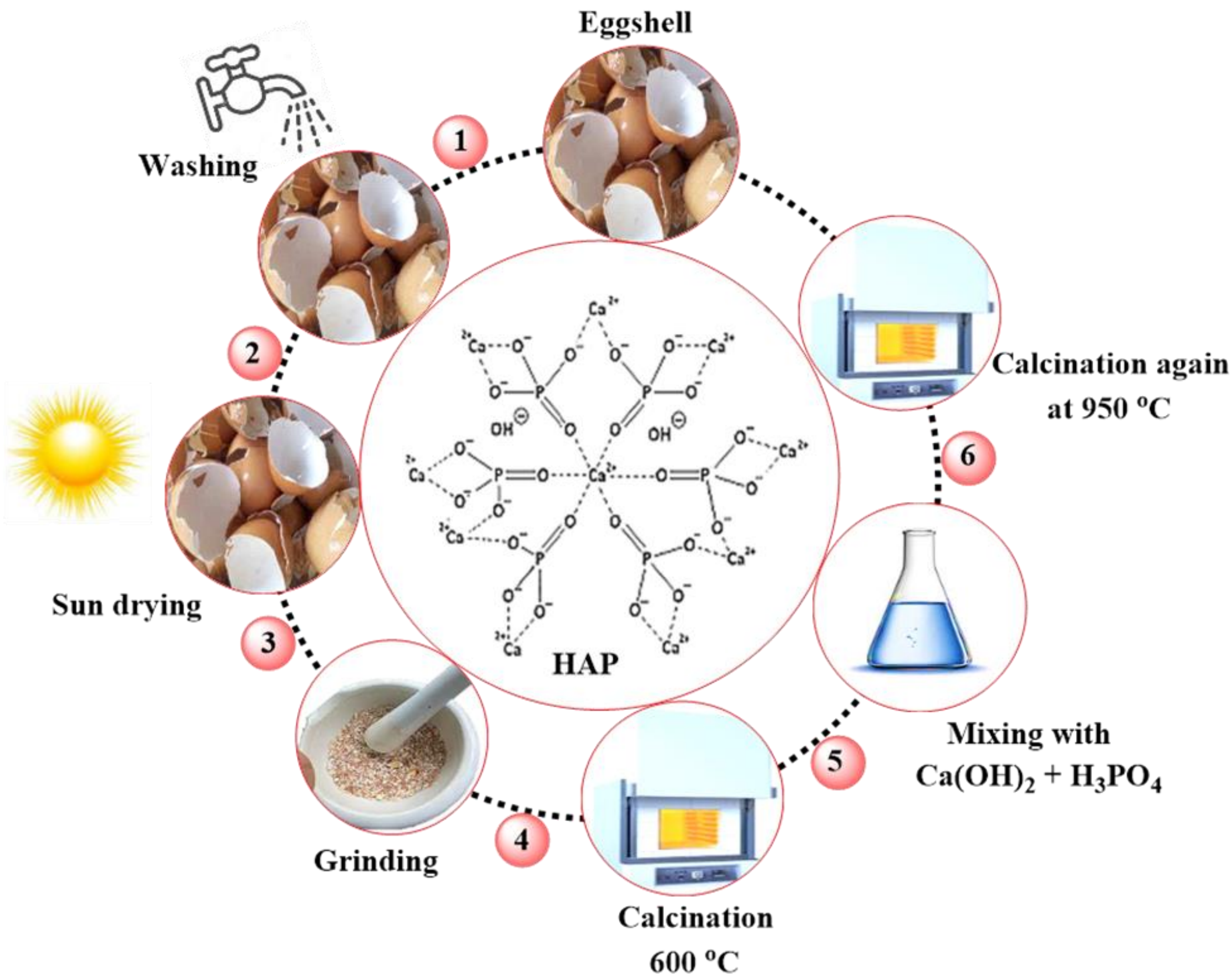

Figure 3: Conversion of eggshell into useful adsorbent for the removal of toxic metals.

Fig. (**4**) demonstrates the transformation of agricultural waste (e.g., rice husks, coconut shells, or straw) into effective adsorbents for pollutant removal. The figure likely outlines steps such as pretreatment (drying, grinding), activation (chemical or thermal), and application in wastewater treatment. By repurposing low-cost farm residues into porous, high-surface-area materials, this process offers a sustainable and economical solution for tackling contaminants like heavy metals or dyes while reducing agricultural waste.

4.1. Agricultural Waste-Activated Carbon

A carbonaceous material with an amorphous and microcrystalline structure is called activated carbon. It possesses notable porosity, physicochemical durability, adsorptive capability, mechanical robustness, level of surface reactivity, and surface area [60].

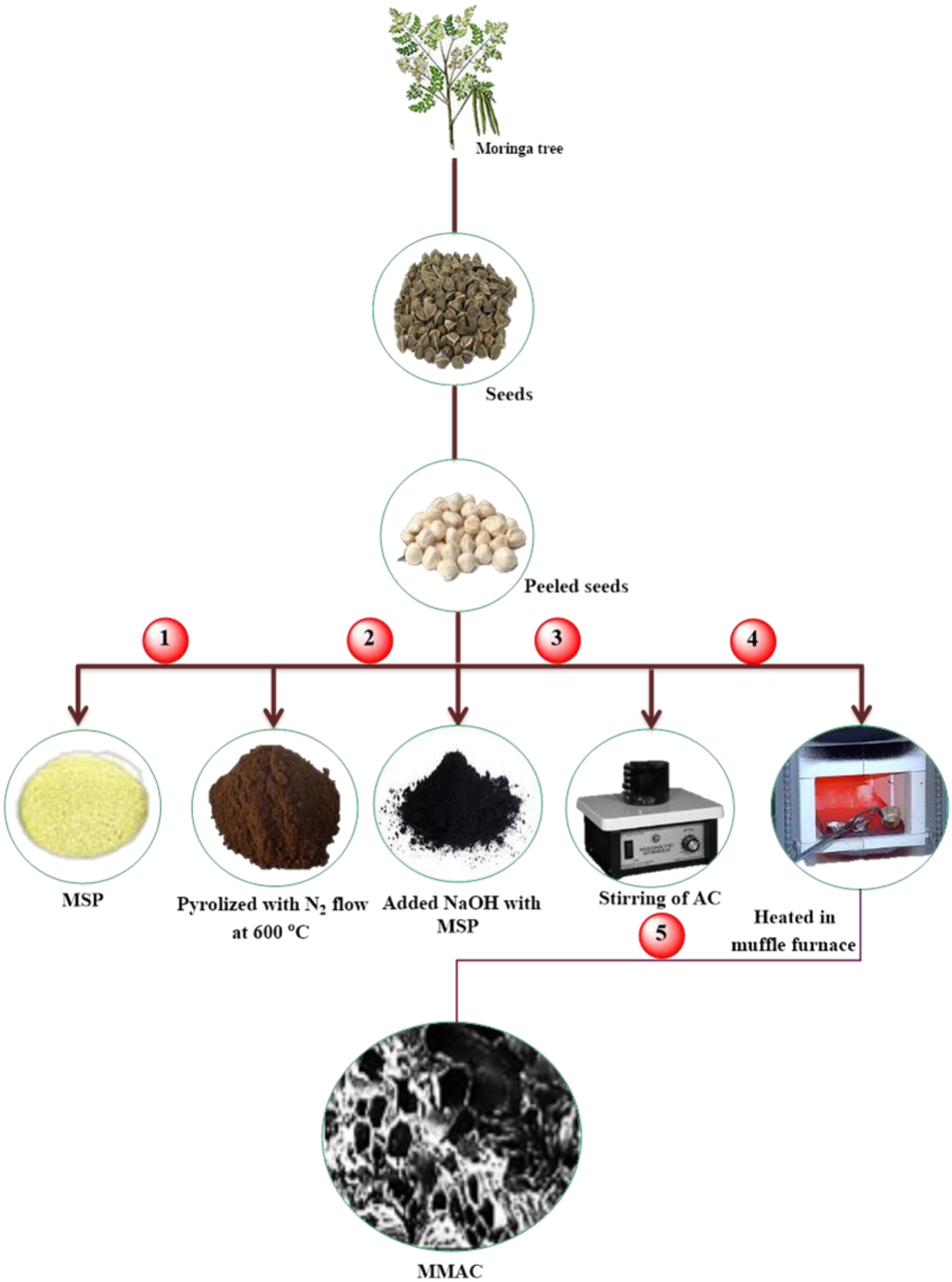

Figure 4: Conversion of agricultural wastes to useful adsorbents.

Because of the release of dangerous Cr^{6+} and other pollutants, the leather tanning industry contributes significantly to environmental pollution. To treat tannery effluents, two novel adsorbents were investigated: hydroxyapatite (HAP) and moringa-modified activated carbon (MMAC), which is made from eggshell and moringa seeds. They exhibited significant Cr^{6+} removal capacities: 295 mg/g for HAP, 280 mg/g for MMAC. These adsorbents also effectively eliminated Fe, Pd, Cu, and Zn (85% removal), as well as Cd, Ni, and Mn (70% removal). Testing in packed-bed reactors demonstrated a 15 min breakthrough time, highlighting their excellent regeneration potential

[61]. Fig. (**5**) compares the adsorption efficiency of two materials MMAC and HAP for removing various heavy metals from contaminated water. The figure likely presents bar graphs or curves showing metal uptake capacities, highlighting differences in performance based on material properties like surface area or chemical affinity. This visual underscores potential of engineered adsorbents in targeted pollutant removal, offering insights for optimizing water treatment strategies.

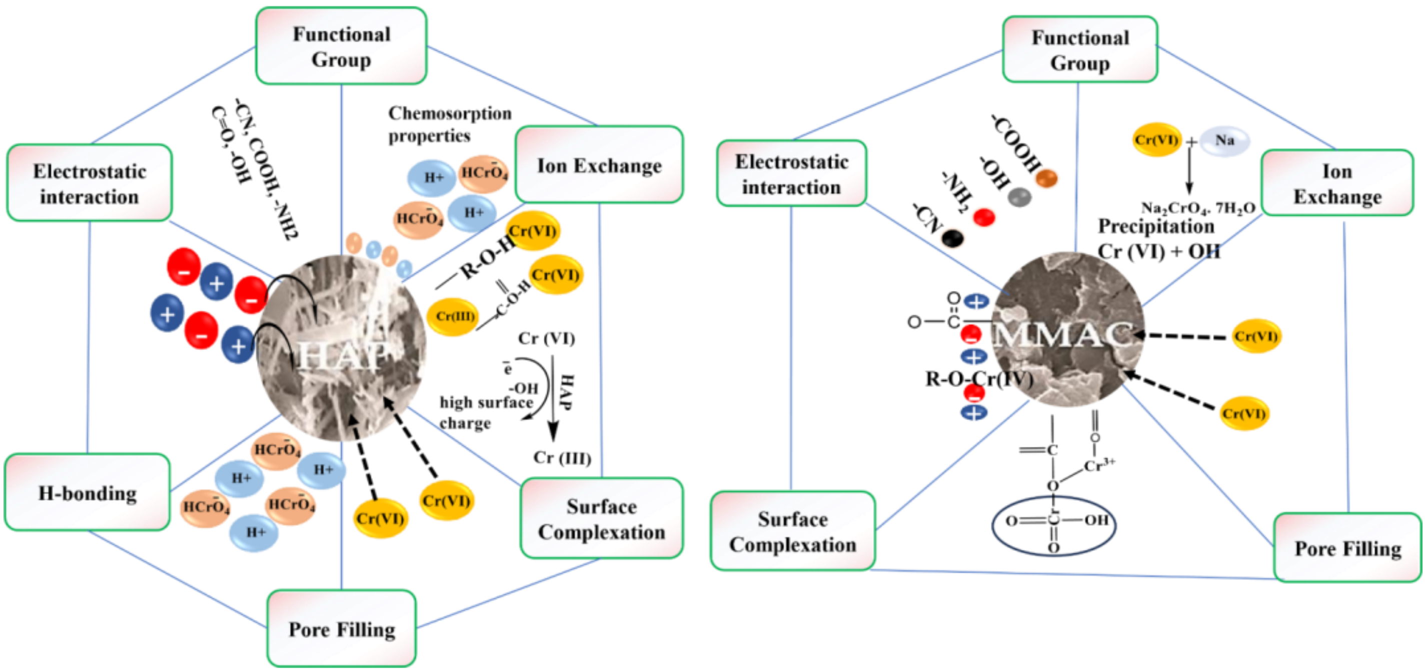

Figure 5: Adsorption of different metals by MMAC and HAP.

The adsorption efficiency of activated carbon in water treatment is largely dependent on its surface characteristics, including specific surface area, porosity, and other crucial surface characteristics. Activated carbon is made from agricultural waste [62]. The specific surface area (SSA), which indicates the available surface for adsorption, varies significantly based on the precursor material and the activation method [63]. For instance, activated carbon produced from rice husk can achieve an SSA of 1200–1800 m^2/g, with higher values generally leading to better adsorption performance. The functionality of activated carbon is also greatly influenced by its porosity, which is commonly divided into three categories: macropores (50 nm), mesopores (2–50 nm), and micropores (<2 nm). Microporous carbons are more effective for adsorbing small molecules like gases, while mesoporous structures are better suited for larger pollutants such as dyes. Coconut shell-derived activated carbon, for example, tends to have a high micropore volume, enhancing its capacity for heavy metal adsorption [64].

Furthermore, the pore volume of agricultural waste-derived activated carbon typically ranges from 0.3 to 1.2 cm^3/g**,** influenced by the type of activation process used. Chemical activators like potassium hydroxide are known to significantly increase the pore development, leading to improved adsorption capacity. Functional groups like hydroxyl, carboxyl, and carbonyl are another important surface characteristic that can increase the carbon's affinity for particular pollutants. Acidic functional groups can be added to the carbon by modifying it with substances like phosphoric acid, which enhances the adsorption of basic pollutants like dyes. To maximize the efficiency of activated carbon in water treatment applications, these surface characteristics SSA, porosity, pore volume, and surface functional groups are essential [65].

The use of industrial and leftover waste materials, as well as agricultural byproducts, to produce activated carbons has gained popularity recently. Activated carbon has been produced using a variety of agricultural waste materials as source materials. This encompasses substances such as walnut, coconut, and almond husks, in addition to peels from corn cobs, bananas and cassava, rice and wheat straw, pine wood, among numerous alternatives [66]. These agricultural waste materials are rich in cellulosic elements, commonly composed of cellulose, hemicellulose, lignin, and residual ash. They are very desirable as sources of carbon production because of their composition [67]. In a recent development, magnetic activated carbon was synthesized using seaweed algae. This unique material displayed magnetic characteristics and was utilized to remove Zn^{2+}, Cd^{2+}, and Cu^{2+} from solution environments. The study demonstrated that the biosorption process achieved an average reduction in the concentration of each metal by at least 90% over a 24 h period [68].

Furthermore, a magnetically enhanced biochar referred to as CMB, derived from banana peels, demonstrated remarkable abilities in biosorption. When only 0.05 mg of CMB was used, it displayed a high capacity for biosorbing Hg^{2+}, Cu^{2+} and Zn^{2+} in separate systems. The biosorption process was particularly efficient at pH 6 and within a short span of 3 h, with biosorption capacities of 72.8 mg/g for Zn^{2+}, 75.9 mg/g for Cu^{2+}, and 83.4 mg/g for Hg^{2+}. However, when examining ternary systems where all three metals were present, it was observed that the presence of Hg^{2+} substantially hindered the uptake of Zn^{2+} and Cu^{2+}. However, within these ternary systems, the CMB substance exhibited a stronger biosorption inclination towards Hg^{2+} when contrasted with Cu^{2+} and Zn^{2+} [69]. Activated charcoal made from a blend of rice pomace, millet stalks, and cashew shells was recently tested as an adsorbent substance. A layer of Fe^{3+} ions was applied to this charcoal to amplify its chemical attraction to the oxyanion As^{4+}. The results revealed a range of adsorption affinities between 0.236 to 0.301 mg/g for the removal of As^{4+} [70]. Activated carbon adsorbents have been widely used for the extraction of a variety of organic compounds in addition to efficiently removing metal ions. This utilization has been observed both within controlled laboratory environments and with wastewater samples obtained directly from sources. While most biosorption experiments have been conducted using the batch mode, there have also been endeavors to explore column-based studies.

By way of illustration, activated carbon sourced from coconut shells was utilized as a segregating medium to appraise the separation of pentachlorophenol using simulated solutions. With a sorption capacity of 36.82 mg/g, the resulting biosorbent demonstrated its efficacy under mild and commercially feasible conditions. This was particularly noticeable when a temperature of 37°C and a contact time of 6 hours were taken into account [71]. These promising outcomes provide a strong basis for extending the use of biosorbents in real-world wastewater treatment systems. The adsorption of ammonia nitrogen and S^{2-} ions from leachate was examined in a study by Erabee *et al*. For this, they used coconut shells that had been chemically altered and treated with $KMnO_4$.

The research suggested that the sorbent's positively charged surface enabled a successful attachment of ammonia and S^{2-}, resulting in biosorption capacities of 0.1979 and 0.0065 mg/g, respectively [72]. Carbamazepine, a common pharmaceutical contaminant in surface waters, was effectively removed by pine wood-derived activated carbon at very low concentrations (0.5–20 μg/L) and over a wide pH range (3.0–8.0). After three hours, nano-biochar showed 0.074 μg/g of adsorption capacity. Furthermore, the efficiency of adsorption was increased by raising the pH from 3 to 8 [73]. Carbon with a hierarchical porous structure derived from banana peels demonstrated proficiency in capturing MB and Rhodamine B. This material achieved full adsorption of the dyes when exposed to a laboratory sample with an initial concentration of 1000 ppm. The capacities recorded were 744.39 mg/g for MB and 520.29 mg/g for Rhodamine B [74]. Anaerobic bio-filtration was used to remove 88% of COD, 71% of TSS, and 93% of turbidity from wastewater samples that were directly taken from sources. These treated samples were then subjected to activated carbon separation utilizing rice pomace. This process led to a 52% COD reduction and a 63% turbidity decrease [75]. In 2017, a study conducted by Devi *et al*. confirmed the effectiveness of powdered activated carbon obtained from walnut shells. The study focused on treating refinery wastewater sourced from Oman. This carbon successfully achieved a 79% reduction in COD while operating in a slightly acidic environment at pH 6 [76]. Globally, treating wastewater from industrial, domestic, and agricultural sources is critical. Heavy metals, a major water pollutant, demand attention due to their persistence and toxicity. This study investigated mango seeds in raw and activated carbon/zinc oxide nanocomposite forms for removing lead from water. The adsorbents showed high capacities and efficiency, particularly at 45°C, with favorable kinetics and chemisorption characteristics. Thermodynamic analysis supported their effectiveness in lead removal [77].

Utilizing magnetic carbon nanocomposites derived from agricultural waste has proven highly effective in eliminating various metal contaminants. Using magnetic carbon nanocomposites made from tea waste, kan grass, palm waste, and sugarcane bagasse, this method recently successfully removed arsenic (As) [78-81]. The As adsorption rates, which ranged from 2.0 mg/g to 153.8 mg/g, showed notable variation among the various magnetic carbon composites. The initial As concentration, the properties of the carbon material, the size of the particles, temperature, pH, and the dosage of the adsorbent are some of the variables that affect the As adsorption process [82]. With an astounding maximum rate of 153.8 mg/g, spent tea-derived magnetic carbon composites remarkably demonstrated the most significant As adsorption capacity when wastewater treatment was taken into account. Turning to the adsorption study involving lead (Pb), alternative biomass materials like spent bleaching earth, Myrtus communis leaves, and biomass waste were employed. These materials demonstrated a broad range of Pb adsorption capabilities, spanning from 100 to 480.90 mg/g. Similarly, diverse materials such as walnut shell and rice husk, sunflower head waste, and orange peel powder were investigated for their ability to adsorb cadmium (Cd). Across these materials, the Cd adsorption range extended from 2.15 to 76.92 mg/g. Fig. (**6**) illustrates the synthesis of magnetic activated carbon from agricultural waste using iron chloride ($FeCl_3$) as an activating agent. The figure likely outlines key steps: waste pretreatment, carbonization, $FeCl_3$ impregnation, and magnetization, resulting in a high-efficiency adsorbent. The magnetic property enables easy separation after pollutant adsorption. This process transforms low-value agricultural residues into a functional material for removing contaminants like heavy metals or dyes, combining sustainability with advanced water treatment technology.

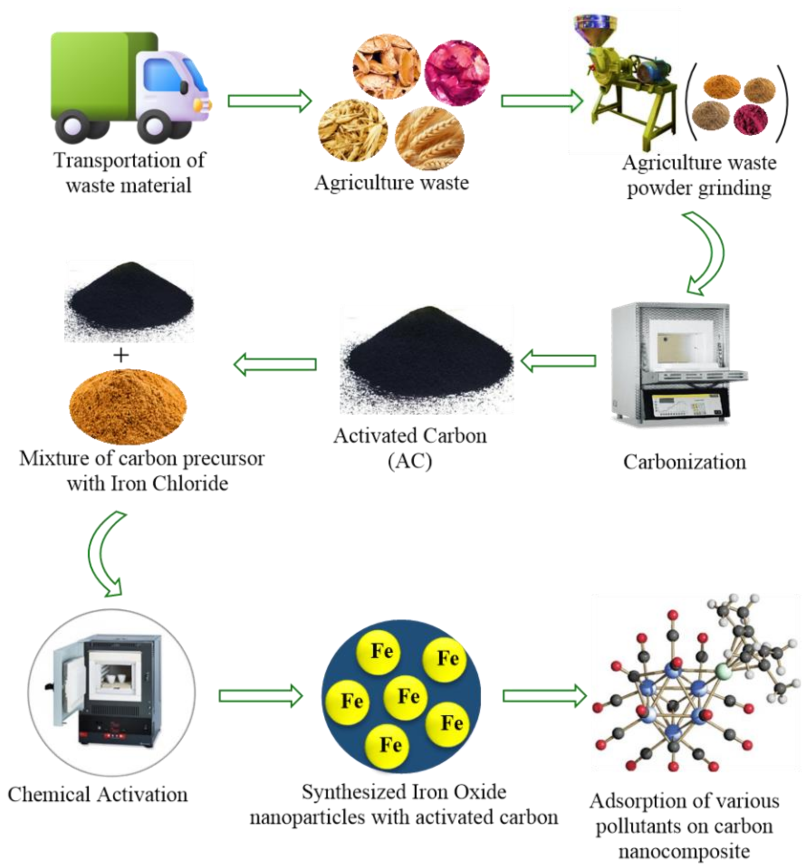

Figure 6: Synthesis of magnetic activated carbon from agricultural waste using iron chloride for pollutant adsorption.

In addition to wastewater treatment, compost derived from mechanical-biological treatment of municipal solid waste has been explored as a low-cost precursor for activated carbon (AC) adsorbents for CO_2 capture [83]. Chemical treatment with sulfuric acid followed by thermal activation at 400–800°C under N_2 yielded a material achieving a CO_2 uptake of 2.6 mol/kg at 40°C. A PSA-based model further validated its potential as a sustainable adsorbent for greenhouse gas mitigation, expanding the versatility of waste-derived carbons [84].

4.1.1. Pretreatment and Modification of Carbon-Based Materials for Activated Carbon

Understanding how various carbonization/activation conditions, the kind of precursor, and the activating agents used affect the final surface and adsorption properties of activated carbons is crucial when pretreatment and modification of carbon-based materials for activated carbon synthesis [85]. Several studies provide insights into these aspects, helping to better understand the performance of biosorbents in wastewater treatment.

4.1.1.1. Pretreatment and Type of Precursor

Effective pretreatments such as water washing, acid washing, and alkaline washing enhanced the activated carbon's adsorption capacity [86]. The physical and chemical properties of the activated carbon are largely determined by the choice of the agricultural waste precursor [85]. Activated carbon frequently has a high micropore volume and specific surface area, which makes it useful for adsorbing heavy metals, dyes, and other pollutants. Agricultural by-products like coconut shells, rice husks, and fruit peels each have distinct qualities like cellulose content, lignin, and hemicellulose that affect their behavior during carbonization and activation [87].

4.1.1.2. Carbonization and Activation Conditions

The porosity, surface area, and pore size distribution of activated carbon are all directly impacted by the temperature and carbonization time [88]. Micropores usually form at lower temperatures (400–600°C), whereas mesopores and macropores prefer to form at higher temperatures (800–1000°C) [89]. Activation conditions, whether physical (using gases like CO_2 or steam) or chemical (using activating agents like KOH, H_3PO_4, or $ZnCl_2$), dramatically influence pore structure and adsorption capacity. One well-known method for creating a well-developed microporous structure and greatly increasing the specific surface area is chemical activation with KOH. This makes it perfect for adsorbing smaller molecules, such as heavy metals [90].

4.1.1.3. Effects of Activating Agents

The final chemical and textural characteristics of activated carbon are determined by the activating agent selection. KOH activation often leads to a higher microporosity, increasing the surface area, while agents like H_3PO_4 tend to generate mesoporous structures suitable for adsorbing larger organic molecules such as dyes. Studies have shown that using $ZnCl_2$ as an activator produces activated carbon with high mesopores volumes, making it effective for organic pollutants [91].

4.1.1.4. Functional Groups

The activation process also influences the surface functional groups, with oxygen-containing groups like carboxyls and hydroxyls significantly improving adsorption performance, especially for heavy metal ions and dyes [92]. There are several methods, both chemical and physical, to add oxygen atoms. Introducing the different functional groups of acid and base modifications makes the surface of activated carbon more efficient for adsorption. Fig. (**7**) highlights the role of pretreatment methods (e.g., chemical, thermal, or physical activation) in enhancing the adsorption capacity of agricultural waste-derived activated carbon. The figure likely compares raw and pretreated materials, showcasing improvements in porosity, surface area, or functional groups that boost pollutant removal efficiency. This optimization step is critical for transforming low-cost agro-residues into high-performance adsorbents, offering a sustainable approach to water purification and waste valorization.

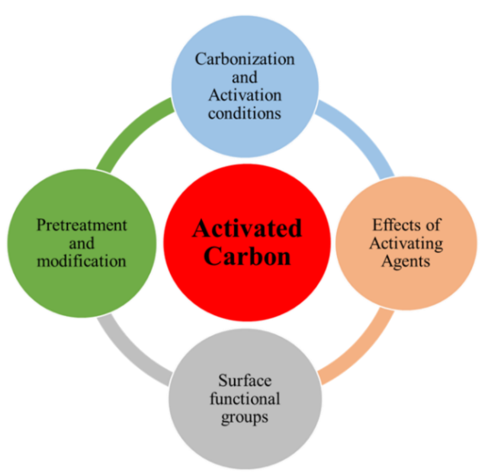

Figure 7: Enhancing adsorption via pretreatment of agri-waste activated carbon.

By adjusting the carbonization and activation conditions, and carefully selecting both the precursor material and activating agent, the surface area, pore structure, and chemical functionality can be tailored to meet specific wastewater treatment needs. The various methods employed to enhance the dye and heavy metal removal performance of materials, along with a comparison of their differences in performance among various materials, are tabulated in Table **1**. This comprehensive overview highlights the key strategies and their respective effectiveness, enabling a clear understanding of the advancements in material performance.

Table 1: Discussed various methods to enhance the dye/heavy metal removal performance of the materials while also comparing the differences in performance among different materials.

Category	Agricultural Waste Materials	Performance/Effect	Comparison	Ref.
Raw AgriculturalWaste	Rice husk	Moderate adsorption capacity for heavy metals and dyes	Rice husk performs well for low-cost applications but may require modification for better efficiency.	[93]
	Corncob	Moderate dye removal efficiency	Corncob-derived materials show moderate performance but are widely available and cheap.	[94]
	Sugarcane bagasse	Good adsorption for both dyes and heavy metals	Sugarcane bagasse is an effective low-cost adsorbent with potential for surface modifications.	[95]
Biochar from Agricultural Waste	Rice husk biochar	Enhanced surface area and adsorption capacity for heavy metals	Biochar derived from rice husk shows improved performance over raw rice husk, especially for lead and cadmium removal.	[96]
	Corncob biochar	High dye adsorption efficiency, especially for organic dyes	Corncob biochar shows significant improvement in dye removal compared to raw corncob.	[97]
	Coconut shell biochar	High surface area, good adsorption capacity for metals and dyes	Coconut shell biochar outperforms many other agricultural biochars, with high porosity and adsorption capacity.	[98]
	Sawdust biochar	Good adsorption for cationic dyes and metal ions	Sawdust biochar is low-cost but requires activation or modification for competitive performance.	[99]
Surface Modification of Waste	Acid-treated rice husk	Higher adsorption capacity for dyes and heavy metals	Acid treatment of rice husk enhances removal efficiency through increased surface area and functional group exposure.	[93]
	Chemically activated coconut shell biochar	Excellent adsorption capacity for heavy metals (Pb, Cd)	Chemical activation significantly enhances coconut shell biochar's adsorption properties, making it competitive with synthetic adsorbents.	[100]
	Magnetically modified corncob biochar	Easy recovery, high removal efficiency for metal ions	Magnetic modification enables easy separation, maintaining high adsorption capacity.	[101]
Thermal/ Physical Activation	Rice husk ash (thermal activation)	Increased porosity, improved heavy metal adsorption	Rice husk ash performs well due to its increased surface area, especially in lead and chromium adsorption.	[96]
	Physically activated sawdust biochar	Higher surface area, better adsorption capacity	Physical activation enhances sawdust biochar's adsorption, making it comparable to more expensive adsorbents.	[102]
Composite Formation	Corncob biochar with graphene oxide	Synergistic effects, high adsorption capacity for dyes and heavy metals	Corncob biochar/graphene oxide composites show much better performance than raw or biochar alone.	[103]
	Bagasse-based composites with metal oxides	Enhanced metal ion removal through improved surface interactions	Metal oxide composites improve bagasse biochars metal ion removal, especially for arsenic and chromium.	[104]

Table 1 contd….

Category	Agricultural Waste Materials	Performance/Effect	Comparison	Ref.
pH Optimization	Rice husk biochar (pH sensitive)	Improved adsorption of cationic heavy metals at low pH	pH control is crucial, as rice husk biochar performs best under acidic conditions.	[93]
	Sugarcane bagasse biochar (pH sensitive)	Effective dye removal at acidic to neutral pH	Bagasse biochar shows good dye removal, especially for cationic dyes under acidic conditions.	[95]
Adsorption Capacity	Coconut shell biochar	High capacity for heavy metals	Coconut shell biochar often shows superior adsorption capacity compared to other agricultural wastes like rice husk.	[105]
	Banana peel biochar	High adsorption for organic dyes	Banana peel biochar has high dye adsorption capacities, especially for methylene blue and other organic dyes.	[106]
Selectivity	Rice husk biochar	Selective adsorption for metal ions (Pb, Cu, Cd)	Rice husk biochar shows selective removal of specific heavy metals based on ionic radius and charge.	[107]
	Orange peel biochar	High selectivity for anionic dyes	Orange peel biochar works well for anionic dyes like Congo red.	[108]
Adsorption Kinetics	Corncob biochar	Fast kinetics for dye adsorption	Corncob biochar achieves equilibrium quickly compared to other waste-derived adsorbents.	[109]
	Coconut shell biochar	Moderate to fast kinetics for heavy metal removal	Coconut shell biochar shows better kinetics for metal ions than most other biochar materials.	[110]
Reusability & Regeneration	Rice husk biochar	Up to 5 cycles with moderate loss of efficiency	Rice husk biochar can be reused multiple times, though efficiency decreases after each cycle.	[111]
	Sugarcane bagasse biochar	4-6 cycles with stable efficiency	Bagasse biochar shows good reusability, retaining high performance over several regeneration cycles.	[112]
Environmental/ Economic Impact	All agricultural waste biochars	Low cost, eco-friendly, sustainable	Agricultural waste-based adsorbents are cost-effective and environmentally friendly, though sometimes less efficient than synthetic materials.	[113]

4.2. Agricultural Plant-derived Biosorbents

Effective materials for eliminating organic pollutants, dyes, and heavy metals from contaminated sites and wastewater are currently receiving attention. The source of these materials is agricultural plants. Metal ions or other contaminants attaching to the surface of a biosorbent made from biological sources is known as biosorption, a metabolically passive physicochemical phenomenon [114]. Biosorbents can originate from a variety of sources, such as microorganisms, plant-derived materials, industrial or agricultural waste, biopolymers, and other materials used for biological removal [115]. One of the advantages of using plant-derived biosorbents is their operational simplicity and low operational cost.

Variables like pH, temperature, and contact time have a big impact on how well agricultural waste biosorbents treat water. Because the surface charge of the biosorbent and the ionization state of the contaminants are highly dependent on pH, the majority of biosorbents show optimal adsorption efficiency in mildly acidic to neutral conditions, usually within a pH range of 5.0 to 7.0. Temperature also plays a crucial role, with adsorption efficiency generally increasing within an optimal range of 25–30°C due to the enhanced mobility of contaminants and faster diffusion into the biosorbent's pores. Additionally, prolonged contact time allows for more effective contaminant-biosorbent interactions, with an ideal range typically between 60 and 150 minutes, depending on the specific contaminant and the type of biosorbent used. Understanding these optimal conditions helps in assessing and optimizing the performance of biosorbents for various water treatment applications, thus reinforcing their efficiency and practical applicability. Acid blue 193 has been adsorbed from contaminated water using apricot seed shell powder (ASP), an adsorbent substance. Acid blue 193's ability to adsorb onto ASP was shown to be affected by the adsorbent dose, pH, contact time, and dye concentration in the solution. At these optimal conditions, the maximum adsorption of acid Blue 193 was 104.65 mg/g [116]. Another study sought to determine whether it was feasible to extract the metal ions from the adsorbent for later use and how well sugarcane bagasse removed Pb (II) and Ni (II) from untreated wastewater. Investigated were the effects of temperature (30–70 °C), pH (4-6), contact time (30–150 min), and adsorbent dosage (0.3–0.7 g). At pH 6.0, 30 °C, 90 minutes of contact time, and 0.5 g of adsorbent dosage, the highest removal efficiency of Pb (89.31%) and Ni (96.33%) was attained [117].

Biosorption is a rapid and reversible process that occurs when ions bind to the functional groups on the surface of the biosorbent in watery solutions. This process does not require additional nutrients or increased chemical oxygen in water, and it generates a low quantity of sludge. Additionally, plant-derived biosorbents have the ability to be regenerated and reused, further enhancing their cost-effectiveness. The application of nitric acid and tetraethylenepentamine to amino-functionalized wheat straw was employed for the purpose of eliminating Cr^{6+} from a wastewater sample. This sample, stemming from the production of electrical panels in China and possessing a pH of 2.2, achieved a purification level exceeding 90% [118]. Additionally, using Eupatorium adenophorum weeds and wheat straw together showed an adsorption capacity of 89.22 mg/g over three hours, effectively removing Cr^{6+} from the solution at a pH of 1.0 [119]. The experiment encompassed treating barley straw with phosphoric acid impregnation and subjecting it to microwave radiation. This was done to modify the straw for the removal of norfloxacin at concentrations within the milligrams per liter spectrum. Conducting adsorption tests under neutral pH conditions, using 5.0 mg of adsorbent and a pollutant concentration of 100 ppm, revealed notable sorption capacities. These capacities were 349 mg/g, 359 mg/g, 387 mg/g, and 441 mg/g, corresponding to experimental temperatures of 25°C, 35°C, 45°C, and 55°C [120]. Corn cob and sugar cane, both regarded as waste materials, were employed to effectively remove the organic pollutant chlortetracycline. Notably, both biosorbents showcased removal efficiencies exceeding 90%, achieving their best performance with an optimal reaction duration of 20 h [121]. Distinct variations were noted in the optimal pH value required for the effective removal of MB. The enhanced adsorption was particularly noticeable in conditions ranging from slightly acidic to acidic.

By enhancing corn straw through citric acid and graphene oxide modification, a removal rate of over 80 % for MB was attained at a pH of 8 [122]. Similarly, the processed residue of Salvia miltiorrhiza Bunge achieved a removal rate exceeding 90% for methylene blue at pH 7. The effectiveness of eliminating methylene blue from wastewater was showcased through a synergistic approach that combined biodegradation and biosorption. As an example, the pairing of rice straw with the white rot fungus *Phanerochaete chrysosporium succeeded* in removing 88% of MB at a pH of 5.0. Of the dye's removal, 28.4% was attributed to biodegradation by P. chrysosporium, while the biodegraded rice straw and fungal cells adsorbed the remaining portion [122]. A similar investigation was carried out using rice straw and *Bacillus subtilis* [123]. By utilizing 0.5 g of rice straw and 0.2 mL of spore suspensions, this method accomplished a removal rate that surpassed 90% for methylene blue under a pH of 7.0. The collaboration of both *P. chrysosporium* and *B. subtilis* led to expanded specific surface areas and the creation of extra functional groups on the straw, resulting in a substantial improvement in the removal of methylene blue. Moreover, microbial biodegradation also played a pivotal role in eliminating the dye. The extent of (azo) dye removal was notably influenced by various experimental parameters, with reaction duration emerging as a consistent influencing factor.

The effectiveness in removing (azo) dyes exhibited significant variability, underscoring the significance of evaluating biosorbents derived from plant materials due to their widespread availability and economical production on a global level. The efficacy of agricultural plant-derived biosorbents in eliminating heavy metals has been convincingly demonstrated in numerous research studies. As an illustration, biosorbents originating from agricultural waste materials have demonstrated their efficiency in adsorbing heavy metal copper (Cu) from wastewater. The attributes of the biosorbent, including surface area and pore structure, hold a pivotal role in determining its capacity to adsorb heavy metals [124]. Similarly, bacterial augmented floating treatment wetlands (FTWs) using plant-based biosorbents have shown high removal rates of heavy metals from dye-enriched wastewater [125]. The use of agricultural waste as biosorbents is particularly promising due to their high surface areas, microporous attributes, and surface chemical nature. These waste-derived biosorbents offer a low-cost alternative to expensive materials like activated carbon, which is commonly used for adsorption [126]. Moreover, biosorbents sourced from agricultural waste have proven to be efficient in the elimination of heavy metals from both water and wastewater [127].

4.3. Stone Fruit-based Sorbents

Stone fruit-derived adsorbents have been recognized as a cost-effective solution for the removal of dyes and heavy metals from wastewater. These materials can be directly applied without the need for chemical or physical alteration, making them convenient for wastewater treatment. Fig. (**8**) illustrates the modification of fruit waste seeds into functionalized biochar for wastewater treatment. The figure likely depicts steps such as pyrolysis, chemical activation, or surface modification to enhance the biochar's porosity and introduce oxygen/nitrogen-rich groups. These modifications improve its affinity for dyes and heavy metals, enabling efficient adsorption. The process repurposes agricultural byproducts into a sustainable, high-performance adsorbent, addressing both waste management and water pollution challenges [128].

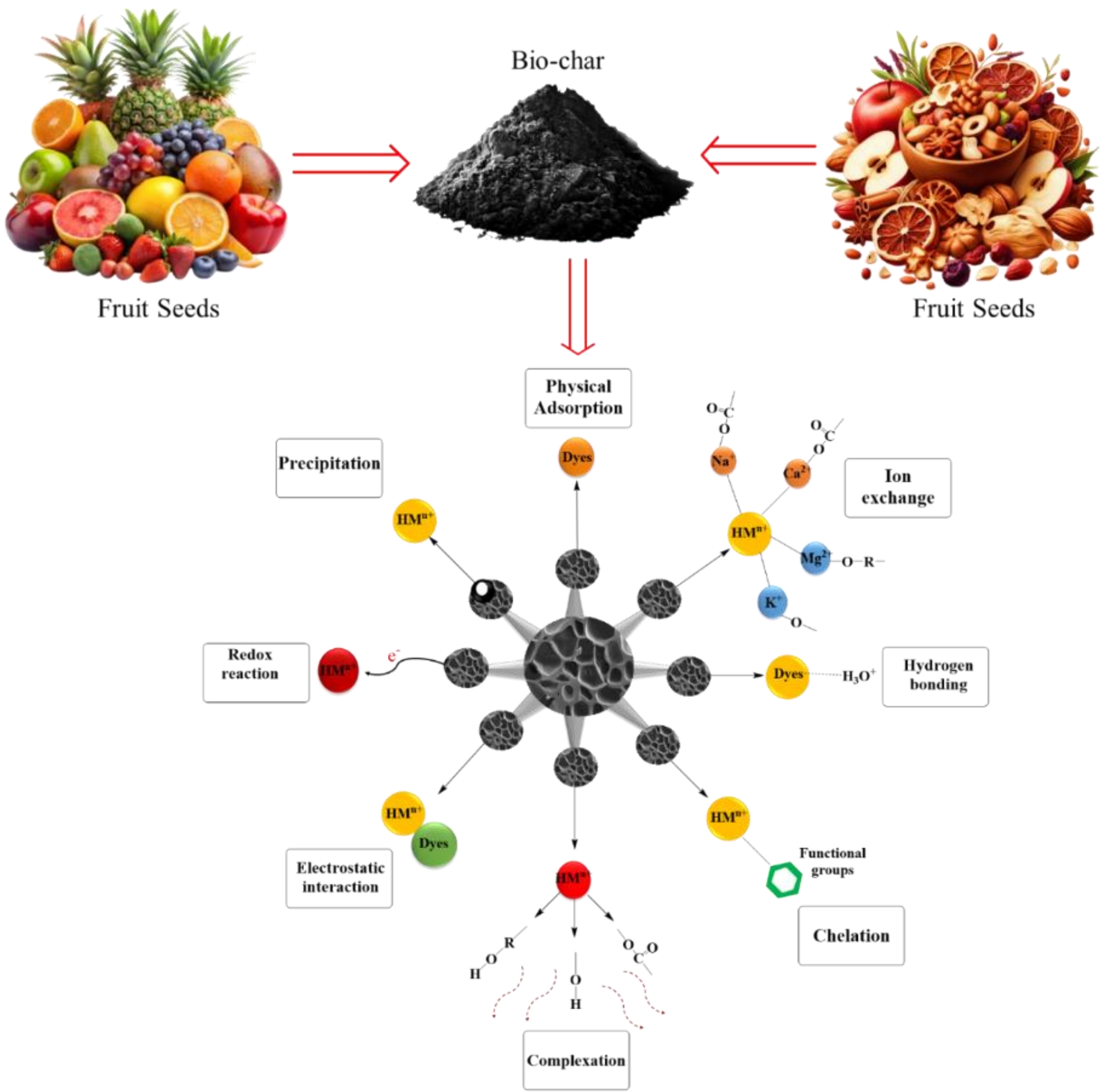

Figure 8: Modified fruit waste seeds form biochar rich in functional groups for dye and heavy metal adsorption in wastewater treatment.

The adsorption of different heavy metals or other organic pollutants by stone fruit-based sorbents is strongly pH-dependent. Materials derived from stone fruits exhibit their highest adsorption efficiency for a variety of metal ions, such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+}, within the optimal pH range of approximately 5 to 5.5 [129, 130]. Nevertheless, the optimal pH levels diverged, with a pH of 6 identified for As^{3+} and a pH of 2 for Cr^{6+}. In the case of eliminating methylene blue dye, both peach shell and stone materials showcased their highest efficiency at a pH of 5.5 [131]. The case of simultaneous biosorption provides an illustrative example of the competitive mechanism. This is evident from the lower efficiency observed when using Carica papaya seed-modified feldspar clay for removing Cu^{2+} and Pb^{2+} ions compared to the removal efficiency for individual metal solutions [132]. This phenomenon, known as antagonistic biosorption, led to decreasing percentage removals of both metal ions as their initial concentrations enhanced from 100 to 600 ppm. Specifically, the removal rates dropped from 89.6% to 62.3% for Cu^{2+} and from 94.7% to 68.9% for Pb^{2+}. The decline in removal efficiency with increasing metal concentration can be attributed to the saturation of the available active sites on the adsorbents. This observation holds significance due to the potential use of waste materials for purifying wastewater samples containing various inorganic and organic impurities [133]. In such situations, the simultaneous adsorption of adsorbates that are not chemically related may lead to competition, highlighting the need for a thorough investigation involving representative molecules from all the specific chemical categories being targeted. The potential of discarded fruit stones/pits as bio-waste materials for the removal of methylene blue has been substantiated. Within the pH range of 5.5, across initial concentrations spanning 200 to 400 ppm and utilizing adsorbent masses from 0.001 to 0.1 g, these materials displayed sorption capacities varying from 178.25 to 444.4 mg/g [131, 134, 135]. Biosorbents that have undergone chemical or physical alterations have demonstrated enhanced biosorption capabilities when compared to their untreated counterparts. Monroy-Figueroa's comparative study on the biosorption of Cd^{2+} and Ni^{2+} ions using both unmodified and chemically modified *Byrsonima crassifolia* endocarp emphasized the significant potential of chemical modification in this context [136]. The activation of peach material with citric acid revealed encouraging prospects, as it effectively eliminated Cu^{2+}, Pb^{2+}, and Cd^{2+} with sorption capacities measuring 118.76, 93.4, and 89.6 mg/g, respectively [134]. Following treatment with tartaric, citric, or sulfuric acid, avocado pits demonstrated elevated sorption capacities for Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} (ranging from 3.3 to 21.8 mg/g), which were notably higher than those exhibited by untreated avocado seeds (ranging from 2.5 to 5.6 mg/g) [130]. Furthermore, when alkalized apricot stone waste was employed, it displayed effective elimination of Cu^{2+}, Pb^{2+}, and Zn^{2+} from a solution containing 400 ppm of metal ions and maintained at a pH of 5.0. With a biosorbent mass of 0.5 g, it accomplished removal rates of 81% for Cu^{2+}, 87% for Pb^{2+}, and an impressive 97% for Zn^{2+}. Notably, alkalized peach kernels demonstrated 2 to 3 times higher sorption capacities than their natural counterparts [129].

4.4. Husk and Shell-based Adsorbents

The use of husks and shells as biosorbents has gained attention due to their abundant availability and potential for heavy metal removal. Fig. (**9**) demonstrates the detoxification of pollutants using modified agricultural husks and shells as adsorbents. The figure likely showcases the treatment process, where these low-cost materials chemically or thermally enhanced are employed to capture and neutralize contaminants like heavy metals or organic dyes from wastewater. By leveraging their natural porosity and modified surface properties, these adsorbents provide an eco-friendly and cost-effective solution for water purification while repurposing agricultural byproducts [137]. The high surface area and presence of functional groups in husks and shells contribute to their adsorption capacity. Volatile organic compounds (VOCs) and odors, key indoor air pollutants affecting health, were studied. Ammonia adsorption onto biomass rice husk-based adsorbents (silica carbon composite, activated carbon, silicon dioxide) was investigated using time-resolved infrared spectroscopy. About 85% reduction in concentration was achieved under optimized conditions. Adsorption capacities for ammonia were 7.28, 11.22, and 6.61 mg/g, respectively, at 298 K. Kinetic data fit a pseudo-second-order model well for all adsorbents [138]. Recently, repurposing agricultural byproducts as affordable adsorbents to clean water has gained attention. Yet, there's limited focus on eco-friendly disposal of resultant solid residues. A walnut shell powder, a local agricultural waste, was used successively to remove Fe^{2+} and Cr^{6+} metals from water [139]. In another study, researchers created adsorbents from coconut shells and rice husks. The coconut shell adsorbents exhibited 70 % efficiency in nickel removal, while rice husk adsorbents showed 65 % efficiency. Copper removal rates were higher at 75-76% for both adsorbents compared to nickel. Moreover, both adsorbents successfully reduced metal ion concentrations in industrial wastewater to below the permissible limit of 3 mg/L [140]. Yousef *et al*. investigated ibuprofen removal using natural cocoa shell biomass and modified versions. Raw biomass demonstrated a saturation IBP adsorption capacity ranging from 16.67 to 23.81 mg/g, while biomass that underwent functionalization exhibited even greater capacities, ranging from 30.59 to 38.95 mg/g. The efficiency of the adsorbents in extracting ibuprofen from water was largely influenced by the density of adsorption sites and their corresponding energies [141]. In recent trials, unprocessed coconut shell was utilized to isolate CA, CBZ, NAP, and DCF from both controlled ultrapure water and actual secondary wastewater effluents. Remarkably, for sourced samples employing an adsorbent mass/volume of 250 mg/L, reduced removal percentages were documented (26.9% for CA, 57.9% for CBZ, 44.7% for NAP, 31% for DCF) in contrast to simulated samples with an adsorbent mass/volume of 133 mg/L (with removal percentages of 63% for CA, 85.5% for CBZ, 79.1% for NAP, 68.8% for DCF). The authors ascribed this variability to the existence of suspended solids and soluble organic compounds within the wastewater [142]. They suggested further purification for real-world scenarios. The matrix effect, influenced by multiple pollutants, governs pollutant removal in practical situations [143]. Modification of *Camellia oleifera* shell with citric acid yielded excellent removal efficiencies for crystal violet (97%) and Pb^{2+} (86.9%) under specific conditions. Surface adsorption and intra-particle diffusion complemented chemical interactions [144]. Employing rice husk in constructed wetlands augmented with microorganisms achieved effective (azo) dye removal through biosorption, phytoremediation, and bioremediation processes. The study emphasized pH-dependent efficiency, with lower pH favoring anionic dye removal. For 0.2 g biosorbent and 100 mg/L solution concentration, black-5 azo dye elimination efficiencies were 84%, 52%, and 55% at pH values 4, 7, and 10 respectively [145].

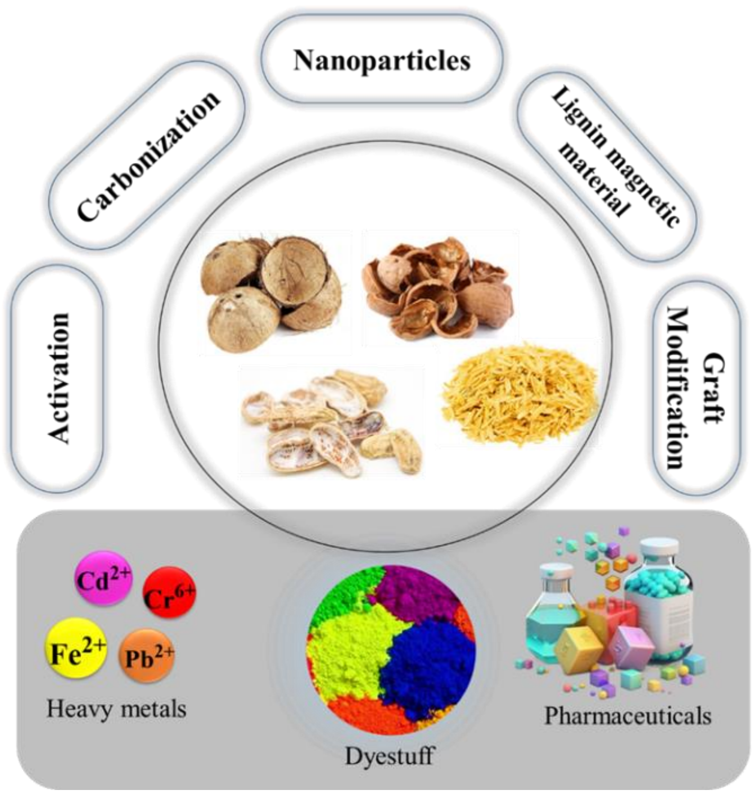

Figure 9: Pollutant detoxification using modified husk and shell-based adsorbents.

4.5. Peels of Fruits and Vegetables as a Source of Adsorbent

In the context of wastewater treatment, fruit and vegetable peels have been studied as adsorbents for organic and inorganic pollutants. Particularly, an in-depth examination has been carried out on the effectiveness of adsorbents derived from fruit wastes (including citrus, mango banana, grapes, and apples) and vegetable wastes like cauliflower, potatoes, cabbage, tomatoes, carrots and broccoli [146]. In a particular investigation involving pomelo peel as a biosorbent, the optimization of Pb^{2+} metal adsorption was achieved by immobilizing pomelo peel within Ca-alginate. The research highlighted that the fruit peel effectively eliminated 89 % of Pb^{2+} from wastewater [147]. Similarly, combining banana waste with alginate was employed for heavy metal removal (Cr, Cu, Pb, Zn). The ALG–BPA composite exhibited the highest efficiency, achieving 100 % uptake of Zn, Cu, Pb, and Cr from model solutions [148]. An exploration was conducted into the potential use of cellulose beads derived from orange peel (OPC) as adsorbents for removing metals from wastewater. The presence of functional groups and elements on the adsorbent was confirmed by FT-IR and SEM-EDS. At a pH that is neither acidic nor basic, the OPC adsorption sequence demonstrated the trend of Pb^{2+} having the highest adsorption, followed by Cd^{2+}, and then Cr^{6+}, resulting in corresponding removal percentages of 98.33%, 93.91%, and 33.50% respectively [149]. Ahmad *et al*., employed Jackfruit peel as a means to eliminate cationic dye from a solution. Their findings indicated that the process of MB adsorption onto the Jackfruit peel adsorbent adhered to the kinetics of pseudo-second-order (PSO) and the Langmuir isotherm model. The maximum biosorption capacity recorded was 232.55 mg/g [150]. In new research, *Tilia cordata* (little leaf linden) and *Foeniculum vulgare* (fennel) were employed as bio-sorbents for copper removal. Optimal conditions included an initial copper concentration of 10 mg/L, 0.2 g mass of each bio-sorbent, and pH 5.5 and 5.23. Langmuir isotherm described adsorption, with max capacities of 29.35 mg/g and 32.98 mg/g for *Tilia cordata* and *Foeniculum vulgare*. Adsorption was spontaneous and endothermal. *Tilia cordata* and *Foeniculum vulgare* showed high removal efficiency (93.34% and 95.4%) at 0.5 M, indicating stability and renderability [151]. To eliminate Neutral Red (NR) and Methylene Blue (MB), researchers applied a technique involving the application of a silica layer onto soya waste, which was then utilized as the sorbent material. This modified soya waste adsorbent exhibited notably improved removal efficiency, reaching approximately 97.1% for MB and 93.8% for NR. In contrast to other biomass-derived adsorbents documented in existing literature, the silica-coated soya waste adsorbent demonstrated heightened speed and effectiveness in adsorbing pollutants, achieving equilibrium within a mere 15-minute interaction period [152]. An investigation was conducted on an inexpensive, readily accessible adsorbent made from agricultural waste derived from Anchote peels.

The application of this adsorbent was employed for the purpose of eradicating the methyl orange (MO) dye from wastewater. Implementing the anchote peel adsorbent yielded a notable efficacy in eliminating the MO dye from water, achieving a removal efficiency of 94.47% [153]. Recently, economical adsorbents such as tangerine peel, bovine gut, tea waste, and sunflower seed hull have found application in adsorbing heavy metals like chromium and iron from solutions that are tainted with contaminants. Regarding the elimination of chromium metal ions from water-based solutions, various materials such as bovine gut, tangerine peel, sunflower seed hull, and tea waste exhibited distinct adsorption capacities. Specifically, they showed capacities of 85%, 51%, 46%, and 34% respectively. Fig. (**10**) illustrates the use of fruit peels as natural adsorbents to purify wastewater

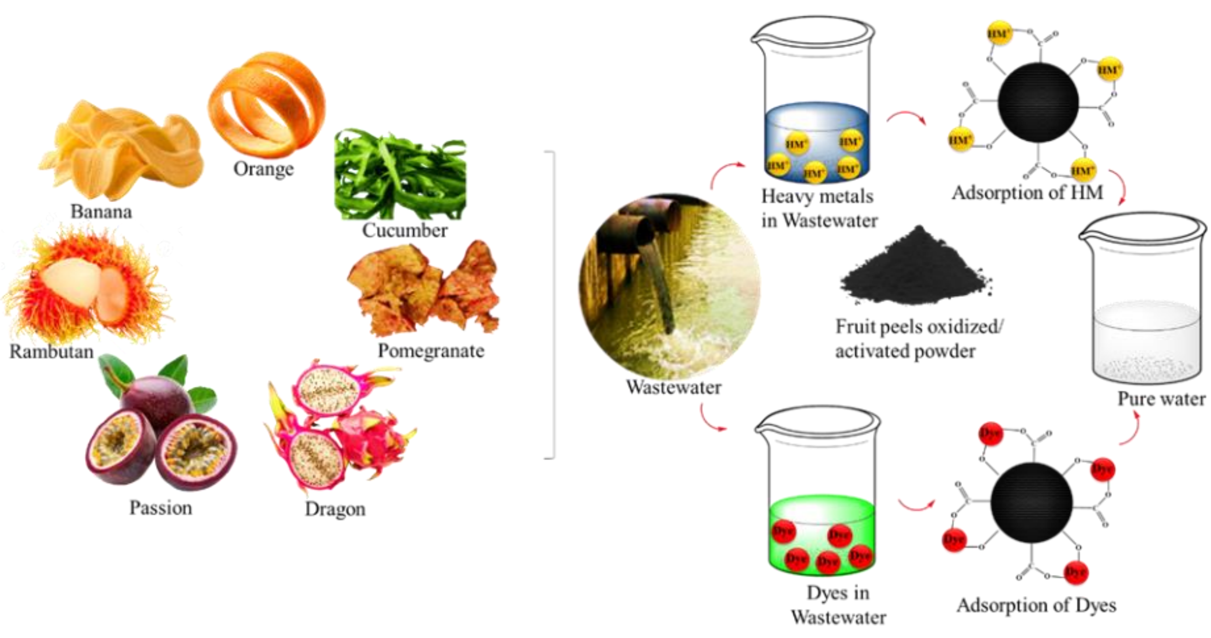

Figure 10: Illustrate how the fruit peels are used against heavy metals and dye to purify the wastewater.

contaminated with heavy metals and dyes. The figure likely depicts the process of preparing the peels (e.g., drying, grinding, or chemical activation) and their application in adsorbing pollutants. Rich in functional groups like carboxyl and hydroxyl, fruit peels effectively bind contaminants, offering a low-cost, biodegradable, and sustainable solution for water treatment while reducing organic waste.

Meanwhile, in the context of capturing Fe3+ ions, the adsorption capacities manifested as follows: both tea waste and bovine gut showcased an identical capacity of 96%, whereas tangerine peel and sunflower seed hull demonstrated capacities of 87% [154]. The feasibility of utilizing lemon peels as a starting material to produce an adsorbent substance was examined. The objective of this material was to effectively remove both heavy metals and dyes from wastewater in a simultaneous manner. It's important to highlight that the resulting material, denoted as LPZn, displayed noteworthy peak adsorption capacities of 0.85 mg/g for Cu^{2+} and Congo Red for 618.35 mg/g [155]. In Table **2**, different agro-waste-derived adsorbents are listed with their corresponding adsorption capacities for dyes and heavy metals.

5. Characterization of Biosorbents from Agricultural Waste

The characterization of biosorbents derived from agricultural waste using advanced techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and field emission scanning electron microscopy (FESEM) provides substantial insights into their structural and functional attributes. This characterization is crucial for the optimization and effective application of these biosorbents in pharmaceuticals, dye, and heavy metal removal from wastewater. The combination of these methodologies enables a comprehensive understanding of the surface properties, morphology, and chemical functionalities that facilitate the biosorption process.

XRD plays a fundamental role in identifying the crystalline structure of biosorbents, which is pivotal in understanding their interactions with pollutants. For example, XRD studies on biosorbents derived from agricultural products such as coconut coir or rice husk have highlighted the presence of various crystalline phases that may influence their adsorption capacity [186].

The presence of specific minerals can act as active sites for the adsorption of heavy metals or dyes. For instance, the XRD analysis of walnut shells indicated a favorable surface arrangement conducive for the adsorption of heavy metals due to the crystallographic characteristics observed [187].

Additionally, the peak width and intensity derived from XRD can be used to assess parameters like the average crystallite size and the degree of crystallinity, which directly correlate with the pores and surface area of the biosorbent. This characteristic is significant in optimizing the biosorbent design for increasing the active sites available for contaminant binding [188].

SEM and FESEM are essential for examining the surface morphology of biosorbents, which greatly influences their overall effectiveness in pollutant removal. The high-resolution images obtained from FESEM allow for detailed visualization of the microstructural features of biosorbents. For instance, SEM imaging of treated rice husk biosorbent showed a rough and porous surface compared to the untreated variant, signifying an increased adsorptive capacity due to enhanced surface area [189].

In a specific study focusing on the biosorption of methylene blue dye, the morphology of the biosorbent post-adsorption was analyzed using SEM, revealing that the dye is encapsulated within the biosorbent matrix, which enhances the binding efficiency [190]. FESEM results have identified micro-scale pores and rough textures that host dye molecules effectively, optimizing the contact area available for adsorption [191].

The enhanced surface area and porosity as visualized through these techniques not only explain the increased adsorption capacity but also help in tailoring the biosorbents for specific pollutants. For instance, agricultural wastes modified with chemical agents to enhance functionality exhibited significant changes in morphology, resulting in increased adsorption rates of contaminants, confirming the effectiveness of acute surface modifications [192, 193].

Table 2: Agro-waste adsorbents for the remediation of dyes and heavy metals.

Adsorbent	Dyes	q_e (mg/g)	Metals	q_e(mg/g)	Ref.
Chicken egg shell	AO7, TBO	75.8, 114.18	Cu^{2+}, Zn^{2+}	175.6, 153.6	[156]
Flax processing waste-based adsorbent	MB, MG, CR	163.9, 94.3, 85.5	Zn^{2+}, Pb^{2+}, Cu^{2+}	8.3, 13.3, 7.1	[157]
Sugarcane bagasse	-	-	Pb^{2+}, Ni^{2+}	1.61, 123.4	[117]
Ultrasonic-assisted jujube seeds	-	-	Zn^{2+}, Pb^{2+}	221.1, 119.9	[158]
Straw (Lingo-cellulosic sorbent)	MB	68.8	Fe^{3+}, Cu^{2+}	29, 37	[159]
Straw based adsorbent (WS-CA-AM)	MO, MB	3053.4, 120.8	Cu^{2+}	17.8	[160]
PCRAC	MG	128.1	Cu^{2+}, Ni^{2+}	176.9, 167.9	[161]
Biochar derived from coconut shell, groundnut shell, rice husk	Basic red 09	10, 46.3, 44	-	-	[162]
Coconut coir	-	-	Cu^{2+}	7.8	[163]
Biochar agro-waste	MO	12.3	-	-	[164]
Agr-waste-Juncus effuses-magnetic cellulose powder	CIRR195, CIRB222	58.2, 86	-	-	[165]
Agro-waste walnut shell-biochar	-	-	Ni^{2+}	13.2	[166]
Mangrove fruit-AC	EBT, MO, MG, MB	588.2, 588.2, 666.6, 666.6	-	-	[167]
ATAB & GS-GO@FeNPs	-	-	Cr^{6+}	369, 387.5	[168]
AC-Millettia thonningii seed pods	CV, MB	7.7, 14	-	-	[169]
Agro-waste (Ash seed)	CB	12.1	-	-	[170]
Sorghum stem	MB	98.1	-	-	[171]
Sorghum root	-	-	Pb^{2+}	197.6	[171]
MgAl-LDH@RHB	-	-	Cd^{2+}, Cu^{2+}	125.3, 104.3	[172]
Jackfruit seed-biochar	-	-	Fe^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Mn^{7+}	76.4, 79.4, 97.9, 79.9, 79.8	[173]
Magnetic biochar-peanut husk	-	-	Cr^{6+}	75.6	[174]
AC-MFS	-	-	Pb^{2+}	322.2	[175]
Peanut shell-derived sorbent (g-PS)	MB, BR	538.3, 687.5	Cd^{2+}	62	[176]
Ag@ES	-	-	Cr^{6+}	93	[177]
Banana rachis-biochar	MB	243.4	Pb^{2+}	179.7	[178]
Pyrolized rice husk biochar	MG	19.9	-	-	[179]
Coffee husk	-	-	Cd^{2+}, Pb^{2+}	116.3, 139.5	[180]
modified S. officinarium (MSO)	-	-	Cr^{+6}	243.90	[181]
Jackfruit leaves (*Artocarpus heterophyllus*)	-	-	Pb^{+2}	87.7	[182]
nMgO@ GHBC	-	-	Cr^{+6}	96.80	[183]
Agricultural waste biochar (SLB)	BF	174.5	-	-	[184]
SAAES/SA/MNPs	MB and CV	256.62 mg/g and 240.62 mg/g	-	-	[185]

The results from various studies indicate substantial efficiencies in heavy metal and dye removal using biosorbents derived from agricultural waste. For example, a biosorbent derived from rice straw demonstrated a methylene blue removal capacity of up to (97.09 mg/g) under optimal conditions [190]. Similarly, the maximum adsorption capacities for lead ions from agricultural waste biosorbents, like coffee and cocoa residues, were reported to be (158.7 mg/g) and (134.5 mg/g), respectively [193, 194].

Characterization techniques like FTIR can complement XRD, SEM, and FESEM in elucidating the specific functional groups responsible for heavy metal and dye binding. Functional groups, such as hydroxyl (-OH) and carboxyl (-COOH), identified in various agricultural waste biosorbents, play a critical role in the adsorption mechanism by providing sites for metal ion complexation [191]. Studies suggest that the functionalization of agricultural waste enhances these critical groups, improving the biosorbents' performance through mechanisms such as ion exchange, electrostatic attraction, and complexation [195].

For instance, various trials conducted on the adsorption of both nickel and cobalt ions revealed that the modified biosorbents from agricultural waste, such as corn cob, displayed significantly higher adsorption profiles due to the enhanced functional group density, further establishing the relationship between surface chemistry and adsorption capacity [192].

6. Environmental Implications and Logistical Challenges

Environmental implications of biosorbents involves considering their biodegradability and the impact of their production and disposal [196]. Biosorbents derived from agricultural waste are typically biodegradable, making them more environmentally friendly compared to synthetic adsorbents. This biodegradability ensures that, after their use in water treatment, they can decompose naturally without leaving harmful residues, contributing positively to waste management strategies [197]. The production of biosorbents, however, comes with certain environmental impacts. Although they are made from renewable agricultural by-products, their conversion into effective adsorbents (e.g., activated carbon) often requires energy-intensive processes such as carbonization and chemical activation [198]. These processes may involve the use of activating agents like phosphoric acid or potassium hydroxide, which, though effective at enhancing adsorption properties, can generate waste and emissions if not carefully managed. Furthermore, large-scale biosorbent production may lead to issues such as transportation emissions, especially if the raw agricultural waste must be transported over long distances to processing facilities. On the disposal side, spent biosorbents may present challenges depending on the contaminants they have adsorbed. For example, biosorbents loaded with heavy metals or organic pollutants can pose disposal risks if not handled correctly [199]. Incineration, composting, or safe landfilling are possible disposal methods, but they require appropriate management to prevent secondary contamination. Some biosorbents may even be regenerated and reused, reducing the overall environmental impact. Overall, while biosorbents offer clear advantages in terms of sustainability and biodegradability, their environmental footprint depends on the efficiency and environmental safeguards implemented in their production, use, and disposal processes.

The management of biosorbents derived from agricultural waste faces significant logistical challenges, particularly in the collection and distribution processes [200]. Collecting agricultural waste materials like fruit peels, husks, and plant residues is complicated by their decentralized nature, as they are often dispersed across farms or processing facilities, increasing transportation costs and emissions. Additionally, the seasonal availability of some agricultural by-products can disrupt continuous supply, requiring storage solutions that add to the logistical burden [201]. Transportation challenges further arise when moving bulky, low-density materials over long distances to processing facilities, contributing to both financial and environmental costs. Storage also poses difficulties, as some raw materials, such as fruit peels, are biodegradable and must be processed quickly to prevent decomposition, which can compromise their effectiveness as biosorbents. The heterogeneity of agricultural waste also necessitates pretreatment and sorting to ensure consistency in biosorbent quality, adding another layer of complexity to the logistics [202]. To mitigate these challenges, localized processing plants, improved supply chains, and partnerships with agricultural producers are essential for optimizing the biosorbent management system.

The utilization of biosorbents derived from agricultural and municipal solid waste presents a promising pathway toward sustainable development. By converting organic residues into value-added materials for environmental remediation, such approaches align with circular economy principles and contribute to climate change mitigation. For instance, industrial-scale production of activated carbon from MSW digestate has demonstrated feasibility in processing over 90,000 tons of waste annually while generating nearly 5,000 tons of CO_2 adsorbent. This not only diverts waste from landfills but also creates a cost-effective, low-carbon material for pollution control. Economic assessments and process optimization techniques, such as Response Surface Methodology, further reinforce the viability of large-scale implementation. These developments support global efforts toward achieving SDGs by integrating waste valorization with environmental protection and economic resilience [203].

7. Economical Overview of Agricultural-based Adsorbents

Adsorbents made from agricultural waste have a number of financial benefits that make them a good choice for a range of adsorption procedures. One of the key factors contributing to their economic viability is their low cost. Agricultural waste, such as almond shells, is readily available locally and often considered a byproduct or waste from agricultural production. The cost of using these waste materials is further decreased by the fact that they are typically used without or with very little processing, such as washing, drying, and grinding [204]. Although activated carbon is one of the most popular and effective adsorbents, its high cost remains a significant drawback. The cost associated with the adsorption process is primarily determined by the expenditure associated with the chosen adsorbent used to remove impurities from wastewater.

As a result, there is a strong need for affordable materials that have the same adsorption capacity as activated carbon, but this is still a significant drawback [205]. An economic analysis of biochars made from agricultural wastes such as rice husk, groundnut shell, and coconut shell was conducted in a recent study conducted by Praveen *et al*. This assessment focused on their capability to eliminate Basic Red 09 from wastewater. Within this evaluation, the comprehensive expense associated with biochar production forms a crucial component, incorporating costs related to production, upkeep, raw materials, conveyance, workforce, and dissemination. These factors are essential considerations for both marketing and the industrial utilization of biochar. Yet, comprehensive cost data for biochar, particularly sourced from a major industrial biochar market, are currently lacking [162]. As of 2018, 91 companies worldwide reported biochar sales, with the average global biochar price amounting to 2.13 €/kg. Prices ranged from 0.072 €/kg in the Philippines to 7.11 €/kg in the UK, which was a substantial variation.

Interestingly, in India, the prices for mixed biochar exhibited a spectrum from 0.064 €/kg to 10.83 €/kg [206]. In order to determine the total overhead for producing biochar, the analysis took into account a number of factors, including feedstock collection, transportation, pyrolysis, drying, grinding, labor, and other expenses. The estimated costs for making one kilogram of adsorbent material were 0.52 € for coconut shell, 0.49 € for groundnut shell, and 0.49 € for rice husk, according to the cost analysis. When compared to the other two types of biochar, groundnut shell biochar was the most cost-effective, with the lowest cost per gram of Basic Red 09 removal at 0.01 €. In addition, the inquiry yielded a significant finding. Compared to other produced biochar, groundnut shell biochar demonstrated an outstanding adsorption capacity of 46.29 mg/g. Most notably, rice husk biochar had an adsorption capacity of 44 mg/g and coconut shell biochar had a capacity of 10 mg/g. The cost of extracting one gram of Basic Red 09 from rice husk and coconut shell biochars was calculated to be 0.011 € and 0.052 €, respectively. The economic feasibility of using commercial adsorbents (granular activated carbon, or GAC, Zeolite 13X, and Zeolite 4A) for the removal of fluoxetine was the subject of another evaluation by Silva *et al*. [207].

8. Gap in Literature and How to Fill this Gap

Numerous studies have explored the adsorption efficiency of agricultural waste-based biosorbents but significant gaps remain in their real-world applicability, particularly under complex wastewater conditions with mixed contaminants. Limited work has been done on long-term regeneration and reuse of these biosorbents, and their integration into existing water treatment infrastructure requires further investigation. Additionally, the environmental impact of spent biosorbents and their safe disposal has not been comprehensively addressed. The scalability and economic feasibility across different geographic and industrial contexts also need more in-depth analysis. Future research should focus on pilot-scale studies, standardization of biosorbent preparation methods, and techno-economic evaluations to bridge the gap between laboratory findings and practical applications.

9. Conclusion

This review comprehensively explored the potential of agricultural waste-derived biosorbents as sustainable and cost-effective alternatives for the removal of heavy metals, dyes, and organic pollutants from wastewater. By classifying a wide variety of agro-waste materials—including husks, shells, peels, and plant residues the study highlighted their physicochemical properties, surface modifications, and pollutant-specific adsorption capacities. It also presented the influence of critical parameters such as pH, temperature, and contact time on biosorption efficiency. One of the key contributions of this work is the incorporation of an economic analysis, assessing the feasibility and cost-effectiveness of biosorbents compared to conventional adsorbents like commercial activated carbon. The environmental implications and challenges related to large-scale implementation, logistics, and disposal were also critically discussed. Furthermore, the review provided updated insights into advanced material enhancements, including magnetic modification and chemical activation, to improve adsorption performance and reusability. Overall, this work serves as a valuable resource for researchers and industry stakeholders seeking scalable, eco-friendly solutions to wastewater treatment, and it supports the integration of agricultural waste management within a circular economy framework.

Conflict of Interest

The authors have no conflict of interest.

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Authors Contribution

The authors confirm their contribution to the article as follows: conception and design of the study: MK and FH; data review and search: SM and TA analysis and interpretation of results. All authors reviewed the results and approved the final version of the manuscript. The authors confirm sole responsibility for the following: study conception and design, data collection, analysis and interpretation of results, and manuscript preparation.

List of Abbreviations

COD	=	Chemical oxygen demand
AC	=	Activated Carbon
CA	=	Clo fibric Acid
CBZ	=	Carbamazepine
NAP	=	Naproxen
DCF	=	Diclofenac
ALG–BPA	=	Alginate microbeads Banana peel ash
ES-M-CEW	=	Egg shell metal -Chicken egg white protein biosorbent
Flax-biosorbent	=	Flax Fiber Crop
SCB	=	Sugar cane bagasse
UAJS	=	Ultrasonic assisted jujube seeds
WS-CA-AM	=	Acrylamide and citric acid with waste straw
PCRAC	=	Phosphoric acid activated Chrysopogon zizanioides roots AC
CSB	=	Coconut shell biochar
GnSB	=	Groundnut Shell biochar

RHB	=	Rice husk biochar
CC	=	Coconut Coir
BA	=	Wattle bark carbonaceous biochar
BM	=	Mimosa husk carbonaceous biochar
BC	=	Coffee husks carbonaceous biochar
Cellulose M-JEPs	=	Magnetic cellulose Biomas-Juncus effusus powders
WSBA	=	Walnut shell biochar adsorbent
ATAB	=	Acid treated active biochar
GS-GO@FeNPs	=	Graphene oxide iron nanoparticles
MgAl-LDH@RHB	=	Treated Rice husk biochar
JSW	=	Ackfruit seed waste
MBCPH	=	Magnetic biochar-peanut husk
AC-MFS	=	Mahogany fruit seed AC
g-PS	=	Peanut shell derived sorbent
Ag@ES	=	AgNPs immobilized on eggshells
BW-BC	=	Banana rachis-biochar
AO7	=	Acid Orange
TOB	=	Toluidine blue
MG	=	Malachite green
MB	=	Methylene blue
CR	=	Congo Red
MO	=	Methylene orange
CIRR195	=	C.I. Reactive Red 195
CIRB222	=	C.I. Reactive Blue 222
NR	=	Neutral Red
EBT	=	Eriochrome Black-T
CB	=	Cibacron Blue
BR	=	Basic red 46
SLB	=	Sycamore leaf biochar
BF	=	Basic fuchsin dye

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