Removal of Methylene Blue by Activated Carbon beads and Agricultural waste: A Review

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Abstract

Methylene Blue (MB), commonly used cationic dye in industries such as textiles and printing, offers substantial environmental and health problems due to its toxicity, persistence, and carcinogenic potential. This review looks at the effectiveness of two adsorption-based techniques for MB removal: activated carbon beads and agricultural waste-derived adsorbents. Activated carbon beads, made from carbon-rich precursors like mangosteen peels and modified with alginate, have high adsorption capacities (up to 230 mg/g) and removal efficiencies of over 98% under ideal circumstances like pH 9.5 and ambient temperature. Agricultural wastes, such as Corn husks, rice husks, and grape wood, show promise as low-cost and sustainable alternatives, with removal efficiencies of 83-97% and adsorption capacities of up to 98 mg/g. This research investigates preparation methods, adsorption mechanisms, and the effects of various parameters such as pH, adsorbent dose, and contact time. A comparison analysis demonstrates the cost-effectiveness and environmental friendliness of agricultural waste, as well as the higher performance of activated carbon beads. The review concludes with recommendations for improving adsorbent characteristics, filling research gaps, and scaling up these methods for industrial wastewater treatment.

Keywords: Methylene blue, activated carbon beads, mangosteen peels, alginate

1. Introduction

Methylene Blue (MB) is a synthetic dye that is commonly used in industries such as textiles, printing, and medicine due to its vivid hue and chemical adaptability. [1] Regardless of its utility, improper discharge of MB-containing effluents into natural water systems has raised serious environmental and health problems. Industrial processes, particularly in the textile sector, dump over 10-15% of dyes directly into the environment, making MB a significant contributor to water pollution. MB dye is currently one among the most used dyes for cotton, wood, and silk. The dye is widely found in industrial wastewater, which has disastrous environmental consequences. [1,2] Given the solubility and durability of azo dyes, standard methods of flocculation, sedimentation, and adsorption are ineffective for removing these compounds since they just move materials between phases without effectively degrading the compounds. Currently, such physicochemical approaches are the most commonly utilized for treating wastewater produced by the textile sector, resulting in acceptable effluents but producing waste materials with significant levels of toxicity. [3]

The removal of dyes from wastewater is critical to protecting the environment and public health. Synthetic dyes, which are widely utilized in industries such as textiles, leather, and paper, are frequently released into water systems without proper treatment. These dyes, particularly Methylene Blue, have serious environmental and ecological effects because of their stability, toxicity, and resistance to degradation. [4,5]

- ***Environmental Protection:*** Dyes limit sunlight penetration in water bodies, impeding photosynthesis in aquatic plants and algae. This disruption reduces oxygen production, causing oxygen depletion and damaging aquatic creatures like fish. Dyes can also change the temperature and pH of water, causing significant disruptions to aquatic ecosystems. [4]
- ***Toxicity:*** Synthetic dyes can be harmful to humans and aquatic life due to their toxicity and carcinogenic properties. Long-term contact to contaminated water can cause skin irritation, respiratory issues, and organ damage in people. Dye-contaminated water frequently reduces reproductive rates and increases death among aquatic animals. [4]
- ***Bioaccumulation and Persistence:*** Non-biodegradable dyes can accumulate in ecosystems. These persistent contaminants can eventually enter the food chain, hurting both people and animals. [4]

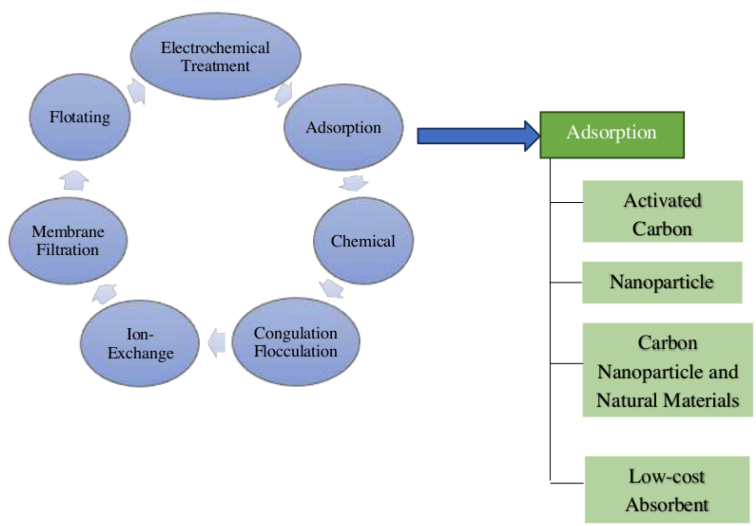


Fig 1: Schematic diagram of tertiary treatment for dye (MB)-removal technologies [1]

2. Activated Carbon

Activated carbon is commonly considered as one of the most effective adsorbents for extracting pollutants such as Methylene Blue (MB) and other toxins from wastewater due to its outstanding physical and chemical characteristics. Its great adsorption capacity is due to its large surface area, well-developed porous structure, and rich functional groups, which include hydroxyl (-OH), carboxyl (-COOH), and aromatic groups. Activated carbon may efficiently adsorb dye molecules by a variety of methods, including electrostatic interactions, hydrogen bonding, π-π interactions, and pore filling. [6]

Activated carbon can be manufactured from a variety of precursors, including non-renewable materials like coal, peat, and wood. However, the increased desire for cost-effective and ecological solutions has prompted the investigation of agricultural and industrial waste as antecedents. Coconut shells, rice husks, peanut shells, corn stover, and fruit peels are examples of abundant and carbon-rich materials that have been widely researched for activated carbon synthesis. These materials not only offer an environmentally beneficial option, but they also address waste disposal concerns by transforming waste into value-added goods. [7,8]

The production of activated carbon involves two main steps:

2.1. Carbonization: Carbonization involves heating raw materials to high temperatures (400-900°C) in an inert environment, such as nitrogen or argon, to remove volatile chemicals and concentrate carbon content. This stage leads to the creation of a char with fundamental porosity. [8]

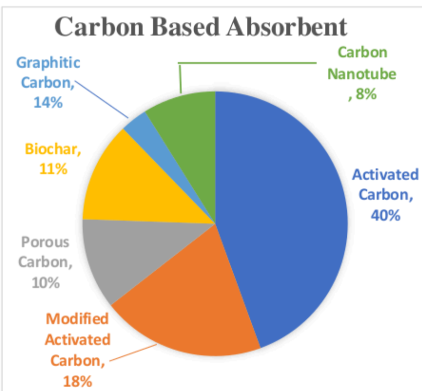
2.2. Activation:

- ✓ **Physical Activation:** The char is further treated with gases such as steam or carbon dioxide at high temperatures to improve pore growth and surface area. [8]
- ✓ **Chemical activation**: It involves treating char with substances like phosphoric acid (H_3PO_4), potassium hydroxide (KOH), or zinc chloride ($ZnCl_2$) to increase porosity and add functional groups to the carbon surface. This approach is typically used at lower temperatures and is more energy efficient. [8]

A number of variables, including as pH, temperature, contact time, and initial dye concentration, affect activated carbon's capacity to adsorb MB. Because of the improved interaction between the cationic dye molecules and the negatively charged carbon surface, optimal adsorption is frequently seen at basic conditions (pH 8–10). Because of better molecular diffusion and interaction kinetics, adsorption efficiency rises at intermediate temperatures (25–35°C). [9]

Activated carbon's relatively high production cost, which is mostly caused by the energy requirements of the activation process, is one of its main drawbacks despite its effectiveness. Furthermore, it might be difficult to regenerate used activated carbon, which frequently leads to a decrease in adsorption capacity over time. These difficulties have spurred researchers to concentrate on sustainable and affordable substitutes, especially those made from bio-waste. Recent research has demonstrated that agricultural waste may be successfully used to create activated carbon that performs on par with or better than that of conventional sources. For instance, because of its dense carbon content and inherent hardness, activated carbon derived from coconut shells has shown strong MB adsorption capabilities. Similar to this, chemically activated rice husks and fruit peels have increased porosity and functional group availability, which makes them excellent dye removers. [10]

Activated carbon is widely utilized not just to remove dyes but also to adsorb other pollutants, such as organic compounds, heavy metals (including lead and chromium), and even newly discovered toxins like medications. To further increase efficiency and sustainability, research is still being done to improve regeneration techniques, optimize activation procedures, and investigate hybrid materials that combine activated carbon with other functional adsorbents. [11]



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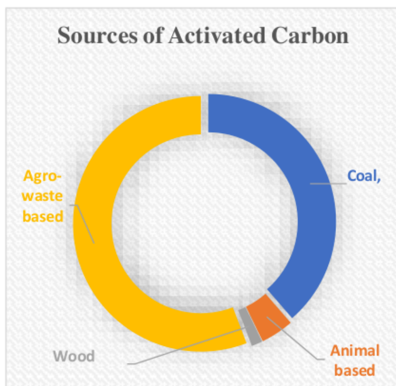

Figure: 3

Figure 2 and 3 shows Research on carbon-based adsorbents and sources of activated carbon for methylene blue elimination from 2008 to 2021. [1,8]

3. **Sodium Alginate beads with Activated Carbon as Adsorbents –**

3.1. Activated Carbon Beads: Activated carbon beads are very efficient adsorbents with a huge surface area, high porosity, and abundant functional groups such as hydroxyl and carbonyl. These beads are typically created by carbonizing organic precursors such as fruit peels or biomass, followed by chemical or physical activation to improve adsorption capabilities. Their homogeneous size and shape make them excellent for use in industrial applications, particularly wastewater treatment. Activated carbon beads efficiently remove dyes like Methylene Blue using electrostatic attraction, hydrogen bonding, and π-π interactions, resulting in high adsorption capacities and quick dye removal rates. [12,13]

3.2. Properties

- ***High Surface Area and Porosity:*** Activated carbon beads have a porous shape that enhances surface area and adsorption capacity. This shape aids in the adsorption of dye molecules, particularly those with larger molecular sizes, such as Methylene Blue. [13]
- ***Uniform Shape and Size:*** The spherical shape of activated carbon beads allows for regular flow in column operations and prevents clogging, making them excellent for large-scale industrial wastewater treatment. [13]
- ***Chemical and Thermal Stability:*** Activated carbon beads maintain their structural integrity and adsorption efficiency across a wide range of temperatures and pH conditions, enabling their use in diverse wastewater scenarios. [13]
- ***Rich Functional Groups:*** The beads contain functional groups such as hydroxyl (-OH), carbonyl (-C=O), and carboxyl (-COOH), which contribute to the electrostatic interactions and hydrogen bonding with MB molecules, enhancing adsorption efficiency**.** [13]

3.3. Preparation Methods

- ***Selection of Precursors:*** The availability and carbon content of organic, carbon-rich materials, such as fruit peels, biomass, or lignocellulosic wastes, are taken into consideration. [14]
- ***Carbonization:*** The precursor material is heated at high temperatures (400-900°C) in an inert environment (such as nitrogen or argon) to remove volatile chemicals and turn it into carbon-rich char. [14]
- ***Chemical activation:*** Carbonized materials are activated with substances such as zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), or potassium hydroxide (KOH).

Chemical activation enhances porosity by eliminating contaminants and adding adsorption sites to the carbon structure's surface. [14]

- ***Formation of beads:*** Slurry is formed by mixing activated carbon with a binder, such as sodium alginate.
  The slurry is deposited into a cross-linking agent, commonly calcium chloride ($CaCl_2$), and forms spherical beads through a gelation process. [14]
- ***Drying and storage:*** The beads are cleaned to eliminate superfluous chemicals before drying at a moderate temperature (60-105°C). The dried beads are kept in sealed containers for use in adsorption experiments. [15]

3.4. Adsorption Mechanisms

- ***Electrostatic interactions:*** Positively charged MB molecules attract negatively charged functional groups on the bead surface. [16]
- ***π-π Interactions:*** MB's aromatic structure interacts with π-electrons on the carbon surface. [16]
- ***Hydrogen Bonding:*** Functional groups like as -OH and -COOH establish hydrogen bonds with MB molecules, which improves adsorption. [16]
- ***Pore Filling:*** MB molecules penetrate into the porous structure of the beads, occupying accessible adsorption sites. [16]

3.5. Factors Affecting Adsorption

- ***pH:*** Adsorption is most effective at basic pH (9-10), when the adsorbent's surface is negatively charged, which promotes electrostatic interactions.
  At lower pH, hydrogen ions compete with MB molecules for active sites, reducing adsorption. [17]
- ***Temperature:*** Moderate temperatures (25-30°C) increase adsorption by increasing dye molecules' mobility and penetration into pores.
  Extremely high temperatures might cause desorption or deterioration of the adsorbent. [17]
- ***Contact time:*** Adsorption occurs quickly in the early phases because to the amount of accessible active sites.
  Equilibrium is usually reached in 60-120 minutes, depending on the dye concentration and adsorbent dosage. [17]

4. Performance of Activated Carbon for Methylene Blue Removal

The superior physicochemical properties of activated carbon beads allow them to remove Methylene Blue (MB) more effectively than other adsorbents. Their effectiveness depends on a number of factors, including kinetics, isotherm behavior, adsorption capacity, and removal efficiency. [18,19]

4.1. Adsorption Capacity: High adsorption capabilities are exhibited by activated carbon beads, which frequently outperform other adsorbents.

- **Typical Capacity:** Under ideal circumstances, adsorption capacities range from 200 to 230 mg/g, which makes them quite efficient at extracting MB from wastewater.
- **Optimal Conditions:** A basic pH (9–10) solution, a moderate temperature (25–30°C), and an appropriate dosage of beads all maximize the adsorption capacity.

The amount of dye adsorbed per unit mass of adsorbent at equilibrium is calculated as:

$$q_e = \frac{(C_0 - C_e).V}{m}$$

Where:

- q_e: Adsorption capacity (mg/g)
- C_0: Initial concentration of MB (mg/L)
- C_e: Equilibrium concentration of MB (mg/L)
- V: Volume of the solution (L)
- m: Mass of adsorbent used (g)

4.2. Removal Efficiency (%R)

- ***Efficiency:*** At dye concentrations of up to 100 mg/L, removal efficiencies for MB frequently surpass 98%.
- ***Consistency:*** The high porosity and vast surface area of the beads allow for good efficiency over a variety of initial dye concentrations.

The percentage of MB removed during the adsorption process is given by:

$$\%R = \frac{C0 - C_e}{C_0} \times 100$$

Where:

- C_0: Initial concentration of MB (mg/L)
- C_e: Equilibrium concentration of MB (mg/L)

4.3. Kinetics

- ✓ ***Pseudo-Second-Order Kinetics:*** Chemisorption is the main mechanism, as the adsorption process exhibits pseudo-second-order kinetics. This implies that functional groups like hydroxyl and carbonyl have strong interactions with the bead surface through MB molecules.
- ✓ ***Equilibrium Time:*** Adsorption proceeds quickly, and equilibrium is usually reached in 60 to 120 minutes. Because there are many active sites on the beads, the initial adsorption rates are substantial.

4.3.1. Pseudo-First-Order Kinetic Model [20]

Describe the rate of adsorption based on the adsorbent capacity:

$$\text{Log}\ (q_e - q_t) = \log q_e - \frac{{}_{1}t}{2.303}$$

Where:

- q_t: Adsorption capacity at time ttt (mg/g)
- k_1: Rate constant of pseudo-first-order adsorption (min^{-1})
- t: Time (min)

4.3.2. Pseudo-Second-Order Kinetic Model [20]

Represents chemisorption and is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where:

- k_2: Rate constant of pseudo-second-order adsorption (g/mg·min)

4.3.3. Isotherm Model

- ✓ ***Freundlich isotherm*:** Multilayer adsorption on heterogeneous surfaces is suggested by adsorption data that frequently match the Freundlich isotherm. This is in line with the various pore diameters and functional groups found on the beads of activated carbon. [20]
- ✓ ***Langmuir Isotherm:*** The Langmuir isotherm, which denotes monolayer adsorption under particular circumstances, is occasionally followed by the adsorption process. [20]

Describes monolayer adsorption on a homogeneous surface:

$$q_e = \frac{q_{max}\, bC_e}{1+bC_e}$$

Where:

- q_{max}: Maximum adsorption capacity (mg/g)
- b: Langmuir constant related to adsorption energy (L/mg)

5. Agricultural Waste as adsorbents –

5.1. Agricultural Waste: Agricultural waste, such as maize husks, rice husks, coconut shells, and fruit peels, provides a sustainable and cost-effective alternative to traditional adsorbents. These materials are abundant, biodegradable, and sustainable. Agricultural waste can be turned into effective adsorbents with porous architectures and functional groups capable of binding dye molecules using simple procedures such as washing, grinding, and chemical activation. Agricultural waste-based adsorbents are both environmentally friendly and effective, having proven performance in extracting Methylene Blue and other contaminants from wastewater. [21]

An environmentally favourable and economical method of treating wastewater is agricultural waste, a by-product of the farming and food sectors. These materials are a huge and renewable resource that can be used for environmental purposes, even though they are frequently thrown away or burned. Since agricultural waste naturally contains cellulose, hemicellulose, lignin, and other organic components that give it a porous structure and active functional groups, it is very useful as an adsorbent. [21,22]

There are various benefits to using agricultural waste, including Methylene Blue (MB), for colour removal. It offers an inexpensive substitute for more costly and energy-intensive traditional adsorbents, such as commercial activated carbon. Additionally, using waste materials is in line with sustainable practices, which address the pressing problem of water contamination while lessening the environmental impact of agricultural wastes. Through pore-filling mechanisms, hydrogen bonds, and electrostatic interactions, agricultural residues' porous structure and natural surface chemistry enable them to effectively absorb colours. [23]

5.2. Common Types of Agricultural Waste Used

- ***Rice Husks:*** It is plentiful by product of grinding rice. It is made up of lignin, cellulose, and silica, all of which increase the material's capacity for adsorption. [24]
- ***Coconut Shells:*** They are perfect for producing activated carbon because of their hard shells and high carbon content. Both chemical and physical activation techniques work well. [24]
- ***Corn Husks:*** Good adsorption potential due to its high cellulose and lignin content. It is demonstrated to be 90% effective at neutral pH for removing colors such as Methylene Blue. [24]
- ***Fruit peels, such as those from oranges, bananas, and mangosteen:*** It is abundant in cellulose, lignin, and pectin, all of which improve adsorption ability. When activated, mangosteen peels have adsorption capabilities of up to 98 mg/g. [24]

Figure 4: Schematic clarification of activated carbon derived from bio-waste and its potential uses[25]

5.3. Properties

✓ ***Abundance and Renewability:*** Large amounts of agricultural waste are produced globally as a result of the food and farming industries. Fruit peels, coconut shells, corn husks, and rice husks are a few examples. These materials are renewable and available year-round, making them an inexpensive and sustainable option. [26]

- ✓ ***Chemical Composition:*** These materials have a lot of surface area for dye molecules to stick to because of their inherent porosity, which is increased by chemical or heat activation. [26]
- ✓ ***Surface Functional Groups:*** Polar functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and phenolic groups, are found in agricultural waste and are essential for attaching dye molecules through electrostatic and hydrogen bonding interactions. [27]
- ✓ ***Eco-friendly and affordability:*** By using agricultural waste, sustainable behaviours are encouraged and the environmental impact of trash disposal is lessened. Additionally, the expensive raw materials that are normally used for the creation of adsorbents are eliminated. [27]

5.4. Preparation Methods

- ***Collection and Cleaning:*** Agricultural residue is gathered from farms or processing facilities. Examples include rice husks from milling, coconut shells from oil extraction, and fruit peels from food preparation.
  The garbage is thoroughly cleansed with water to eliminate dust, grime, and contaminants. Additional organic solvents may be employed to remove greasy deposits. [28]
- ***Drying:*** To remove moisture, the cleaned materials are dried in an oven at 60-110°C for 24 to 48 hours. This process improves grindability and prevents microbial deterioration. [28]
- ***Grinding:*** A grinder or mill is used to finely grind the dried trash. Finer particles have more surface area, which improves adsorption efficacy. [28]

5.5. Activation of Chemicals

Chemical agents are added to the powdered waste to improve porosity and add functional groups:

- ➢ ***Acids (such as HCl and HPO_4):*** To improve dye adsorption, eliminate contaminants and raise surface acidity. [29]
- ➢ ***Bases (such as KOH and NaOH):*** For cationic dyes like Methylene Blue, increase surface alkalinity and generate more reactive sites. [29]

- ***Thermal Activation:*** To create a highly porous structure, the material is heated to temperatures between 400 and 900°C in an inert atmosphere, such as nitrogen gas. This stage increases the adsorption capability and eliminates volatile components. [30]
- ***Cleaning and Neutralization:*** To get rid of any remaining chemicals, the material is repeatedly cleaned with distilled water after activation. Depending on the activation technique, diluted acid or base is applied to neutralize the adsorbent if chemical activation was employed. [30]

6. Adsorption capacities of different biosorbent for the removal of MB from wastewater;

Given the recent advancements in the use of inexpensive adsorbents, this review has worked extremely hard to cover a broad range of recent studies on unconventional adsorbents in order to inform researchers about the adsorption capacities of various biological materials used recently, as indicated by the tables above. Kinetic analyses and equilibrium isotherms were found to be accurate in every study that was completed. [31]

To analyze the fit, a variety of adsorption isotherm models were employed, including Langmuir, Freundlich, BET, Temkin, and Redlich-Peterson. Furthermore, the process of biosorption research should be expanded in light of bioabsorbent regeneration and recovery, based on the knowledge already available. [31]

The tables below provide an overview of the superior performance and financial potential of adsorbents made from biomass that demonstrated strong sorption qualities in a few chosen publications during the past four years.

6.1. Table 1: Bio-waste-derived adsorbent studies in 2016 – 2017

Biosorbents	Qmax (mg/g)	Most Appropriate Model	pH	Temperature (◦C)	Time (min)	Reference
Palm shell	163.3	F-K2	NA	25	NA	[32]
Fe_3O_4 -activated montmorillonite	106.38	L-K2	7.37	20	25	[33]
Clay (montmorillonite	184.5	L-K2	6.3	25	30	[34]

and vermaculti)/ polyaniline/Fe3O4						
Magnetic chitosan/active charcoal	200	L-K2	7.73	25	200	[35]
Fe_3O_4/poly acrylic acid	73.8	L-K2	NA	45	NA	[36]
Magnetized graphene oxide	306	L-K2	9	25	360	[37]
Corn straw	267.38	F-K2	8	25	20	[38]
Magnetic chitosan and graphene oxide	243.31	K2-L	12	60	60	[39]
Corn shell	357.1	L	4	25	30	[40]
Magnetic activated carbon	2.046	F-K2	10	25	120	[41]
Magnetic halloysite nanotube-nano-hybrid	689.66	L-K2	10	25	180	[42]
Magnetic polyvinyl alcohol/laponite RD	251	L-K2	5.5	25	60	[43]
Aegle marmelos leaves	500	F-K2	6	25	120	[44]
Oak-acorn peel	109.43	L-K2	7	24	120	[45]
Geopolymers	15.95-20.22	S-K2	4-12	25	80	[46]

6.2. Table 2: Bio-waste-derived adsorbent studies in 2018

Biosorbents	Qmax (mg/g)	Most Appropriate Model	pH	Temperature (◦C)	Time (min)	Reference
Carboxymethyl/cellulose/ Fe_3O_4/SiO_2	31.02	L-K1	11	NA	60	[47]
Cellulose-grafted	7.5	L	8		5.5	[48]
$NiFe_2O_4Ca$/alginate	1243	R-K1	6.5	25	180	[49]
Magnetic alginate	161	L	7	20	120	[50]
Magnetic hydrogel, Nanocomposite of poly acrylic acid	507.7	L-K1	7	25	120	[51]
Magnetized graphene oxide	232.56	L-K2	9	30	10	[52]
Soursop	55.397	R-K2	5.5	25	300	[53]
Sugarcane, Bagasse	17.434	S-K2	5.5	25	300	[54]
Palm sawdust	53.476	F-K2	8	25	120	[55]
Eucalyptus sawdust	99.009	F-K2	6	20	60	[56]

6.3. Table 3: Bio-waste-derived adsorbent studies in 2019

Biosorbents	Qmax (mg/g)	Most Appropriate Model	pH	Temperature (◦C)	Time (min)	Reference
Fir bark	330	F-K2	NA	25	40	[57]
Pumpkin peel	198.15	L-K2	7	50	180	[58]
Rice husk	608	L	7	25	60	[59]
Date stones	163.67	F-K2	10	25	360	[60]
Seaweed	1279	L-K2	4	25	50	[61]
Moroccan cactus	14.04	L	5	25	60	[62]
Syagrus oleracea	893.78	L-K2	7	25	20	[63]
Mentha plant	588.24	L	10	25	30	[64]

Palm leaf	500	L	2	30-60	30	[65]

6.4. Table 4: Bio-waste-derived adsorbent studies in 2020

Biosorbents	Qmax (mg/g)	Most Appropriate Model	pH	Temperature (◦C)	Time (min)	Reference
Kendu fruit peel	144.90	L-K2	6	25	100	[66]
Magnesium oxide nanoparticles	163.87	L-K2	7.3	25	70	[67]
Fava bean peel	140	L	5.8	27	NA	[68]
Dicarboxymethyl cellulose	887.60	L-K2	3	25	60	[69]
Alginate-based beads	400	L-K1	7	25	NA	[70]
Black cumin seeds	16.85	F-K2	4.8	25	20	[71]
Dragon fruit peels	195.2	L-K1	3-10	50	60	[72]
Litsea glutinosa seeds	29.03	L-K2	9	40	600	[78]
Moringa oleifera leaf	136.99	F-K2	7	25	90	[79]

6.5. Table 5: Bio-waste-derived adsorbent studies in 2021

Biosorbents	Qmax (mg/g)	Most Appropriate Model	pH	Temperature (◦C)	Time (min)	Reference
Grass waste	364.2	L	10	45	15	[80]
Mangosteen peel	871.49	L-K2	10	25	60	[81]
Coconut shell	156.25	F-K2	4.9	25	360	[82]
Core shell	34.3	L-K2	7	25	120	[83]
Banana stem	101.01	F-K2	7	25	90	[84]
Alginate beads	769	L-K2	8	30	NA	[85]
Ulva lactuca	344.83	L-K2	11	25	NA	[86]
Cassava stem	384.61	L-K2	9.2	25	60	[87]
Corncob	864.58	L-K2	5	25	360	[88]

7. Challenges of uses of Agricultural waste:

Although there are many obstacles to overcome, using agricultural waste as adsorbents for wastewater treatment has a lot of potential. The low adsorption efficiency of raw agricultural waste materials is a major drawback. These materials frequently lack the surface area, porosity, and functional groups necessary for efficient adsorption in their natural condition, making pre-treatment procedures like chemical or heat activation necessary. Although these procedures improve adsorption performance, they complicate and increase the expense of the preparation process. [89]

The diversity of agricultural waste's makeup presents another difficulty. The plant type, geographic region, and harvesting conditions can all affect the material's cellulose, lignin, and hemicellulose contents. This discrepancy makes it challenging to guarantee consistent adsorption performance and standardize the manufacture of adsorbents. Large-scale application is further complicated by the possibility that different sources of the same agricultural waste will provide varying adsorption capabilities. [89]

Other challenges are introduced by the preparation process itself. It can take a lot of time and resources to clean, dry, grind, and occasionally chemically activate agricultural waste. Concerns over the pre-treatment processes' effects on the environment are raised by the possibility of chemical waste from the use of activating agents like bases and acids. Additionally, with time, particularly during repeated adsorption cycles, the adsorption effectiveness of adsorbents based on agricultural waste may deteriorate. Their practical usefulness in long-term applications is limited since their stability and reusability are frequently lower than that of commercially available activated carbon. [89,90]

There are additional difficulties in producing agricultural waste-based adsorbents on a large scale for industrial application. Despite the apparent cost-effectiveness of laboratory-scale production, switching to industrial-scale manufacturing can be expensive, especially when it comes to raw material transportation and activation. The scalability issue is compounded by the lack of selectivity in agricultural waste-based adsorbents, as they may adsorb multiple contaminants present in real wastewater, reducing their efficiency in removing specific pollutants like Methylene Blue. [89, 90]

The use of agricultural waste as adsorbents raises further environmental problems. The environmental advantages of employing renewable waste materials may be negated by the high energy input required for thermal activation operations, which are frequently required to improve adsorption efficacy. Furthermore, improper treatment of used adsorbents may cause them to release absorbed contaminants back into the environment, which raises concerns about their regeneration or safe disposal. [90]

Despite these obstacles, research is still being done to find creative ways to maximize the utilization of agricultural waste as adsorbents. The promise of agricultural waste as an economical and environmentally beneficial substitute for conventional adsorbents can be fully realized with advancements in preparation techniques, enhanced characterisation methodologies, and more sustainable activation processes. [90]

8. Handling of Materials after Adsorption

The adsorbent can be handled in a number of ways following use, such as regeneration, reuse, and secure disposal. There are several methods for achieving regeneration, such as heat regeneration, chelating desorbing agents, alkali desorbing agents, and salt desorbing agents. Apart from the previously described methods, other methods for regenerating organic pollutants include ozonation, photo-assisted oxidation, electrochemical oxidation, microwave-assisted regeneration, thermal regeneration, chemical regeneration, microbiological regeneration, and ultrasonic regeneration. [91]

The effectiveness of the adsorbent declines after numerous cycles of adsorption and regeneration. The process makes the adsorbent unnecessary after numerous adsorption–regeneration cycles with the same contaminant. The used adsorbent can be recycled, burned, or dumped in a landfill. Prior to landfill disposal, old adsorbents containing hazardous elements can be stabilized/ solidified, thus raising the expenditure of the adsorbent's life cycle evaluation. Reusing and appropriately disposing of the adsorbent in several applications might improve its sustainability. There are numerous applications for the employed adsorbent, such as in cement clinkers, brick formulations, road construction, and as a catalyst. The three principal applications of discarded adsorbents are as follows: as a catalyser, in the making of ceramics, and as a fertilizer. [91]

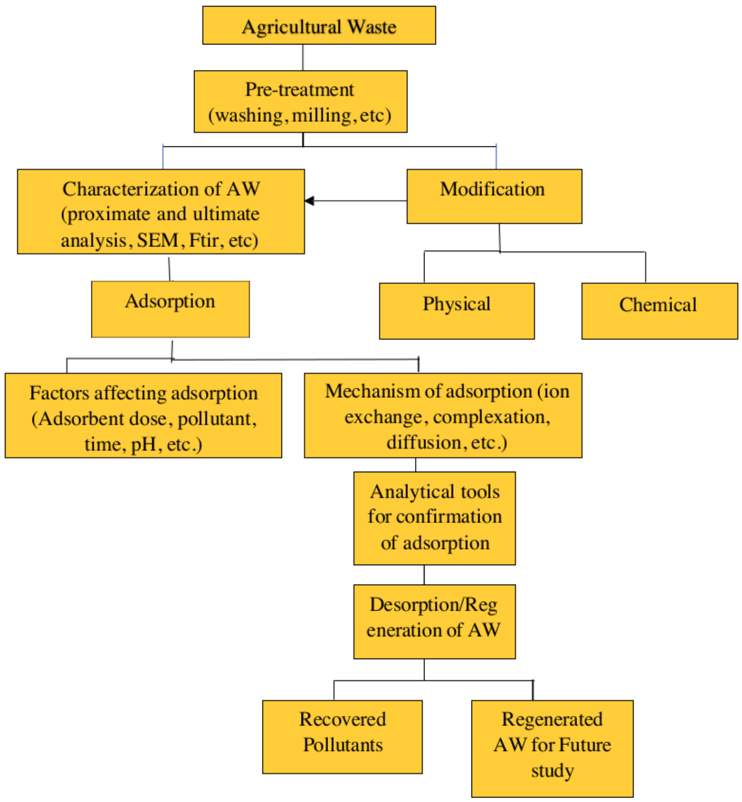

Figure 5: A flowchart presenting the overall adsorption process for pollutant removal

9. Cost-Effectiveness: Disposal vs. Desorption

After the adsorption process, adsorbents can be desorbed and regenerated until the effluent's pollutant content is kept below the allowable limit set by regulatory agencies. The used adsorbent can either be thrown away or used again for various purposes such pollutant removal, ceramic production, and catalyst synthesis. A chelating agent, salt, or an alkali or acid reagent can be used to desorb contaminants; for organic pollutants, chemical, thermal, microwave, or other methods can be employed. When an acid, alkali, chelating molecule, or chemical is used as a desorbing agent, waste (secondary pollution) is produced in the polluted eluent. Because of this, this method has the same disposal problems as other methods, like wasted adsorbent, which have an impact on the environment and the economy. However, in rare cases, metals that are mixed with other heavy metals can be recovered. For example, chromium (Cr) can be recovered from barium chloride (baCl), and mercury (Hg) can be recovered as mercury chloride (HgCl) from the ethylenediaminetetraacetic acid (EDTA)–Hg combination. [92]

10. Limitations

The main drawback of the previously published adsorption studies is that they are often conducted in laboratories without the use of commercial-scale column filtration systems or pilot trials. Aside from the limitations of the adsorbents used, only a small number of the studies used actual wastewater; the majority used batch mode experiments with simulated mono-pollutant solutions. The majority of studies on bio-waste adsorption concentrated on eliminating a single impurity from actual effluent that contained dye. Further study in multipollutant systems using actual textile wastewater is necessary to meet wastewater treatment requirements. Even when these methods are effective against a particular pollutant, the review also shows some inherent limitations of recent advancements in the use of activated carbon in terms of operational efficiency, overall costs, energy consumption, and the potential to form harmful by-products. The possibility for comparative studies is limited since different characteristics were utilized as indicators in earlier research projects, despite the fact that the majority of bio-wastes had high elimination efficiency up to 99%. Lastly, cost assessments were limited because the majority of earlier studies on biomass-based adsorption were conducted at a laboratory scale using simulated effluent. [92]

11. Conclusions

One of the most affordable and plentiful sources of carbon synthesis is bio-waste, which is regularly transformed into activated carbon. Bio-waste has emerged as a viable, economical, and sustainable source of activated carbon for the elimination of Methylene Blue (MB) between 2012 and 2021. Initial cost, local availability, stability, environmental friendliness, ease of transportation, treatment procedures, recyclability, longevity, regeneration potential, and pore volume after deactivation are some of the criteria used to evaluate low-cost bio-waste-based adsorbents. Higher pH values are necessary to maximize the uptake of cationic dyes, making pH one of the most important factors affecting adsorption efficacy. The initial dye concentration, temperature, adsorbent type and dosage, and contact time throughout the adsorption process are other critical variables. Adsorption studies use a variety of activation methods, such as chemical, steam, and carbon dioxide activation. While chemical activation is known to produce adsorbents with the maximum porosity and surface area, steam activation is clearly the most cost-effective technique. Thermal treatment, acid or base treatment (such as sodium hydroxide or nitric acid), organic solvents, vacuum processes, and biological treatments are some of the desorption techniques used for regeneration.

A cost-effective adsorption system should take into account a number of parameters, including the volume of adsorbent utilized, ease of production, adherence to green chemistry principles, and the activation method selected. Furthermore, post-adsorption materials exhibit the potential to be recycled for use in fertilizers, ceramics, and catalysis.

12. References

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