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# REVIEW ARTICLE

# The Use of Adsorption Technology in the Removal of Dyes and Heavy Metals From Aqueous Solution by Agricultural Wastes

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#### Abstract

The removal of dyes and heavy metals from wastewater has been a source of concern, both in terms of appearance and health. The removal of dyes and heavy metals from textile effluents on a continuous industrial scale has received a lot of attention in recent years. Various plant-derived wastes are often suggested for the treatment of heavy metals and dyes; these pollutants are sustainable due to their natural abundance, efficacy, and low cost. Adsorption process has emerged as the most widely used and successful method for water and wastewater treatment. The present study's focus, however, is on popularizing sustainable solutions for pollution remediation and developing a variety of solid waste-based adsorbents that enhance the effectiveness of the adsorptive separation process. As a result, a wealth of published data regarding the use of unprocessed agricultural biomass-based substitutes as efficient adsorbents for aqueous-phase heavy metal ion removal in batch adsorption experiments is available. In this study, different agricultural waste materials are assessed as low-cost adsorbents for the removal of dyes and heavy metals from wastewater. The review also discusses some of the fundamental principles of dye adsorption on adsorbents. This review primarily focus on evaluating plantderived adsorbents and their modifications, particularly for heavy metal and dye adsorption. Overall, the mechanism of adsorption and the suitability of the current methods are discussed, and their future potential is explored. Also, this review shows that many studies are required to explore the wide-ranging laboratory, industrial, and environmental applications of agricultural wastes as adsorbents.

Keywords: Adsorption, Agricultural waste, Dyes, Heavy metals, Low-cost adsorbents, Mechanisms of adsorption

## 1. Introduction

W ater is a vital component of life and energy, yet millions of people worldwide struggle due to a lack of access to fresh, clean water. It is commonly recognized that  $70-80$  % of illnesses in underdeveloped nations, especially those that affect vulnerable populations like women and children, are caused by contaminated water [\(Alprol et al.,](#page-8-0) [2023a\)](#page-8-0). The buildup of pollutants such as toxic metals (copper, zinc, iron, chromium, lead, cadmium, nickel, etc.), is a result of industrial activity, which is the primary cause of most environmental pollution issues and ecosystem degradation ([Pino](#page-10-0) [et al., 2006](#page-10-0)). Apart from this, residual dyes, surfactants, auxiliary chemicals, chlorinated compounds, and salts make up the majority of the wastewater released by the textile industry ([Khan et al., 2013](#page-10-1)).

Heavy metal ions are considered to be particularly dangerous pollutants, which is a significant environmental problem because of their mobility in the liquid phase of ecosystems, toxicity to higher life forms, and accumulation throughout the food chain. Moreover, these ions are nondegradable and thus persistent, leading to both ecological and health problems ( $\ddot{O}$ [zcan et al., 2005](#page-10-2)). Regarding dyes, they

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are used in food, paper, pharmaceutical, textile, and cosmetic industries. These substances have the potential to be poisonous, mutagenic, and carcinogenic, which make them hazardous to cells and other living things when contaminated ([Al Prol, 2019](#page-8-1)).

Therefore, before releasing aqueous pollutants into the environment, industrial effluents must be cleaned of these metal ions and dyes. Evaporation, solvent extraction, ion exchange, reverse osmosis, membrane filtration, chemical precipitation, coagulation, ozonation, photocatalysis, electrochemical oxidation, activated carbon adsorption, and Fenton reagent oxidant techniques are among the frequently used conventional techniques for removing heavy metal ions and dyes from water and wastewater ([Alprol et al., 2019, 2021](#page-8-2); [Abualnaja](#page-8-3) [et al., 2021b;](#page-8-3) [Bal and Thakur, 2022](#page-9-0)).

However, these traditional methods have their own set of intrinsic drawbacks, including delicate operating environments, higher costs, lower efficiency, the creation of secondary sludge, and more expensive disposal [\(Abualnaja et al., 2021a](#page-8-4)). A large quantity of natural materials or certain agricultural waste products may also have value as low-cost adsorbents. These materials are inexpensive, so after they are used up, they can be disposed of without having to be renewed.

Adsorbents are typically seen to be inexpensive if they do not need to be processed, are plentiful in nature, or are leftovers or waste products from another industry ([Ashour et al., 2021\)](#page-8-5). The preparation of activated carbons from rice husk ([Menya](#page-10-3) [et al., 2018\)](#page-10-3), coconut shell carbon [\(Hu and Sriniva](#page-9-1)[san, 1999](#page-9-1)), coconut tree sawdust carbon [\(Couto](#page-9-2) [et al., 2012\)](#page-9-2), and various forms of activated carbon from agricultural by-products [\(Gad and El-Sayed,](#page-9-3) [2009\)](#page-9-3) has been documented in reports.

It is imperative to adhere to environmental restrictions concerning the release of dyes and heavy metals into water streams and devise strategies for eliminating them from wastewater. Thus, the aim of this review paper is to present basic knowledge and research on the adsorption of heavy metals and dyes from aqueous solutions using different kinds of agricultural solid wastes as an inexpensive adsorbent, which is also a source of pollution. In addition, an attempt has been made to evaluate the adsorption process in this paper, emphasizing the adsorption efficiency, optimal parameters, and applicability of adsorbents.

#### 2. Environmental pollution

According to [Gichana et al. \(2015\)](#page-9-4) environmental pollution is any alteration to a region's natural composition that has a negative impact on both plant and human life. The primary causes of environmental pollution are the growing human population, fast industrialization, unplanned urbanization, deforestation, scientific and technological advancements, and much more. Environmental contamination can be categorized as follows according to the media in which it manifests itself.

There are three types of pollution: (a) air pollution, which happens in the atmosphere; (b) water pollution, which occurs in aquatic media; and (c) soil contamination, which occurs in the lithosphere. Among all the natural resources, water is the most important because it is necessary for all living things to survive.

Wastewater is defined as water that has been collected in the main sewer system and has had its composition altered by industrial and human use. The environment, economic growth, and development of Egypt are all highly influenced by water and the quality of surface and groundwater. The nation's surface water is unprotected from runoff pollution from chemical fertilizers and pesticides, untreated industrial effluents, and municipal wastewater [\(Ara,](#page-8-6) [2015](#page-8-6)).

### 2.1. Heavy metals in wastewaters: definition and sources

The term 'heavy metal' describes 20 metals, such as cadmium, chromium, mercury, lead, copper, and nickel, that are hazardous or poisonous at low concentrations and have a density of more than 5 g/  $cm<sup>3</sup>$  [\(El Zayat and Smith, 2009](#page-9-5)).

An alternative interpretation encompasses transition metals, some lanthanides, metalloids, and actinides, such as Cd, Pb, Cu, Zn, and Hg. While Cd, Hg, and Pb are among the nonessential metals that have no known function for organisms and are toxic even at low levels, some heavy metals, like Se, Fe, Cu, Zn, and Ni, are essential elements that are necessary for maintaining the metabolism of all living organisms (cofactors for enzymes or proteins) and can be toxic at high concentrations [\(Karaca](#page-9-6) [et al., 2008](#page-9-6)).

The primary industries responsible for heavy metal pollution in surface water and wastewater include surface treatment and electroplating, metallurgy, metallurgy of easily fusible alloys, metal and plastic coating, paint manufacturing, electrotechnics industry and rechargeable battery manufacturing (Ni-Cd), inorganic pigments, dye finishing, leather industry, and oil refining and mining.

Heavy metal cations are hydrated with distinct bipolar water molecules when they come into contact with surface water. Because they are absorbed more quickly and interfere with enzyme functions, hydrated ions are more hazardous than metal atoms.

#### 2.1.1. Heavy metal effects on human health

Heavy metals are nonbiodegradable, persistent pollutants that can accumulate in organisms even at low concentrations and cause serious illness ([Khalef](#page-9-7) [et al., 2022](#page-9-7)). Common effects on humans include increased salivation, severe stomach irritations that result in vomiting, abdominal pain, diarrhea, damage to the pancreas, liver disease, high blood pressure, choking, low blood iron, and damage to the nerves or brain. Ingestion-related poisoning causes vomiting, coma, jaundice, hypotension, and gastrointestinal pain ([Isangedighi and David, 2019](#page-9-8)).

#### 2.1.2. Heavy metal effects on aquatic environment

Contamination of lakes, rivers, and oceans with heavy metals is a serious issue. As a result of heavy metals' inability to decompose like organic pollutants, it may be said that the problem of heavy metal pollution necessitates quick action in order to be solved ([Rathoure, 2020](#page-10-4)).

Heavy metals in the environment have a negative impact on aquatic life. According to [Ahalya et al.](#page-8-7) [\(2005\)](#page-8-7) the toxicity is mostly determined by the water chemistry and sediment composition in the surface water system.

In an aquatic habitat, metal ions have the potential to bioaccumulate. Microorganisms mineralize the metals, which are then absorbed by plankton and other aquatic organisms, where they are biomagnified many times. Humans picked it up when they ate contaminated seafood. Aquatic creatures may experience the following sublethal effects from slightly higher metal levels in natural waters ([Aha](#page-8-7)[lya et al., 2005](#page-8-7)):

- (1) Changes in the histology or morphology of tissues.
- (2) Physiological alterations, such as impaired swimming ability, altered circulation, and inhibition of growth and development.
- (3) Modifications to biochemistry, including blood chemistry and enzyme function.
- (4) Modifications to reproduction.

The level of metal in a tissue can be controlled by many different organisms. Bivalves and aquatic plants are unable to effectively control the intake of metals, whereas fish and crustacea can excrete

nonessential metals like mercury and cadmium as well as necessary metals like copper, zinc, and iron. Bivalves frequently act as biomonitor organisms in areas of suspected contamination in estuarine systems [\(Kasiotis and Emmanouil, 2015](#page-9-9)).

Fish and other invertebrates' capacity to adsorb metals is mostly determined by the physical and chemical properties of the metal, whereas zooplankton and phytoplankton frequently absorb accessible metals rapidly (de Paiva Magalhães et al., [2015](#page-9-10)). There are three primary ways that metals might enter the systems of aquatic creatures:

- (1) Free metal ions that easily diffuse into the bloodstream after being absorbed by the gills.
- (2) The bloodstream passively diffuses free metal ions that have been deposited onto body surfaces.
- (3) Free ions swallowed with water as well as metals adsorbed onto food and particulate matter may be consumed.

#### 2.2. Dyes in wastewater

Any colored material that may impart its distinctive colors is referred to as a dye or dyestuff. Due to their preferential absorption of certain light wavelengths, pigments and dyes both give the appearance of being colored. A pigment, as opposed to a dye, is often insoluble and has no affinity for the substrate. Depending on the salt used, certain dyes can precipitate with an inert salt to create lake colors, such as calcium, aluminium, or barium [\(Ara, 2015\)](#page-8-6).

Organic chemicals, whether natural or synthetic, are used as dyes in a variety of sectors. A variety of items, including leathers, fibres, papers, edibles, etc., can be colored with dyes. The components of auxochromes and chromophores, which include NO,  $NO<sub>2</sub>$ , and N=N, improve the dye's affinity for the fibers while chromophores (NH<sub>2</sub>, OH, NR<sub>2</sub>, NHR, Cl, and COOH) are responsible for producing colors in the dye's molecules [\(Salleh et al., 2011](#page-10-5)).

In textile, food, rubber, paper, and paint industries, a variety of dyes are used, including acid, reactive, basic, azo, direct, vat, and disperse dyes [\(Demirbas, 2009\)](#page-9-11). With the exception of vat and disperse dyes, all dyes have concentrations of metals including chromium, zinc, lead, copper, and cobalt in their aqueous solution.

These industries' dye-bearing wastewater is distinguished by its strong color, high organic content, and potential for hazard.

#### 2.2.1. Environmental concern of dyes

Textile industry wastewater is a complicated mixture of many pollutants, from heavy metals

linked to dyes or the dyeing process to insecticides with an organochlorine base. In water, several colors can be seen at concentrations as low as 1 mg/ l. Wastewaters from textile production, which typically have dye contents among 10 and 200 mg/l, are consequently frequently vividly colored, making their discharge into open waters an aesthetic concern (O'[Neill et al., 1999\)](#page-10-6). They are extremely persistent in natural settings because they are dyes that are intended to be both chemically and photolytically stable. Most dyes can be harmful to human health and other living things. These colors have been linked to allergic reactions, dermatitis, skin dermatoses, and adverse effects on the immune system, lungs, liver, vasco-circulatory system, and reproductive system of experimental animals as well as humans ([Mansour et al., 2022b\)](#page-10-7). For instance, substitutions containing halogen atoms, nitro, methyl, or methoxy groups may be more harmful than those containing carboxyl or sulfonate groups, which typically have the opposite effect [\(Chung and Cerniglia, 1992\)](#page-9-12).

It is crucial to understand the possible risks associated with sulfonated aromatic amines because the majority of soluble commercial dyes contain one or more sulfonate groups.

# 3. Treatment of wastewater containing organic dyes and heavy metals

Because heavy metals are hazardous to a wide variety of living forms in addition to contaminating water bodies, their removal from industrial effluent is crucial ([Mansour et al., 2022a\)](#page-10-8). Metal ion removal has traditionally involved the use of a number of methods, including oxidation, chemical precipitation, reduction, coagulation, ion exchange, filtration, solvent extraction, electrochemical treatment, reverse osmosis, evaporation recovery, membrane technologies, and adsorption [\(Mansour et al., 2022c](#page-10-9)). The common techniques used to extract heavy

metals from industrial wastewater are listed in [Table 1](#page-4-0) along with the benefits and drawbacks of each method. Wastewater containing dyes is difficult to treat because the organic molecules are resistant to aerobic digestion and are designed to have good resistance to light. Three categories can be used to categorize dye removal techniques: chemical, biological, and physical. Depending on the wastewater load, these techniques have benefits and drawbacks [\(Al Prol, 2019\)](#page-8-1). [Table 2](#page-5-0) enumerates a number of benefits and drawbacks of techniques used for the removal of organic dyes' color.

#### 3.1. Adsorption

Adsorption is the separation of a material from one phase and accumulation or concentration of that substance on the surface of another. The substance concentrated at the surface of the adsorbing phase is known as the adsorbate, and the adsorbent is the adsorbing phase. Adsorption and absorption are not the same thing. According to [Alprol et al.](#page-8-8) [\(2023b\)](#page-8-8), absorption is the process of material being transported from one phase to another (such as a liquid) to produce a solution [\(Alprol et al., 2023b\)](#page-8-8), while adsorption has been shown to be more effective than alternative methods for reusing water in terms of starting cost, design simplicity, operational ease, and insensitivity to harmful contaminants [\(Meshko et al., 2001\)](#page-10-10). A common practice in commercial settings, adsorption is found in a multitude of biological, physical, chemical, and natural systems. In this case, a solid phase (rarely a liquid phase) and a fluid phase (gas or liquid) coexist. Absorption, or the fluid or gas's penetration into the solid phase, occurs concurrently with the adsorption process.

#### 3.1.1. Mechanisms of adsorption

Interactions between molecules, ions, and the adsorbent surface cause adsorption to occur. These

<span id="page-4-0"></span>Table 1. Conventional metal removal technologies ([Vieira and Volesky, 2000\)](#page-10-11).

| Method                                   | Advantages   | <b>Disadvantages</b>   |
|--|--|--|
| Chemical precipitation and<br>filtration | Cost effective, simple, and requires low<br>maintenance                | Results in the generation of large volume<br>of sludge affected by low pH and<br>presence of other salts |
| Chemical oxidation or reduction          | Ease of operation and mineralization                                   | Requires the addition of chemicals   |
| Electrochemical treatment                | Pure metal can be recovered for recycle<br>and no<br>reagents involved | Require quite large amounts of electricity   |
| Reverse osmosis                          | Minimal maintenance and effective                                      | Not cost efficient   |
| Evaporation                              | Does not require addition of chemical<br>reagent                       | Energy-intensive high operating cost   |
| Ion exchange                             | Effective and pure effluent metal re-<br>covery is possible            | Expensive resins highly sensitive to<br>pH of solutions  |

| No. | Method                                     | Advantages  | <b>Disadvantages</b>   |
|-----|--|---|--|
| 1   | Bleaching in the presence<br>of fungicides | High bleaching of anthraquinone and<br>indigoid dyes                            | Low rate of azo dyes bleaching Requires<br>a bioreactor and an external source of carbon |
| 2   | Ozonation                                  | Gases are applied No alteration of the<br>volume                                | Small half-life (20 min)   |
| 3   | Oxidation with NaOCl                       | Initiates and accelerates the breaking of<br>azo bonds                          | Aromatic amines release  |
| 4   | Photochemical oxidation                    | Does not generate sludge  | By-product formation   |
| 5   | Coagulation-flocculation                   | Removal of insoluble dyes Economi-<br>cally feasible Simple                     | Sludge generation  |
| 6   | Ion exchange                               | Regeneration possibility The adsorbent<br>is not lost                           | Not effective for all types of dyes  |
| 7   | Irradiation                                | Effective at laboratory scale   | Requires a large amount of dissolved O <sub>2</sub>                                      |
| 8   | Micro-ultrafiltration                      | Low pressure needed   | Low quality of treated water   |
| 9   | Nano-filtration                            | Separation of low molecular weight<br>organic compounds<br>and of divalent ions | High operation costs   |
| 10  | Reverse osmosis                            | Removal of mineral salts, dyes, and<br>chemical reagents                        | High pressure is needed  |

<span id="page-5-0"></span>Table 2. Advantages and disadvantages of removal methods for dyes from wastewater [\(Fiessinger et al., 1981](#page-9-16); [Valavala et al., 2011;](#page-10-13) [Kabsch-Kor](#page-9-17)[butowicz and Urbanowska, 2012](#page-9-17); [Chaplin, 2018](#page-9-18); [Crini and Lichtfouse, 2019;](#page-9-19) [Youssef and Khodzinskaya, 2019](#page-10-14)).

integrations are dependent on the kinds of molecules or ions that are present, the crystalline or amorphous adsorbent surfaces that are available, the bonds that form, and the kind of solution (electrolyte or nonelectrolyte). Depending on the type of substrate and the adsorbed molecule (nonpolar or polar), the type of binding among the sorbite and the substrate might be ionic, covalent, dipole-dipole, or van der Waals (Dą[browski, 2001](#page-9-13)). Adsorbents can be either organic or inorganic, and surfaces can likewise be either way. A positive or negative charge is typically present on inorganic surfaces, which are extremely polar. However, organic surfaces can vary in charge from extremely polar to nonpolar ([Ara and Usmani, 2015](#page-8-9)). A cation may create an inner-sphere or outer-sphere complex with a surface based on the formation of a chemical connection between the metal and the oxygen ion that is donating electrons (in this case, an inner-sphere complex) or the proximity of the cation to the surface-negative groups up to a certain distance. It is important to distinguish between physisorption, which solely relies on the surface-based physical forces of interfacial imbalance and attraction (e.g. van der Waals), and chemisorption, which requires chemical binding. In addition, there is a difference between passive metal sequestration by dead biomass and active metabolically driven metal uptake by living cells [\(Febrianto et al., 2009\)](#page-9-14).

#### 3.1.2. Steps of adsorption processes

According to [Soller et al. \(2003\),](#page-10-12) the adsorption process typically involves the following steps:

#### (1) Transport of bulk solutions.

Adsorbents go from the bulk solution to the fixed film liquid's boundary layer that surrounds them in this step. In adsorbent contactors, advection and dispersion act as the dynamic force for this step.

#### (2) Transport by film diffusion.

In this step, adsorbate spreads from inert liquid film to the entry of the pores of the adsorbent.

#### (3) Adsorption and pore transport.

In this stage, molecule diffusion through the pore and/or distribution along the adsorbent's surface will group the adsorbate and attach it to the adsorbent at accessible adsorption sites.

#### 3.1.3. Types of adsorption

Adsorption can be achieved through two different methods: chemisorption and physisorption. Both processes occur when the kinetic energy of the contaminant (adsorbate) molecules is overcome by the attractive forces at the solid surface (adsorbent), which cause the molecules in the liquid phase to adhere to the solid surface.

This kind of adsorption is also sometimes referred to as perfect adsorption. Chemical adsorption, also known as active adsorption or chemisorption, is the process by which the adsorbate and adsorbent interact chemically [\(John Thomas and Crittenden,](#page-9-15) [1998](#page-9-15)). [Table 3](#page-6-0) provides a summary of some significant characteristics that differentiate physical and chemisorption adsorption.

<span id="page-6-0"></span>Table 3. Some important features that distinguish between physical and chemisorption adsorption [\(Webb, 2003](#page-10-16); [Lavrenko et al., 2018;](#page-10-17) [Aljamali et al.,](#page-8-10) [2021\)](#page-8-10).

|                | Chemisorption   | Physisorption (van der Waals)  |
|----------------|---|--|
| 1              | Is dependent on the reactivity of the adsorbent and adsorbate   | Is a phenomenon with low degree of interaction   |
| $\overline{2}$ | Molecules are linked to reactive parts of the surface and the<br>adsorption is a monolayer                                  | At high relative pressures physisorption generally occurs as<br>a multilayer   |
| 3              | Chemisorbed molecules lose their identity (result is a new chem-<br>ical compound) and cannot be recovered after desorption | In physisorption the molecules keep their identity and in<br>desorption in liquid they maintain their original structure |
| $\overline{4}$ | Adsorption enthalpy is related strength of the chemical bonds,<br>$E = 80 - 600$ kJ/mol                                     | Physisorption is always exothermic, typically $(E = 5-40 \text{ kJ})$<br>mol)  |
| 5              | Often is an activated process that may be slow and irreversible   | Reversible process   |
| 6              | Kinetics of adsorption, highly variable. Hard desorption can be<br>irreversible   | Fast kinetic, because it is a nonactivated process and<br>reversible; easy desorption, the process can be reversible     |
| 7              | Adsorption enthalphy ( $kcal/mol$ ) > 20  | Adsorption enthalphy (kcal/mol) $<$ 10   |
| 8              | Surface covered incomplete  | Surface covered complete   |
| 9              | Involves formation of chemical bonds between adsorbate and<br>adsorbent   | Involves van der Waals force between adsorbate and<br>adsorbent  |
| 10             | May take a longer time to achieve equilibrium   | Equilibrium can be achieved quickly  |

#### (1) Physical adsorption.

The adsorbate is not bound to the adsorbent as firmly as it is during chemical adsorption, which is why physical adsorption is typically more prevalent at low temperatures and has a relatively low adsorption energy. The strength of the attractive forces between the adsorbent and the adsorbate determines the reversibility of physisorption.

#### (2) Chemical adsorption.

Chemical interaction between the adsorbent and the adsorbate is favored at higher temperatures because chemical reactions proceed more rapidly at elevated temperatures than at lower temperatures.

#### 3.1.4. Factors affecting adsorption process

- (1) The properties of the adsorbent, such as its surface area, pore size, and chemical makeup.
- (2) The adsorbate's physical and chemical properties, such as its chemical composition and molecular polarity.
- (3) The adsorbate's concentration in the liquid phase (solution).
- (4) The liquid phase's properties, such as temperature and pH.
- (5) The system's residence time.

#### 4. Adsorbents: selectivity and types

The adsorbent's ability to provide active sites for molecule binding makes it essential to the adsorption process [\(Ghoneim et al., 2014\)](#page-9-20). However, the cost or low adsorption capacity of adsorbents is the main disadvantage of the adsorption process. An adsorbent is a material that may adsorb chemicals onto its surface by intermolecular forces; it is often porous and has a large surface area ([Zhou et al.,](#page-10-15) [2019](#page-10-15)).

Adsorbents ought to possess these qualities to be used in commercial settings:

- (1) A micropore volume or surface area that is reasonably high.
- (2) Chemistry of the surface.
- (3) High selectivity to allow for precise divisions.
- (4) Great capability to reduce the quantity of adsorbent required.
- (5) Fast sorption due to advantageous kinetic and transport characteristics.
- (6) Chemical and thermal stability, which includes very little solubility in the contacting fluid to maintain the adsorbent's quantity and characteristics.
- (7) Mechanical strength and hardness to stop erosion and crushing.
- (8) Reasonably inexpensive.

### 4.1. Types of modification of agricultural materials

Three basic categories can be used to categorize the modifications made to these materials: (a) chemical, (b) mechanical, and (c) thermal ([Fig. 1\)](#page-6-1). The primary goal of mechanical modification is to

<span id="page-6-1"></span>

Fig. 1. Types of modification of agricultural materials.

<span id="page-7-0"></span>Table 4. Adsorption capacity qmax (mg/g) of some agricultural waste adsorbents for the removal of organic dyes.

| Agricultural wastes adsorbent               | Dye                | $q_{\text{max}}$ (mg/g) | References                   |  |
|---|--------------------|-------------------------|------------------------------|--|
| Date stones and jujube shells               | Congo Red          | $45.08 - 59.55$         | El Messaoudi et al. (2017)   |  |
| Jujube seeds                                | Congo Red          | 55                      | Reddy et al. (2012)          |  |
| Waste banana pith                           | Direct Red         | 5.92                    | Namasiyayam et al. (1998)    |  |
| Cotton plant wastes                         | Remazol Black B    | $35.7 - 50.9$           | Tunc et al. (2009)           |  |
| Waste of corn silk                          | Reactive Blue      | 71.6                    | Değermenci et al. (2019)     |  |
| Banana peel, cucumber peel, and potato peel | Orange G           | $20.9 - 40.5$           | Stavrinou et al. (2018)      |  |
| Ash seeds                                   | Cibacron Blue      | 67.114                  | Grabi et al. (2023)          |  |
| Jute processing waste                       | Congo Red          | 13.18                   | Banerjee and Dastidar (2005) |  |
| Eucalyptus bark                             | Solar Red BA       | 43.5                    | Tahir et al. (2016)          |  |
| Bean peel                                   | Cibacron Blue      | 28.490                  | Grabi et al. (2021)          |  |
| Almond shell                                | Eriochrome Black T | 123.92                  | Ben Arfi et al. (2017)       |  |
| Corn stigmata ground                        | Indigo Carmine     | 64                      | Mbarki et al. (2018)         |  |
| Cotton gin trash film                       | Acid Blue 25       | 35.46                   | Haque et al. (2020)          |  |
| Peanut husk                                 | Light Green        | 60                      | Su et al. (2013)             |  |
| <b>Rice Husk</b>                            | Congo Red          | 580                     | Jiang and $Hu$ $(2019)$      |  |

decrease the starting material's particle size through cutting or mechanical milling [\(De](#page-9-21)g[ermenci et al.,](#page-9-21) [2019\)](#page-9-21).

Chemical groups or ionic behavior may not necessarily change, but it might require some chemical treatment (for cleaning, for example). However, the second concept's principle that of chemical modification is precisely the reverse, with

Table 5. Adsorption capacities for adsorption of heavy metal ions by numerous agricultural waste materials at optimum conditions.

| Raw agricultural<br>by-products | Heavy<br>metal<br>ions | $q_{\max}$<br>(mg/g) | References               |
|---------------------------------|------------------------|----------------------|--------------------------|
| Jackfruit peels                 | Cu(II)                 | 17.5                 | Ibrahim (2020)           |
|                                 | Pb(II)                 | 10.1                 |                          |
|                                 | Cd(II)                 | 20                   |                          |
|                                 | Mn(II)                 | 76.9                 |                          |
| Vigna radiata husk<br>biomass   | Cu (II)                | 11.05                | Naseem et al. (2019)     |
|                                 | Co(II)                 | 15.04                |                          |
|                                 | Ni(II)                 | 19.88                |                          |
| Date palm empty<br>fruit bunch  | Cr(VI)                 | 70.49                | Rambabu et al. (2020)    |
| Coffee pulp                     | Cr(VI)                 | 13.48                | Ayob et al. (2021)       |
| Canola seeds                    | Pb(II)                 | 4.25                 | Gonçalves et al. (2019)  |
|                                 | Cd(II)                 | 52.36                |                          |
| Orange peel                     | Cd(II)                 | 170.3                | Chen et al. (2018)       |
| Avocado peel                    | Pb(II)                 | 4.93                 | Ahmad and Danish (2022)  |
|                                 | Ni(II)                 | 9.82                 | Mallampati et al. (2015) |
| Coconut husk                    | Cu(II)                 | 443.0                | Malik and Dahiya (2017)  |
|                                 | Ni(II)                 | 404.5                |                          |
| Corn straw                      | Cd(II)                 | 38.91                | Chi et al. (2017)        |
| Date seed biochar               | Ni(II)                 | 19.54                | Mahdi et al. (2019)      |
| Banana peels                    | Cu(II)                 | 14.3                 | Van Thuan et al. (2017)  |
|                                 | Ni(II)                 | 27.4                 |                          |
| Eucalyptus bark                 | Zn(II)                 | 131.6                | Afroze et al. (2016)     |
| Orange peel                     | Hg(II)                 | 7.46                 | Chinyelu et al. (2015)   |
| Mango leaves                    | Cd(II)                 | 4.08                 | Al Prol et al. (2017)    |
| Rice husk                       | Cu(II)                 | 133.34               | El-Moselhy et al. (2017) |
|                                 | Cd(II)                 | 41.15                |                          |

chemical groups modified in order to increase their chemical interaction with anionic dyes ([Munaga](#page-10-18)[pati and Kim, 2016\)](#page-10-18). Although chemical treatments are what primarily drive the dye adsorption in this approach, mechanical milling may be used as a prior step. The other idea is thermal modification, which can involve both chemical and mechanical milling processes. The basic idea here is to use high-temperature carbonization processes to turn biomass into carbonaceous materials like activated carbon [\(Aziz et al., 2018\)](#page-9-22). These processes frequently produce high surface areas, which is what makes the adsorption property so much better. Each of the three approaches has advantages and disadvantages and is promising in their own right.

## 5. Various agricultural and plant-based adsorbents for the removal of dyes and heavy metals

The use of agricultural waste adsorbents has sparked a lot of interest in environmental studies these days because traditional methods of treating heavy metals and poisonous dyes are expensive and produce large amounts of hazardous chemical sludge. Because agricultural wastes contain functional groups that may bind metals and remove them from water and waste water, they are readily available, reasonably priced, environmentally friendly, and have a high capacity to adsorb heavy metals. The primary constituents of agricultural waste materials are cellulose and lignin; additional ingredients include hemicellulose, lipids, proteins, simple sugar, starches, water, and hydrocarbons. Agricultural waste materials have a distinct physical and chemical makeup. Operational divisions for instance, the surface hydroxyl and carboxylic groups

of agricultural waste material play a significant role in binding activities that lead to a high affinity for metal cations.

Because agricultural wastes are underutilized resources and can pose significant disposal issues, their use is becoming an increasingly important topic. A variety of agricultural waste materials, including rice husks [\(Vieira et al., 2014](#page-10-32)), corncobs, peanut hulls, hazelnut shells, corn starch, waste tea leaves, blast furnace slag, sugar beet pulp, lignite, lignin, and powdered waste sludge, have been used as adsorbents recently. [Malik et al. \(2017\)](#page-10-33) have researched various adsorbents, including, red mud, fly ash, wood charcoal, sunflower stalks, and petiolar felt-sheath, in order to identify more affordable and efficient alternatives for adsorption. Several research groups have studied adsorption utilizing agricultural adsorbents to remove heavy metals and organic dyes from wastewater; the results are shown in [Tables 4 and 5.](#page-7-0)

## 5.1. Conclusion

The problem of heavy metal ion and dye contamination in water, from diverse sources such as agricultural practices and untreated industrial effluent discharge, is a worldwide concern. Adsorption-based separation technology is one of the most widely used conventional remediation techniques for treating heavy metal-contaminated water and wastewater because of its easy-to-use design, low energy consumption, high separation efficiency, efficiency at lower pollutant concentrations, high molecular selectivity, ability to separate multiple pollutant components, and minimal secondary pollution.

These adsorbents work better with cationic dyes by nature than with anionic dyes, though. This review paper included current batch adsorption results using a variety of unconventional and affordable agricultural solid waste-based adsorbents under different process settings, as well as an amalgamation of data from numerous scattered literature sources. The review has also shown that, in certain situations, adsorption's removal effectiveness was enhanced by the adsorbent modification. A variety of physicochemical process factors as well as the properties of the adsorbent determine the effectiveness of metal and dye removal from the aqueous phase. The current review makes it evident that unconventional raw or modified agricultural solid waste-based adsorbents are becoming more and more efficient, although lowcost adsorbents for heavy metal ions have issues with decontamination.

#### Declaration of Competing Interest

There are no conflicts of interest.

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