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*Review*

# Cadmium Ion Removal from Wastewater Utilizing Biomass-Based Materials: A Review

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**Abstract:** The world is struggling with the increasing rate at which water bodies are constantly polluted due to rapid modernization and industrialization. The different types of water contaminants include both anthropogenic and natural contaminants. Environmentalists are mainly concerned about heavy metals such as cadmium ions, as they are considered poisonous and carcinogenic even if they are present at a minimum concentration, and they are considered an immediate concern, according to the World Health Organization. Recently, many methods, such as solvent extraction, ion exchange, electrochemical precipitation, and reverse osmosis, have been developed to remove heavy metals from wastewater. These methods have been reported to be expensive and inefficient; hence, more cost-effective and eco-friendly alternative strategies are needed. Amidst these challenges, a ray of hope emerges in the form of biosorbents. These abundant, eco-friendly, and cost-efficient materials have shown promise as an alternative method for removing heavy metals from wastewater. They are equipped with functional groups that can effectively absorb metal ions onto their surfaces, offering a potential solution to our water contamination woes. This review is significant as it delves into the potential use of several biosorbents to decontaminate cadmium ions from wastewater. This review is significant as it delves into the potential use of several biosorbents to decontaminate cadmium ions from wastewater

**Keywords:** biosorbent; heavy metals; wastewater; agricultural wastes; eco-friendly; decontamination

## 1. Introduction

Anthropogenic activities, increasing human population, industrialization, and urbanization have contributed immensely to water, air, and soil pollution worldwide [1]. With the rapid development of industries such as metal plating, fertilizers, and mining operations, heavy metals are directly or indirectly discharged into effluents, especially in developing countries where environmental laws are not enforced. This has resulted in increased water demand globally. The environmental pollution associated with heavy metals is a global nuisance and is considered life-threatening when heavy metal tolerance levels are exceeded. Hazardous heavy metals of particular health and ecological concerns in industrial wastewaters include zinc (Zn), copper (Cu), nickel (Ni), mercury (Hg), cadmium (Cd), lead (Pb), and chromium (Cr) [2].

Cadmium pollution has become a severe problem facing environmentalists worldwide due to its carcinogenic importance and ability to accumulate in human organs and cells readily. $Cd^{2+}$ pollution emanates from sources such as electroplating and smelting from nonferrous metals, phosphate fertilizers, and batteries [3]. Exposure to different degrees of $Cd^{2+}$ is associated with a wide range of conditions, including kidney and bone damage, developmental and neurobehavioral disorders, elevated blood pressure, and potentially even lung cancer. Exposure to $Cd^{2+}$ has therefore been classified as a type I carcinogen by the World Health Organization (W.H.O.), the International Agency for Research on Cancer (I.A.R.C.), and the National Toxicology Program (N. TA, U.S.A.) [4]. The W.H.O. and the US Environmental Protection Agency (U.S. E.P.A.) have set permissible concentration limits of 0.003 and 0.005 mg/L for cadmium ions in drinking water, respectively [5]. For this reason, government agencies have grown interest in achieving permissible limits. Several

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treatment methods have been employed, such as filtration, chemical precipitation, coagulation, solvent extraction, ion exchange, adsorption, membrane processes, and electrochemical treatment. Among these existing methods, adsorption has been widely acknowledged due to its cost-effectiveness, simplicity of operation, high efficiency, and easy recovery. The effectiveness of the adsorption process is affected by factors such as the solution pH, temperature, contact time, initial metal ion concentration, agitation speed, adsorbent size and dosage, and other internal competing factors.

*Review Approach*

Due to humans' rapid modernization and industrialization, the world faces health implications associated with daily water pollution. Governments and environmentalists are primarily concerned with heavy metals present in wastewater. These contaminants have been reported to have detrimental health effects on human and aquatic life, even at low concentrations. Conventional methods to decontaminate wastewater have been reported to be expensive, complicated, inefficient, and non-environmentally friendly. Hence, more cost-effective and eco-friendly alternative strategies are needed. Biosorbents are abundant, inexpensive, eco-friendly, and cost-efficient and contain functional groups capable of absorbing heavy metal ions onto their surfaces. This review, therefore, discusses the sources and potential health effects of $Cd^{2+}$ in wastewater and the various biosorbents (microorganisms and plant parts) utilized for removing $Cd^{2+}$ from sewage.

## 2. Chemical Properties of Cadmium

Cadmium belongs to group XII of the periodic table of chemical elements. This soft, silvery-white metal is chemically similar to zinc and mercury in its physical and chemical properties (Table 1). It is a post-transition metal with two electrons in the s orbital and a completed orbital. $Cd^{2+}$ is resistant to corrosion and is used as a protective plate; it is water-insoluble and not flammable. $Cd^{2+}$ burns in the air, forming cadmium oxide [6].

**Table 1.** Physical and chemical properties of cadmium.

| | |
|---|---|
| Atomic number | 48 |
| Atomic weight | 112.41 u |
| Atomic radius | 155 pm |
| Electronic configuration | $[Kr]4d^{10}5s^2$ |
| Melting point | 321.07 °C |
| Boiling point | 767.3 °C |
| Density at 20 °C | 8.65 g/cm$^3$ |
| Reduction potential $Cd^{2}+ + 2e^- \rightarrow Cd(s)$ | −0.40 E° |
| Heat of fusion | 6.21 kJ/mol |
| Heat of vaporization | 99.6 kJ/mol |
| Electronegativity (Pauling scale) | 1.69 |
| First ionization energy | 867.8 kJ/mol |
| Second ionization energy | 1631.4 kJ/mol |

## 3. Sources of Cadmium Pollution

There are many sources of $Cd^{2+}$ pollution in effluents. The rapid pace of industrialization, urbanization, population expansion, modernization, and anthropogenic activities are mainly attributed to environmental cadmium pollution. These include fossil fuel burning, incineration of municipal waste, metal plating, nuclear reactors, welding and soldering, photography, production of iron, steel, and cement, production of nickel-cadmium batteries, manufacturing industries, paints

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and pigments, plastic stabilizers, electroplating, pesticides, phosphate fertilizers, discharge of untreated toxic industrial wastes and dumping of industrial effluents [7,8].

## 4. Exposure to Cadmium and Toxicity

As a potent pollutant and a Category-I carcinogen by I.A.R.C. and W.H.O., $Cd^{2+}$ readily accumulates in living cells and adversely affects humans and the environment. Cadmium has been well investigated, and its toxicity to the environment and human health has been documented. The persistent accumulation of cadmium has adverse effects on aquatic flora and fauna and should be a significant concern for public health. The ingestion of soluble cadmium ions above the maximum permissible level has been reported to cause many health-related issues, including the development of kidney stones, bone damage, cancer, hypertension, weight loss, Itai-Itai disease, endocrine disruption, interference with calcium regulation in biological systems, renal failure, and chronic anemia [8–10]. Cadmium ions have also been reported to induce alterations in steroidogenesis, disorders of the menstrual cycle and reproductive hormones, delays in puberty and menarche, pregnancy loss, premature birth, and reduced birth weight [11].

## 5. Conventional Methods for Removing Heavy Metal Ions from Wastewater

Several conventional methods have been employed to mitigate heavy metal pollution, but the most common methods include chemical precipitation, ion exchange filtration, reverse osmosis, electrochemical, coagulation, and flocculation methods [12].

### *5.1. Chemical Precipitation*

Chemical precipitation is the addition of precipitating agents, resulting in a chemical reaction that converts the soluble compound into an insoluble form. It is the most common method for removing heavy metal ions up to parts per million (ppm) from an aqueous solution. Although the process is cost-effective, its efficiency is affected by low pH and the presence of other salts (ions). This process requires the addition of different chemicals, which ultimately leads to the generation of sludge with a high water content, the disposal of which is cost-intensive [13].

### *5.2. Iron Exchange Filtration*

As the name suggests, ion exchange involves the exchange of problematic dissolved ions in water with less problematic ones. Although it is relatively expensive compared to the other methods, it can achieve ppb clean-up levels while handling a large volume. The disadvantage of this method is that it cannot handle concentrated metal solutions because organics and other solids in wastewater quickly foul the matrix. Moreover, ion exchange is nonselective and is highly sensitive to the pH of the solution [14].

### *5.3. Reverse Osmosis*

Reverse osmosis, also known as desalination, deionizes wastewater by pushing it under pressure through a partially semipermeable membrane. In this process, relatively small molecules can pass through the membrane, but not larger ones. Despite the high quality of reverse osmosis filtration, its effectiveness and safety require professional maintenance and are, hence, costly.

### *5.4. Coagulation and Flocculation*

Coagulation and flocculation are two essential processes in wastewater treatment. Coagulation occurs when a chemical reaction occurs after using a coagulant or chemical in wastewater. In an aqueous solution, colloidal materials form flocs or small aggregates. Suspended materials such as metals are attracted to these small aggregates or flocs. Slow mixing of water could help form small flocs that could increase in size such that they settle inside the solution. This process is known as flocculation [15].

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### *5.5. Electrochemical Process*

The electrochemical treatment of wastewater involves an electron transfer reaction that may include either electro reduction or electrooxidation [16]. Electrolytic metal recovery has been investigated for a long time. This method passes a direct current through an aqueous solution containing metal ions between the cathode plates and insoluble anodes. Positively charged metal ions adhere to negatively charged cathodes [17]. The removal efficiencies of metals have been reported to be influenced by the type of cell and the electrode used. Overall, electrochemical processes provide the following advantages: (1) metal selectivity, (2) no additional chemical requirements, (3) rapid and well-controlled operation with high removal efficiency, and (4) a lower level of produced sludge. Limitations include (1) a pH-sensitive process, (2) the need for the replacement of sacrificial electrodes, and (3) the requirement for high-cost electrodes and their subsequent electrical energy requirements, increasing the cost of this technology [18].

## 6. Adsorption

Adsorption is a mass transfer process in which a substance is transferred from a liquid or gas phase to the surface of a solid or liquid (adsorbents) and becomes bound by physical and chemical interactions (12). Adsorption can be divided into physical and chemical adsorption, physisorption and chemisorption

The most common and effective method for the removal of heavy metals is activated carbon, but this approach is not attractive due to the high regeneration cost [19].

Using biological adsorbents such as plant biomass, microorganisms, and other biomaterials to mitigate heavy metals has shown promising application prospects due to high efficiency, cost-effectiveness, and less secondary pollution. These adsorbents can adsorb, transform, and degrade $Cd^{2+}$ in water through a series of physical, chemical, and biological processes. The use of biological adsorbents is considered better because of their convenience, ease of operation, simplicity of design, and broader applicability in water pollution control [20].

### *6.1. Microorganism Biomass-Based Materials for Cadmium Ion Removal*

In biological treatment methods, heavy metal ions are degraded by employing microorganisms (Table 2) under either aerobic (in the presence of oxygen) or anaerobic (without oxygen) conditions. Microbial biomass (fungi, bacteria, yeasts, and algae) and non-living biomass (shrimp, krill, squid, crab shells, etc.) are used in the biodegradation process [21]. Bacteria such as *Bacillus cereus* [22], *Pseudomonas aeruginosa* [23], *Pseudomonas putida* [24], Streptomyces *rimosus* [25], *Staphylococcus xylosus* [26], *Nostoc muscorum* [27], Fungi such as *Fomitopsis pinicola, Penicillium chrysosporium and Trametes versicolor* [28], *Penicillium canescens* [29], *Penicillium purpurogenum* [30], *Saccharomyces cerevisiae* [31], and Algae such as *Bifurcaria bifurcate, Saccorhiza polyschides, Ascophyllum nodosum, Laminaria ochroleuca and Pelvetia caniculata* [32] have all been reported to effectively remove cadmium ions in aqueous solutions to the desired degree. The functional groups of heavy metal ions, such as amine, carboxyl, hydroxyl, sulfate, sulfhydryl, and imidazole, bind to the cell walls of these living organisms. Biological methods are associated with sludge bulking, rising sludge, and floc formation [33], which can affect the efficiency of heavy metal degradation. However, microorganisms such as yeast and fungi quickly grow, produce high biomass yields, and can be modified genetically and morphologically; hence, recent attention has been given to this method for remediating heavy metal ions.

**Table 2.** Microorganisms employed as adsorbents for cadmium ions removal from aqueous solutions.

| Adsorbent | $Q_{max}$ (mg/g) | Reference |
|---|---|---|
| *Alcaligenes eutrophus* | 122 | [84] |
| *Galaxaura oblongata* (Red algae) | 85.5 | [85] |

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| | | |
|---|---|---|
| *Pelvetia canaliculate* (Brown algae) | 140 | [86] |
| *Chondracanthus chamissoi* (Red algae) | 85.4 | [87] |
| Marine algae, dead biomass | 80 | [88] |
| Nile water algae | 37.43 | [89] |
| Green algae *Ulvalactuca* | 29.2 | [90] |
| Red algae *Hypnea valentiae* | 28.4 | [91] |
| Alginate Carriers | 220 | [92] |
| *Ascophyllum nodosum* | 38 | [32] |
| *Saccorhiza polyschides* | 95 | [32] |
| *Aspergillus niger*, living | 15.50 | [93] |
| *Fucus spiralis* | 64 | [94] |
| *Saccorhiza polyschides* | 95 | [32] |
| *Eichhornia crassipes* | 2.44 | [95] |
| Baker's yeast | 91.74 | [96] |

### *6.2. Agricultural Biomass-Based Materials for Cadmium Ion Removal*

In recent years, many researchers and environmentalists have successfully employed agricultural biomass-based materials to remove heavy metal ions such as cadmium from wastewater.

Agricultural-based materials are usually characterized by lignin and cellulose as the significant components. Functional groups such as acetamido groups, carbonyls, phenolics, polysaccharides, amides, amino acids, sulfides, carboxyl groups, alcohols, aldehydes, ketones, carboxylic acids, and esters present in agricultural biomass-based materials can bind to heavy metals by donating electron pairs to form complexes with metal ions in aqueous solutions [34,35]. Some biosorbents are nonselective and tend to bind to various heavy metals, whereas others are specific to certain kinds of metal ions in solution.

These biosorbents have successfully been reported to remove heavy metal ions from aqueous solutions. The use of these agricultural wastes as alternative adsorbents to mitigate heavy metals in wastewater is increasing because of their low cost, high efficiency, abundance, eco-friendliness, presence of metal-binding functional groups, biodegradability, ease of processing, minimized sludge generation, etc.

Many authors have highlighted the potential use of agricultural byproducts for heavy metal ion removal due to their advantages in decontamination processes. Examples of plant parts, such as sawdust, leaves, rice husk, peels, brains, and seeds, have been discussed as promising adsorbents for removing cadmium ions from wastewater.

#### 6.2.1. Saw Dust as a Biosorbent for Cadmium Removal

Readily available and inexpensive, Sawdust has been extensively reported to effectively remove heavy metals, including $Cd^{2+,}$ from aqueous systems [36]. Sawdust Contains various organic compounds, such as lignin, cellulose, hemicellulose, and polyphenolic groups, that bind heavy metal ions. Sawdust from the untreated fir tree of Romania, *Abies Alba fir,* was reported to have a removal efficiency of up to approximately 83% and a maximum adsorption capacity of 2.08 mg/g $Cd^{2+}$ within a pH range of 5.5-8.0 [37]. Untreated *Pinus halepensis* sawdust was also investigated as an adsorbent for removing $Cd^{2+}$ from aqueous solutions. A maximum adsorption rate of 97.7–100% was achieved in the first 10–20 minutes of contact at a pH of 9.0, adsorbent dose of 10 g/L, and cadmium concentration of 5 mg/L [38]. The ability of polyaniline coated on sawdust as a synthetic adsorbent for the adsorptive removal of $Cd^{2+}$ from aqueous solutions by batch operation. Investigated polyaniline coated on sawdust can be an effective adsorbent for removing $Cd^{2+}$ from aqueous solutions. Adsorption was found to be rapid and occurred within 20 minutes for a cadmium

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concentration range of 10:40 mg/L at a pH of 6.0 [39]. A similar study by Saima et al. (2006) demonstrated the ability of sawdust (Cedrus deodar wood) waste. It successfully removed $Cd^{2+}$ ions from an aqueous solution with a maximum sorption of 97% within 8 min at pH 8 [40].

#### 6.2.2. Leaves as Biosorbents for Cadmium Removal

Leaves are structurally composed of different biological polymers enriched in hydroxyl and phenolic groups participating in metal-binding activities.

Research conducted by Mahvi et al. (2008) using Ulmus leaves for cadmium uptake revealed that cadmium uptake was rapid and reached 85-92% of the equilibrium biosorption capacity in 15 minutes at an optimum pH of 6 [41]. The dead leaves of the typical ornamental plant *Dracaena draca*, also known as the dragon tree, were reported by Mahmoud et al. (2015) to remove $Cd^{2+}$ ions from wastewater, attaining a maximum sorption rate of 79.60% at 10 ppm, a pH of 7, and a biosorbent dosage of 0.5 g [42]. The adsorption of $Cd^{2+}$ by *Psidium guvajava* leaf powder increased from zero to 63.7% as the pH of the aqueous solution increased from 2 to 5.5 [43]. The ability of *Arundo donax* reed leaves to remove $Cd^{2+}$ from aqueous solutions was investigated. A $Cd^{2+}$ removal percentage of 92% occurred in 20 mg/l $Cd^{2+}$ solutions at pH 5.5 containing 5 g/l powdered leaves of *A. donax*. The adsorption percentage increased to 97% as the adsorbent dose decreased to 2.5 g/l [44].

#### 6.2.3. Seeds as Biosorbents for Cadmium Removal

The effectiveness of the *Crambe abyssinica* Hochst seed byproduct as a biosorbent for the removal of $Cd^{2+}$ from wastewater was analyzed by Rubio et al. (2013). The optimum adsorption conditions reported were 400 mg of biomass in a solution of pH 6.0 and a contact time of 60 min to remove 19.342 mg/g $Cd^{2+}$. The percentage of cadmium metal recovery was 79%, indicating possible biosorbent reuse [45]. *Peganum harmala* seeds were assessed as biosorbents for removing $Pb^{2+}$, $Zn^{2+,}$ and $Cd^{2+}$ ions from aqueous solutions. Approximately 95% of the lead, 75% of the zinc, and 90% of the cadmium ions could be removed from 45 ml of an aqueous solution containing 20 mg/l and 2 g of adsorbent at pH 4.5 after 15 min [46]. The optimum conditions for the removal of $Cd^{2+}$ (85.10%) using *Moringa oleifera Lam* were as follows: biomass dose (4.0 g), metal concentration (25 mg/l), contact time (40 min), and volume of the test solution (200 ml) at pH 6.5 [47].

#### 6.2.4. Peels as Biosorbents for Cadmium Removal

Peels are the major byproducts obtained during the processing of various fruits. Because of their low cost and ready availability, they have been used to remove heavy metals. Peels reportedly contain functional groups that interact with metal ions in aqueous solutions.

Somaia et al. (2015) investigated the ability of Egyptian banana peel to remove $Cd^{2+}$ from wastewater. The biosorbent successfully removed 98.35% of $Cd^{2+}$ from an aqueous solution containing 20 mg/l $Cd^{2+}$, 0.8 g of adsorbent, and a pH of 4.0 [48]. A similar study on dried banana peels by Pairate et al. (2015) showed that biosorption depended on particle size, solution pH, and initial cadmium ion concentration. A maximum adsorption rate of 17.94% was achieved at a pH of 5.0 on a batch scale at 25 ℃ [49]. The ability of pomelo peel, a natural biosorbent, to remove $Cd^{2+}$ ions from aqueous solution by biosorption was investigated by Wanna et al. (2009). It was reported that $Cd^{2+}$ removal increased significantly as the pH of the solution increased [50]. A similar study by Saikwaew and Kaewsarn (2009) revealed that corn, durian, pummelo, and banana peels can remove significant amounts of cadmium ions from wastewater. The results showed that banana peels had the highest $Cd^{2+}$ removal rate, followed by durian, pummelo, and corn peels, at $Cd^{2+}$ removal rates of 73.15%, 72.17%, 70.56%, and 51.22%, respectively, at a pH of 5.0 [51]. A study by Ibisi and Chizaram (2018) also showed that at a pH of 5.0, a concentration of 50 mg/l, and a contact time of 45 min, plantain peels effectively and efficiently removed approximately 90% of cadmium (II) ions from wastewater [52].

6.2.5. Rice Husks as Biosorbents for Cadmium Removal

Rice husks, the outer covering of rice grains, contain abundant floristic fiber, amorphous silica, cellulose, hemicellulose, lignin, protein, and functional groups such as carboxyl groups participating in metal binding processes. These properties have prompted the use of rice husk as an environmentally friendly adsorbent material for the energy-efficient and cost-effective removal of $Cd^{2+}$ from wastewater. The ability of rice husk to adsorb $Cd^{2+}$ from wastewater was investigated by Ajmal et al. (2003). They reported that the adsorption rate decreased while the metal uptake per unit weight of adsorbent increased as the initial $Cd^{2+}$ concentration increased from 10 to 50 mg/L with increasing contact time [53]. $Cd^{2+}$ sorption from an aqueous solution by rice husk was investigated using simple modifications. The pH of the aqueous solutions affected $Cd^{2+}$ removal, and the removal efficiency increased with the increase in solution pH. The maximum reported adsorption was 98.65% at a solution pH of 6.0, a contact time of 60 min, and an initial concentration of 25 mg/L [54]. The chemical modification of rice husk was reported by Kumar and Bandyopadhyay (2006) to increase the $Cd^{2+}$ uptake of raw rice husk from 75% to 97%, 80%, and 97% at a pH of 6.6 for NaOH-treated rice husk, epichlorohydrin-treated rice husk, and sodium bicarbonate-treated rice husk, respectively [55]. Researchers have suggested that NaOH-, epichlorohydrin-, and sodium bicarbonate-treated rice husks could be alternatives for remediating $Cd^{2+}$ from wastewater. In another study, biochar, rice husk, wheat straw, and corncob reported $Cd^{2+}$ uptake capacities of 94.73%, 93.68%, and 95.78%, respectively [56]. The removal of Cd (II) and Se (IV) from aqueous solution was studied at various times, and the pH, metal concentration, temperature, and sorbent status (wet and dry) were analyzed by El-Shafey (2007). Cd (II) sorption quickly reached equilibrium within ~two h, while Se (IV) sorption slowly reached equilibrium within ~200 h, with better performance for the wet sorbent than the dry sorbent. Cd(II) sorption was extremely low at low pH values (pH 1.5–2) and increased with increasing pH with a decrease in the final pH due to proton release, indicating an ion exchange mechanism [57].

**Table 3.** Adsorption capacity of various biomass of plant origin for the removal of cadmium ions from aqueous solution.

| Biomass resource | Adsorption capacity (mg/g) | Reference |
|---|---|---|
| Rice husk | 103.09 | [53] |
| Rice husk | 8.58 | [55] |
| Rice husk | 21.28 | [54] |
| Rice husk ash | 3.04 | [47] |
| Rice husk | 73.96 | [97] |
| NaOH-treated rice husk | 20.24 | [55] |
| Epichlorohydrin-treated rice husk | 11.12 | [55] |
| NaHCO-treated rice husk | 16.18 | [55] |
| Peat peels | 118.91 | [82] |
| Yam peels | 113.89 | [82] |
| Banana peels | 100.00 | [82] |
| Orange peels | 148.67 | [82] |

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| | | |
|---|---|---|
| Cassava peels | 59.88 | [82] |
| Peas peels | 118.91 | [98] |
| Apple peels | 0.8 | [99] |
| Modified orange peels | 40.56 | [100] |
| Pomelo peel | 21.83 | [50] |
| Coffee waste | 15.65 | [101] |
| Tea waste | 11.29 | [102] |
| Onion waste | 2.56 | [103] |
| Garlic waste | 2.3 | [103] |
| Cassava waste | 18.05 | [104] |
| *Terminalia catappa* Linn leaf | 35.83 | [105] |
| Tree fern | 16.30 | [106] |
| *Psidium guvajava* l leaf powder | 31.15 | [43] |
| *Platanus orientalis* leaves | 110.00 | [107] |
| *Ficus religiosa* leaf powder | 27.14 | [105] |
| Fig leaves | 103.09 | [98] |
| *Syzygium cumini* leaf powder | 34.54 | [108] |
| Wheat bran | 15.71 | [109] |
| Wheat bran | 0.70 | [110] |
| Wheat straw | 11.60 | [111] |
| Cashew nutshell | 436.7 | [112] |
| Walnut shell | 11.6 | [113] |
| Seaweed (*Ascophyllum nodosum*) | 106.3 | [114] |
| Reed plant (*Phragmites australis*) root | 1168.6 | [114] |
| Sunflower plant | 35.97 | [115] |
| Juniper fibre | 29.50 | [116] |
| Kraft lignin | 137.14 | [117] |
| Modified lignin | 6.7-7.5.0 | [118] |

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## 7. New Adsorption Materials for Heavy Metal Removal

Due to the unplanned discharge of untreated industrial wastewater from different industries and anthropogenic activities, the need to explore different adsorption materials to remove heavy metal ions from wastewater is critical. In addition to employing conventional methods and using biological adsorbents to remove heavy metal ions and other contaminants from wastewater, many other adsorbents, such as polymers, metal nanoparticles, metal oxide nanoparticles, and carbon-based nanomaterials, have also been used [58,59]. Recently, nanotechnology has been integrated with most conventional techniques for removing heavy metals from water systems to improve removal efficiency. Nanotechnology is a rapidly growing sector in the current developed world, and nanoparticles (NPs)/nanomaterials are substances used to produce nano-enabled engineered products in the technology field. Nanomaterials have been reported to be superior and have many advantages over conventional methods. Nanomaterials have proven to be excellent adsorbents due to their exotic properties, including small size, catalytic potential, high reactivity, large surface area, and many active sites available for interactions with various impurities. These properties contribute to their exceptional adsorption capacities [60]. Among different nanomaterials used as sorbents, carbon nanotubes have been investigated in depth because of their large surface area, chemical inertness, light mass density, porous structure, and strong affinity for pollutants. Modifying surfaces with different functional groups provides another edge to these tubular structures as one of the best nano adsorbents with easily modifiable surfaces [61,62]. Various functional groups (e.g., hydroxyl, carboxyl, amine, and ligands) can be quickly introduced on the surface of carbon nanotubes through functionalization to make them more selective and specific for certain pollutants. Similarly, many particular contaminants can be removed from wastewater using chemically modified carbon nanotubes [63,64].

**Table 4.** Merits and demerits of some of the standard methods employed for heavy metal removal.

| Methods | Merits | Demerits |
|---|---|---|
| Chemical precipitation | Simple and cost-effective | Sludge forms in large amounts |
| Chemical coagulation | Sludge settling and economically feasible | High cost, High consumption of chemicals |
| Ion-exchange | High regeneration of materials and metal selective | High cost due to disposal, less number of metal ions removed |
| Electrochemical method | Metal selective and no chemicals are needed | High energy consumption |
| Membrane filtration | Good removal of different heavy metals | Expensive |
| Biosorption | Feasible in removing some metals | Biosorbents require further modifications to increase the number of active binding sites and make them readily available for sorption |

## 8. Factors Affecting Adsorption Study

Several physical and chemical factors, including the solution pH, biosorbent dosage and size, temperature, agitation time, initial metal concentration, contact time, ionic strength, etc., influence adsorbents' use to remove metal ions from wastewater. These factors usually determine the overall efficiency of adsorption by affecting the uptake rate, selectivity, and removal of some heavy metals.

**Effect of contact time**: The biosorption of heavy metals from aqueous solutions has been reported to increase directly proportional to increasing contact time. This is attributed to the transfer

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of more heavy metal ions from the solution phase to the active sites of the biosorbent as the contact time increases. [65,66]. Another reason for the increased sorption of metal ions with prolonged agitation time might be the reduced boundary layer resistance to the transfer of biomass in solution [67].

**pH**: Among several factors of adsorption, the pH of an aqueous solution is an important parameter influencing the biosorption of heavy metals. The surface charge of adsorbents, ionization, speciation of heavy metals, and competing metal ions in solution are primarily affected by differences in pH. [68]. The pH dependency of adsorbents is attributed to the involvement of functional groups present in metal ion uptake, chemistry, and on the surface of their cell walls [69]. As the pH of the adsorption solution increases, the sorptive removal of cationic metals increases, whereas that of anionic metals decreases. At lower pH, the overall surface charge of the adsorbents will be positive. $H^+$ ions compete effectively with metal cations, causing a decrease in the biosorption capacity. When the pH increases, the surface of the adsorbent becomes increasingly negatively charged, favoring metal ion uptake due to electrostatic interactions. At a very high pH, biosorption stops, and hydroxide precipitation starts [70,71].

**Effect of temperature:** The change in solution temperature affects the diffusion rate of metal ions and the solubility of metal ions [68]. The temperature impacts the adsorption capacity depending on the surface functional groups of a given adsorbent. However, it is common for many studies to conclude that the influence of temperature is limited and only within a specific temperature range [72]Temperature can affect the biosorption process in different ways, depending on whether it is exothermic or endothermic.

**Effect of initial metal ion concentration:** Heavy metal ions can be transported from the solution to the surface of adsorbents owing to a driving force generated by the initial metal concentration [70]. The maximum adsorption of an adsorbent increases as the initial metal ion concentration increases due to more significant collisions between metal ions and adsorbents. However, increasing the metal ion concentration usually leads to decreased removal efficiency. Adsorption researchers have attributed this behavior to the saturation of adsorption sites on adsorbents and the lower rate of transporting metal ions [73,74].

**Effect of particle size:** Adsorbents' adsorption capacities are primarily influenced by their particle size due to changes in the total surface area, which is necessary for metal adsorption. Several authors have suggested that the smaller the particle size, the more significant the removal efficiency [74–76].

**Effect of adsorbent dosage:** Many authors have reported that the removal percentages of metal ions are directly proportional to the adsorbent dosage. As Kumar et al. (2012) reported, the efficiency of $Cd^{2+}$ removal increased rapidly as the cashew nut shell dosage increased. This phenomenon is attributed to the large quantities of available adsorption sites. Nevertheless, the adsorption efficiency of adsorbents has been reported to decrease with increasing adsorbent dose, which can be ascribed to the overlap of adsorption sites leading to a decrease in the total surface area. [76].

**Effect of pretreatment on adsorption:** Different authors have employed raw or untreated adsorbents to remove heavy metals in aqueous solutions. However, they have been reported to have significant drawbacks, including low adsorption capacity and high release of soluble organic compounds into the solution. For these reasons, it is highly recommended that adsorbents be pretreated before being used as adsorbents [77]. There has been an increasing call and suggestion to increase the efficiency of heavy metal adsorption, remove soluble organic compounds, and eliminate the coloration of the solutions by modification [58]. This call has led to the use of different methods to achieve maximum adsorption of heavy metals from wastewater. The modification methods employed to improve adsorbent efficiency include physical modification (size reduction, cutting, grinding, etc.), heat treatment (boiling, freezing, drying, etc.), chemical treatment (acid treatment, base treatment, oxidation with organic solvents, treatment with metal salts) and cell modification (enhancement of binding sites, elimination of inhibiting groups, craft polymerization). Several modifications are used/combined in the adsorption processes to achieve high effectiveness. Although physical modifications are considered simple and inexpensive, they are combined with other

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modifications to achieve high effectiveness. Chemical pretreatment mainly removes lignin, cellulose, hemicellulose, pectin, etc., increasing the surface area and enhancing the metal adsorption capacity. Chemical modification of plant biomass can be a practical approach for improving agricultural waste adsorption properties and performance. The treatment of raw biomaterials is likely to remove part of the organic matter and increase the surface area and porosity needed before using the material for heavy metal ion removal [66].

## 9. Advantages of Employing Agricultural Wastes as Low-Cost Adsorbents

Exploring biomaterials as suitable adsorbents among many agricultural wastes has been a daunting task for researchers in the field of bioremediation. To simplify this task, adsorption researchers have performed much work in selecting suitable adsorbents. According to Park et al., local availability and low cost are the critical factors in choosing agricultural byproducts and wastes for practical application [68]. These characteristics play crucial roles in industrial applications, thus making agricultural wastes superior to conventional adsorbents [78]. Based on these factors, they proposed agricultural wastes and biomaterials as potential sources of adsorption. The available literature reveals that numerous farming by-products and waste materials, including rice husk and bran, wheat husk and bran, sawdust of many kinds of wood, the bark of trees, coconut and ground-nut shells, waste tea leaves, apple, banana, and orange peels, sugarcane bagasse, coffee beans, sugar beet pulp, Cassia fistula leaves, sunflower and cotton stalks, walnut shells and many others, have been employed in remediating heavy metal ions from aqueous solution [79]. The primary reasons for employing these agricultural wastes in wastewater treatment over other conventional methods are their high versatility for a wide range of operational conditions, their ease of availability, low cost, abundance, biodegradability, ease of processing, regeneration, and recycling of biosorbents; minimized sludge generation; high efficiency, environmental friendliness; high selectivity for metals; low influence of alkaline earth and common light metals; high tolerance to organics; independence of concentration and good regeneration [80–82]. Moreover, agricultural by-products can be quickly processed, recycled, and recovered without causing devastating effects on the environment [58]. Furthermore, utilizing these waste products solves solid waste management problems and the environment. Finally, recycling agricultural wastes and byproducts for heavy metal ion treatment is said to reduce waste in an eco-friendly way. Hence, it agrees well with practical, innovative, and sustainable waste management [82].

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Despite the numerous advantages of biosorption methods, there are a few shortcomings, including a shorter lifetime of biosorbents compared with that of conventional sorbents [21]. Despite the numerous advantages of biosorption methods, there are a few shortcomings, including a shorter lifetime of biosorbents compared with that of conventional sorbents [21].

## 10. Conclusion and Future Perspective

The significant increase in the industry's production and use of heavy metal ions has contributed to environmental pollution due to the release of high amounts of contaminated water into effluents. This increasing heavy metal pollution, especially cadmium ions, in water bodies is alarming and life-

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threatening to humans and aquatic organisms. The removal of cadmium ions, considered one of the most notorious and lethal heavy metals in wastewater, is imminent due to their ability to damage many vital organs and cells of humans. In attempts to create a cadmium-free environment and fulfill the W.H.O. guidelines, many environmentalists and researchers are working on several eco-friendly and cost-effective methods and technologies to achieve this aim. Methods such as chemical precipitation, coagulation/flocculation, ion exchange, adsorption, flotation, and membrane processes have been extensively studied. All these methods aim to improve the quality of water that is ultimately discharged to the environment. Agricultural-based biomass has proven to be an effective alternative adsorbent for removing cadmium ions from wastewater due to its eco-friendliness, cost-effectiveness, availability, abundance, biodegradability, ease of processing, application, and recovery without negatively affecting the environment. These advantages make agricultural biomass-based adsorbents an economical alternative to conventional methods for decontaminating cadmium ions from wastewater.

Despite the many benefits of biosorption, a few shortcomings still need to be addressed. A shorter lifetime [21], early saturation of metal ions [83], and delays in long-term usage are possible due to recycling properties [72]. Future studies should address the above problems to realize commercial utilization and application of biosorbents. Additionally, the use of diverse chemicals for pretreatment may lead to the discharge of unexpected compounds into water bodies [73]. For this reason, it is very prudent to determine the best, most effective, and most efficient methods to mitigate the adverse effects of pretreatments while enhancing the adsorption capacity of adsorbents.

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