PHYSICAL AND CHEMICAL ADSORPTION MECHANISMS IN AGRICULTURAL WASTE ADSORBENTS

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Abstract

Agricultural waste-based adsorbents have emerged as promising low-cost materials for the removal of heavy metals from contaminated water and textile wastewater. Their effectiveness is mainly linked to the presence of lignocellulosic components and active functional groups such as hydroxyl, carboxyl, amino, and phenolic groups, which participate in metal binding. Heavy metal removal by these materials occurs through several mechanisms, including ion exchange, complexation, chelation, physical adsorption, precipitation, and electrostatic attraction. The present paper focuses on the physical and chemical adsorption mechanisms involved in agricultural waste adsorbents and explains how these mechanisms contribute to the removal of toxic metals such as lead, cadmium, chromium, and nickel. The study also highlights the role of factors such as pH, metal concentration, and surface characteristics in controlling adsorption performance. It concludes that understanding these mechanisms is essential for improving adsorption efficiency and developing sustainable wastewater treatment systems based on agricultural residues.

Keywords

Agricultural waste adsorbents, heavy metal removal, physical adsorption, chemical adsorption, ion exchange, complexation, chelation, textile wastewater

I. INTRODUCTION

Heavy metal pollution has become a serious environmental issue due to the discharge of untreated or poorly treated industrial wastewater into natural water bodies. Textile wastewater often contains toxic metals such as lead, cadmium, chromium, and nickel, which are non-biodegradable and harmful to both human health and ecosystems. In recent years, agricultural waste has gained importance as an alternative adsorbent because it is abundant, inexpensive, biodegradable, and rich in functional groups capable of binding metal ions. Materials such as rice husk, sawdust, bagasse, and fruit peels have shown significant potential in removing heavy metals from wastewater.

The adsorption behavior of agricultural waste adsorbents is not governed by a single process. Rather, heavy metal removal occurs through multiple physical and chemical mechanisms working simultaneously. Physical adsorption mainly involves weak intermolecular forces and surface attraction, while chemical adsorption includes stronger interactions such as ion exchange, complexation, and chelation. In addition, precipitation and electrostatic attraction may also support the overall removal process under suitable treatment conditions. A proper understanding of these mechanisms is important because it helps explain adsorption efficiency, metal selectivity, regeneration potential, and the suitability of agricultural residues for wastewater treatment applications.

II. MECHANISMS OF HEAVY METAL REMOVAL BY AGRICULTURAL WASTE

The effectiveness of agricultural waste as a low-cost adsorbent for heavy metal removal from textile wastewater is largely attributed to the diverse physicochemical mechanisms involved in the adsorption process. Agricultural residues are primarily composed of lignocellulosic materials containing cellulose, hemicellulose, lignin, proteins, and various functional groups that actively participate in metal binding. These functional groups—including hydroxyl (–OH), carboxyl (–COOH), amino (–NH_2), and phenolic groups—serve as active sites for interaction with dissolved metal ions.

Heavy metal removal by agricultural waste does not occur through a single pathway; rather, it involves multiple simultaneous mechanisms such as ion exchange, complexation, chelation, physical adsorption, precipitation, and electrostatic attraction. The dominance of a particular mechanism depends on factors such as pH, metal concentration, temperature, and the chemical nature of the adsorbent surface (Fu & Wang, 2011). According to Tchounwou et al. (2012), biosorption processes in natural materials are often complex and involve both chemical and physical interactions.

Understanding these mechanisms is essential for optimizing adsorption performance and improving the design of wastewater treatment systems. Regulatory bodies such as the United States Environmental Protection Agency emphasize the need for efficient heavy metal removal technologies to meet permissible discharge standards (USEPA, 2020). The following subsections explain the major mechanisms involved in heavy metal removal by agricultural waste materials.

Ion Exchange Mechanism

Ion exchange is one of the primary mechanisms responsible for heavy metal removal using agricultural waste adsorbents. This process involves the reversible exchange of metal ions in solution with naturally occurring ions present on the surface of the biosorbent.

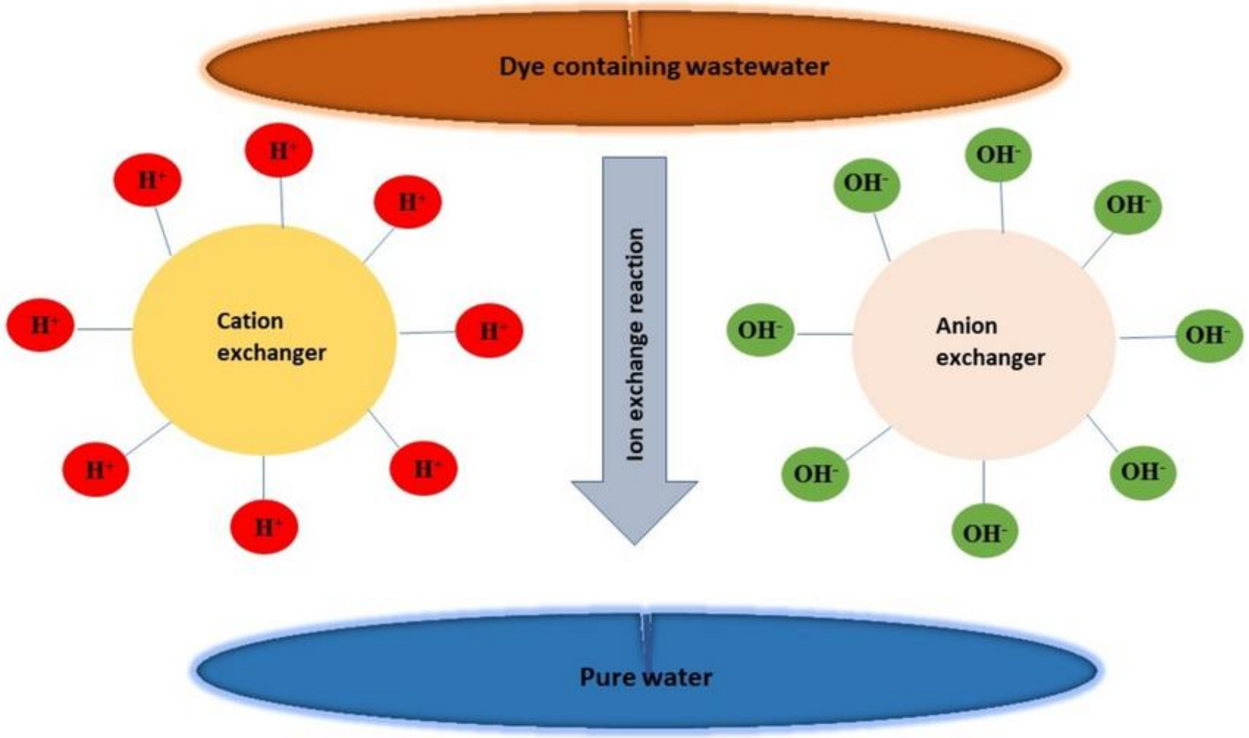

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Figure 1.1Ion Exchange Mechanism

- **Basic Principle**
    - Agricultural residues contain exchangeable cations such as H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}.
    - When wastewater containing heavy metals comes into contact with the adsorbent, metal ions replace these lighter ions.
    - This exchange occurs due to electrostatic attraction and charge balance requirements.
- **Role of Functional Groups**
    - Carboxyl (–COOH) groups are particularly important in ion exchange.
    - At suitable pH levels, carboxyl groups dissociate to form negatively charged sites ($-COO^-$).
    - These negatively charged sites attract and bind positively charged metal ions such as Pb^{2+}, Cd^{2+}, and Cu^{2+}.
- **Influence of pH**
    - Ion exchange is highly pH-dependent.
    - At low pH, high concentrations of H^+ ions compete with metal ions for binding sites, reducing adsorption efficiency.
    - At optimal pH (usually 4–6 for many metals), ion exchange efficiency increases (Fu & Wang, 2011).
- **Reversibility and Regeneration**
    - Ion exchange is generally reversible.
    - Adsorbents can often be regenerated by washing with dilute acid or salt solutions.
    - This property enhances the economic feasibility of agricultural waste adsorbents.

Studies have shown that materials such as rice husk, sawdust, and sugarcane bagasse remove heavy metals effectively through ion exchange processes. Tchounwou et al. (2012) reported that ion exchange contributes significantly to biosorption capacity in lignocellulosic materials due to their high density of carboxyl and hydroxyl groups.

Complexation and Chelation

Complexation and chelation are chemical adsorption mechanisms involving the formation of coordination bonds between metal ions and functional groups present on the adsorbent surface.

- **Complexation Mechanism**
    - Occurs when metal ions form coordinate bonds with electron-donating groups.
    - Functional groups such as –COOH, –OH, $-NH_2$, and phenolic groups act as ligands.
    - These ligands donate electron pairs to metal ions, forming stable metal–ligand complexes.
- **Chelation Mechanism**
    - A specific type of complexation.
    - Involves formation of ring-like structures between a single metal ion and multiple binding sites on the adsorbent.
    - Chelation results in stronger and more stable metal binding compared to simple adsorption.
- **Chemical Bond Formation**
    - Unlike physical adsorption, complexation and chelation involve stronger chemical bonds.
    - Often classified as chemisorption.
    - May be partially irreversible under certain conditions.
- **Selectivity**
    - Complexation provides selectivity toward specific metals.

    - For example, copper and lead show strong affinity for amino and carboxyl groups.

Fourier Transform Infrared Spectroscopy (FTIR) analyses in various studies have confirmed shifts in functional group peaks after metal adsorption, indicating chemical interactions between metal ions and adsorbent surfaces (Fu & Wang, 2011). According to Tchounwou et al. (2012), chelation is particularly important for divalent metal ions due to their ability to form stable coordination complexes.

The stability of these complexes depends on:

- Metal ion properties (charge density, ionic radius)
- Type and density of functional groups
- Solution pH and temperature

Complexation and chelation significantly enhance adsorption capacity and contribute to the long-term retention of heavy metals on agricultural waste materials.

Physical Adsorption

Physical adsorption, also known as physisorption, involves weak intermolecular forces between metal ions and the adsorbent surface. Unlike chemical adsorption, physical adsorption does not involve the formation of chemical bonds.

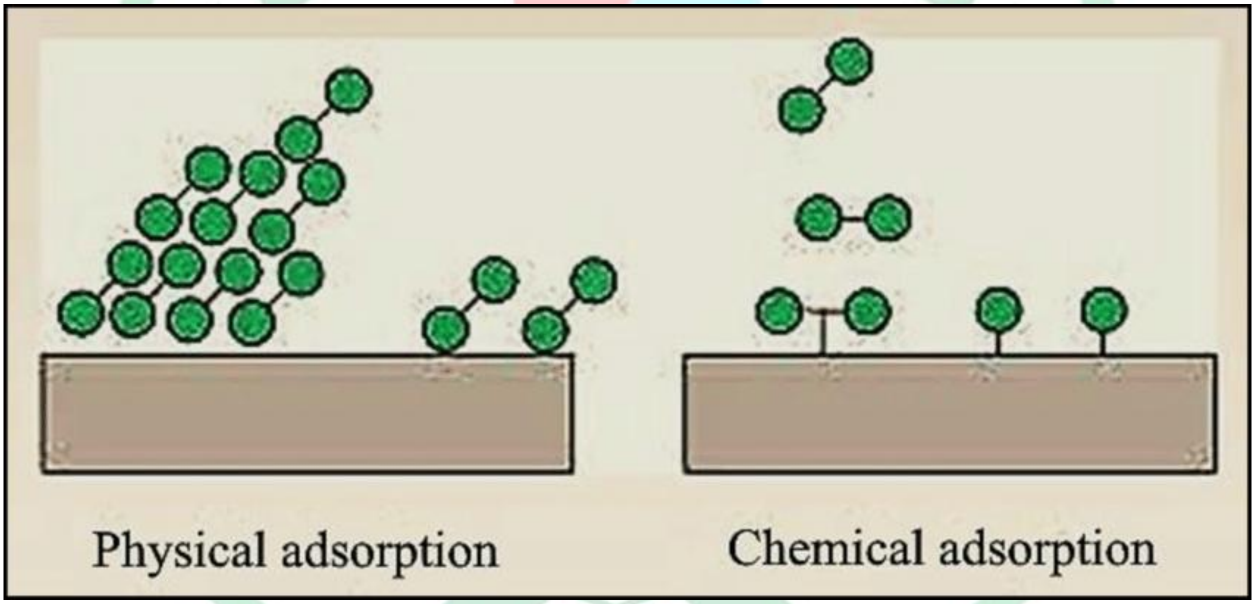

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Figure 1.2 Physical Adsorption

- **Nature of Interaction**
    - Governed by van der Waals forces.
    - Relatively weak and reversible.
    - Occurs rapidly at the initial stage of adsorption.
- **Role of Surface Area and Porosity**

  - Adsorbents with high surface area and porous structure enhance physical adsorption.
  - Agricultural wastes can be thermally treated or carbonized to increase porosity.
  - Biochar derived from agricultural waste exhibits improved physical adsorption properties.
- **Multilayer Formation**
  - Physical adsorption may involve multilayer adsorption.
  - Often described using Freundlich isotherm models.
- **Temperature Influence**
  - Physisorption is generally exothermic.
  - Increased temperature may reduce adsorption efficiency.

Although physical adsorption is weaker compared to chemisorption, it plays an important role in the overall adsorption process, especially during the initial phase of metal uptake. Fu and Wang (2011) reported that physical adsorption contributes to rapid metal removal before chemical interactions dominate.

One advantage of physical adsorption is ease of regeneration. Because the bonds are weak, desorption can occur with mild treatment, making the adsorbent reusable.

Precipitation and Electrostatic Attraction

In addition to ion exchange and complexation, heavy metal removal may also occur through precipitation and electrostatic interactions.

Precipitation Mechanism

- **Formation of Insoluble Compounds**
  - At higher pH levels, certain metal ions form insoluble hydroxides.
  - These precipitates may deposit on the adsorbent surface.
  - For example, chromium and copper form metal hydroxides under alkaline conditions.
- **Surface-Induced Precipitation**
  - The adsorbent surface may act as a nucleation site.
  - Promotes localized precipitation of metal compounds.
- **Contribution to Overall Removal**
  - Precipitation may enhance total removal efficiency.
  - However, it is often difficult to distinguish from adsorption experimentally.

Precipitation is more significant at higher pH values, where metal solubility decreases. However, excessive pH adjustment may not be economically feasible in industrial systems.

Electrostatic Attraction

- **Charge-Based Interaction**
  - Occurs between oppositely charged metal ions and adsorbent surface.
  - Surface charge depends on pH and point of zero charge (pHpzc).
- **pH Influence**
  - Below pHpzc, the surface is positively charged.
  - Above pHpzc, the surface becomes negatively charged.
  - Negatively charged surfaces attract positively charged metal cations.
- **Rapid Initial Adsorption**

  - Electrostatic attraction contributes to fast initial uptake.
  - Often followed by stronger chemical interactions.

According to the World Health Organization, maintaining optimal treatment conditions is essential to ensure heavy metal concentrations remain within safe discharge limits (WHO, 2017). Electrostatic attraction plays a supportive role in achieving these limits by enhancing adsorption efficiency.

III. REVIEW OF PREVIOUS STUDIES ON AGRICULTURAL WASTE ADSORBENTS

The growing body of global research on agricultural waste as adsorbents demonstrates their potential as effective, sustainable alternatives to synthetic and commercial adsorbents for removing heavy metals from textile wastewater. Agricultural waste materials—composed primarily of lignocellulosic biomass—have been shown to effectively adsorb toxic metals such as lead (Pb), cadmium (Cd), chromium (Cr) and nickel (Ni) due to their high surface area and surface functional groups (Fu & Wang, 2011). This section critically examines scientific studies related to (1) removal of major heavy metals using agricultural waste, (2) comparison of adsorption capacities among different wastes, and (3) the effects of chemical and physical modification/activation on adsorbent performance.

Removal of Lead (Pb), Cadmium (Cd), Chromium (Cr), and Nickel (Ni)

A significant number of studies have investigated the removal of toxic heavy metals using agricultural wastes, with many reporting high removal efficiencies under optimized conditions.

Lead (Pb): Lead is one of the most studied metals due to its severe toxicity and persistence in aquatic environments (Tchounwou et al., 2012). Rice husk, one of the most abundant agricultural wastes, has shown strong affinity for Pb(II) ions. Gupta et al. (2013) reported Pb(II) adsorption of up to 95% using untreated rice husk at pH 5–6 under batch conditions, attributed largely to ion exchange and complexation mechanisms involving hydroxyl and carboxyl groups. Similarly, banana peels, rich in pectin and cellulose, demonstrated Pb(II) removal efficiencies above 90% in aqueous systems due to their abundant carboxyl functional sites (Annadurai et al., 2003; Mohan & Pittman, 2007).

Cadmium (Cd): Cadmium is another priority pollutant often targeted in adsorption studies. Sugarcane bagasse has been widely applied for Cd(II) removal; Ahmad & Hameed (2010) reported up to 88% removal at pH 6. The authors attributed this performance to ion exchange between Cd(II) and native Ca^{2+}/Mg^{2+} ions in the biomass, along with complexation with surface ligands. Wheat straw also demonstrated significant Cd(II) uptake, with adsorption capacities comparable to commercial activated carbon under optimal conditions (Gupta & Suhas, 2009). These findings suggest that cereal residues can be effective Cd adsorbents—especially after surface activation.

Chromium (Cr): Chromium, particularly hexavalent chromium, is highly toxic and carcinogenic. Several studies have demonstrated high Cr(VI) removal using agricultural wastes. Coconut shell powder exhibited up to 85–92% Cr(VI) adsorption at acidic pH, driven predominantly by electrostatic attraction and reduction of Cr(VI) to Cr(III) on the adsorbent surface (Mittal et al., 2009). Another study showed that groundnut shells achieved more than 90% Cr(VI) removal after alkaline activation—highlighting the importance of modifying surface chemistry to target specific metals (Reddy & Pattabhi, 1997).

Nickel (Ni): Nickel is commonly present in textile effluents due to dyeing and finishing operations. Modified sawdust adsorbents removed up to 80% Ni(II) from model solutions, with adsorption following pseudo-second-order kinetics, suggesting chemisorption as the dominant mechanism (Demirbas, 2008). Olive pomace and grape waste were also effective for Ni(II) removal, with adsorption capacities near or exceeding those of commercial activated carbon under certain conditions (Aljeboree et al., 2017).

IV. COMPARATIVE ADSORPTION CAPACITIES OF DIFFERENT AGRICULTURAL MATERIALS

Comparative studies are essential for identifying the most effective agricultural adsorbents based on adsorption capacity (q_max), percentage removal, cost, and reusability.

Unmodified vs. Modified Wastes: Unmodified agricultural wastes often exhibit moderate adsorption capacities, but when compared side-by-side, their performance varies widely. For example, rice husk was found to have q_max values of ~35.7 mg/g for Pb(II), whereas wheat straw often demonstrated q_max values in the range of 40–60 mg/g for the same metal under identical conditions (Sarkar et al., 2012). Coconut husk and banana peels similarly showed competitive performance, with their ranking often depending on solution pH and initial metal concentration.

Comparison with Commercial Adsorbents: Although commercial activated carbon generally exhibits higher adsorption capacities, low-cost biosorbents frequently approach these levels. For example, activated coconut shell carbon often shows q_max values above 100 mg/g for Pb(II), whereas modified agricultural wastes such as phosphoric acid-activated sugarcane bagasse can reach q_max of ~90–95 mg/g for Pb(II), highlighting that modification significantly narrows the performance gap (Ahalya et al., 2003).

Multi-metal Adsorption Systems: Real textile wastewater contains mixtures of heavy metals, and competitive adsorption studies have shown different capacities compared to single-metal systems. For example, in a multicomponent solution containing Pb, Cd, and Cr, banana peels showed selective adsorption with 76% Pb removal, 61% Cr removal, and 54% Cd removal—indicating competitive inhibition at shared active sites (Ho & McKay, 2003). These competitive effects underscore the need for comprehensive evaluations under real-world conditions.

Ranking Based on Applications: In a comparative analysis of agricultural adsorbents, researchers often rank materials using performance indices such as adsorption capacity, cost per unit adsorbed, and regeneration efficiency. For example:

- **Rice husk** — high capacity for Pb and Cd, moderate for Ni.
- **Bagasse** — high capacity for Cd and Cr after activation.
- **Fruit peels** — excellent for Pb and Ni, moderate for Cd.
- **Nut shells** — strong performance for chromium species.

The variability in performance confirms that no single agricultural waste is universally superior; instead, selection depends on target metals, treatment scale, and wastewater characteristics.

Modification and Activation of Agricultural Adsorbents

Raw agricultural wastes often contain limited active sites and relatively low surface area compared to commercial adsorbents. Consequently, researchers have developed numerous physical, chemical, and thermal modification techniques to enhance adsorption performance.

Chemical Activation: Chemical activation involves treating biomass with acids, bases, or oxidizing agents to increase porosity and surface functional groups:

- **Acid treatments (H_3PO_4, HCl):** Increase surface area and expose carboxyl/phenolic groups. For example, H_3PO_4-activated rice husk showed nearly double the adsorption capacity for Cr(VI) compared to the unmodified material (Lo et al., 2010).

- **Base treatments (NaOH, KOH):** Enhance pore development and increase negative charge sites that attract metal cations (Ghaedi et al., 2011).
- **Oxidizing agents (H_2O_2):** Introduce oxygenated functional groups, improving complexation and chelation capacity (Rout et al., 2014).

Thermal Activation & Carbonization: Thermal activation involves heating biomass in limited oxygen at high temperatures to produce biochar or activated carbon-like materials:

- Biochar from coconut shells, rice husk, and sugarcane bagasse exhibits enhanced surface area and stable pore structure (Inyang et al., 2016).
- Biochar derived at 500–700°C often shows significantly improved adsorption capacities for Pb, Cd, and Ni compared to untreated residues due to increased porosity and exposed functional groups (Tan et al., 2015).

Physical Modification: Physical treatments such as grinding, sieving, and steam activation improve adsorption by increasing accessible surface area:

- Grinding smaller adsorbent particles reduces diffusion limitations and enhances removal.
- Steam activation develops additional micropores and improves metal uptake (Perez et al., 2014).

Composite and Nanostructured Materials: Advanced research has explored combining agricultural wastes with nanoparticles (e.g., Fe_3O_4, TiO_2) to create magnetic or hybrid adsorbents. These composites facilitate easier separation after treatment and often show enhanced metal affinities (Deng et al., 2010). For example, magnetic sugarcane bagasse biochar coated with iron oxide exhibited significantly improved removal of Cr(III) and Pb(II) due to synergistic surface interactions.

Performance Improvements: Modified adsorbents frequently achieve 1.5–3× higher adsorption capacities compared to their raw forms:

- Acid-activated bagasse for Cd(II): q_max increased from ~25 mg/g (raw) to ~75 mg/g (activated) (Gupta et al., 2016).
- Thermally activated rice husk biochar for Pb(II): q_max improved from ~45 mg/g to ~110 mg/g (Tan et al., 2015).
- NaOH-treated sawdust for Ni(II): q_max increased by over 50% compared to untreated sawdust.

Regeneration & Reusability: An important aspect of activation is the ability to regenerate adsorbents. Several studies demonstrate sustainable regenerability:

- Acid-desorbed rice husk retained over 80% of its initial capacity after 3 adsorption–desorption cycles (Singh & Sharma, 2017).
- Biochar materials often show stable adsorption over multiple cycles, enhancing economic viability.

V. CONCLUSION

Agricultural waste adsorbents provide an effective and sustainable option for heavy metal removal from wastewater because of their low cost, availability, and strong adsorption potential. Their performance is influenced by both physical and chemical adsorption mechanisms, including physisorption, ion exchange, complexation, chelation, precipitation, and electrostatic attraction. Among these, chemical interactions often contribute to stronger and more stable metal binding, while physical adsorption supports rapid initial uptake and easier regeneration. Overall, the study shows that a clear understanding of adsorption mechanisms is essential for optimizing treatment conditions and enhancing the practical application of agricultural waste materials in wastewater remediation. These adsorbents hold strong potential for environmentally friendly and economically feasible treatment systems.

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