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A COMPREHENSIVE REVIEW ON ASSESSMENT OF AGRICULTURAL CROP WASTE MATERIALS AS BIOADSORBENTS FOR ENVIRONMENTAL REMEDIATION

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Abstract

Agriculture, a legacy from our ancient ancestors, is fundamental to human survival and prosperity. Each year, the agricultural industry generates a substantial volume of agricultural and horticultural waste. Concurrently, the disposal of solid waste, particularly heavy metal ions originating from a variety of metal manufacturing industries, poses a significant societal challenge and constitutes a considerable environmental hazard. Hence, bioadsorbents are viable alternate components in comparison to conventional tactics for the wastewater purification and are capable of competing graciously in the eradication of heavy metal ions from wastewater. The review deliberates the impending use of different agricultural waste and their utilization for the removal of heavy metals and contaminants in wastewater based on their adsorption capacities and operating factors, cost-effectiveness, and practical engineering solutions. Biosorption is considered as operational and eco-friendly alternative to conventional techniques such as chemical precipitation, ion exchange, and membrane filtration for removing toxic metal ions. This review emphasizes the exploitation of readily available agricultural waste as adsorbents for mitigating environmental pollutants. It further scrutinizes the influence of various treatment methodologies on augmenting their efficacy in pollution reduction.

Key words: agro-waste, bioadsorbent, environmental remediation, heavy metal, waste water treatment

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1. Introduction

The agricultural and industrial sectors are instrumental in the socio-economic progression of developing nations globally. The rapid population growth in countries such as India and China has led to an escalation in agricultural and industrial outputs. While this increase is associated with economic advancement, it is crucial to recognize the adverse environmental implications of the waste generated from these sectors (Kumar et al., 2023). Notably, untreated discharge of wastewater having nutrient loading into the rivers and canals results in water pollution caused by various contaminants, including fungi, microbes, residual pesticides, and heavy metals (Kumar et al., 2020a; Taher et al., 2023). Industrial wastewater is useful in completing agricultural production through inland irrigation thus posing a potential health risk (Arshad et al., 2023; Taher et al., 2023). Agriculture is liable for 21 percent of GHGs emissions that occur although a sustainable course of agriculture is yet to be discovered in light of the

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expected increase in the world population is projected to expand to 10 billion by 2050. To address the limitations of natural resources, it is necessary to reduce the consumption of fossil fuels, decrease carbon emissions, and minimize solid waste (Duque-Acevedo et al., 2020). Solid waste management is carried out by reducing the bulky waste assembled at the source, or, in lieu reusing the unavoidable waste material generated (Yaashikaa et al., 2021). To mitigate the environmental impact of agricultural waste, industries such as food and cosmetics, textiles, tanneries, and agriculture must establish a closed-loop system. This system involves reprocessing waste materials into valuable resources, thereby reducing transportation and storage costs and eradicating emissions of greenhouse gases (Hamulczuk and Pawlak, 2022; Karic et al., 2021).

Water is considered to be a tremendously significant and precious resource for preserving the aquatic ecosystem and its diversity on Earth. Recently, global water consumption has been rising at a rapid pace due to varied factors such as overpopulation, urbanization, industrialization, and economic upswing. Water quality is severely hampered and degraded because of wastewater having high loading of heavy metals (cadmium, lead, zinc, chromium), dyes of textiles, polycyclic aromatic hydrocarbons (PAHs), and oil residues of liquid petroleum hydrocarbons (Chen et al., 2022; Mishra et al., 2017). In impoverished nations where access to sanitation and hygiene facilities is limited, a deficit of clean and accessible water might jeopardize both human health and the biosphere (Chong et al., 2023). Accumulation of a large array of highly hazardous heavy metals occurring and depositing in groundwater and surface water leads to chronic health conditions notably nausea, and mental and neurological disorders (Khan et al., 2022; Zahedifar et al., 2021). Water scarcity has posed a fuss in developing an efficacious wastewater treatment method (Chen et al., 2022). The application of various remediation techniques, such as adsorption, membrane filtration, electrodialysis, precipitation, biological remediation, electrochemical methods, ion exchange, and others, has been employed to eliminate pollutants from the wastewater (Anirudhan and Radhakrishnan, 2008; Tee at al., 2022; Zahedifar et al., 2021). Adsorption is an enormously most extensively used wastewater treatment technique ascribable to its low price and capital expenditure. The adsorption process is advantageous as it is attributable to a cost-effective design with minimal equipment expenses, minimal carbon footprint, and use of inexpensive adsorbents for operation and supplementary. Adsorption is environmentally friendly and ecologically benign due to its facile operational status and exemplary regeneration efficacy. In the middle of the 1990s, living or inert microorganisms were utilized for the treatment of sewage and waste and are considered to be the first bioadsorbent created for the adsorption of contaminants (Chong et al., 2023; Hlihor et al., 2009). In a couple of decades, biochar was generated from diverse sorts of biomass waste likely animal faeces food waste, and municipal waste solids for the elimination of the pollutants (Kumar et al., 2023; Taher et al., 2023).

Metals are intrinsically found on the external shell of the Earth, attaining the water partitions owing to anthropogenic activity, particularly metal mining and chemical transformation of metal compounds in industries, metal-based industries, leachates from waste deposits of landfills, animal excreta, automobile manufacturing and construction and demolition of agricultural runoff, roadwork’s, collaborating with natural events such as the volcanic eruption of hot lava, corrosion of heavy metals and metalloids, soil erosion (Duque-Acevedo et al., 2020; Kumar et al., 2023; Taher et al., 2023; Yaashika et al., 2021). These metals pose a substantial hazard to ecology and human health attributable to their eco-toxicological impact, bioaccumulation, and carcinogenic characteristics (Kumar et al., 2020b). The diverse organic compounds are pernicious, non-biodegradable, and tenacious in the domains of natural habitat thus bearing a greater influence on water pollution. Organic pollutants refer to a wide range of substances, both natural and anthropogenic, including chemical pesticides, pharmaceuticals, cosmeceuticals, hormones such as estradiols and esterons, as well as drugs of abuse. These pollutants are released into the environment through various sources, such as the discharge of industrial wastewater (whether treated or untreated), runoff from agricultural, livestock, and aquaculture activities, leaching from landfills, and the release of effluents from domestic and hospital sources (Chen et al., 2022; Chong et al., 2023; Karic et al., 2021). The pharmaceutical industry and agricultural production are essential for the manufacturing of pharmaceuticals, personal hygiene, skin care merchandise, and pesticides (Karic et al., 2021).

Numerous studies reconsidered agricultural waste materials alike stone fruits, nuts and husks of coconut, fruits and vegetable peels, forest residues, wood, and plants; in an attempt to cost-effective, and sustainable bioadsorption resources for remediating water pollutants (Karic et al., 2021; Sharma et al., 2024). Agricultural waste primarily consists of cellulose, hemicelluloses, and lignin. These components contain various functional groups such as aldehyde, carboxyl, carbonyl, hydroxyl, phenolic, and ether groups. Through specific binding mechanisms and interactions, these functional groups can interact with hazardous chemicals present in wastewater. Despite this, agricultural waste-derived bioadsorbents are less effective at bioadsorption than synthetic, commercial adsorbents. A significant amount of research on the adsorption of impending pollutants via the process of valuing waste from wood, agricultural products, and other sources was done. (stem and cobs), and cereals (rice, corn, wheat) (Karic et al., 2021; Shaheen et al., 2019; Tee et al., 2022). Consequently, several pre-treatment approaches have been developed to improve the sorption properties of raw biomass, thereby enhancing its potential for use in wastewater treatment (Bhattacharjee et al., 2020; Enaime et al., 2020). This scholarly article synthesizes findings on the utilization of agricultural waste and its ancillary applications in wastewater management, specifically through the use of bio-waste adsorbents for the removal of metals and organic waste (Martini et al., 2023).

The review explores the potential for agro-waste to mitigate water pollution by substituting traditional bioadsorbents with more sustainable and viable alternatives. The efficacy of bioadsorbents and bioadsorption techniques is underscored, with particular emphasis on their cost-effectiveness, binding mechanisms, and operational parameters such as pH, initial concentration, temperature, dosage, and pre-treatments. Furthermore, comprehensive and comparative studies are discussed, examining various factors including the types of bioadsorbents used, experimental conditions, targeted pollutants, sorption capacity, and overall contaminant removal efficiency.

2. Issues related to agricultural waste

Agriculture plays a pivotal role in the Indian economy (Harshala and Wagh, 2022). In recent decades, India has made significant progress by adopting contemporary cultivation techniques have led to substantial advancements by implementing efficient techniques. From being called a “begging bowl” to a “breadbasket”; agricultural Science and engineering have recast their image and have progressed into an established and modern trade. India holds the distinction of being the second-largest global producer of various agricultural commodities, including wheat, rice, vegetables, fruits, spices, and spice products (Kesavan and Swaminathan, 2020). As stated by the United Nations, agricultural waste is elucidated as agricultural operations generate substantial waste. The dependence on the system and the specific agricultural activity can vary; the waste generated can take any form of liquid, solid, or slurry (Obi et al., 2016). An unfeasible development of agriculture induces undesirable consequences on the rural and global ecosystem (Nguyen, 2017). Indian Ministry of New and Renewable Energy (MNRE) claims that India generates 500 million tonnes (Mt) of agricultural crop residues annually. According to the Ministry of Agriculture (2014), despite using crop residues as fuel or fodder, there remains a surplus of 140 Mt, with 92 Mt being burned annually (Ministry of Agriculture, 2014). Rice and wheat contribute about 70% of the crop residues, as rice- wheat is the best planting system in India.

The waste generated from the production of agricultural and horticultural produce increases with the increase in production and the readily accessible, cheap waste could be availed for removing heavy metal ions from the effluents as bioadsorbent could be in their natural or modified form (Sadh et al., 2018). The objective behind utilizing agricultural food wastes for the eradication of hazardous heavy metals could vanquish the aforementioned difficulties to a prominent extent. Industries such as Agrochemicals, energy-related, and textile exhibited a wide range of pollutants in water. The release of significant quantities of heavy metals into the ecosystem by different organizations presents a substantial risk due to their intrinsic toxicity, persistence in the environment, and propensity to accumulate in living organisms. This concern is particularly pronounced in developing nations, where it can occur either through direct or indirect means. The bioaccumulation of Heavy metals in the crops consumed by humans poses a high risk to health to the health of people varying from diarrhoea, cancer, mental and central nervous dysfunction, anaemia, and childbirth complications (Al-Huqail et al., 2022). Sufficient monitoring of different resources of water is crucial to prevent the transmission of diseases like cholera and typhoid, it is important to consume water that is safe and suitable for both personal use and agricultural purposes (Adelodun et al., 2022).

3. Types of agricultural crop waste

The utilization of agricultural food waste materials or by-products of crops and their residue straw, Husk, shell peel, pomace, bagasse, seeds, bran, corn cob, pulp, plant biological yield and cotton stalks, etc., as bioadsorbent for eradicating pollutants, is a novel technique as an alternative substitute (Alalwan et al., 2020; Burakov et al., 2018; Sari et al., 2023). The procedure offers several advantages compared to the conventional method, including lower cost, greater effectiveness, reduced sludge production, and bioadsorbent regeneration (Dai et al., 2018). The huge wastage occurs at different stages of the supply and handling chain (Alalwan et al., 2020; Burakov et al., 2018; Chong et al., 2023). High bioadsorption capacity is found in the waste material generated from agro-and-food industry, as it contains components likewise cellulose, hemicellulose, lignin, lipids, starch, proteins, hydrocarbons and several functional groups in their molecular structures that could adsorb pollutants such as aldehydes, alcohols, ether groups, ketones, and aromatic rings accelerating metal complexation facilitates the efficient elimination of heavy metals (Dai et al., 2018; Krishna et al., 2018). Consequently, the unique composition and structure of bioadsorbent make them advantageous for interacting with pollutants in different aqueous effluents. For instance, the sorption capability of bioadsorbent prepared from seeds has been estimated to eliminate divergent metals from the environment posing better results (Sheikh et al., 2021). The technique of altering such substances enhances the attraction of cations and anions onto adsorbents, hence offering potential benefits such as cost reduction in waste disposal and serving as an alternate treatment method to replace commercially available active carbon (Ahmad and Zaidi, 2020). The topic of discussion pertains to palm kernel fiber. The materials utilized in this study include rice husk, sawdust, tea waste, peanut shell, orange peels, wheat husk, pineapple stem, and sorbents derived from coconut, including bagasse coconut mesocarp, coconut husk, and coconut shell fiber (Table 1). The utilization of coconut copra meal, coconut coir pit, and coconut bunch waste in various applications has been a subject of academic interest (Sari et al., 2023; Uddin and Nasar, 2020).

Dry rice husk comprises organic compounds such as cellulose, lignin, carbohydrates, and others which make up 70-85% whereas, Silica present in the cellular membrane makes up the remaining portion (Malarvizhi et al., 2022). For the expulsion of lead and copper, batch experiments employing tartaric acid-altered rice husk as an adsorbent have been conducted. The results have elucidated the consequences on various parameters, namely pH, initial adsorbate concentration, particle size, and temperature. There have been reports indicating that modified rice husk has favourable characteristics for the removal of copper (Cu) and lead (Pb) from aqueous solutions (Dharsana and Jose. 2022; Purwiandono and Lestari, 2023).

Ground nut shells (GNS) can be employed due to their carbonate-based, which presents challenges in terms of disposal but also offers potential for its application as a cost-effective adsorbent for removing heavy metals from wastewater, owing to their high carbon content (Bayuo et al., 2019). Bayuo et al. (2019) found that groundnut shells have a significant capacity to eliminate chromium ions from aqueous solutions, even without undergoing any physical or chemical alterations. The adsorption process of chromium ions was found to be affected by several elements, such as pH level, duration of contact, initial levels of metal ions, the volume of adsorbent used, and temperature. The coconut husk is composed of two main components: the coconut pit and fiber. Additionally, the coir dust refers to the coarse material obtained from the robust mesocarp of the coconut, which is shredded during the extraction of the flesh for oil production (Droepenu et al., 2020). Coir dust which is 7% of coir husk; is a brown, weighed particle possessing lignin, tannins, cellulose, pentosane, and furfural (Etim et al., 2016). Husk and coir are beneficial owing to their structural stability, high absorptivity, and porous structure thus enabling them to be excellent bioadsorbent for wastewater contaminants (Hashem et al., 2017).

Table 1. Agricultural waste and its utilization

Type of waste	***Crop***	***Properties***	***Usage***	***References***
Food processing waste	all types of fruit and vegetables starch, dairy waste, meat, fruit peels, vegetable trimmings, spent grains, and pulp trash	rich in cellulose hemicellulose lignin ash, enzymes and nutrient content	Extremely nutritious, Waste, inexpensive use to make primary and secondary metabolites. Use for making biochar and bioadsorbent.	Bayram et al. (2022); Cho et al. (2023); Sari et al. (2023)
Fresh biowaste	most of the climacteric and non-climacteric fruits peel, skin, rind shell, stalk branches and twigs	rich in cellulose hemicellulose lignin ash and nutrient content	Use for making biochar and bioadsorbent.	Bayram et al. (2022); Sari et al. (2023)
Edible oil waste	sesame, mustard, cotton	rich in cellulose hemicellulose lignin ash and nutrient content	Used as manure; nutrient source and feed for the animal use for making biochar and bioadsorbent	Cho et al. (2023); George et al. (2021); Jagadeesan et al. (2023)
Kitchen waste	leftover household cooked food waste, leftover vegetables and fruits, egg shells,	rich in carbohydrates, amino acids, fatty acids, cellulose lignin, organic acids, inorganic salts,	For the enzyme production use for making biochar and bioadsorbent.	Saharan et al. (2023); Sołtysik et al. (2022)
Animal waste	the animals, the egg, and livestock industries, like skin, hairs, feathers, hooves, horns, deboning residues, and other materials	rich in organic carbon, minerals and fats	High amount of OM, protein, and fat. Use for making biochar and bioadsorbent.	Martini et al. (2023)
Agricultural waste	bagasse, rind, twings, offshoots, and stems	rich in carbohydrates, amino acids, fatty acids, cellulose lignin, organic acids, inorganic salts	Use for making biochar and bioadsorbent.	Chi et al. (2023); Karic et al. (2021); Tee et al. *(*2022)

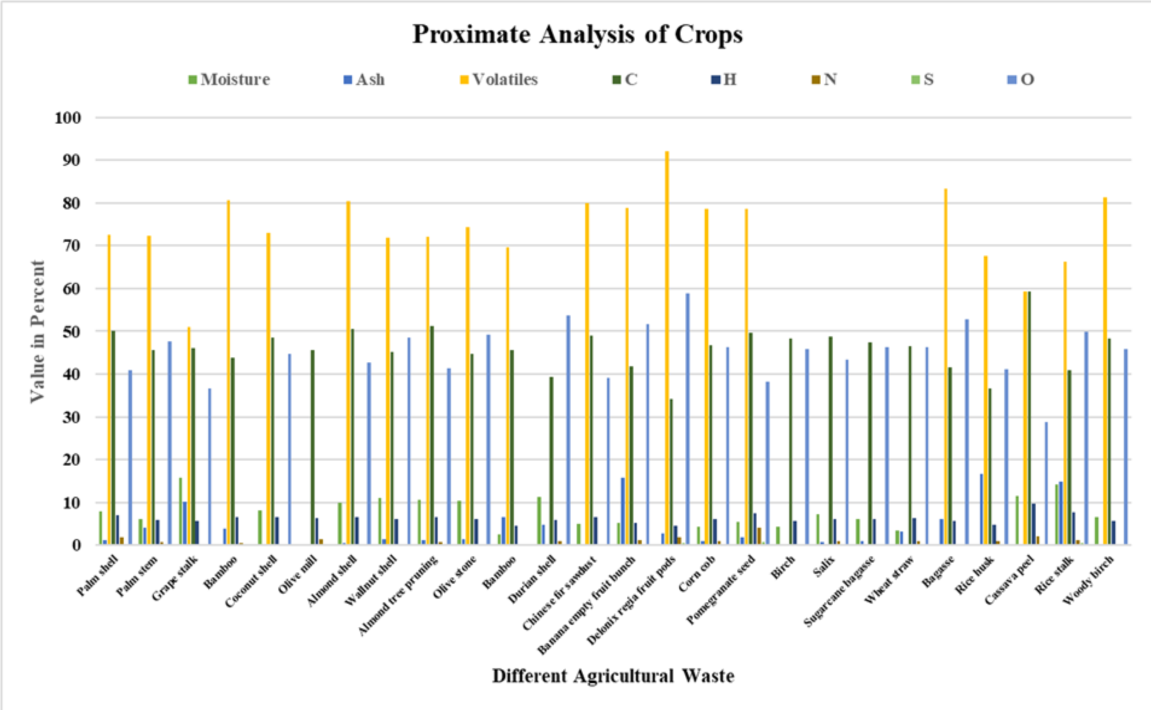

Fig. 1. Proximal analysis of the different agricultural waste

Some other materials also can be utilized for the manufacturing of Bioadsorbent (Fig. 1). Seeds of *Moringa oleifera* besides possessing nutritional benefits and medicinal properties also play a vital role as bioadsorbent due to an assortment of functional groups of carboxyl, amino acids, and phosphate. Seeds are utilized as a source of oil-rich flavonoids, tannins phenolic compounds, and hydrolyzable carbohydrates, thus being a promising biodegradable bioadsorbent with low cost.

4. Sustainable management of agricultural waste

Inadequate wastewater treatment disrupts the quality of water and enhances water pollution in developing countries, despite an increase in the efficiency of water use (Sniatala et al., 2023). The predicament coupled with poor water quality ascribed to the existence of heavy metals like Cr, Fe, and Cu leads to an insufficiency of water resources thus reducing the availability of clean water for public usage (Kurniawan et al., 2023; Maiurova et al., 2022). The UN's 2030 Agenda now encompasses environmental sustainability among its primary objectives.

However, achieving one of the targets of sustainable development goals (SDGs), which is to ensure sustainable access to potable water, is hindered due to water contamination caused by industrial and anthropogenic activities. This pollution leads to the release of effluents that contain hazardous heavy metals (Kurniawan et al., 2023). Consequently, this issue jeopardizes both public health and global economic growth. Water contamination in underdeveloped nations is a prevalent issue mostly attributed to the insufficiency of water technologies that exhibit a low capacity for excluding heavy metals (Liang et al., 2022).

Massive amounts of agricultural waste produced in the course of cultivation activities of the crop provide a source of energy supply for processing, production, and domestic activities in rural areas. In agri-based industries processing of rice, sugarcane, vegetables, coconut, and fruits, produces large secondary residue although on average tonnes of crop leftovers are produced for every tonne of the main product that is processed.

Waste generated from food industries signifies a considerable loss of the items produced and the vivacious resources such as land, water, labor, and energy (Ahmad and Zaidi, 2020). Agricultural and horticultural waste especially the ones comprising cellulose, lignin, and hemicellulose. These substances accommodate diverse functional groups such as aldehydes, alcohols, ether groups, ketones, and aromatic rings) in their molecular structures for the adsorption of contaminants (Dai et al., 2018). The divergent wastes produced include identical functional groups and chemical components at varying levels which are insulated or sterically hindered within the massive structure of the organic matrix interpreting it to be inaccessible to interact with the contaminants directly thus reducing the adsorption efficacy.

5. Green chemistry and adsorption by bioadsorbent

The primary objective of green chemistry is to facilitate the utilization of sustainable resources incorporate strategies that minimize waste generation and embrace the ideas of a circular economy (Omran and Baek, 2022; Sari et al., 2023).

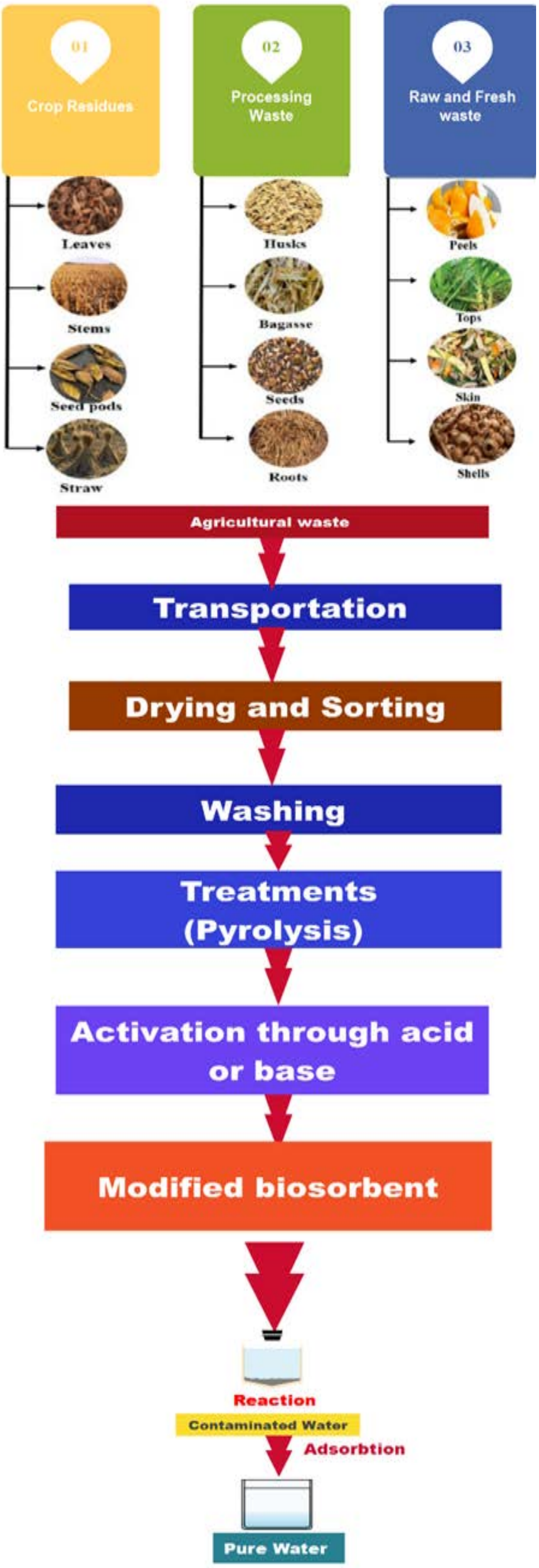

Fig. 2. Preparation of bioadsorbent from agricultural waste

Osman et al. (2020) proposed a set of twelve principles that outline the whole scope of green chemistry. These principles serve to underscore the multifaceted nature of the concept of green chemistry. Affordable waste materials can be used to make useful products like membranes and active photo-catalysts and bioadsorbents (Lau et al., 2022; Osman et al., 2020). The products are cost-effective for an array of applications likely water remediation, energy storage, and gas separation. The use of renewable feedstock is a principle of Green Chemistry and the adsorption by bioadsorbent aligns with it (Lima and Asencios, 2021) Bioadsorbent frequently generated from agricultural and horticultural waste are utilized as value-added goods to remove varied kinds of hazardous pollutants from water. The concoction of the bioadsorbent was prepared using the green chemistry principles given by Anastas and Warner (Osman et al., 2020) of synthesizing less dangerous chemicals and intrinsically safer chemistry to prevent accidents and avoid the use of hazardous chemicals (Chong et al., 2023).

Salt-activated bioadsorbent are presumed to be primarily activated by sodium chloride (NaCl) because of their inherent neutrality. The seeds of *Raphia hookeri* with the application of biochar demonstrate ecologically friendly attributes and reduced corrosive properties. In addition, it is worth noting that the manufacturing process employed for the synthesis of polydopamine and modified cyclodextrin polymers (CD-CA/PDA) is characterized by its ecologically conscious nature. This is primarily because both the raw materials utilized and the conditions under which the preparation takes place pose no harm to human health or the surrounding ecosystem. According to the study conducted by Chen et al. (2022), the regeneration and recovery of exhausted bioadsorbent is a viable waste management strategy in the context of promoting sustainability and efficient waste management practices.

Moosavi et al. (2020) developed magnetic bioadsorbent by incorporating magnetic particles into bioadsorbent to facilitate the recovery process. Regeneration of adsorption can be accomplished by employing the green chemistry principle of waste prevention and design for energy efficiency (Ahsan et al., 2018)

6. Generation of bioadsorbent from the waste agricultural material

Agricultural waste material that is discarded including seed, pulp, and peels of fruits and vegetables can be utilized for removing heavy metal ions as they possess varied properties. Waste materials which include cellulose show a notable potential for the bioadsorption of metals. Mathew et al. (2016) worked on the Banana peel taken as a green solution for the removal of metal toxins from contaminated water and is a feasible, readily available, cost-effective technique. In the past years, several researchers also used agricultural waste to eradicate toxic metals from wastewater (Burakov et al., 2018). Khatoon and Rai (2016) reviewed the sugarcane bagasse possessing cellulose (50%), ployoses (27%), and lignin (27%) which makes biopolymers a rich adsorbent. Saw dust was also retrospected as a copious agro-waste for the exclusion of heavy metal ions and dyes. In an experiment to investigate the absorption of malachite green on powdered activated carbon derived from groundnut shell waste; it was postulated that peanut shells exhibited the lowest loading capacity compared to rice and coconut shells. However, all three types of shells demonstrated higher efficiency in removing five heavy metal ions compared to commercial adsorbents.

Activated carbon and biochar produced from biomass are auspicious bioadsorbent for water management (Kumar and Kumar, 2020; Kumar et al., 2020c). The valorization of agricultural waste material by transforming the coconut husk shells, corncobs and rice straw into biochar for wastewater treatment (Chong et al., 2023). Biochar beads are highly economical and efficient adsorbents enabling the separation and recovery of fie biochar particles (Jang et al., 2017; Yu-Jin et al., 2023).

The highly porous carbonaceous material possesses high adsorption properties for the removal of organic contaminants. Biochar is prepared by pyrolysis of biomass at high temperatures and in an environment free from oxygen below 700˚C to increase yield and preserve the functional groups (Hassan and Carr, 2021). Contrastingly a temperature of 600-2000˚C is essential for the combustion of activated carbon and its porosity can be improved by subjecting it to physical (steam, O_2, or CO_2) or chemical (salt, acid, and base) activation processes. The treatment and reduction of contamination can be accomplished when biomass-based adsorbent is used to treat wastewater (Dai et al., 2018; Mengting et al., 2022). Harshala and Wagg (2022) stated that it was acceptable to recover the ecological contaminants owing to their porosity, loose surface, chemical stability, and exceptional mechanical strength. The performance of different bioadsorbent has been summarized in Table 2.

7. Physiognomies of bioadsorbent

The primary focus of concern in understanding the metal binding mechanism on the outermost layer of biomass is in an investigation of the physical and chemical properties of bioadsorbent. The investigation of the structure and surface chemistry of bio-adsorbents holds significant importance in the advancement of adsorption and separation techniques. Various techniques that are effective for bioadsorption can be categorized based on the nature of bioadsorbent. These techniques include X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) spectroscopy, and Fourier-Transform Infrared Spectroscopy (FTIR), and nitrogen sorption, among others (Fig. 2).

Bioadsorption alludes to a technique of employing organic substances or parts as adsorbents to remove hazardous metallic and non-metallic ions, as well as smaller particles, from wastewater created by various industries such as ore refinement, metallurgy, fertilizers, and papermaking (Basu et al., 2022; Mengting et al., 2022). The physicochemical qualities of the solution have a significant impact on its efficiency. Various factors such as pH, temperature, beginning concentration, and others can significantly influence the outcome of a given experiment or reaction. Bioadsorbent can be categorized into three main classifications: natural, biological, and waste-oriented. Several natural adsorbents, such as sand, zeolite, and silicon dioxide materials, possess desirable adsorbent characteristics and are readily accessible within the ecosystem (Singh et al., 2020). The primary sources of biological adsorbents are microorganisms, such as fungi, bacteria, and algae (Mathew et al., 2016). Other biological adsorbents derived from biological sources, such as chitin, peat, and biomass, have been reported (Ahmad and Zaidi, 2020).

8. Factors affecting the bioadsorption

The bioadsorption process can be influenced by a multitude of variables that are associated with environmental characteristics.

8.1. Temperature

Bioadsorption effectiveness is unaffected by temperature (20-35°C). Bioadsorption activity and adsorbate kinetic energy rise beyond 50°C, probably destroying the physical structure of the bioadsorbent. For a particular adsorbate, modifications in the equilibrium capacity of the adsorbent might be due to a slight change (+ / -) in the temperature where higher temperatures show significant improvement in adsorption (Harshala and Wagh, 2022).

8.2. pH

pH plays a vital role in the mobility of the functional groups in the adsorbent, competition between metallic ions and the solution chemistry of the metals (Sari et al., 2023). Besides, pH of the solution has a significant impact on the cation's affinity in the functional groups present on the cellular surface. At a lower pH, the biosorption capability decreases although it increases with the increase in pH until it reaches an optimum value. At a higher level (pH > 5.5), metal ions precipitated because the solution included a lot of hydroxyl anions (Li et al., 2019).

8.3. Pre-treatment

The adsorption qualities of bioadsorbent are modified as a result of physical treatments (e.g., drying, autoclaving, boiling, and mechanical disruption), owing to the specific purposes for which these treatments are employed. The potential for bioadsorption is increased by chemical processes like alkali treatment which is particularly evident in some fungal systems with greater metal affinities.

8.4. Acidity

The ion-exchange technique, wherein biomass serves as a natural ion-exchange substrate characterized by weakly acidic and basic functional groups, bears similarity to the process of bioadsorption. This methodological comparison underscores the shared principles of these two approaches in the context of environmental remediation. Notably, metal bioadsorption has been demonstrated to be substantially pH-dependent. Cu, Cd, Ni, Co, and Zn metal absorption are often decreased because cations and protons compete for binding sites at low pH.

8.5. Biomass concentration

It was postulated that at a given equilibrium concentration, the adsorption of metal by biomass is stronger at low cell densities. The adsorption of the specific metal escalated with lower biomass concentrations due to an increase in the bioadsorbent content actively promoting the interference between binding sites. The high biomass content prevents metal ions from reaching the precise position of the binding site (Alalwan et al., 2020; Sari et al., 2023).

8.6. The initial concentration of metal ions

The concentration of the metal ion at the beginning of the process plays a crucial role in regulating the barrier to mass transfer of all metals between the fluid and adsorbed phases. When the concentration of metallic ions in a solution is initially high, all metal ions readily bind to the available binding sites, resulting in a significant acceleration of the adsorption process by 99 percent until saturation is achieved (Sari et al., 2023).

8.7. Agitation speed

The acceleration of bioadsorption of adsorptive materials can be achieved by reducing the barrier to mass transfer. However, it is important to note that this increase in agitation speed may result in physical harm to the bioadsorbent, leading to a subsequent decrease in the resistance to mass transfer (Sari et al., 2023).

8.8. Contact time

The process of physical adsorption of metal ions onto the cellular surface is characterized by a rapid initial phase. This phase, however, is transient and diminishes over time. As the system approaches equilibrium, the activity of the adsorption sites on the adsorbent progressively decreases, indicating a reduction in their capacity to sequester additional metal ions (Sari et al., 2023). This phenomenon underscores the dynamic nature of the adsorption process and its dependence on contact time.

8.9. Bioadsorbent size

Reduced size of bioadsorbent size is favourable for the batch process owing to its higher surface area. It is less suitable for column processes due to lower mechanical strength and potential column clogging (Sari et al., 2023).

9. Mechanisms involved in bioadsorption

The utilization of bioadsorbent encompasses the capture of metal ions via various mechanisms such as the chelation process, complexity, ion transfer, chemosorption, and adsorption on the surface and pores. This process can be achieved using a wide range of naturally occurring materials, including agricultural waste (Yang et al., 2019). The waste produced from agricultural operations such as straw, trash, branches, peels, pulp, etc. endures modification processes that alter an assortment of their physicochemical characteristics, involving their hydrophilic/hydrophobic traits, physical attributes, functional groups, resistance to microbiological attack, and thermal stability. This phenomenon increases the ability of sorption to effectively eliminate contaminants from aqueous solution (Fig. 3).

9.1. Chelation

It is a technique where a chelate, an organic compound, links the metal ions at more than one location simultaneously intending to create a ring structure (Billah et al., 2023). Ligands are molecules that attach to an organic compound and display different coordination modes. Their interaction with a metal forms what is termed a coordination complex. The link between the meal or cation and the crystal lattice becomes weaker as the number of coordination complexes increases on mineral surfaces, leading to dissolution.

Chelates are more stable than complexes because they form several bonds with the metal ion at multiple points (Ahmad and Zaidi, 2020).

9.2. Complexation

An intricate system is created when two or more species are linked together through this process. Mononuclear complexes are those that are created when metal ions and ligands combine in a way that positions a single metal atom in the center. A polynuclear complex forms when more than one metal ion is present in the core. Depending on the number of binding ligands involved, the metal atom may have a negative, positive, or neutral charge during the assembly of polynuclear complexes (Ahmad and Zaidi, 2020).

9.3. Chemisorption

Chemical sorption is a synonym for chemisorption. It is attributed to an adsorption procedure wherein the surface and the adsorbate undergo a chemical reaction. Chemisorption involves the formation of a single layer of adsorbate on the adsorbent, characterized by a high enthalpy of adsorption. The chemisorption rate initially rises with temperature, but eventually decreases as the temperature continues to increase.

9.4. Ion exchange

A crucial part of adsorption is performed by this mechanism. The counter ions on the surface of the bioadsorbent are exchanged with the binary metal ions at the time of the process of bioadsorption. The technique of ion exchange has been employed by several widely accessible technologies for the purification of water. Ion exchange is usually accomplished by cation or anion exchange. For instance, anion exchangers are amino groups, whereas carboxyl groups serve as cation exchangers (Ahmad and Zaidi, 2020).

9.5. Surface precipitation

This process suggests that metal ions in water-based solutions interact with functional groups on microbial cell surfaces, forming a precipitate that keeps the metal ions associated with the cells. Adsorption methods often lead to both organic and inorganic metal precipitates. The use of microbial cells results in organic metal precipitates, which are a byproduct of the excretion of extracellular polymeric material.

9.6. Reduction

The bioadsorption of heavy metals, including gold and palladium, depends heavily on reduction, and thus this mechanism plays a vital role in bioadsorption. The metal ion links with the functional group during the process of reduction and it gets reduced thus experiencing the growth of crystals. The reduced metal links the bioadsorbent in numerous locations. Numerous heavy metals, including chromium, gold, palladium, and others, may be efficiently eliminated using the reduction process. For instance, by converting Cr (VI) into Cr (III) from the aqueous solution utilizing the bioadsorption method, it is simple to remove Cr (VI) (Krishna et al., 2018).

Nevertheless, these approaches have plenty of drawbacks, notably low metal concentration specificity, the production of massive amounts of hazardous sludge, and significant capital expenditures. In contrast, adsorption has been identified as an extremely successful approach due to its distinct characteristics, affordability, user-friendliness, high adsorption capacities, and versatility. This accounts for the cost-effectiveness of the adsorption method in the elimination of toxic substances and organic dyes (Khatoon and Rai, 2016). Considering the biological-based material's features, many carboxyl, hydroxyl, and amino groups on their surface thereby promoting the bioadsorption process. Scientists have recently placed a lot of emphasis on using them to remove contaminants from various fluids.

Table 2. Treatment of wastewater by agricultural wastes with certain operating factors

Crop name	***Waste***	***Method of activation***	***Adsorbate***	***Conditions***				***Adsorption capacity (mg/g)***	***References***
				Application (g/L)	***pH***	***Temp (˚K)***	***Time (h)***		
Onion *Allium Cepa*	Seeds	Sorption	Cadmium (II)	1.50	Neutral	297.85	1.5	1.50	Sheikh et al. (2021)
Almond *Prunus amygdalus*	Shell	Sorption	Crystal violet	0.51	Slightly acidic	292.85	3.0	1.085	Goksu and Tanaydin (2017)
Apricot *Prunus armeniaca*	Stone	Chemical activation (H_2SO_4)	Lead (II)	1.02	Slightly acidic	292.85	0.5	21.38	Mouni et al. (2011)
Apricot *Prunus armeniaca*	Shell	Chemical modification with (NaOH)	Lead (II)	-	Neutral	ART	2.0	171.78	Mouni et al. (2011)
Bael *Aegle marmelos*	Shell	Chemical activation with phosphoric acid	Hexavalent chromium	20.03	Acidic	292.85	4.0	17.30	Anandkumar and Mandal (2009)
Banana *Musa spp.*	Skin	Hydrothermal carbonization	Lead (II)	10.02	Neutral	297.85	3.0	359	Zhou et al. (2017)
Broad bean *Vicia faba*	Shoots	Chemisorption mechanism	Chromium (VI)	5.00	Acidic	ART	1.0	100.00	Fawzy et al. (2015)
Carrot *Daucas carota*	Skin	Atomic Absorption Spectrometer	Chromium (VI)	2-10	Slightly acidic	ART	0.5	88.28	Bhatti et al. (2010)
Cassava *Manihot esculenta*	Peel	Aqueous solution of MAA (Mercaptoacet ic acid)	Copper (II)	0.5	Neutral	ART	-	127.3	Horsfall et al. (2004)
Citrus *Citrus spp.*	Flaved o	Carbonisation and activation with $ZnCl_2$	Copper (II)	-	Neutral	ART	-	59.77	Dutta et al. 2011
Corn *Zea mays*	Stalks	Elemental analysis	Cadmium ion	-	Neutral	297.85	-	12.73	Zheng et al. (2010)
Dates *Phoenix dactylifera*	Seeds	Washing and grinding	MB (Methylene Blue dye)	10.01	Neutral	303.01	1.0	43.47	Belala et al. (2011)
Garlic *Allium sativum*	Straw	Desorption by HCl	Methylene Blue dye	0.04	Neutral	297.85	3.3	256.47	Kallel et al. (2016)
Litchi *Litchi chinensis*	Peel	Washing and grinding	Cadmium (II)	-	Slightly acidic	ART	-	23.05	Chen et al. (2018)
Mango *Mangifera indica*	Skin	Soaked with HCl, CH_3OH and HCHO	Lead (II)	2.58	Slightly acidic	ART	1.0	99.05	Iqbal et al. (2009)
Groundnut	Shell	Fourier Transform Infrared Spectroscopy (FT-IR)	Chromium (VI)	-	Acidic	297.85	0.5	131.02	Owalude and Tella (2016)
Musk melon *Cucumis melo*	Peel	Saponification with Ca $(OH)_2$	Lead (II)	1605	Slightly acidic	ART	0.2	167.8	Huang and Zhu (2013)
Neem	Bark	Aqueous solution	Lead (II)	7.50	Slightly acidic	422.85	1.0	84.75%	Naiya et al. (2008)
Palm	Shell	Impregnation with sodium nitrate and carbonization	Sulphur Dioxide Fumes (Gaseous)	-	-	292.85	-	121.67	Sumathi et al. (2010)
Palm	Stone	Chemical activation with H_3PO_4	Lead (II)	2.01	Alkaline	ART	0.6	172.43	Pap et al. (2017)
Papaya (*Carica papaya*)	Seed	Defatted with hexane	Cadmium(I I)	-	Alkaline	297.85	0.4	1000	Adie et al. (2011)
Passionfruit (*Passiflora edulis*)	Peel	Washing and grinding	MB	10.01	Neutral	ART	-	44.70	Pavan et al. (2008)
Peach(*Prunus persica*)	Stone	Steam activation	Hexavalent Chromium	04.01	Acidic	292.85	-	143	Duranoglu et al. (2010)

Peanut (*Arachis hypogaea*)	Hull	Washing and grinding	MB (Methylene Blue dye)	2.00	Slightly acidic	302.85	12.3	67.99	Hashem and Amin (2016)
Pea	Pod shell	Physical adsorption (Isotherm)	Chromium (VI)	30	Acidic	322.85	-	4.33	Sharma et al. (2016)
Pistachio (*Pistacia vera*) hull	Hull	Washing and Grinding	MB (Methylene Blue dye)	2.01	Alkaline	292.85	1.2	601.08	Moussavi and Khosravi (2011)
Pomegranate (*Punica granatum*)	Seed	Washing and Grinding	Crystal violet	8.05	Slightly acidic	297.85	1.0	434.782	Uddin and Nasar (2020)
Pomegranate(*Punica granatum)*	Peel	Carbonization	Lead (II)	2.53	Slightly acidic	317.85	2.3	95	El-Ashtoukhy et al. (2008)
Pomelo *itrus paradise*	Peel	Washing and Grinding	Crystal violet	-	Slightly acidic	302.85	1.0	254.16	Saeed et al. (2010)
Potato *Solanum tuberosum*	Waste	Aqueous solution	Methylene blue	0.5-3.0	Neutral	ART	0.5	52.6	Gupta et al. (2011)
Rice *Oryza sativa*	husk	Adsorption of ascorbic acid	Iron (III) chloride	0.875	-	ART	0.6	49.01	Ashrafi et al. (2015)
Sesame *Sesamum indicum*	Shell	Desorption by HNO_3	Cadmium (II)	0.02	Slightly acidic	ART	8.0	84.74	Cheraghi et al. (2015)
Sorghum *Sorghum bicolor*	Plant waste	Thiourea mediated treatment	Cadmium (II)	-	Slightly acidic	303	-	17.24	Salman et al. (2020)
Sugarcane	Bagasse		Lead (II)	0.37	Slightly acidic	332.85	1.5	-	Ezeonuegbu et al. (2021)
Tamarind Shell *Tamarindus indica*	Seed and Shell	Graft Copolymerization with $K_2S_2O_8$	Copper (II)	-	Slightly acidic	312.85	1.0	64.08	Bulut and Baysal (2006)
Walnut *Juglans regia*	Shell	Carbonized and chemically modified with $ZnCl_2$	Mercury	-	Slightly acidic	333	1.0	151.55	Zahibi et al. (2009)
Wheat *Triticum aestivum*	Bran	Sorption (Delta S_0)	Lead (II)	-	Slightly acidic	297.85		87.00	Bulut and Baysal (2006)

10. Agricultural-based versus other available bioadsorbent

Adsorbents derived from waste biomass are innovative tools for green chemistry and ecological technology, providing a sustainable method for removing harmful water pollutants. These cost-effective bioadsorbents have been developed for wastewater reclamation, with process variables such as pollutant levels, dose, stabilizers, temperature, gravity, and pH needing calibration for optimal contaminant removal (Sari et al., 2023). While other adsorbents like activated clay particles, carbon, graphene industrial by-products, zeolite, and polymer-based materials exhibit higher efficiency, their production costs are significantly higher than bio-based adsorbents, limiting their large-scale implementation (Kalengyo et al., 2023). Bioadsorbents have shown potential in removing dyes from aqueous solutions, albeit with modest effectiveness.

However, their environmental sustainability and economic viability make them a viable alternative for contaminant removal (Kalengyo et al., 2023). In some cases, their efficiency matches that of other adsorbents (Teshome et al., 2023). For instance, a bio-based adsorbent from agricultural waste demonstrated high performance in dye removal, achieving up to 70.25 and 98.41% removal, respectively (Temesgen et al., 2018). Thus, bio-waste adsorbents present a practical solution for wastewater contamination removal.

11. Bottlenecks and future perspective

Utilizing bio-based fruit waste adsorbents is a noteworthy approach for the effective management of soil waste. Bio-based efforts provide a viable alternative to traditional adsorbents. The efficacy of these bioadsorbent can be attributed mostly to their high content of hemicellulose and lignin. Moreover, due to the comparatively lower cost of fruit-based bioadsorbent in comparison to alternative absorbent materials, the financial burden associated with these solid wastes is significantly reduced. The decreased cost of solid fruit waste has emerged as a significant determinant in the utilization of fruit-based bioadsorbent during the past several years (Kumar et al., 2023; Kurniawan et al., 2023; Temesgen et al., 2018; Teshome et al., 2023). The use of solid waste as bioadsorbent necessitates the investigation of many characteristics, including pore space, surface area, and reusability, alongside chemical qualities such as pH, dosage, and adsorption rate. The application of adsorbents encompasses several benefits; however, there exist numerous limitations in the utilization of adsorbents derived from fruits (Sari et al., 2023). Moreover, several potential future outlooks have been indicated below. These potential prospects may prove beneficial for further study and addressing the existing gaps in the widespread application of adsorbents

(Kumar et al., 2023; Kurniawan et al., 2023; Temesgen et al., 2018; Yu-Jin et al., 2023).

The utilization of bioadsorbent is driven by their intriguing and promising qualities, which make materials appropriate for the elimination of pollutants in a manner that is both ecologically benign and sustainable. Furthermore, following the implementation of diverse alternatives, including physical and chemical stimuli, the bioadsorbent demonstrates remarkable adsorption characteristics and efficiencies. This study explores the comprehensive examination of modified bioadsorbent and their applications in the remediation of several emerging pollutants, including dyes, heavy metals, polycyclic aromatic hydrocarbons (PAHs), and oil. Additionally, the diverse adsorption mechanisms employed by these modified bioadsorbent are thoroughly investigated. Numerous studies have already been conducted on the utilization of bioadsorbent for the bioadsorption and remediation of diverse pollutants.

However, there are a few topics that necessitate further investigation. The existing body of literature mostly focuses on investigating the adsorption capabilities of bioadsorbent. These studies often employ synthetic solutions that include only one type of contaminant. Additionally, researchers aim to enhance the synthesis of bioadsorbent through the pyrolysis process, including both physical and chemical modifications. The utilization of a combination of diverse contaminants can be employed as a means to investigate the adsorption efficacy, hence enhancing our understanding of the effectiveness and long-term viability of bioadsorbent in practical industrial scenarios. However, to evaluate the effectiveness of bioadsorbent, it is necessary to conduct an absorption study using industrial effluent. The efficacy of pollutant removal was boosted due to the improved physical and chemical features of the modified bioadsorbent. When considering the energy-intensive process of pyrolysis for biomass and the associated chemical usage, it is important to acknowledge that the modification of biochar as adsorbents leads to increased production costs. To ensure the viability of enhanced bioadsorbent for commercial application, it is necessary to optimize the synthesis-related parameters on an industrial scale to facilitate mass production. To select the most suitable adsorbents, it is important to conduct a feasibility analysis encompassing the evaluation of preparation costs and performance assessment.

The challenging process of recycling bioadsorbent continues from a sustainability standpoint. The long-term viability of bioadsorbent is a persistent challenge that restricts their effectiveness in industrial adsorption processes. In-depth research is imperative to improve the bioadsorbent's mechanical characteristics and stability, which will conclusively result in less bioadsorbent waste disposal. Not much comprehensive research on the sustainability assessment of bioadsorbent-based water treatment is in the literature at the moment. As a result, a thorough life cycle assessment (LCA) of the bioadsorbent is necessary, including everything from the manufacture of the bioadsorbent to the safety assessment in terms of handling risk, the environment, and human health.

12. Conclusion and way's forward

The review featured a description of the dispersal patterns and detrimental effects of pollutants in water, while also highlighting the potential of these pollutants as cost-effective and environmentally-friendly bioadsorbent. India, the world's largest economy, produces crops year-round, resulting in agricultural waste and residue. Inefficient agricultural waste management pollutes the environment, making food production harder, especially in rural areas. The utilization of bioadsorbent derived from Agro-waste exhibits a plethora of functional groups, rendering them highly suitable materials for the effective removal of heavy metals, organic dyes, and oil pollutants.

Numerous viable processes for the treatment of contaminants have been presented to gain a deeper understanding of the involvement of chemisorption, electrostatic contact, ionic exchange, chelation and hydrophobicity.

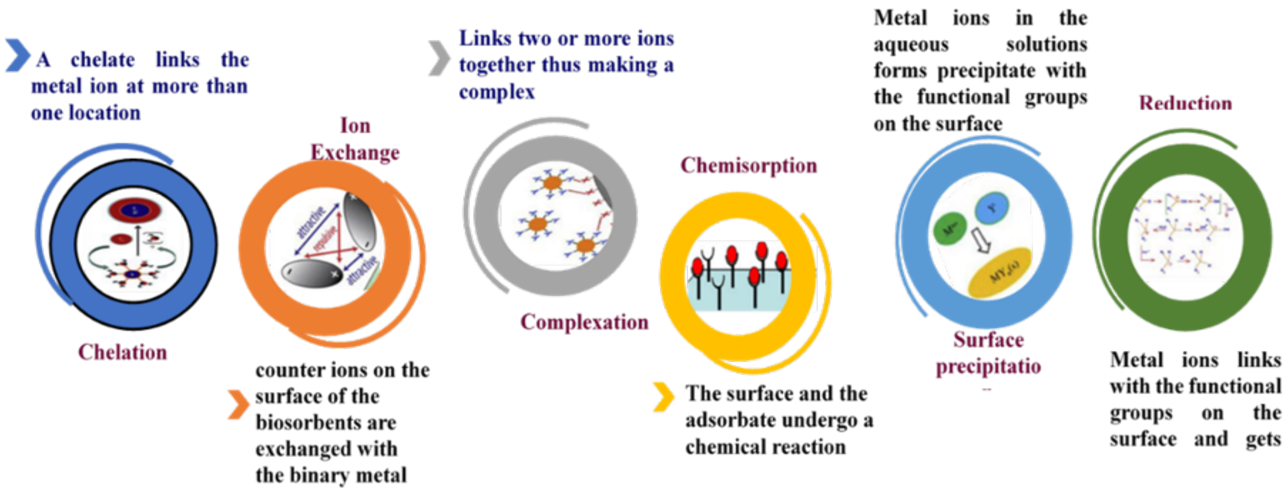

Fig 3. Mechanisms involved in bioadsorption process

Additionally, the practical significance of bioadsorbent made from biowaste has been elucidated through the discussion of desorption and regeneration processes. This review identifies many potential applications of agricultural waste-based adsorbents in the field of environmental clean-up. Besides, highlights the research gaps that require additional investigation. The advancement of effective green conversion and technology could accelerate the aggrandizement of biological adsorption. From the future perspective of environmental sustainability, recycling bioadsorbent will remain another challenge. There is an urgent need for advanced research and development (R&D) to improve the mechanical attributes and stability of bioadsorbents, factors that currently obstruct the effective disposal of bioadsorbent waste.

The biosorption process is a complex system, with its efficiency influenced by numerous variables. These include the nature of the biomass utilized as the adsorbent material, the concentrations of heavy metals, and physicochemical parameters such as temperature, pH, and contact time. Addressing these challenges through targeted R&D initiatives is crucial for optimizing the biosorption process and advancing sustainable waste management practices.

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