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Exploring the Relationship Between Food Waste and Heavy Metal Extraction through Biosorption

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Abstract Heavy metal elimination from polluted water is a prerequisite as they are hazardous to the environment as well as the health of people. Heavy metal removal from wastewater may be done effectively and economically via biosorption. Using waste materials as biosorbents from the food industry is an eco-friendly approach to waste management and pollution control. A considerable amount of waste is being generated from the food industry, such as grape pomace, coffee grounds, citrus peels, banana peels, coconut coir, tea waste, and rice husks, which are dominant in functional groups comparatively like carboxylic, hydroxyl, and amino groups that are proficient of binding heavy metals. A number of variables, consisting of temperature, pH, time of contact, and initial metal concentration, have an impact on the biosorption process. The routine technique for utilization of waste materials with respect to the food industry as biosorbents has several advantages, such as their abundance, budget-friendly, and ability to get rid of heavy metals effectively. In conclusion, waste materials from the food industry have the weightage to be utilized as effective biosorbents for heavy metals, providing a sustainable and eco-friendly solution for managing waste and pollution.

Keywords: heavy metal; biosorption; food; waste material; capacity.

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1. Introduction

Metal pollution is recognized as the most widespread and multifaceted environmental problem today. Food contamination is the major route by which heavy metals via soil and water accumulate in the body, causing major effects [1]. Several industries generate and release wastes from various heavy metals in the environment, like labor, photography, electrical appliance manufacturing, metal surface treatment, aerospace facilities, nuclear power plants, etc. Therefore, metal causes thoughtful pollution of the environment, affecting the well-being of humans and threatening the ecosystem. Three forms of heavy metals are of interest: toxic metals, valuable metals, and radionuclides [2,3]. Considering heavy metals, their unrestrained release into the soil and water leads to serious impairment of human health via bioaccumulation in the food chain [4-6]. As an outcome of their chemical complexity, low degradability, and toxicity, heavy metal contaminants are poorly degradable and can be transformed from their higher form of toxicity to relatively lesser form of toxicity or eliminated by either chemical/biological actions. [7-11]. Due to the increased urge for the usage of water for various conditions like the cultivation of crops, house-hold materials, industrialization, and recreational purposes, the recovery and reuse of polluted water is a top priority worldwide [12-14]. For removing heavy metals with the help of wastewater treatment, which consists of a higher concentration of metal, a number of traditional methods like membrane filtration, chemical precipitation, electrolysis, carbon adsorption, ion- exchange, and co-precipitation/adsorption are being used. [15-28]. These methods have drawbacks, such as the high cost of apparatus and operation to produce the sludge. Another disadvantage is energy and space, which has led to their limited application. Hence, it is strongly recommended that cost-effective ways to eliminate water pollution be identified and diagnosed; the routine practice of adsorbents for removing heavy metals is an inexpensive and practical procedure that has fascinated the attention of researchers today [29-31]. Pollutant removal from waste water, mainly from aqueous solutions, is a new and promising approach in heavy metal biosorption [32-36]. Cost-effective attractions Adsorbents are typically considered inexpensive because they are easy to process, plentiful in nature, or produced as a by-product of other industries. The major source of low-cost absorbents is environment-friendly materials or run-offs from commercial or agronomic operations [37]. In general, these materials are plentiful and inexpensive. Low-cost heavy metal removal may be achieved by utilizing readily available adsorbents. Agricultural and industrial waste were used to construct these attractions [38]. Commercially, the adsorbent must have a high selectivity to aid in separation, be simple to transport, have kinetic characteristics, be thermally and chemically stable, be mechanically robust, resist sedimentation, be regenerable, and have a low solubility in liquids. In comparison to conventional heavy metal removal methods, the adsorption technique offers significant benefits.

Figure 1. Countries in the world with respect to research outcomes based on heavy metal extraction via waste food.

The adsorption process has several benefits, including affordability, selectivity of metal, playability, lack of harmful algae, recovery of metal, and, utmost crucial, technique efficiency. Most absorbents comprise agronomic waste, industrial derivatives, natural materials, or modified biopolymers. [38]. Various food industry waste products have been tested in a variety of settings, including seafood processing waste sludge [39], sugar beet pulp [40], banana peel [41-43], papaya wood [44], grape stalk wastes [45], tea-waste [46,47], tamarind hull [48], potato peel waste [49], orange peel [50], etc. The adsorption capability of various food waste products is reportedly superior to that of activated carbons and industrial ion exchangers, making them effective adsorbents. Additionally, a lot of the investigations have been carried out using specific aqueous-phase applications and a certain kind of waste. The current study evaluates the literature on using waste products from the food sector, mainly water, to remove heavy metals, as shown in Figure 1.

2. Chemical and Physical Properties of Waste Food Material

Heavy metal ions are prevalent in wastewater from diverse sources, and numerous traditional techniques exist to remove them. Physical-chemical and biological techniques can be used to separate these traditional techniques [51]. Many businesses have heavily utilized physical and chemical approaches in recent years; however, they are not now preferred for various connected reasons, such as high price and disposal issues. Among the physical techniques are membrane filtration, gravity concentration, flotation, mechanical shielding, & magnetic separation. Reverse osmosis, ultrafiltration, nanofiltration, and electrodialysis are the different types of membrane filtration. Adsorption has been demonstrated as one of the appropriate and actual ways to remove heavy metals compared to membrane filtration and adsorption, as there can often be several issues with membrane separation, such as fouling [52]. Heavy metal elimination from wastewater can be done efficiently by implementing these chemical techniques, but they are quite costly and not particularly appealing from a business standpoint. These chemical methods have some restrictions, such as a high energy need and significant chemical reaction consumption, just as the physical approaches. Numerous studies demonstrate that when heavy metals are present in low quantities, physical and chemical removal procedures are inefficient and expensive [53,54]. Some researchers have used metal nanoparticles and metal oxide to decontaminate and purify water [55]. Biological procedures, often known as bioelimination, are one of the alternative approaches that can successfully lower the concentration of heavy metals to an ecologically acceptable level with modest effort [56]. In past years, various studies have been directed at removing toxic metal ions from wastewater using various plant products and by-products [52,57,58]. They additionally defined the value of agricultural by-products or products as sorbents for removing metal.

Additionally, they suggested that this method is an excellent and effective substitute for removing heavy metals, but only when using sorbents because they are cheap and do not need to be pre-treated. Other scholars have also noted the biological method's drawbacks in addition to its many positives. It needs a lot of space, has limited design flexibility, and has limited operating modes. Additionally, it is advised against using the method while handling significant amounts of wastewater. Researchers from several fields have suggested the biosorption process as an affordable and environmentally friendly method to solve the drawbacks of the aforementioned methodologies. A possible application of organic waste (food and agricultural waste) is biosorption, which is both a technique for removing heavy metals and an example of how it may be done. A low-cost, ecologically responsible, and simple-tobuild approach for creating an adsorbent from food and agricultural waste is also one that produces no harmful or dangerous compounds [57].

3. Potential of Waste Food Material in Removing of Heavy Metals

It is estimated that a huge quantity of food/agricultural waste is created worldwide per year. This waste consists of the discarded mass of fruits and vegetables, such as peels, crumb residue, seeds, and parts unfit for human consumption [59]. This widespread and inexpensive waste works as a biosorbent and tends to eradicate heavy metals from wastewater. This new and potentially alternative process has attracted much interest in recent years. It causes agricultural waste to have an adsorption capacity equal to or higher than the traditionally used processes [60]. These agricultural biosorbents can be applied in raw and altered forms [61]. A variety of agro/food waste products, including wheat bran, sugarcane bagasse, rice husk, rice bran, waste tea leaves, coffee beans, groundnut shells, hazelnut shells, maize corn cob, apple and banana peels, coconut shells, sugar beetroot pulp, soybean hulls, and cotton stalks. etc., can be used to eradicate heavy metals [62,63].

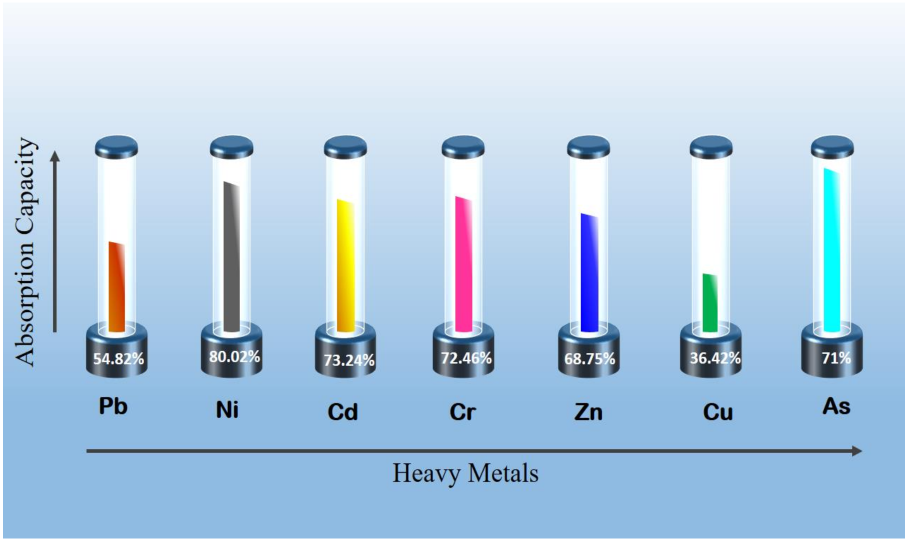

Figure 2. Heavy metals and their absorption capacity (Average) in percentage.

It contains ingredients like cellulose, hemicellulose, lignin, starch, protein, lipids, hydrocarbons, and other functional groups that form metal complexes with high adsorption capacity, helping eliminate heavy metals [64,65]. The effectiveness of agricultural and food waste depends on its affinity, adsorption capacity, and its physical and chemical nature. Different adsorbents show different efficiencies for different heavy metals [66]. For example, coconut waste, orange peel, rice husk, cereal grain, fig leaf, jackfruit, and olive branch are waste, which have excellent cadmium (Cd) removal efficiency [67]. In the case of chromium (Cr), the residues used are oranges, lemons, banana peels, and hazelnut peels [68]. In addition to these waste products, promising results are shown by powdered neem leaves, cactus leaves, coco coir, and pine needles, with about 90-100% effectiveness in removing chromium at optimal pH [69,70]. Different forms of agricultural waste have been used to remove (Ni) from wastewater in natural or modified forms, such as maple sawdust, hazelnut and peanut shells, tea leaf waste, etc. The effectiveness of the waste also depends on the form used. For example, sugarcane bagasse has been shown to be over 80% efficient at removing nickel in its natural form [71].

Similarly, other food waste such as corn cobs, soybeans, cottonseed, and coco coir have also been used to remove nickel in its modified form [72,73]. Removal of nickel up to 99-100% is efficiently done by the natural form of cassia fistula biomass [74,75]. Similarly, for Lead (Pb), numerous farm-based food materials have been used, such as orange peel, lemon grass, ground nut, rice husk, chitosan, coir waste of coconut, etc [76]. Orange peel removes higher levels of silver (Ag), copper (Cu), and zinc (Zn) at low pH, while coffee waste, decaffeinated coffee waste, and carob peel removers have shown to be more actual at eliminating these metals at relatively high pH [77]. This food waste is readily available, less expensive, and environmentally friendly, can be operated effectively within optimal pH range concentrations and in natural or modified form and potentially removes heavy metal contaminants and represents an effective method of waste management compared to traditional ones as it produces a large amount of sediment [78,79] Showin in Figure 2 and Table 1.

Table 1. Absorption capacity of different wastes and targeted heavy metals.

S. No.	Waste	Metal	Absorption Capacity(%,mg,mg/g/%)	References
1	Rice bran	Pb	69-87	[80]
2	Wheat bran	Cu	27.81	[81]
3	Black gram husk	Cd	19.56-49.97	[82]
4	Dal husk	Cr (VI)	96.05	[83]
5	Coffee husk	Cu	7.5	[84]
6	Tea residue	Cu/Pb	48-65	[85]
7	Almond shell	Pb	8.08-28.18	[86]
8	Nut shell	Cr (VI)	1.47	[87]
9	Walnut shell	Cr (VI)	1.33	[87]
10	Chestnut shell	Cu	12.56	[88]
11	Peanut shell	Cu	21.25	[89]
12	Mango peel	Cu	46.09	[90]
13	Grape bagasse	Pb	0.428	[91]
14	Barley straw	Cu/Pb	4.64,23.2	[86]
15	Coir fibre	Pb	263	[92]
16	Pumpkin waste	Cu	68	[93]
17	Sugar beet pulp	Cr (VI)	31.4	[94]
18	Pea waste	Cr (VI)	21.2	[95]
19	Sugarcane bagasse	Cr (VI)	99.8	[96]
20	Banana peel	Zn	5.80	[97]
21	Orange peel	Ni	6.01	[98]
22	Cornelian cherry	Cd	85	[99]
24	Papaya seeds	Cu	212	[100]
25	Corncobs	Cu	31.45	[101]
26	Oat biomass	Cr (VI)	<80%	[102]
27	Jatropha oil cake	Cr (III)	Upto 97%	[103]
28	Hazelnut shell	Cd (II)	High metal adsorption	[104]
29	maize cob	Cu (II)	High metal adsorption	[104]
30	Soybean hulls	Ni (II)	High metal adsorption	[104]
31	Jack fruit	Zn (II)	High metal adsorption	[104]
32	cottonseed hulls	Cu (II)	87%	[105,106]
33	Mustard oil cake	Ni(II)	Upto 94%	[107]
35	Coconut coir	Pb	26.5	[108]
36	Mangosteen shell	Pb	3.6	[108]
37	Mangosteen shell	Cd	3.15	[108]
38	Yellow passion fruit shell	Pb	151.6	[108]
39	Grape waste	Cr	1.91	[108]
40	Papaya wood	Cd	19.88	[108]
41	Papaya wood	Cu	19.89	[108]
42	Mango peel	Pb	99.05	[108]

S. No.	Waste	Metal	Absorption Capacity(%,mg,mg/g/%)	References
43	Mango peel	Cd	68.92	[108]
44	Wheat bran	Cd (II)	>82%	[109]
45	Green coconut shell powder	Cd (II)	98%	[110]
46	Rice polish	Cd (II)	>90%	[111]
47	Waste tea leaves	Pb (II)	92%	[112]
48	Black gram husk	Pb (II)	93%	[113]
49	Saw dust of rubber wood	Pb (II)	85%	[114]
51	Sugarcane bagasse	Cr (III)	Up to 97%	[103]
52	Saw dust of oak	Ni (II)	70-90%	[115]
53	Tea waste	Ni (II)	86%	[105]
55	Rice hush	As (III)	71%	[107]
56	Coir fiber	Zn (II)	>70%	[116]
57	Papaya wood	Zn (II)	67%	[44]
58	Almond shell	Cr (VI)	3.40	[117]
59	Banana peel	Cr (VI)	131.56	[97]
60	Hazelnut shell	Cr (VI)	8.28	[86]
61	Bael fruit	Cr (VI)	17.27	[86]
62	Wheat straw	Cr (VI)	21.34	[96]
63	Pinusroxburghii back	Cr (VI)	4.15	[110]
64	Wheat bran	Cd (II)	15.82	[92]
65	Banana peel	Cd (II)	5.71	[101]
66	Orange peel	Cd (II)	47.60	[97]
67	Mango peel	Cd (II)	68.92	[103]
68	Tea waste	Cd (II)	11.29	[114]
69	Orange peel	Cd (II)	136.05	[111]
70	Raw coffee	Cd (II)	15.65	[114]

4. Biosorption and its Classification

It is a physicochemical procedure in which a selected substance is removed from an aqueous solution using biological material, called biosorption [118-133].

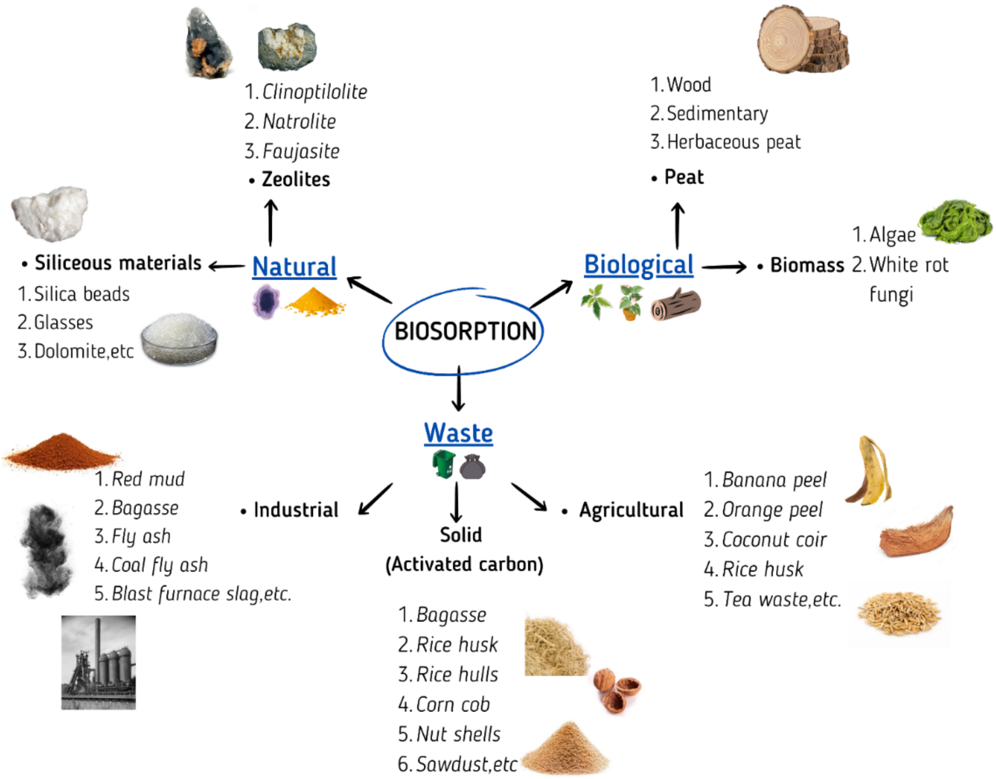

Figure 3. Types of Biosorption along with its classification.

Green chemistry, also known as sustainable chemistry, is receiving greater attention as a result of the growing desire for eco-friendly methods to remove contaminants from the environment [134]. Biosorption is a process that has various principles, such as the replacement of toxic reagents, utilization of safer reagents, evading the production of secondary waste that can not be recycled, reagent reuse, energy utilization should be reduced, and use of eco-friendly techniques.

Adsorption and biosorption are comparable processes, but the latter uses a biological matrix as the adsorbent. The biosorption procedure may include a number of processes, depending on the kind of sorbets used, the biosorbent used, along with other environmental factors. Physiochemical and metabolic processes involving ion chelation, exchange, adsorption, electrostatic interaction, precipitation, redox reactions, and surface complexation are just a few that may be involved in biosorption [135]. Biosorption is classified into three parts: natural, biological, and waste biosorbent.

4.1. Natural biosorbent.

Because natural absorbents, such as clay, zeolite, and others, have strong absorption capabilities, natural biosorbents arise spontaneously from the ecosystem and are readily available in the environment [136]. Natural biosorbents are further divided into two main parts, as shown in Figure 3, such as zeolite and silicious material, whereas zeolite includes clinoptilolite and natrolites, etc., and silicious material includes glasses, silica beads, and domolites, etc., as shown in Figure 3.

4.2. Biological biosorbent.

Biological absorbents include microorganisms that help in biosorption, such as bacteria, fungi, algae, and yeast [137]. In addition to the biological absorbents, biological sources like peats and chitosan, chitin, and biomass are also taken into consideration. Biological biosorbent is further divided into two parts, such as peat biomass. Peats include wood, sedimentary, and herbaceous Peats, and biomass includes algae and white rot fungi, as shown in Figure 3.

4.3. Waste biosorbent.

Waste biosorbents include biosorbents that are obtained from biological and natural waste. This waste biosorbent is obtained from solid (activated carbon) garbage, agricultural waste, industrial waste, waste vegetables peels and fruits, and industrial waste include sugar beet pulp, sawdust, rice husk, bamboo, and cassava peel, orange as well as banana peels, the shell of the egg, corn stack, bagasse, nutshell, etc. [136] as shown in Figure 3.

5. Mechanism of Biosorption

A challenging process called sorbate binding to the biosorbent occurs during biosorption [64]. Agricultural wastes may be used to create biosorbents, which fix metal ions by several methods, including chelation, complexation, ion exchange, chemisorption, reduction, precipitation, and adsorption on the surface and pores [137,138]. In biosorbents, particularly those prepared from agricultural and food waste, substances like starches, cellulose, simple sugar, hemicellulose, lignin, proteins, hydrocarbons, and various functional groups such as carbonyl, amine, sulfonate, carbonyl, phenolic, amide, carboxyl groups, alcohols, and esters can fascinate and separate ions of metals. Recent studies considering biosorbents have established the presence of these functional groups by observing the complexation of the aforementioned functional groups in the biosorption method with the help of heavy metals shown in Figure 4 and toxic effect-related data found in Table 2 [140,141].

The following are the factors responsible for the mechanism of biosorption:

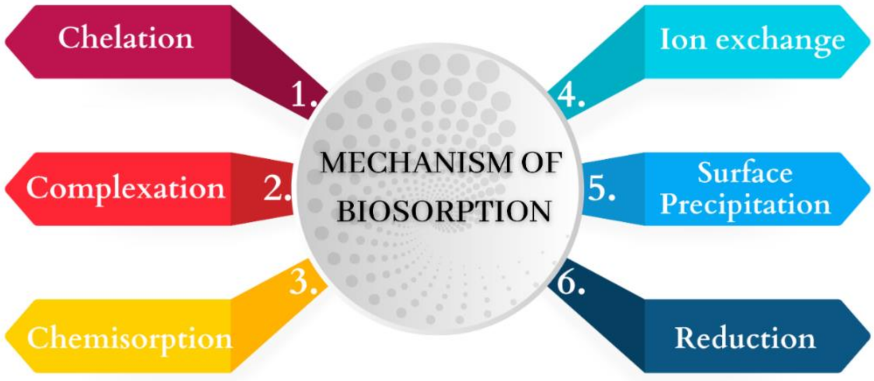

Figure 4. Mechanism of biosorption.

5.1. Chelation.

Multiple metal ions are simultaneously bound in a complex organic substance (chelate) to produce a ring structure. The ligand molecules create these types of coordination on an organic compound, and the interaction between ligands and metals is referred to as a coordination complex [142]. Dissolution happens as a result of a weakening of the link between the metal/cation and the crystal lattice brought on by a rise in coordination complexes on mineral surfaces. Chelates are more stable than complexes due to their many connections with the metal ions in various locations [142].

5.2. Complexation.

The mineral surfaces become less stable as a result of an increase in coordination complexes. In order to form a complex, two or more species must link with one another through this process. Mononuclear complexes are formed when metal ions and ligands combine to form an arrangement with a single metal atom at their core. The forming of a polynuclear complex results when the core contains several metal ions [143]. The metal atom might have neutral, positive, and negative charges depending on how many binding ligands are present during the creation of polynuclear complexes. According to various studies, mononuclear ligands are preferable to polynuclear ligands for complex formation since the latter comprise several ligands and result in the binding of a variable number of species.

5.3. Chemisorption.

The term "chemical adsorption" is often used. It is an adsorption method in which the surface and the adsorbate interact chemically. It frequently happens when chemical interactions or forces of attraction bind the adsorbent and adsorbate together [144]. When chemisorption occurs, a single layer of adsorbate with a high enthalpy of adsorption is produced on the adsorbent. The rate of chemisorption first increases as the temperature rises.

5.4. Ion exchange.

This mechanism is also important for adsorption. With respect to the biosorbent surface, binary metal ions are exchanged for counterions during the biosorption process. Many water filtration systems that are sold on the market employ the ion exchange process. The most typical kind of ion exchange is the interchange of cations or anions. In contrast to cation exchangers, which carboxyl groups represent, anion exchangers are represented by amino groups [136]. Several research has shown how the ion exchange bioabsorption process works to eliminate ions of toxic metal, including chromium, Pb(II), Zn(II), Cu(II), and cadmium, which aids different agricultural food wastes like watermelon peel, rice, and others [64,145].

5.5. Surface precipitation.

This maintains the metal ions in place with the microbe by precipitating them on the surface of an aqueous solution with functional groups. The adsorption process commonly results in the production of organic and inorganic metal precipitates. Utilization of microbial organisms causes extracellular polymeric polymers to be expelled, which causes the development of organic metal precipitates. Other situations can also lead to the formation of insoluble inorganic metal precipitates. In a number of studies, the rind of a watermelon, soybean meal, and the husk of a green tomato have all been used to demonstrate how surface precipitation mechanisms are employed to remove Pb (II), Cu (II), Cu (III), Zn (II), Fe, and Mn [70,145].

5.6. Reduction.

In the adsorption process of the biosorption with respect to heavy metals, including gold and palladium, reduction plays a significant role—the metal bonds with the functional group during the reduction process, which results in reduction. The decreasing metal binds to the biosorbent in several places. Chromium, gold, and palladium are just a few of the heavy metals that the reduction process may be able to remove successfully. For instance, it is easy to change Cr (VI) to Cr (III) and eradicate it from an aqueous solution using the biosorption approach [64,67].

Table 2. Toxic effects of heavy metals on biotic factors.

Heavy metal	Toxic state in nature	Source	Permissible limits (in ppm) in drinking water (USEPA)/ (WHO)	Toxic effects on humans and animals	Toxic effects on plants	References
As	As^{3+}	-Metal smelting -atmospheric deposition -burning of fossil fuels -mining -pesticides, herbicides, and processing of wood	0.01/ 0.05	Causes cancer, lesions of/on skin, cardio-pulmonary diseases, diabetes, GI discomfort, liver damage, and developmental disorders	Disrupts biochemical and physiological activities, suppresses plant growth, causes oxidative damage	[147,148]
Cu	Cu^{2+}	-Wood processing -paints and dyes, -electroplating -steel industry -petroleum refining -metallurgy and mining	1.3/ 1.5	Causes renal and hepatic damage, liver cirrhosis, intestinal irritation, and chronic anemia; Hereditary illnesses due to Cu homeostasis dysfunction.	Causes severe wilting, leaf discoloration, stunting, and necrosis; suppresses the growth of the plant; and causes damage to the root and	[149]

Heavy metal	Toxic state in nature	Source	Permissible limits (in ppm) in drinking water (USEPA)/ (WHO)	Toxic effects on humans and animals	Toxic effects on plants	References
					shoot tips; generates oxidative stress and ROS	
Cd	Cd^{2+}	-Electroplating - dyes and pigments -mining -phosphate fertilizer industry -iron and steel production	0.005/ 0.005	Causes cardiovascular, gastrointestinal, reproductive, and neurological diseases, Proteinuria, Glucosuria, Osteomalacia, Aminoaciduria, Emphysema, and cancer, and affects calcium regulation in the biological systems	Causes leaf curling, chlorosis, and stunting; disturbs opening of stomata; affects transpiration along with photosynthesis; causes oxidative damage; and affects nutrient accessibility, chlorosis, inhibition of growth, root tips turning brown, and finally death	[148]
Fe	Fe^{2+}	-Iron and steel industries -smelting -mining -fertilizers -refractory industry	0.1/ 0.30	Causes hepatic necrosis, anemia, liver failure, hyperglycemia, and gastrointestinal bleeding	Causes bronzing and stippling of leaves, damages the structure of cells, resulting in reduced plant growth, and hinders nutrient uptake	[150,151]
Hg	Hg^{2+} and $Hg_2{}^{2+}$	-Volcano eruptions, -soil leaching - hydroelectric mining -burning of fossil fuel -fungicides -dental amalgams - incinerators -old latex paint	0.002/ 0.001	Causes renal damage, circulatory diseases, high blood pressure, gingivitis, gastrointestinal discomfort, renal dysfunction, hepatotoxicity, pulmonary edema, neurological disorders, CNS injuries, and fetal toxicity	Impairs germination, decreases biomass and water absorption, inhibits photosynthesis, causes protein denaturation, disrupts cell membranes, decreases plant height, increases its bioaccumulation in the shoot and root of the seedling	[152]
Zn	Zn^{2+}	-Mining, -smelting, -paint -electrolysis -galvanization - fertilizers	5.0/ 5.0	Causes anemia; diarrhea; dizziness; nausea; vomiting; depression; malnutrition; and hepatic, renal, and neurological disorders	Causes chlorosis, reduces yield, inhibits many plant metabolic functions, causes senescence, reduces germination, and suppresses plant growth	[153,154]
Pb	Pb^{2+}	-Paints and pigments	0.015/ 0.010	Causes neurological disorders, CNS	Inhibits seed germination and root elongation;	[155]

Heavy metal	Toxic state in nature	Source	Permissible limits (in ppm) in drinking water (USEPA)/ (WHO)	Toxic effects on humans and animals	Toxic effects on plants	References
		-automobiles batteries -fossil fuel burning -Metal plating and finishing operations -fertilizers and pesticides -smelting of ores -soil wastes		injuries, lung dysfunction, and damage of liver, heart, and blood vessels, with potentially fatal consequences, including developmental defects	affects seedling development; causes oxidative damage; disrupts ATP synthesis and lipid peroxidation	
Ni	Ni^{2+}	-Metallurgy -food processing -chemicals -fossil fuel burning - mining	0.2/ 0.02	Causes cancer of the respiratory tract, contact dermatitis, lung cancer, asthma, cardiovascular diseases, genotoxicity, reproductive and developmental toxicity	Causes leaf and meristem chlorosis, induces oxidative damage, disrupts iron uptake, inhibits photosynthesis, and disrupts nitrogen assimilation	[156,157]
Cr	Cr^{3+} and Cr^{6+}	-Leather tanning -dyes -fabric preservatives - catalysis	0.1/ 0.05	Causes mutagenic, carcinogenic, and genotoxic diseases; perforation/ulceration of the nasal septum; skin allergy; reproductive and developmental birth defects; kidney dysfunction	Plant growth and germination of seed are suppressed, inhibits enzymatic activities and nutrient uptake, causes oxidative stress, impairs photosynthesis, causes severe damage to cell membranes, degrades photosynthetic pigments, causing a decline in growth	[7,158]
Mn	Mn^{2+}	-Welding -fuel addition -ferromanganese production	0.26	Damage to the nervous system and respiratory tract, hallucinations, forgetfulness, and nerve damage.	Deficiency in photosynthesis, necrotic spots on older leaves, and chlorosis.	[159]

6. Thermodynamics

Temperature changes have an impact on both the degree of adsorbate molecules diffusing from the solution to the adsorbent and their solubility (particularly in the case of dye biosorption). Three thermodynamic parameters may be used to represent the adsorption characteristics of a material: the Gibbs free energy change (G), change in enthalpy (H), and change in entropy (S). The co-efficient of thermodynamic equilibrium, identified at various concentrations and temperatures, may be employed to assess these properties, and its assessment offers insight into probable adsorption mechanisms. The G value is the primary criterion of spontaneity under constant temperature and pressure. Adsorption would occur, indicating the reaction was spontaneous if this value was negative. It is simple to compute G using the Gibbs expression implementing the equilibrium constants from the Langmuir model at each temperature, whereas the Van't Hoff plot may be used to determine H and S. It is crucial to remember that the G may be calculated from the data of equilibrium adsorption under the supposition that a batch system equilibrium state is created and that a molecule's adsorption is reversible [160]. Also emphasized is the requirement that the adsorbate concentration employed in the equation of Langmuir isotherm be given as the concentration of the molar [162, 163]. However, the volume concentration of the adsorbate has been frequently employed in the Langmuir isotherm equation in the literature on biosorption studies without any theoretical justification. This ultimately resulted in the incorrect use of the equation of Langmuir isotherm to calculate the G in the research related to thermodynamics [161,162].

6.1. Langmuir isotherm equation.

With respect to the surface of solids, gas adsorption was theoretically investigated by Langmuir, who viewed sorption- as a chemical process. This equation fundamentally takes the shape of a hyperbola, where $Qe = Qeth\, KeqCe\, /1 + KeqCe$ (1) Qe = Equilibrium adsorption capacity by weight, Qeth = Maximum adsorption capacity (theoretical) by weight, Keq = Equilibrium constant (adsorption reaction), and Ce = concentration of adsorbate at equilibrium. The equilibrium analysis of biosorption has been the most frequent use of this isotherm equation, although it must be remembered that in the mechanistic characteristics of biosorption, no insights are offered by Langmuir isotherm [148].

6.2. Freundlich isotherm equation.

$Qe = kFCe1/nF$ (2), where Freundlich constants (Kf and nF) include the empirical equation of isotherm that Freundlich proposed. Due to its exponential nature, the Freundlich isotherm equation can only be useful in low – intermediate concentration ranges. Eq. (2) has also been used extensively in biosorption studies, much like the Langmuir isotherm equation [164].

6.3. Sips isotherm equation.

According to Sips, an empirical isotherm equation could be written as $Qe = Qeth\, (KeqCns\, /1 + KeqCens)$ (3), where ns is the Sips constant. Sips [167] stated that "we do not know whether or not this form of isotherm actually represents any experimental results" at the time that he proposed the aforementioned empirical isotherm. According to Kumar and Porkodi's, the finest fit for experimental data is being offered by the Sips isotherm, Langmuir isotherm equation, and Redlich-Peterson isotherm equation in the decreasing order and [168] comparison analysis of various equations of isotherm implemented to the methylene blue sorption on lemon peel. Two methods were created for deriving the empirical Sips equation and are discussed in the following sections.

6.4. Derivation from a thermodynamic approach.

Sips equation was developed by Liu et al. [150] from a thermodynamic view. The complete biosorption reaction might be viewed as a straightforward modification of the adsorbate's state [166], i.e., $C \rightarrow Cads\, \Delta G\, \circ$ (4) where G = Effective free energy change of biosorption (deviates as the reaction of biosorption progresses) and C = Molar concentration of adsorbate in bulk solution and Cads = adsorbed at time t, respectively. G would decrease as the metal concentration increased because the adsorption is more favorable when the concentration of adsorbate (C) increases in bulk solution [167]. By Morel and Hering [151], ΔG◦ can be indicated as,

$$\Delta G \circ = \Delta G \circ \ - nLRT \ln C \ (5)$$

Where the positive coefficient, nL, is present. According to evidence, the amount that a unit of biosorbent, in fact, adsorbs (Q) at a given concentration of adsorbate and the amount that it could conceptually adsorb at that particular concentration (Qth), constituting the real force driving behind biosorption. This driving force gradually decreases as the biosorption reaction approaches equilibrium [167]. As the biosorption progresses, it will diminish adsorption's driving force and resistance. It makes sense to assume that as adsorption resistance increases, the entire change in free energy of the biosorption (G) process will decrease as the adsorption reaction driving force increases. Liu et al. [165] suggested formulating the biosorption reaction's total change in free energy, resulting in the driving force and resistance of adsorption, which results in,

$\Delta G = \Delta G \circ \ + RT \ln Resistance/Driving\ force$ (6)

Theoretically, Eq. (6) is reliable, along with the expression for the change in free energy for an ideal gas and solution [151]. As previously said, as the adsorption process continues, the adsorption reaction becomes less favorable; therefore, G must rise in accordance with this. These appear to indicate that Q represents the resistance of adsorption strength. Behind the process of biosorption, the actual driving force is, on the other hand, which may be seen in the difference between Qth and Q; a bigger difference results in a (smaller value) of G. As a result, Eq. (6) can be expressed as follows:

$\Delta G = \Delta G^{\circ\prime} + RT \ln Q/Qth\ Q$ (16)

According to Eq. (7), "G°" is equal to "G" for Q = 0.5Qth. This implies that "G°" might be seen as the total change in free energy when Q = 0.5Qth, i.e., when the resistance force and the driving force of biosorption are equal. This is in keeping with Morel and Hering's assertion that additional adsorption becomes energetically impossible as Q approaches Qth and G goes to infinity [166]. Substituting Eq. (5) into Eq. (7) results,

$\Delta G = \Delta G \circ \ - nLRT \ln C + RT \ln (Q/Qth - Q)$ (8)

ΔG becomes zero when adsorption reaches its equilibrium.

Hence, 0 $= \Delta G \circ \ - nLRT \ln Ce + RT \ln (Qe/Qeth - Qe)$ (9)

in which Ce, Q_e, and Q_e^{th} are the respective values of C, Q, and Q^{th} at equilibrium.

Solving Eq. (18) for $Qe\ gives\ Qe = Qeth\ (CenL/\ e\Delta Go/RT + CenL)$ (10)

Eq. (19) can be repositioned as $Qe = Qeth\ (CenL\ /Kads + CenL)$ (11)

in which $Kads = e\Delta Go/RT$ (12)

In actuality, Eq. (11) and Eq. (3), the Sips isotherm equation, have a similar formulation. The equilibrium constant of thermodynamics of the biosorption process (Keq), which may be thought of as an analog to a chemical reaction, is described as,

$Keq = e - \Delta Go/RT$ (13)

Comparing Eqs. (12) and (13) depict that,

$Kads = (1\ /Keq)$ (14)

The physical significance of Kads is revealed by equation (14). It should be noted that Eq. (14) can be substituted for Eq. (11) to provide Eq. (12). Here, it is shown that the above-discussed thermodynamic technique may also be used to derive the Sips isotherm equation. Eq. (11) is made further simpler to the Langmuir adsorption isotherm at nL=1:

$$Qe = Qeth\,(Ce\,/Kads + C)\;(15)$$

Eq. (15) demonstrates that the Langmuir adsorption isotherm is only a certain case of Eq. (11) at nL is equal to 1. When C^{nL} e is considerably less than K_{ads}, Eq. (11) is therefore simplified to the Freundlich-type isotherm:

$$Qe = (Qeth\,/Kads)\;CenL\;(25)$$

It seems that Q_e^{th}/K_{ads} is the correct value for the Freundlich constant. It should be noted that two of the constants in the Freundlich isotherm equation, denoted as an empirical formula, are not physically meaningful. Eq. (16) offers a theoretical foundation for more accurately interpreting the empirical Freundlich isotherm equation. Therefore, Eq. (11) can be seen as a generalized version of the Langmuir and Freundlich models.

7. Conclusion and Future Aspect

Utilizing the waste materials as biosorbents from the food industry for heavy metals is a promising approach to further control contamination and waste management. The food industry generates a significant waste quantity that can be practiced in order to eradicate heavy metals from contaminated water. As a result of several factors, the biosorption process and the performance of biosorbents varies on the type of waste material used. However, using waste materials as biosorbents has several benefits, such as affordability, eco-friendliness, and abundance. As water is becoming contaminated day by day, in order to minimize its toxic effects, an hour must be cleaned. So, a well-planned futuristic approach and sustainability are required to do a detailed study on green solutions for the analysis. Further research is required to optimize the biosorption process, identify the most effective waste materials, and evaluate the feasibility of large-scale applications. Overall, utilizing waste materials as heavy metal biosorbents from the food industry is a promising solution that contributes to sustainable waste management and environmental protection.

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Conflicts of Interest

The authors declare no conflict of interest.

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