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Heavy Metal Remediation from Water/Wastewater Using Bioadsorbents - A Review

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ABSTRACT

This paper aims to emphasize heavy metals' impact on water and its removal mechanism with a focus on adsorption. Furthermore, factors affecting bio adsorption, such as temperature, pH, RPM, and initial heavy metal concentration, have been studied for different heavy metals and bioadsorbents. A comparison of their adsorption capacities and efficiencies has been made. This review reviewed different bioadsorbents for their suitability in removing cadmium, lead, and copper ions from water and wastewater, typically by using adsorption as a methodology. A suitable summary compares various heavy metal removal techniques and their advantages and limitations. For adsorption, the characteristics of bioadsorbents and their activation steps have been consolidated. Furthermore, the effects of operational parameters and adsorption mechanisms have been discussed in the review. Apart from assessing the suitability of bioadsorbent, a novel bioadsorbent has been suggested for copper ions removal. The findings shall be significantly useful in applying bioadsorbent in water/wastewater treatment fields to reduce heavy metal pollution. Thorough and well-planned research in this field can facilitate the creation of sustainable and durable technology for wastewater treatment, addressing the increasing demand for safe and dependable water resources, focusing on making it cost-effective and recyclable.

INTRODUCTION

Water serves as an important raw material to most of the industries. Protection of this key component becomes a pivotal task for the present and future. Aside from industries, it is a vital food source for humans, animals, and other living beings, the basis for a wholesome environment. Water pollution due to heavy metals remains a key challenge, making it unsuitable for safe consumption (Malik et al. 2017, Sehyeong et al. 2021).

The inception of heavy metal pollution can be attributed to major operations such as smelting, foundries, mining the metal, and other operations in metal-based industries (Pham et al. 2019, Vaishnavi & Shelly 2015, Qasem et al. 2021). Common and toxic heavy metals in wastewater and sewage sludge include cadmium (Ca), chromium (Cr), mercury (Hg), copper (Cu), arsenic (As), nickel (Ni), silver (Ag), lead (Pb), and zinc (Zn). Each of these heavy metals has a detrimental effect on the health of living species, thus, these pollutants must be kept under limits (Pham et al. 2019, Malik et al. 2017).

Presently, significant work has been done for its removal using precipitation/coagulation, filtration, electrochemical treatment, and ion exchange treatment (Manisha et al. 2021, Malik et al. 2017). Considering most of these methods, there are limitations to versatility in treatment, high cost of buildup, sludge disposal, and less technical maturity (Manisha et al. 2021, Malik et al. 2017, Naif et al. 2021).

Therefore, in this study, we will evaluate the work done on bio adsorbents (natural adsorbents) for removing heavy metals from wastewater with suitable operating conditions. The removal efficiency for different heavy metals (Pb, Cd, and Cu) will be compared using various agricultural waste-derived adsorbents.

NEED OF HEAVY METAL REMOVAL FROM WATER

The presence of heavy metals poses a serious threat to human health. These metals are known to be lethal and carcinogenic, causing substantial damage to aquatic ecosystems and human health (Jamdade & Gawande 2015, Deniz et al. 2022). Contamination is a major challenge in modern times to provide quality potable water to mankind (Nadeem et al. 2021). Health disorders may range from nausea and skin irritation to neurological dysfunction and cancer (Vaishnavi & Shelly 2015, Qasem et al. 2021, WHO Guidelines for

Drinking Water Quality, 2011, 2017). Since these heavy metals are not biodegradable, there is a need for their removal by certain chemical/mechanical separation techniques (Mane et al. 2013). Data summarized below in Table 1 depicts the hazards associated with these heavy metals and their most prominent generation sources and limits defined by WHO.

As elucidated by Fig. 1, some heavy metals have their thresholds even at a concentration above 0.001 $mg.L^{-1}$. Studies have shown that apart from industrial wastewater, rivers, major water supply sources in cities & towns have particularly high heavy metal content (Vaishnavi & Shelly 2015, Jamdade & Gawande 2015).

METHODS FOR HEAVY METAL REMOVAL

Various techniques have been developed to bring down the level of heavy metals in water. Broadly, there are three categories for reducing heavy metal concentration: physical, chemical, and biological, as shown in Fig. 2. There are certain techniques prominently used, currently being actively employed in industries/organizations, such as physical treatment: filtration (Zahra et al. 2023), sedimentation (Noureddine & Harvey 2020), coagulation/flocculation (Abujazar et al. 2022), adsorption (Nadeem et al. 2021), membrane filtration (Zahra et al. 2023), magnetic separation (Boruah et al. 2015), chemical treatment (Liang et al. 2020): chemical precipitation, ion exchange, reverse osmosis (Al-Alawy et al. 2017), electrochemical treatment (Trần et al. 2017), oxidation/reduction, co-precipitation, and biological treatment: advanced techniques like bioremediation (Monika & Surajit 2021), phytoremediation (Ram & Sangeeta 2010), biofiltration (Stefano et al. 2015), enzymatic treatment, microbial fuel cells (Wu et al. 2020) are employed.

Table 1: Heavy metals, WHO limit, and their effect.

S.No.	Heavy Metal	WHO limit [$mg.L^{-1}$]	Primary Generation Source	Effect on humans	References
1.	Cadmium	0.003	Batteries, paints, steel industry, plastic industries, metal refineries, and corroded galvanized pipes	Carcinogen, Kidney Dysfunction	(Vasihnavi & Shelly 2015, WHO Guidelines for Drinking Water Quality 2011,2017)
2.	Chromium	0.05	Steel and pulp mills and tanneries	Carcinogen, Nausea, Diarrhea	(Vasihnavi & Shelly 2015, WHO Guidelines for Drinking Water Quality 2011,2017)
3.	Mercury	0.001	Electrolytic chlorine and caustic soda production, runoff from landfills and agriculture, electrical appliances, Industrial and control instruments, laboratory apparatus, and refineries	Neurotoxin, Kidney dysfunction, Circulatory & Neurological Disorder	(WHO Guidelines for Drinking Water Quality 2011, 2017)
4.	Copper	2	Corroded plumbing systems, electronic and cables industry	Liver Damage, Convulsions, Insomnia	(Vasihnavi & Shelly 2015, WHO Guidelines for Drinking Water Quality 2011, 2017)
5.	Arsenic	0.01	Electronics and glass production	Skin Problems, Visceral Cancer	(WHO Guidelines for Drinking Water Quality 2011, 2017)
6.	Nickel	0.02	Stainless steel and nickel alloy production	Carcinogen, Dermatitis, Gastrointestinal Disorder, Lung, Kidney Damage	(Vasihnavi & Shelly 2015, WHO Guidelines for Drinking Water Quality 2011, 2017)
7.	Silver	0.1	electroplating, semiconductor manufacturing, photograph processing, and silver mining	bluish-gray discoloration of the skin, eyes, and mucous membranes, gastrointestinal symptoms, neurological effects, including tremors, seizures, and coma	(WHO Guidelines for Drinking Water Quality 2011, 2017)
8.	Lead	0.01	Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes, and plastic stabilizers	Central Nervous System Damage, Cerebral Disorders, Kidney and liver Reproductive System Dysfunction	(Vasihnavi & Shelly 2015, Qasem et al. 2021)
9.	Zinc	3	Brass coating, rubber products, some cosmetics, and aerosol Deodorants	Skin irritation, nausea, depression, anemia, neurological symptoms	(Vasihnavi & Shelly 2015, WHO Guidelines for Drinking Water Quality 2011, 2017)

Fig. 1: Graphical representation of WHO limit in $mg.L^{-1}$ for various heavy metals.

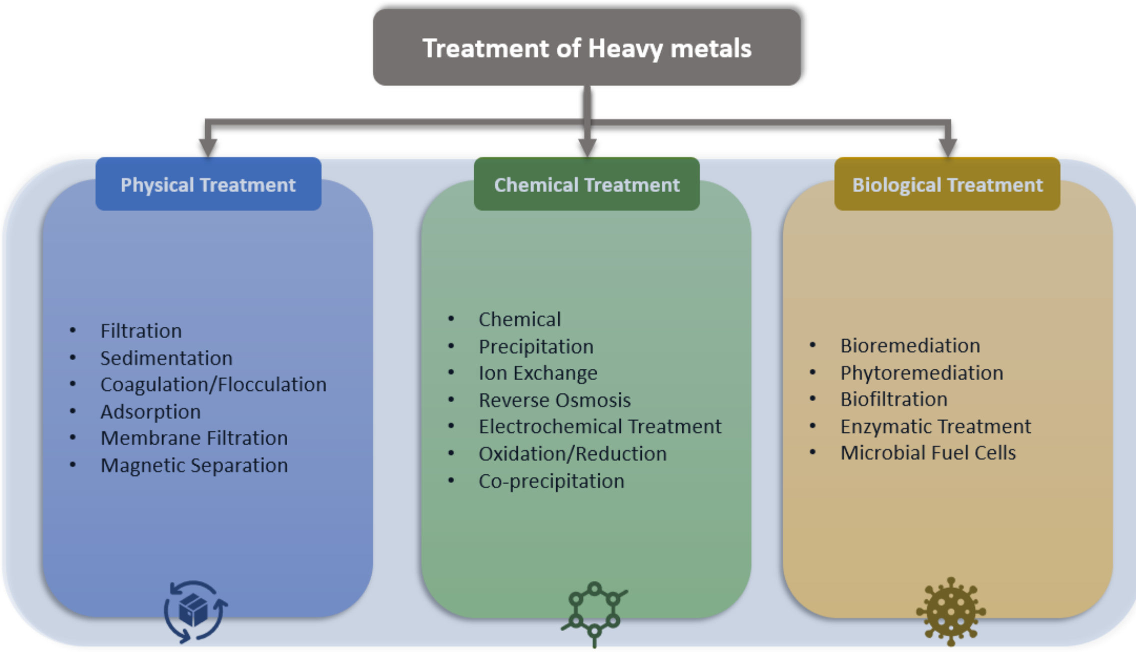

Fig. 2: Techniques available for heavy metal treatment in water/wastewater.

Despite significant efforts to remediate polluted environments using conventional techniques, many of these methods have proven ineffective in removing toxicants completely (WHO Guidelines for Drinking Water Quality 2011,2017, Abubakar et al. 2022). They often have significant drawbacks, including high energy requirements, production of secondary waste products, solvent loss, high operating and maintenance costs, operational complexity, phase separation difficulties, low efficiency, emulsion formation, and incomplete metal removal (Renu et al. 2017, Naseem 2012). Moreover, some traditional methods, such as electrodialysis, ultrafiltration, ion exchange, reverse osmosis, and precipitation, are not only expensive but also generate considerable amounts of sludge and secondary toxic waste products (Renu et al. 2017, Deen et al. 2021). Therefore, there is a need to consider a more efficient and sustainable remediation strategy to tackle the challenges of environmental pollution.

Considering the parameter mentioned earlier, as illustrated and summarized in Fig. 3, adsorption is found to be one of the most efficient methods in terms of cost, scalability, and operability (Manisha et al. 2021, Malik et al. 2017, Nadeem et al. 2021, Qasem et al. 2021).

Suitability of Adsorption

Adsorption has proven to be an efficient technique for the

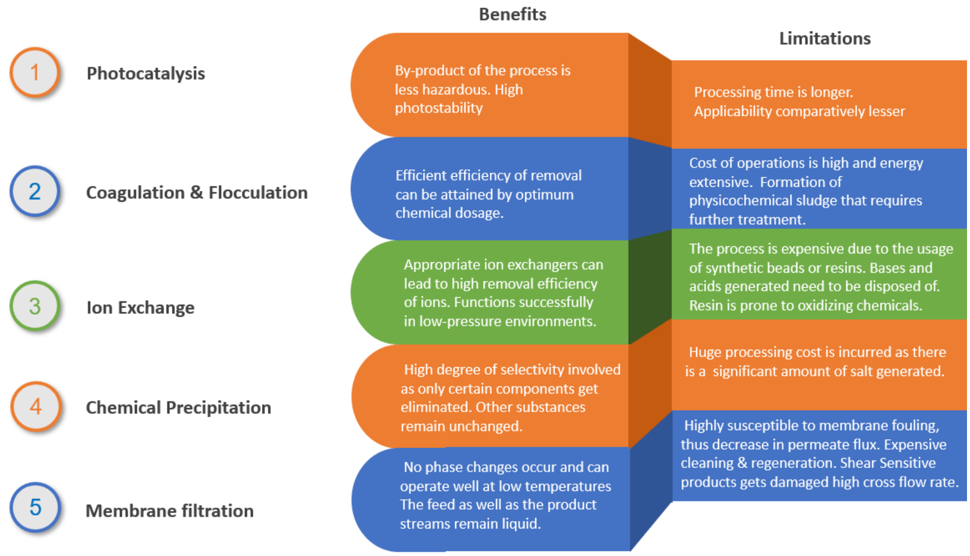

Fig. 3: Advantages and limitations of other treatment techniques.

removal of heavy metals due to multiple reasons. Various researchers have identified that high removal efficiency, even at low metal concentrations, can be obtained by adsorption techniques (Shahinur et al. 2015, Qasem et al. 2021, Deniz et al. 2022, Torres 2020). The rationale behind this is the mechanism by which adsorption works. Heavy metal ions attach to the adsorbent's surface (Malik et al. 2017, Gu et al. 2019).

We can choose and customize the adsorbent for each heavy metal, which makes this process highly selective (Sarthak et al. 2020, Gu et al. 2019). It allows us to target a specific heavy metal based on its functional group, surface charge, and pore size. The adsorption process is also versatile (Manisha et al. 2021) regarding operating parameters such as temperature, pressure, and pH (Naif et al. 2021). Additionally, it is found to produce minimum

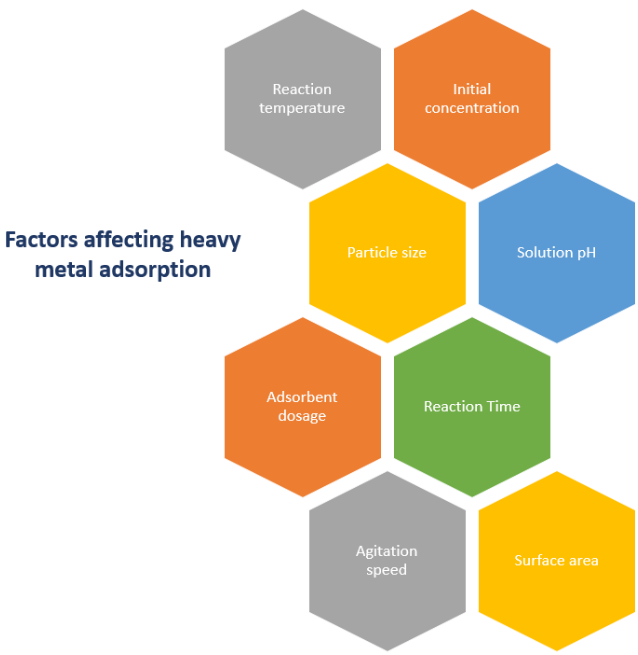

Fig. 4: Factors affecting heavy metal adsorption.

waste and even offer great recyclability (Sarthak et al. 2020), thus making it a low-cost and sustainable technique, an ideal choice for the remediation of heavy metals. (Wai et al. 2021), Some commonly used adsorbents are activated carbon (Myalowenkosi et al. 2016), zeolites (Noureddine & Harvey 2020), chitosan (Zujin et al. 2019), clay mineral (Gu et al. 2019), like halloysite, bentonite, montmorillonite, vermiculite, organic water material derived material like biochar (Sarthak et al. 2020), and few advanced compounds such as nanoparticles (Boruah et al. 2015). All relevant factors which are found to have an impact on adsorption efficiency are shown in Fig. 4.

Bio-Adsorbents as Suitable Adsorbent Media

There is a certain limitation to the usage of chemical adsorbents. Among these, the primary issue is its high environmental impact and poor cost-effectiveness (Adewuyi 2020). As a sustainable alternative, bio-adsorbents can be utilized for similar purposes. There are many sources (refer to Fig. 5) and types of bio-adsorbents that can be customized for removing various heavy metals from water (Malik et al. 2017, Naif et al. 2021, Qasem et al. 2021). The source of generation can be plant-based, animal-based, microbial-based, algae and seaweed-based, or derived from fruit, vegetable, or food waste (Manisha et al. 2021, Nadeem et al. 2021, Abujazar et al. 2022, Deen et al. 2021). Several plants have lignin, cellulosic material, and other organic compounds normally utilized as bioadsorbent. Similarly, chitin and chitosan are derived from animal-based materials and have proven to have high adsorption capacities. Materials like eggshells (Carvalho et al. 2013, Zahir & Sheriff 2014) also can treat heavy metals. Aquatic plants such as algae and seaweed with high polysaccharides, protein, and other organic compounds also serve a similar purpose (Sarthak et al. 2020, Adewuyi 2020, Redha 2020). Food and fruits are proven adsorbents due to their abundance and organic content (Thachanan et al. 2018, Nadeem et al. 2021).

Apart from being eco-friendly, many properties make them typically suitable for such applications, which include large surface area, chemical composition, porosity, selectivity, low cost, and wider availability (Sabino et al. 2016). Generally, most of the bioadsorbents have substantial lignocellulosic content (refer Fig. 6), which provides them with a high surface area and porous structure, enabling a high number of active adsorption sites (Nadeem et al. 2021, Wu et al. 2020). This lignocellulosic structure contains multiple functional groups like amine, carboxyl, and hydroxyl, which enhances their affinity towards heavy metals (Naif et al. 2021).

Another important aspect is the elemental composition of bioadsorbent, which means the variety and content of elements present in the material. Testing methods, such as CHNS (Thachanan et al. 2018, Mohd et al. 2021), quantify this. Adsorption typically happens through chemical and electrostatic interactions (Naseem 2012, Sehyeong et al. 2021), where functional groups and metal ions interact on the surface of the adsorbent. Additional binding sites are made available if elements like sulfur, nitrogen, and oxygen are present, thus helping increase their adsorption capacity (Guat et al. 2022). These elements are even responsible for the structural stability of adsorbents, particularly phosphorus

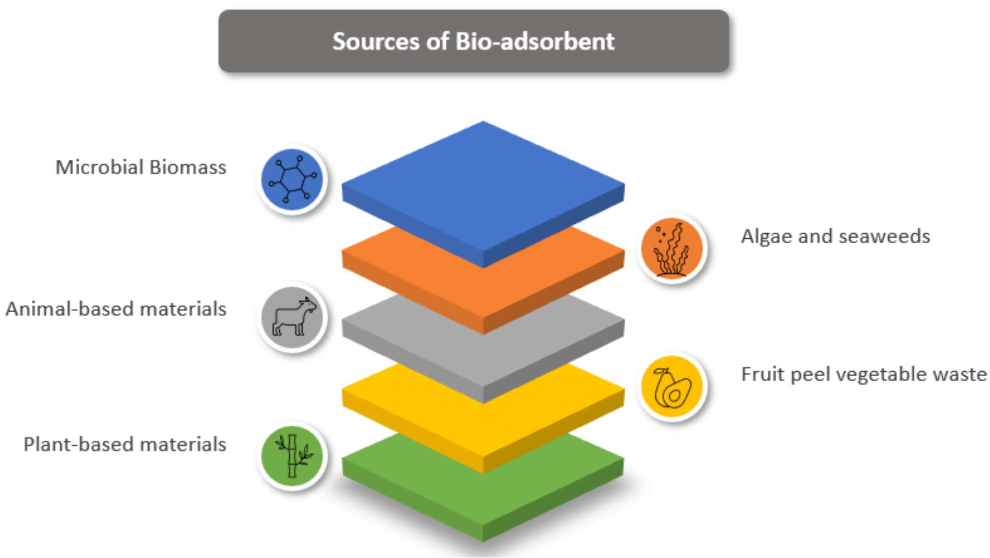

Fig. 5: Various sources of bio-adsorbent from nature.

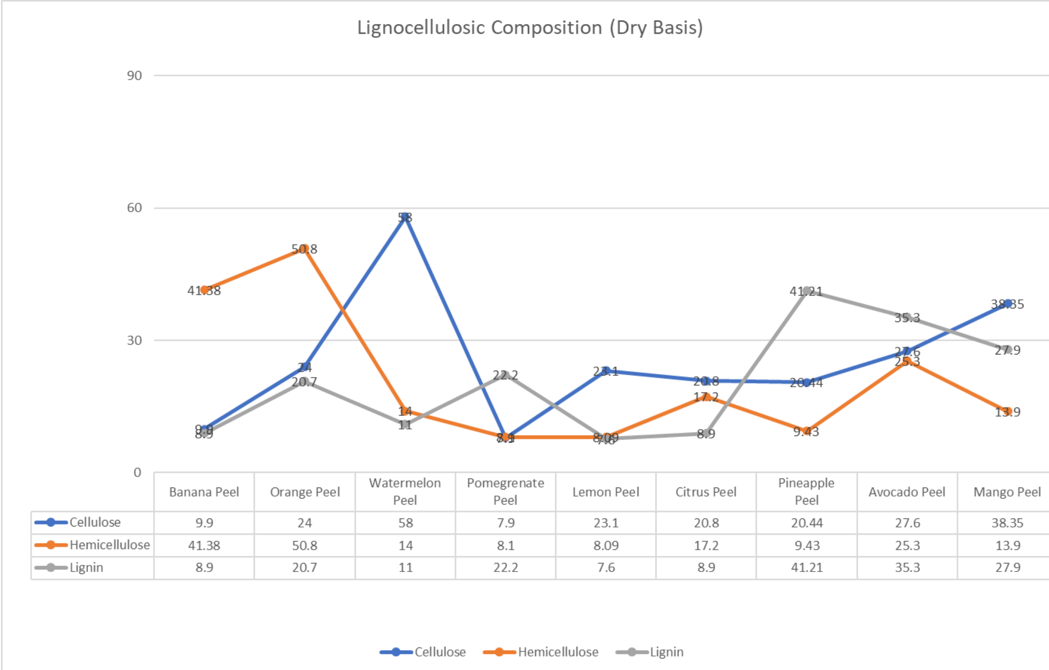

Fig. 6: Lignocellulosic composition in different fruit waste (peels) (Nadeem et al. 2021, Kabenge et al. 2018, Wu et al. 2020, Pathak et al. 2017, Dammak et al. 2019).

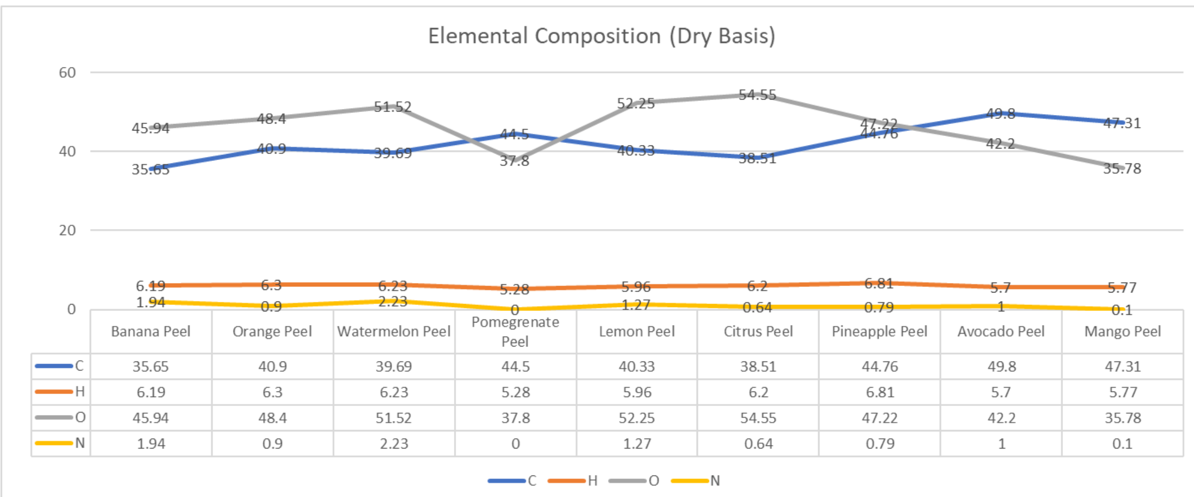

Fig. 7: Elemental composition in different fruit waste (peels) (Nadeem et al. 2021, Kabenge et al. 2018, Wu et al. 2020, Pathak et al. 2017, Dammak et al. 2019).

and silicon. In contrast, some elements like calcium and magnesium make them more resistant to degradation in acid or basic medium. Testing data of many agricultural wastes (Fig. 7) indicates a substantial presence of such elements, which makes them a suitable candidate for usage.

Mechanism of Adsorption

Adsorption is a process where ions, molecules, or atoms from the first material (also known as adsorbate) form a thin layer on the second material (also known as adsorbent) due to forces of attraction that may be chemical or physical. The process can lead to single or multi-layer formation basis the external factors involved. It has varying applications, such as purification, separation, storage, etc. A few important terms that are associated with adsorption and are frequently used are adsorbate and adsorbent. Adsorbate is the material being adsorbed, while adsorbent is the material on which it is adsorbed. The efficiency and interaction of adsorbate and adsorbent depend a lot on their characteristics and composition. There are two types of adsorptions: Physical adsorption (Sarthak et al. 2020) and Chemisorption (Thachanan et al. 2018). The adsorption process is majorly exothermic. Either physisorption or chemisorption, as the former causes a decrease in system entropy and free energy, while the latter involves the formation of new chemical bonds. As a result, physical adsorption is reversible, and chemisorption is not. Both adsorptions may occur concurrently in any given system, provided the process parameters are favorable. Thus, it can be said that entire bonding in adsorption happens by the bonding of adsorbates to the adsorbent surface via Van der Waals interactions, electrostatic interactions, and/or hydrogen bonds (Abujazar et al. 2022, Sabino et al. 2016, Sehyeong et al. 2021) (Maftouh et al. 2023).

The entire adsorption process depends on the concentration of adsorbate and adsorbent, surface area, pressure, temperature, and characteristics. While developing/ design of any adsorption system, adsorption isotherm must be established. Prominently, Freundlich and Langmuir isotherms are developed. Both these isotherms determine how adsorption occurs in a system.

Mathematically, Freundlich isotherm can be written as

$$q = K_f \times Ce^{(1/n)}$$

Where,

q = Amount of adsorbate adsorbed/ mass of adsorbent

Ce = Equilibrium concentration of the adsorbate in bulk phase

K_f = Freundlich constant for determining adsorption capacity if the adsorbent

n = Freundlich exponent for determining the intensity of adsorption

Langmuir adsorption isotherm can be written as

$$q = (q_{max} \times K \times Ce)/(1 + K \times Ce)$$

where

q = Amount of adsorbate adsorbed/ mass of adsorbent

Ce = Equilibrium concentration of the adsorbate in bulk phase

q_{max} = is the maximum adsorption capacity of the adsorbent,

K = Langmuir constant related to the affinity of the adsorbent for adsorbate.

Isotherms are extensively explained in other research works (Sarthak et al. 2020, Pham et al. 2021, Shagufta et al. 2020, Jianlong & Can 2009), even though it is not detailed in this article.

Preparation of Bio-adsorbent and Trials

The entire cycle of bioadsorbent application consists of multiple steps, starting from the selection of biomass to regeneration. First and foremost is the selection of biomass based on factors like their availability, cost, and efficiency for removing heavy metal. Post identification, the biomass is procured in raw form and is further prepared to make it fit for usage. In most cases, biomass is washed properly to remove external dust, contamination, or any other unwanted material, then dried and ground to a fine powder (Firomsa

Fig. 8: Typical bioadsorbent preparation and usage cycle.

et al. 2020, Jian et al. 2019, Gaurav et al. 2018). Drying temperature and time vary for every adsorbent.

In some cases, it is oven-dried, and in some, it is sun-dried (García-Vargas et al. 2020). The objective is to remove moisture and volatile content from the organic compounds without affecting their properties. Sometimes, the material is converted to carbon at very high temperatures if the objective is to use it in the same form (Sihem et al. 2012, Rajec et al. 2015, Opia 2018). In some cases, biomass is chemically treated to enhance its adsorption capacities (Rajkumar & Swati 2015, Adewuyi 2020). Fig. 8 depicts typical steps for the preparation of bioadsorbent followed and implemented by most researchers.

Once the adsorbent is ready, it is specifically characterized by determining its physical and chemical properties like surface area, composition, functional group, and porosity (Jian et al. 2019, Ali et al. 2019). These properties give a fair idea of the heavy metal impurities that can be removed and their optimization scope. Multiple tests are then performed to test the ability of the adsorbent prepared to remove heavy metals from the aqueous solution. This can be done by either mixing (for batch process) or just by contact through a packed column (for continuous process). The process is further optimized by varying parameters like the initial concentration of heavy metal, the dosage of adsorbent, pH, temperature, stirring time, or contact time to achieve the best removal efficiency (Maryam et al. 2020, Gregorio & Badot 2008). The biomass is sometimes regenerated by desorbing the heavy metal through an appropriate eluent, regenerated biomass and heavy metal removed can be utilized (Lata et al. 2015, Fouda-Mbanga et al. 2021). Based on the data points, the cost-effectiveness and efficiency of the adsorbent can be determined compared to other adsorbents.

For every trial, it is necessary to calculate adsorption efficiency. Typically, adsorption efficiency can be calculated as:

$$\text{Adsorption efficiency } \% = (C_i - C_f)/C_i \times 100$$

where,

C_i = Initial concentration of heavy metal in aqueous solution before adsorption

C_f = Final concentration of heavy metal in aqueous solution after adsorption.

Similarly, in the case of regeneration, desorption percentage (%) is calculated, which can be given as:

Desorption percentage = (amount of adsorbate desorbed /amount of adsorbate adsorbed) x 100%

It is usually used to determine the effectiveness of the desorption process while regeneration and reusability of bioadsorbent are being considered. It indicates the extent to which heavy metals are removed from the surface of bioadsorbent. A higher value of desorption percentage is a positive indicator for recycling the adsorbent (Fouda-Mbanga et al. 2021, Redha 2020).

Additionally, the adsorption capacity (Opia 2018) of any bioadsorbent can be determined. It is mathematically written as

$$\text{Adsorption capacity (mg/g)} = (C_i - C_f) \times (V/W)$$

Where,

Ci and Cf are initial and final concentrations of heavy metal in water, V is the volume of solution, and W is the weight of the adsorbent. Adsorption capacity is a crucial parameter used to evaluate distinct adsorbents' usefulness in removing pollutants from water as it determines the amount of a pollutant that can be adsorbed per unit weight of the adsorbent.

EFFECTIVENESS OF BIOADSORBENT IN HEAVY METAL REMOVAL

Existing studies have highlighted that different bio adsorbents, such as agricultural waste materials, algae, fungi, bacteria, and plant-based materials, can effectively remove heavy metals from contaminated water. Here, we will evaluate some of the work done to remove copper, lead, and cadmium using bioadsorbents.

Removal of Copper (Cu) by Bioadsorbents

Copper (Cu) is among the toxic heavy metals introduced to water/wastewater due to industrial processes and natural deposits. Copper piping in plumbing systems is also a major source. The biosorption of copper has gained a lot of attention for its removal.

Table 2 shows the results of different studies on the adsorption of various components using different bioadsorbents. The adsorbents used in these studies include lentil shells, wheat shells, rice shells, papaya leaf powder, paddy straw powder, surfactant-modified laterite soil, powdered spent mushroom compost, banana peel, date pits, tea waste, dried marine algae (Hizikia fusiformis), and watermelon rind. The optimum pH, temperature, RPM, initial concentration, adsorption capacity, and removal efficiency for each study are also provided.

Data shows that the adsorbent's adsorption capacity and removal efficiency vary significantly depending on the adsorbate-adsorbent interaction. Date pits show a very high removal efficiency for an initial concentration of 1000 $mg.L^{-1}$, whereas banana peel is just 27.74% for an initial concentration of 5 $mg.L^{-1}$.

Table 2: Various sources of bio-adsorbent from nature for removal of copper.

S. No.	Origin of adsorbent	Component used	Optimum pH	Temperature °C	RPM	Initial conc. $mg.L^{-1}$ or ppm	Adsorption capacity [$mg.g^{-1}$ or ppm]	Removal Efficiency	Reference
1.	Lentil	Shells of the grains	6	59.85	150	500	9.588	89.13%	(Haluk et al. 2008)
2.	Wheat	Shells of the grains	6	59.85	150	500	17.422	51.28%	(Haluk et al. 2008)
3.	Rice	Shells of the grains	6	59.85	150	100	2.954	35.43%	(Haluk et al. 2008)
4.	Papaya	Leaf powder	7	Ambient	-	20	24.63	85.00%	(Geetha & Anil 2016)
5.	Paddy	Paddy straw powder	7	-	-	20	37.17	65.00%	(Geetha & Anil 2016)
6.	Laterite soil	Surfactant-modified laterite soil	6	25+-2	-	10	185	91.56%	(Tien et al. 2017)
7.	Mushroom compost - a mixture of mushroom mycelium, rubber tree sawdust, rice husk, and calcium carbonate	Powdered spent mushroom compost	6	ambient	125	10	0.7	42.21%	(Kamarudzaman et al. 2022)
8.	Banana	Banana peel	-	50	100	5	-	27.74%	(Leong 2018)
9.	Dates	Date pits	7	25	-	1000	-	99.40%	(Thamer et al. 2015)
10.	Tea	Tea waste	7	ambient	-	200	-	94.62%	(Patrick et al. 2021)
11.	Banana	Peels	<7	40	-	5	-	53.28%	(Leong 2018)
12.	Dried marine algae	Hizikia fusiformis	4	25	-	100	45.09	31.60%	(Pham et al. 2021)
13.	Watermelon	Rind	6.48	20	-	10	5.73	56.40%	(Liu et al. 2012)

Table 3: Various sources of bio-adsorbent from nature for removal of Lead.

S.No.	Origin of adsorbent	Component used	Optimum pH	Temperature °C	Initial conc. $mg.L^{-1}$ or ppm	adsorption capacity $[mg.g^{-1}]$	Removal efficiency	Reference
1.	Orange	orange peels	5-6	Ambient	10	0.97	97.87%	(Prasenjit et al. 2020)
2.	Sugarcane	Bagasse	6	30	0.8	1.61	89.31%	(Ezeonuegbu et al. 2021)
3.	Polydopamine composite	-	-	-	1	394	99.80%	(Daniel et al. 2018),
4.	Banana	Peels	<7	50	5	-	27.14%	(Leong 2018)
5.	Banana	Peels	13	RT	-	0.959	100.00%	(Rabiatul et al. 2019)
6.	Dried Marine algae	Hizikia fusiformis	4	25	100	167.73	10.90%	(Pham et al. 2021),
7.	Biochar of pinewood or rice	Husk	5	45	20	4.25	95.00%	(Zhengang and Fu-Shen 2009)
8.	natural American bentonite	-	5.5	25	200	427	95.00%	(Naeema 2014),
9.	*M. oleifera*,	-	6	27	10	5.6	86.00%	(Gautam et al. 2020)
10.	Peanut	Shell	6	27	10	1.7	78.00%	(Gautam et al. 2020)
11.	*P. juliflora*	-	6	27	10	1.4	72.00%	(Gautam et al. 2020)
12.	Sugarcane	Bagasse	6.0	30	0.8	1.61	89.31%	(Ezeonuegbu et al. 2021)
13.	Papaya	Seed	-	Ambient	100	8.5	85.00%	(Zahir & Sheriff2014)
14.	Chicken Egg	Shell	-	Ambient	100	8.2	82.00%	(Zahir & Sheriff 2014)
15.	Coconut	Leaf powder	-	Ambient	100	9	90.00%	(Zahir & Sheriff 2014)
16.	Tea	Brewed tea waste	1.0	20	100	1.197	97.97%	(Hakan et al. 2020)
17.	Tea	Tea waste	5.0	25	100	33.49	85.00%	(Wan 2014),
18.	Walnut	Walnut shell	4.0	20	100	9.912	90.00%	(Çelebi & Gök 2017)

Table 4: Various sources of bio-adsorbent from nature for removal of Cadmium.

S. No.	Origin of adsorbent	Component used	Optimum pH	Temperature °C	Initial conc. $mg.L^{-1}$ or ppm	adsorption capacity $[mg.g^{-1}]$	Removal Efficiency	Reference Name
1.	Natural phosphate	-	5	Ambient	-	-	78.00%	(H.Yaacoubia et al. 2013)
2.	Watermelon	Rind	9.12	20	500	40.16	80.00%	(Husein et al. 2017)
3.	Watermelon	Rind	5	Room temperature	50-200	63.29	-	(Lakshmipathy et al. 2013)
4.	Orange	Dried orange peel powder [DOPP] is chemically modified with nano-silica (SiO_2)	6.5	Ambient	50	142	95% (max)	(Jyoti et al. 2021)
5.	Cork biomass		6	40	10-100	14.77	64.48%	(Fouad et al. 2016)
6.	Papaya	Seed	-	Ambient	100	7.9	79.00%	(Zahir & Sheriff 2014)
7.	Chicken Egg	Shell	-	Ambient	100	8.6	86.00%	(Zahir & Sheriff 2014)
8.	Coconut	Leaf powder	-	Ambient	100	8.5	85.00%	(Zahir & Sheriff 2014)
9.	Tea	Brewed tea waste	4	20	100	1.163	84.74%	(Hakan et al. 2020)
10.	Tea	Tea waste	5	20	5	1.76	99.50%	(Ghasemi et al. 2017)
11.	Tea	Tea waste	5	25	20	16.87	45.00%	(Wan 2014)
12.	*Capparis decidua*	branches and leaves	6	Room temperature	249	248.62	80.00%	(Muhammad et al. 2021)
13.	*Ziziphus mauritiana*	branches and leaves	6	Room temperature	249	235.65	80.00%	(Muhammad et al. 2021)
14.	Rice	Rice husk	9	Room temperature	200	-	80-90%	(Salman & Khan 2015)
15.	Wood	sawdust	9	Room temperature	300	-	80-90%	(Salman and Khan 2015)
16.	Dried Marine algae	Hizikia fusiformis	4	25	100	42.08	14.90%	(Bich et al. 2021)

The optimum pH for most cases is 6-7, with dried marine algae (*Hizikia fusiformis*) as the only exception (Pham et al. 2021, Haluk et al. 2008, Geetha & Anil 2016, Tien et al. 2017, Kamarudzaman et al. 2022, Leong 2018).

Removal of Lead (Pb) by Bioadsorbents

Lead contamination must be removed critically to protect people's health and lives. Exposure to Lead while drinking water can have severe and prolonged health complications, particularly in women and children (Prasenjit et al. 2020, Ezeonuegbu et al. 2021). Even low concentrations of lead exposure can cause growth-related setbacks, reduced IQ, and behavioral challenges in children. For adults' kidney damage, reproductive problems, and high blood pressure are prominent diseases (Deen et al. 2021). Various industries, such as batteries, paint, plastic, automobile, steel, etc., contribute significantly to this increased level of lead in water (Salman & Khan 2015, Ezeonuegbu et al. 2021).

In Table 3, Lead removal data is compared using natural adsorbents and their corresponding adsorption capacities and removal efficiencies for water treatment. It can be observed that some adsorbents, such as polydopamine composite, have an outstanding adsorption capacity of 394 $mg.g^{-1}$, with a remarkable removal efficiency of 99.8%. Additionally, natural American bentonite displays an impressive adsorption capacity of 427 $mg.g^{-1}$, with a 95% removal efficiency. Sugarcane bagasse and banana peels exhibit moderate adsorption capacities, with sugarcane bagasse showing a capacity of 1.61 $mg.g^{-1}$ and banana peels ranging from 0.97 to 27.14 $mg.g^{-1}$, depending on pH and temperature. The removal efficiency of these adsorbents ranges from 78% to 89.31%. Other adsorbents, such as dried marine algae (Hizikia fusiformis), tea waste, and walnut shells, demonstrate good adsorption capacities, ranging from 1.197 to 167.73 $mg.g^{-1}$, with removal efficiencies ranging from 85% to 97.97%.

Adsorbents like papaya seeds, chicken eggshells, and coconut leaf powder exhibit moderate to good removal efficiencies, ranging from 82% to 90%. The optimum pH for most cases is within the range of 6-7.

Removal of Cadmium (Cd) by Bioadsorbents

Like lead and copper, cadmium also possesses considerable health concerns. It can pile up in the body over time, leading to various health problems. Long-term exposure to cadmium-polluted drinking water can cause kidney damage, leading to kidney disease and failure (Lakshmipathy et al. 2013, Ghasemi et al. 2017) (Wan 2014). It can also affect the bones, causing osteoporosis and damage to the liver and lungs. There are various sources of cadmium in water: Natural sources of cadmium include the weathering of rocks and soils, while anthropogenic sources consist of manufacturing processes, mining activities, and improper disposal of waste materials (Vaishnavi & Shelly 2015, WHO Guidelines for drinking water quality 2011, 2017).

Different bioadsorbents have been tried for cadmium removals, such as natural phosphate, watermelon rind, orange peel powder, cork biomass, papaya seed, chicken eggshell, coconut leaf powder, tea waste, *Capparis decidua*, *Ziziphus mauritiana*, rice husk, sawdust, and dried marine algae. Data in Table 4 show that each adsorbent's adsorption capacity and efficiency vary based on the origin, component used, pH, temperature, initial concentration, and other factors. For instance, the highest removal efficiency was observed with orange peel powder chemically modified with nano-silica (Jyoti et al. 2021), with a maximum of 95%. Meanwhile, rice husk and sawdust showed an 80-90% removal efficiency for initial concentrations of 200 and 300 $mg.L^{-1}$, respectively. In contrast, dried marine algae showed a low removal efficiency of only 14.9%. The study highlights the potential of various natural adsorbents as an effective and eco-friendly solution for removing contaminants from water (Wan 2014, Muhammad et al. 2021). The results suggest that orange peel powder chemically modified with nano-silica, rice husk, and sawdust can be an efficient adsorbent for removing contaminants from water. The findings also emphasize the importance of considering the origin, component used, pH, temperature, and initial concentration while selecting an appropriate adsorbent for water treatment. (Yaacoubia et al. 2013, Husein et al. 2017, Lakshmipathy et al. 2013, Jyoti et al. 2021, Fouad et al. 2016).

CONCLUSION

Minimizing pollutant and pollution sources in water is of utmost importance as fresh water is significantly scarce worldwide. Reiterating that these adsorbents are economical and environment friendly makes them quite a suitable option compared to traditional alternatives such as chemical precipitation & ion exchange. The alternatives have been generating residues that are difficult to dispose of. In this study, we learned that the efficacy of bio adsorbents is dependent on factors such as the type of bio adsorbent, its concentration and type of heavy metal ions in the solution, the pH of the solution, the contact time between the bio adsorbent and the solution, and the temperature of the solution. Conclusively, the data presented in this study shows bio adsorbents have an encouraging future as eco-friendly and economical alternatives to conventional water treatment methods and environmental remediation. Research in this direction can subsequently lead to various applications and increased efficiency.

FUTURE OF BIOADSORBENT AND FURTHER SCOPE OF WORK

The multipronged benefits of bioadsorbent usage could play a significant role in addressing environmental challenges, an extreme area of concern, such as water pollution and air pollution. It can additionally pave the path for the development and acceptability of sustainable technologies for multiple industries. Evolutionary advances in Biotechnology and Materials Science can also be expected to contribute to developing innovative bio adsorbents. These adsorbents would certainly aid us with enhanced properties and performance. Principally, the future of bio adsorbents looks up and coming. This ingenuity has notable potential for important contributions to environmental safeguarding and sustainability. During the entire literature survey, it was identified that Lablab purpureus pod/seedcase (locally called Pavta in India) is not yet utilized as a bioadsorbent, particularly for copper removal. It is widely grown in Asia, Africa, and some of America. As a legume crop, *Lablab purpureus* is known to be a good source of lignocellulosic material. Thus, learning from data shows that it has the potential to become an adsorbent. Appropriate study and testing to be done further for its characterization and efficiencies.

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