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Review Article

Sustainable Applications of Bio-adsorbents from Agricultural Wastes for Eradication of Heavy Metals from Aqueous Medium

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ABSTRACT

Remediation of heavy metals from watercourses is of particular concern because of the presence of heavy metals in the environment. There is range of technologies being carried out for the removal of inorganic pollutants from wastewater. The conventional method of removing toxic heavy metals is chemical precipitation, reverse osmosis, coagulation, flotation, and ion exchange are expensive and produces large amounts of sludge and toxic products which have negative impact on environment. Therefore, a green technology using agricultural waste as bio-adsorbent has received more attention for the removal and recovery of heavy metals because it uses environment friendly, sustainable, and cost-effective. The majority of the agricultural waste biomass belongs to the alcohol family, carbonyl, amide, amino, etc., which have an affinity for heavy material ions to form material complexes or chelates. The methodologies of the bio-absorption process include chemisorption, complexation, face adsorption, periphrasis through pores, and ion exchange. The present review presents different types of bio-adsorbents, their uses, and their mechanism of action. Furthermore, these bio-adsorbents can be modified for better efficacy and reused repeatedly. This review also includes several ways for improving the efficiency of bio-adsorbents and physicochemical conditions for extracting heavy metals from waste streams.

Key words: Bio-adsorbents, Agricultural wastes, Eradication, Heavy metals, Remediation.

1. INTRODUCTION

The availability of safe and fresh water is the core of a healthy society, but it is woefully neglected globally. About 71% of earth's surface is covered with water and only 3% of it is available for drinking. Therefore, for the need of fresh and clean water without any contamination is the need of an hour. However, this fresh water is not available in undeveloped countries where numerous waterborne diseases are found. According to the WHO, 1.7 million people die each year from diarrhea, with 90% of them being children under the age of five [1]. More than 50% of India's population doesn't have access to safe regulated drinking water [2]. This is because of growing industrialization, urbanization, and overpopulation around the world, which has had a greater impact on water bodies due to increased pollution containing hazardous heavy metals.

Aquatic systems contain of heavy metals which are highly toxic and non-biodegradable. Heavy metals such as mercury, nickel, lead, copper, zinc, cadmium, and chromium present in huge amount [3]. Various algal species collect heavy metals by biosorption, which causes biomagnification in marine systems leading to the major health issues [4]. They do not decay under normal conditions. Thus, their development under ecological conditions improves, resulting in a proliferation of foodstuffs and water bodies which is then consumed by humans and the environment around the world. Therefore, immediate removal of these heavy metals from the surroundings has become of great importance. For the sustainable removal of unwanted contaminants from water has become a major challenge. There are several strategies available to remove contaminants from water, such as oxidation, membrane partitioning, and electrochemical coagulation, but bio-adsorbent has attracted the interest of researchers due to its utility, renewability, and ecologically friendly nature.

1.1. Heavy Metals

Heavy metals belong to our periodic table that has high atomic mass and a density at least 5 times greater than that of water. As per US-Environmental Protection Agency (USEPA), the most heavy metals are human carcinogens and systematic toxicants that even at the lower levels of exposure. Common heavy metals with their permissible limit as per the WHO, USEPA, Indian Statistical Institute, and Indian council of medical research are shown in Table 1 [5].

1.2. Conventional Methods of for Heavy Metals Removal

Various methods for the treatment of heavy metals removal from contaminated water such as chemical precipitation, ion exchange, electrochemical methods, adsorption using activated carbon, and bio-adsorption. Table 2 shows a comparison of different technologies for eliminating heavy metals [6].

1.3. Processing of Agricultural Waste

For proper extraction of bio-adsorbents such as maize-waste, it is properly homogenized by grinding. Further, it is carbonized using muffle furnace and then oven dried at 105°C for 4 h [7]. Figure 1 represents diagrammatic representation of synthesized bio-adsorbent from agricultural waste.

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Table 1: Represents heavy metals with their permissible limit as per the WHO, United States Environmental Protection Agency, Indian Statistical Institute, and Indian council of medical research

Heavy metals	Permissible limit WHO	USEPA	ISI	ICMR
Copper (mg/l)	1.0	1.3	0.05	1.5
Mercury (mg/l)	0.001	0.002	0.001	0.001
Chromium (mg/l)	0.1	-	0.05	-
Zinc (mg/l)	5.0	-	5.0	0.10
Lead (mg/l)	0.05	-	0.10	0.05
Arsenic (mg/l)	0.05	0.05	0.05	0.05

WHO: World Health Organization, USEPA: United States Environmental Protection Agency, ISI: Indian Standard Institution, ICMR: Indian Council of Medical Research

Table 2: Represents comparison of different technologies for removing heavy metals

S. no.	Methods	Disadvantages	Advantages
1.	Chemical precipitation	Large method of sludge, extra operational cost for sludge disposal	Simple operation, inexpensive, can remove most of metals
2.	Chemical coagulation	High cost Large consumption of chemicals	Sludge settling Dewatering
3.	Ion -exchange	High cost Less number of metal ions removed	High regeneration of materials Metal selective
4.	Electrochemical methods	High capital and running cost Initial solution pH and current density	Metal selective No consumption of chemicals pure metals can be achieved
5.	Adsorption using activated carbon	Cost of activated carbon	No regeneration Performance depends upon adsorbent Most of metals can be removed High efficiency (>99%)
6.	Biosorption	Early saturation, limited potential for biological process improvement, no potential for biologically altering the metal violence is state	Low cost, high efficiency, minimization of sludge, regeneration of biosorbents, no additional nutrient requirement, metal recovery
7.	Membrane filtration	High Operational cost due to membrane fouling	Small space requirement, low pressure, high seperation, Selectivity

Table 3: Represents adsorption of toxic heavy metals on agricultural waste derived bio-adsorbents[19]

Bio-adsorbent	Adsorbate	Adsorbent maximum capacity (mg/l)
Tea waste	Zn (II)	80.90
Maize waste	Cr (VI)	34.48
Rice husk	Cd (II)	73.96
Saw dust waste	Cr (VI)	76.92

1.4. Surface Modification of Bio-adsorbents

The surface of the bio-adsorbents is modified according to the need. Figure 2 represents types of surface modifier, parameters influencing heavy metals biosorption and surface modification of bio-adsorbents [8].

1.5. Characterization of Bio-adsorbent Using Various Techniques

Characterization of bio-adsorbent is done to understand surface, physical, and chemical properties using various analytical tools which is represented in Figure 3 [9].

1.6. Agricultural Waste Materials as Low-cost Bio-adsorbents

A huge number of agricultural surpluses such as tea wastes, maize waste, rice husk, and saw-dust waste can be potentially utilized to eliminate poisonous heavy metals from aqueous media (Table 3). Processing of these bio-adsorbents is already discussed above in Figure 1 and the most of them work as above possible technique.

1.7. Tea Waste-based Bio-adsorbents

Tea waste is also considered as bio-waste. The net dry matter of tea leaves contains mainly about one-third of phenolic, hydroxyl, carboxylate, aromatic, and oxyl groups. It has prolonged ion replacement attribute which in turn improves its pollutant uptake capacity [10]. There have been several studies that utilized either factory-rejected tea waste or spent tea leaves to produce activated carbon which in turn were used as an adsorbent for the removal of organic and inorganic pollutants from wastewater [11]. Orhan and Büyükgüngör (1993) used waste tea, Turkish coffee, granular activated carbon, and nut and walnut shells as adsorbents to remove Cr(IV), Cd(II), and Al(III) metal ions from synthetic waste water [12]. Granular activated carbon has more removal efficiency of 98.5, 99, and 99.8% for Cr(IV), Cd(II), and Al(III) ions as compared to 93, 98, and 98%, respectively, for tea waste.

1.8. Maize Waste-based Bio-adsorbents

Maize cob is another type of agricultural waste, and it contains natural ion-exchange capability, because of this reason, it is mostly used for the removal of heavy metals [13]. Achanai Buasri *et al.* modified bio-adsorbents by treating corn cobs with phosphoric acid and evaluated their properties [14]. The modified maize cob's biosorption capability for removing Zinc(II) from wastewater was evaluated.

1.9. Rice Husk-based Bio-adsorbents

It is one of the most important agricultural wastes produced, particularly in rice-producing continent such as Asia. Around 500 million metric tons of rice are produced worldwide, with rice husk accounting for 10–20% of that. Dry rice husk is composed of 72–85% of organic matter, mainly sugars, lignin 21.44%, cellulose 32.24%, and mineral ash 15.05% as well as % of silica in its mineral ash [15]. Rice husk has been shown to contain a high amount of cellulose and hemicellulose, making it a strong prospect for heavy metal uptake. Adsorption capacity improved by researchers by doing pre-treatment of rice husk for intensifying the loading capacity toward metal ions such as cadmium, so it was treated with Na_2CO_3 or HCL [16].

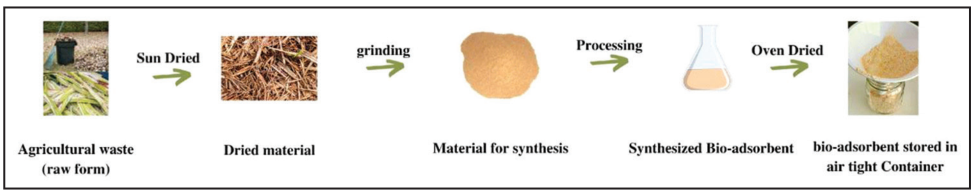

Figure 1: Diagrammatic representation of synthesized bio-adsorbent from agro-waste

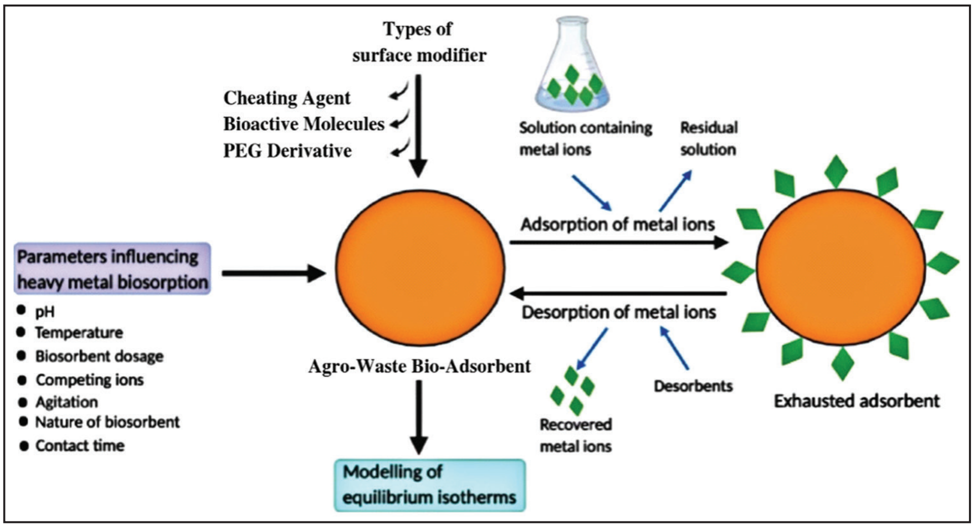

Figure 2: Diagrammatic representation of surface modification of Bio-adsorbents

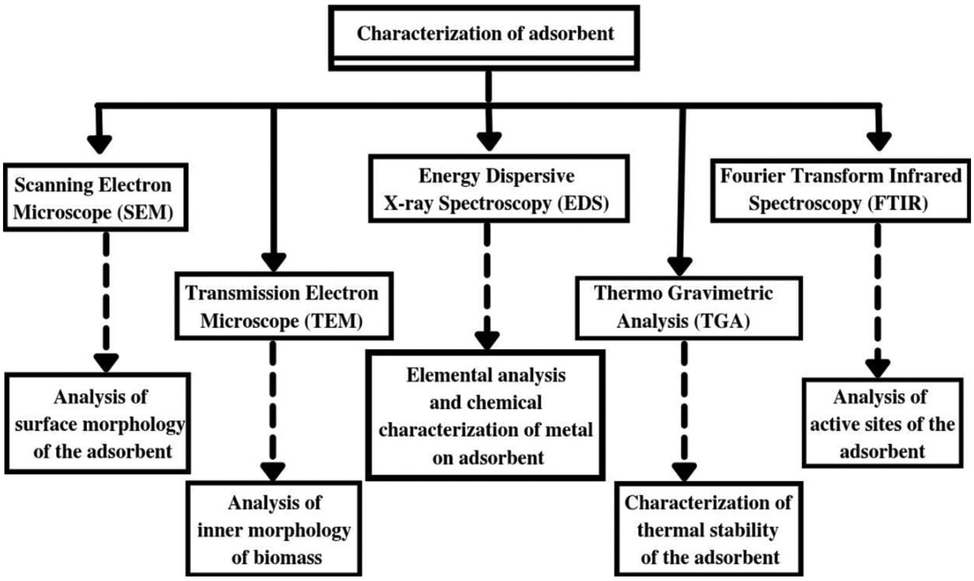

Figure 3: Instrumental analysis for characterization of adsorbents and their outcomes

1.10. Saw Dust Waste-based Bio-adsorbents

Metal ions removed from saw dust, a common agricultural waste. The ability of saw dust from various sources to behave as an adsorbent has been investigated. Ajmal *et al*. evaluated the use of phosphate-treated mango tree saw dust as a potential sorbent for the removal of Cr^{6+} ions from electroplating effluents. The pre-treated saw dust was found to remove Cr^{6+} ions from industrial effluents with a 100% effectiveness [17,18].

1.11. Mechanism of Heavy Metals Removal

Among all the heavy metal removal procedures for wastewater, the adsorption-assisted technique is the most efficient and cost-effective [20]. Physical and sorption adsorption, ion and ligand exchange, chelation, and surface and interior complexation are all examples of adsorption mechanisms. Physisorption, which is common in the low-cost adsorbents, is mostly caused through surface and interfacial adsorption. Diffusion transports metal ions from solution to the adsorbent surface in surface adsorption. Metal ions are strongly attracted to adsorbent surfaces having opposing charges to the adsorbate by electronic forces such as dipole–dipole interactions or H-bonding [21-23]. When metal ions pass through the boundary layer, they quickly adhere to the adsorbent surface and are removed from the solution. Metal ions diffuse from the liquid boundary layer into the interstitial pores of the adsorbent during interfacial adsorption [24]. As a result, adsorption happens on the inside wall of the substrate material which is represented by Figure 4.

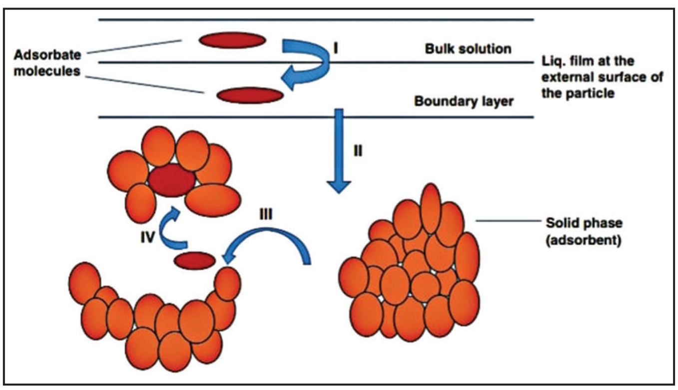

Figure 4: Mechanism of heavy metals adsorption on the surface of adsorbent

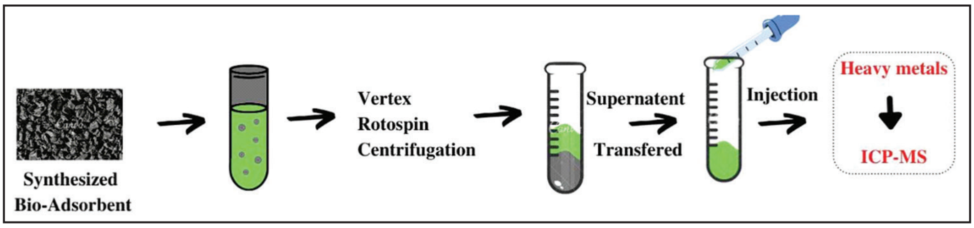

Figure 5: Diagrammatic representation of batch adsorption experiment

2. BIOSORPTION EFFICIENCY DETERMINATION SYSTEM

The efficacy of heavy metal biosorption can be assessed using two alternative methods: Batch and column adsorption [25].

2.1. Batch Adsorption Method

This method can be used to determine the maximum sorption capability of bio-adsorbents for various experimental batches [26]. It is used in laboratories for wastes with a small volume. As a result, the column technique is applied on a huge scale. Figure 5 represents whole process of batch adsorption experiment.

2.2. Column Adsorption Method

This is the most effective method for treating huge volumes of wastewater. In this method, packed column is favored [27]. In batches, the uptake capacity is more than column, but residence time of column is less. Thus, for faster removal of pollutants, column is best [28].

2.3. Regeneration of Adsorbent

It is a technique in which loaded pollutants are recovered from the adsorbent while the adsorbent is also regenerated for reuse. Depending on the active functional group present, the agriculture waste stacked with adsorbent is extracted using a suitable solvent such as acetone, methanol, or dilute nitric acid [29]. Various chemicals such as sodium hydroxide, potassium hydroxide are used to desorb arsenic from biomass [30].

3. CONCLUSION

This study focused on the present research that recognized the potential use of bio-adsorbents such as agricultural wastes for heavy metal removal from polluted water. Bio-adsorbents could also offer commercial objectives in the future; thus, further study should be concentrated on filling the following gaps: Conventional methods used are costly and less efficient in removing contaminants from water. The synthesis of agricultural wastes creates economical and efficient bio-adsorbents for the simultaneous removal of pollutants of various classes of heavy metals from the water courses. To encourage large-scale application of bio-Adsorbents, comprehensive study is needed to characterize novel bio-Adsorbents from agriculture/food industry with maximum heavy metals sorption capacities.

A comprehensive study is expected for the characterization of bio-adsorbents from agro-waste several pre-treatment techniques should be analyzed to prepare the bio-adsorbents productive during the heavy metal remediation procedure. The concept of using bio-adsorbents could be beneficial in the improvement of an accessible green filtration technology for cleansing of heavy metals-polluted drinking water which would provide low-income people to enjoy heavy metals free drinking water to protect them from health hazards.

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5. CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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