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Bionanomaterials for Heavy Metal Detoxification by Adsorption Mechanisms

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***Abstract*— The issue of heavy metal contamination of water resources is a serious environmental and social health problem, and it requires the establishment of effective and sustainable remediation technologies. Green adsorbents Bionanomaterials Engineered nanomaterials based on biological resources (plants, microbes, biopolymers, etc.), are promising as green adsorbents since they are biocompatible and non-toxic and exhibit excellent physicochemical capabilities. They have increased surface area, functional groups and structural versatility that allows them to adsorb toxic metals using electrostatic attraction, ion exchange, complexation, chelation and redox-mediated reactions. Recent developments show that bionanoadsorbents are better than the majority of traditional materials in adsorption capacity, selectivity and regeneration capability. Even with these benefits, there are still limitations with regard to obtaining consistent material synthesis as well as long-term stability, scalable production and consistent performance in complex industrial effluents. Moreover, loopholes still exist in mechanistic knowledge, lifecycle evaluation and field-scale implementation. The synthesis pathways, adsorption mechanisms, influencing factors, and regeneration strategies are critically assessed, and the emerging trends and research needs are brought out. On the whole, bionanomaterials are a promising and sustainable technology in the heavy metal detoxification and have great prospects in use in future in environmental and wastewater treatment.**

***Keywords*— Heavy metal removal; Adsorption mechanisms; Green synthesis; Biopolymers; Nanotechnology; Environmental remediation.**

I. INTRODUCTION

Water pollution by poisonous heavy metals is one of the most ongoing and threatening environmental problems that are experienced around the world. Non-biodegradable, very persistent, and likely to bioaccumulate through the food chain, heavy metals lead (Pb2 +), cadmium (Cd2 +), chromium (Cr6 +), mercury (Hg 2+), nickel (Ni 2 +), and arsenic (As3 +/As5 +) are polluting substances that influence human health, agriculture, and aquatic environment (Fu and Wang, 2011). The World Health Organization states that heavy metal pollution of drinking water is a cause of serious health-related disorders which include a neurological injury and kidney failure to carcinogenic (WHO, 2017). The main causes of heavy metal contamination of wastewater are industrial activities such as mining, textile manufacturing, battery manufacturing, electroplating, and tannery industries (Gupta and Nayak, 2012).

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Chemical precipitation, membrane filtration, ion exchange, reverse osmosis, and coagulation-flocculation are examples of conventional wastewater treatment technologies that have been extensively employed in the removal of heavy metals. Although the techniques are effective in the controlled settings, they are usually limited by factors such as high cost of operation, sludge formation, energy-consuming mechanisms, and low efficiency in low metal concentration (Fu and Wang, 2011; Barakat, 2011). In this respect, it may be noted that adsorption-based treatment has created one of the most promising and efficient methods because of its affordability, simplicity, flexibility and capability to treat even trace forms of metals (Babel and Kurniawan, 2003).

Bionanomaterials have started attracting attention as next generation adsorbents in heavy metal detoxification in the recent years. Nanoscale materials based on biological sources, e.g. plants, algae, bacteria, fungi, and natural polymers, or synthesized by green and environmentally friendly processes, are known as bionanomaterials (Iravani, 2011). The materials are of high quality in terms of physicochemical properties, such as: high surface-area-to-volume ratio, high amount of reactive functional groups (-OH, -COOH, -NH2), tunable surface chemistry, and biocompatibility (Ahmed et al., 2016). Their environmental friendliness in terms of green synthesis, low toxicity, and biodegradation present a major benefit compared to traditional nanomaterials, which may require the use of dangerous chemicals and consume (a lot of energy) to create. The ability of bionanomaterials to adsorb molecules in a unique manner is due to the various mechanisms that include ion exchange, surface complexation, electrostatic attraction, chelation and redox interactions (Ho and McKay, 1999). As an example, plant-extract-mediated nanoparticles have high metal-binding capacity owing to phytochemical capping agents, whereas microbial nanoparticles have the capability of protein mediated metal coordination (Mittal et al., 2013; Narayanan and Sakthivel, 2010). The nanomaterials which have been used in biopolymers like chitosan, cellulose nanofibers and alginate nanocomposites have good availability of functional groups and this leads to a high adsorption efficiency (Rinaudo,2006).

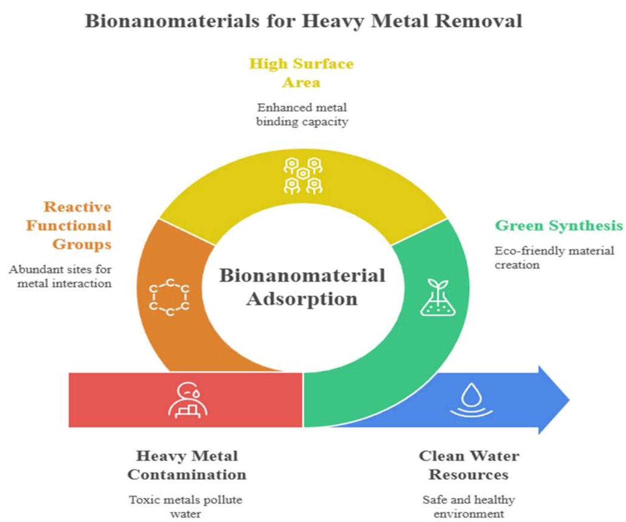

Figure No. 1: Bionanomaterials for Heavy metal removal

Increased use of bionanomaterials is in line with world sustainability as it is seen to facilitate the notion of promoting green chemistry, environmental toxicity, and enhancing the advancement of cheap and scalable wastewater treatment technologies. Furthermore, hybrid bionanocomposites, such as magnetite-biopolymer composites or plant-metal oxide hybrids, are expected to perform synergistic adsorption, and thus are highly promising as industrial effluent treatment (Kumar et al., 2020). Although they have potential, some obstacles exist regarding scale-up, stability and environmental risk assessment and standardisation of synthesis protocols. As a result, the entire knowledge of the synthesis pathways, adsorption processes, efficiency variables, and viable difficulties of bionanomaterials is the key to the development of bionanomaterials in heavy metal detoxification. This review assesses the latest advances in the field of bionanomaterial-based adsorption technologies, points out the mechanistic understanding and also gives gaps on research and opportunities in treating wastewater sustainably.

II. Overview of Bionanomaterials

The bionanomaterials refer to a specific category of nanodegradable materials that are produced by applying biological resources like plants, algae, fungi, bacteria, or natural biopolymers as the starting raw material or as reducing and stabilizing agents. They have their basis in the concept of green chemistry, which focuses on the production of eco-friendly products, lower toxicity, and minimal usage of the dangerous chemicals (Iravani, 2011). These nanomaterials are usually biologically derived and fall within the range of 1-100 nm and have distinct physicochemical properties of high surface-area-to-volume ratio, high concentration of functional groups (e.g., amino, hydroxyl and carboxyl), and tunable surface chemistry, which enhance their reactivity and binding affinity to environmental contaminants, especially heavy metals (Ahmed et al., 2016).

Biosynthesis of bionanomaterials is a process that entails a variety of biological processes. Phytochemicals, flavonoid, alkaloids, phenolics, and terpenoid, which are used as natural reducing and capping agents, mediate the synthesis of nanoparticles at a rapid rate and in a stable form (Mittal et al., 2013). Microbial systems associated with bacteria, fungi, and yeast synthesize metal-ion reduction to nanoparticles intracellularly and extracellularly involving enzymes, proteins, and polysaccharide (Narayanan and Sakthivel, 2010). Also, nanomaterials based on biopolymers, including chitosan, cellulose nanofibers, alginate, and starch nanocomposites, are highly utilized due to their biodegradability, biocompatibility, and chemical modification capabilities in an attempt to improve their application as water treatment agents (Rinaudo, 2006). The diverse synthesis routes enable very delicate control over the shape, size, stability and functionality of nanoparticles.The rising popularity of bionanomaterials is based on their strong beneficial properties to those of the traditional chemically synthesized nanomaterial. They have reduced environmental toxicity, economic production, excellent adsorption capacity, and compatibility with sustainable wastewater treatment methods (Kumar et al., 2020). They are best suited to bind heavy metal ions by adsorption processes like ion exchange, chelation, surface complexation and electrostatic attraction due to their natural origin and inherent functional groups. Moreover, hybrid bionanocomposites, i. e. biopolymer with the metal oxides, magnetic nanoparticles or carbon nanomaterials, demonstrate synergistic behaviour which makes them more stable, reusable and selective to certain contaminants. With the development of research, bionanomaterials are becoming promising solutions that can be scaled and are environmentally responsible in the area of heavy metal detoxification and the range of environmental remediation problems in general.

III. Synthesis Approaches for Bionanomaterials

TABLE I: SYNTHESIS APPROACHES FOR BIONANOMATERIALS

Synthesis Approach	Description	Typical Biomaterials Used	Advantages	Limitations
Top-Down Approach	Mechanical or physical breakdown of bulk materials into nanoscale structures.	Chitin, cellulose, lignin, biopolymers	Simple, scalable, produces uniform particles	Lower control over size/shape, high energy consumption
Bottom-Up Approach	Nanomaterials are assembled atom-by-atom or molecule-by-molecule.	Proteins, peptides, DNA, polysaccharides	High control of size/shape, highly tunable properties	Slow process, requires controlled environment
Green/Biogenic Synthesis	Use of biological organisms or extracts for eco-friendly nanoparticle synthesis.	Plant extracts, microbes, enzymes	Eco-friendly, cost-effective, non-toxic	Batch variability, slower reaction rates
Chemical Synthesis	Chemical reactions produce nanomaterials through reduction, precipitation, etc.	Biopolymer stabilizers (e.g., alginate, gelatin)	High purity, reproducible, scalable	Uses hazardous chemicals, possible toxicity
Physical Synthesis	Energy-based processes such as laser ablation, sonication, thermal decomposition.	Biopolymers used as capping/stabilizing agents	Produces uniform, high-quality nanoparticles	High cost, requires specialized equipment
Hybrid or Bio-Hybrid Synthesis	Combines biological molecules with chemical/physical methods for advanced nanostructures.	DNA, proteins, lipids, polysaccharides	High precision, multifunctional nanomaterials	Complex process, requires expertise

Synthesis of bio nanomaterials is mainly centered on biological or green pathways where biological organisms, derivatives or biomolecules are used as a source of nanoparticles synthesis in an environmentally friendly and greener way. Among these, the plant-mediated synthesis has received significant recognition because of its simplicity and rapidness as well as scalability. Phytochemicals found in plant extracts include flavonoid,

terpenoid, phenolics, alkaloids, and reducing sugars which serve as reducing agent as well as stabilizing agent in the formation of nanoparticles (Iravani, 2011). The biochemical constituents transform metal ions to nanoparticles, hence avoiding the use of dangerous chemical reagents. Parameters that are vital in the control of the size, morphology, and stability of the synthesized nanoparticles include reaction parameters, including pH, temperature, extract concentration, and the type of metal precursor used (Mittal et al., 2013). The process has been extensively used to form metal and metal oxide nanoparticles including Ag, Au, ZnO, TiO2 and Fe3O4.
The other significant strategy is microbial synthesis wherein bacteria, fungi, and yeast are used as natural nanofactories. The microorganisms aid nanoparticle formation by enzyme reduction, metal-binding proteins, and polysaccharides that are found in the cell walls/cytoplasm (Narayanan and Sakthivel, 2010). A range of bacterial species (Bacillus subtilis, Pseudomonas aeruginosa) and fungal species (Aspergillus niger, Fusarium oxysporum) have been studied as forming intracellular gold, silver, and iron nanoparticles and extracellular nanoparticles, respectively, due to their high metal tolerance and release of reductive biomolecules (Dhillon et al., 2012). The benefits of microbial synthesis include an increased uniformity, controlled nucleation, and the potential of large-scale production with the help of bioreactors, although it might also need rigid aseptic conditions and complicated downstream processing.

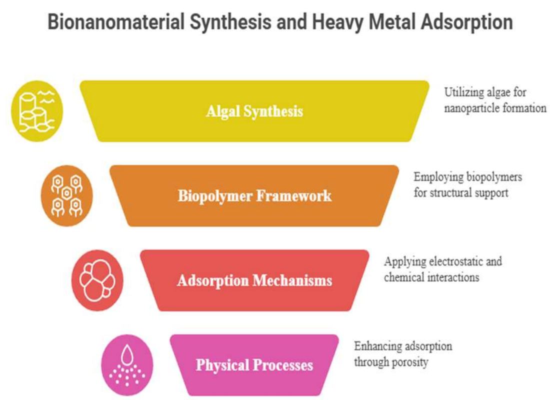

Figure No. 2: Synthesis Approaches for Bionanomaterials

The other sustainable pathway is algal-based synthesis, which takes advantage of the high biochemical content of microalgae and macroalgae. Algae contain pigments, proteins, and polysaccharides that are able to reduce metal ions and stabilize the subsequent nanoparticles (Barwal et al., 2011). Their natural capacity to accumulate metals bioaccumulates metals and this promotes the formation of nanoparticles. Moreover, under the simplest nutrient growing conditions the algae develop at an increased rate thus making them the best candidates in cost-effective manufacturing of nanoparticles. Gold, silver, zinc oxide and iron oxide nanoparticles have been synthesized successfully using Chlorella vulgaris, Sargassum muticum and Spirulina platensis species. Algal-mediated method is thought to be environmentally harmless, but there is still a problem of optimization of biomass harvesting and extract preparation.Besides biological organisms, biopolymers, like chitosan, cellulose, alginate, starch, and gelatin, can be used as flexible structures to prepare nanomaterials and nanocomposites. These biodegradable polymers are naturally occurring and have structures that give them stability, metal binding functional groups and are inherently biodegradable (Rinaudo, 2006). Nanomaterials based on biopolymers may be prepared through chemical crosslinking, ionic gelation, electrospinning or nanoprecipitation and may include metallic or metal oxide nanoparticles to improve adsorption capacity. Hybrid bionanocomposites (e.g., chitosan-magnetite, cellulose-graphene oxide, or alginate-ZnO) exhibit greater mechanical strength, high surface reactivity, and selective adsorption properties because of the synergies between organic and inorganic substances (Kumar et al., 2020). These engineered bionanomaterials are a promising future of scalable, tunable, and application-specific synthesis in waste water treatment and environmental remediation.

IV. Heavy Metal Adsorption Mechanisms

The main factors in the heavy metal adsorption by bionanomaterials are those associated with surface interactions due to the presence of numerous functional groups, large surface-volume ratio, and surface chemistry, which can be controlled. Electrostatic attraction, ion exchange, surface complexation, and chelation are the prevailing ones, and functional moieties (hydroxyl, carboxyl, amino, and thiol groups) are also involved in metal binding (Gupta and Nayak, 2012; Khan et al., 2020). The process of electrostatic attraction between positively charged metal ions and negatively charged bionanomaterial surfaces takes place and highly depends on the pH and ionic strength (Fu and Wang, 2011). Ion exchange: This is the substitution of natural cations (e.g., Na +, H +, Ca2 +) on the surface of the nanomaterial, and is a typically used ion exchange in bio-derived nanoparticles such as chitosan-based or lignocellulosic nanofibers (Babel & Kurniawan, 2003). In the meantime, the coordination of the metal ions and donor groups on biological molecules (proteins, polysaccharides, and phenols) dictates the process of complexation, as well as chelation, which forms stable metal-ligand complexes at the nanoscale (Hussain et al., 2019).The second significant adsorption process is the micro-/nano-scale physical processes, such as filling of the pore, intraparticle diffusion, and p-metal. Synthesized bionanomaterials based on agricultural residues, microbial biomass, or plant extracts are more likely to be hierarchically porous, thereby increasing diffusion of metal ions into internal cavities (Kumar et al., 2021). Moreover, the reduction-based transformations influence adsorption when bio-nanoparticles contain redox-active groups that can convert the metal ions to less toxic or immobilized forms - such as Fe3O4 or phytogenic nanoparticles reducing Cr(VI) to Cr(III) (Sharma et al., 2015). There is also a role of hydrogen bonding of van der Waals interactions in the overall adsorption capacity of hybrid bionanomaterials with organic and inorganic domains. A combination of those mechanisms renders bionanomaterials highly effective in the detoxification of a wide spectrum of heavy metals, including Pb(II), Cd(II), Cr(VI), Ni(II), and As(III/V), and qualifies them as promising materials in efficient wastewater treatment (Wang and Chen, 2016).

V. Bionanomaterials for Heavy Metal Removal

This has seen the appearance of bionanomaterials to be the most efficient adsorbents of heavy metal remediation since they have biologically friendly synthesis routes and have better physicochemical characteristics. They are small in size (nanoscale), which means that they have a high ratio of surface to volume and, therefore, they can react with metal ions more readily in aqueous systems (Khan et al., 2020). Nanoparticles produced by plants through phytochemicals like flavonoids, tannins and phenolics have a great potential to bind metals due to the existence of various functional groups such as, -OH, -COOH and -NH2 (Iravani, 2011). In the same manner, nanoparticles with different surface structures and biocompatibility are formed by microbial routes based on bacteria, fungi, and algae, which are used to adsorb, reduce, or precipitate toxic metals, including Cr(VI), Pb(II), Cd(II), and Ni(II) (Singh et al., 2016).

Figure No. 3: Bionanomaterial for Heavy Metal Removal

Nanomaterials made of biopolymers, such as chitosan nanoparticles, cellulose nanofibers, alginate nanogels, and protein-based nanocomplexes, are highly used in the removal of heavy metals because of their high ability to chelate and structural versatility. Amine and hydroxyl group functionalized chitosan nanoparticles have shown outstanding adsorption capacity to Pb(II), Cu(II), and Cr(VI) due to the presence of strong affinities to positively charged ions (Vakili et al., 2019). Utilizing agricultural by-products, nanocrystals and nanofibers of cellulose have a lot of binding sites and are very stable in water treatment systems (Kumar et al., 2021). The synergist properties of hybrid bionanomaterials of natural polymers with metal or metal oxide nanoparticles including Fe3O4 chitosan or TiO2-cellulose composites, and so on, have increased adsorption, magnetic recovery as well as reusability (Bhattacharya and Gupta, 2008).

TABLE II: BIONANOMATERIALS FOR HEAVY METAL REMOVAL

Bionanomaterial	Biological Source / Precursor	Nanostructure Type	Target Heavy Metals	Adsorption Mechanism(s)	Key Advantages	Limitations
Chitosan-Based Nanoparticles	Chitin from crustaceans, fungi	Nanoparticles, nanofibers	Pb^{2+}, Cd^{2+}, Cr^{6+}, Cu^{2+}	Electrostatic attraction, chelation	Biodegradable, strong chelation	Requires modification for stability
Cellulose Nanocrystals/Nanofibers	Plant biomass, algae	Nanofibers, nanocrystals	Pb^{2+}, Cd^{2+}, Hg^{2+}	Ion exchange, H-bonding	Abundant, renewable	Lower affinity without modification
Biochar Nanoparticles	Agricultural biomass	Nanoporous carbon nanoparticles	Pb^{2+}, Cd^{2+}, As^{3+}, Ni^{2+}	Surface complexation, π–π interactions	Low-cost, eco-friendly	Variable composition
Alginate-Based Nanomaterials	Brown algae	Hydrogels, nanoparticles	Pb^{2+}, Cu^{2+}, Zn^{2+}	Ion exchange, chelation	Biodegradable, selective	Limited mechanical stability
Protein-/Peptide-Based Nanoparticles	Soy protein, microbial proteins	Protein-stabilized nanoparticles	Pb^{2+}, Cd^{2+}, Hg^{2+}	Coordination with functional groups	High affinity	Sensitive to pH
Microalgae-Derived Nanomaterials	Chlorella, Spirulina	Nano-biochar, nano biomass	Pb^{2+}, Cr^{6+}, Ni^{2+}	Biosorption	Renewable, low cost	Pretreatment required
Fungal/Mycelium-Based Nanomaterials	Aspergillus, Pleurotus	Nano-mycelial composites	Pb^{2+}, Cd^{2+}, Cr^{6+}	Chelation, reduction	Robust biosorption	Cultivation time required
Plant-Extract Green Nanoparticles	Neem, tea, fruit peels	Metal/metal oxide nanoparticles	Pb^{2+}, Cr^{6+}, Ni^{2+}	Reduction, adsorption	Eco-friendly, cheap	Stability issues
Bacterial Cell Wall–Derived Nanomaterials	Bacillus, Pseudomonas	Nanocell wall fractions	Pb^{2+}, Cd^{2+}, Cu^{2+}	Surface adsorption	High reactivity	Sensitive to pH/temperature
Enzyme-Immobilized Nanomaterials	Laccase, peroxidase	Nano-enzymatic composites	Hg^{2+}, Cr^{6+}	Biocatalysis, adsorption	High specificity	Enzyme stability issues

Besides the adsorption process, a number of bionanomaterials possess redox activity, which converts toxic metal ions to less toxic forms. As an example, phytogenic Fe3O4 and silver nanoparticles have been demonstrated to convert hexavalent chromium (Cr(VI)) to trivalent counterpart (Cr(III)) and, therefore, enhance the capacity to remove toxic substances (Sharma et al., 2015). Multi-mechanistic removals by complexation, ion exchange, microprecipitation, and surface coordination are also possible with biosynthesized nanoparticles giving them effectiveness in a broad spectrum of industrial effluents. Bio-nanomaterials are an emerging category of novel adsorbents to be used in the remediation of heavy metals because of their sustainable syntheses, biodegradability, and low environmental footprint, which promotes the concept of green nanotechnology and circular-economy solutions to wastewater treatment (Wang and Chen, 2016).

VI. KEY FACTORS INFLUENCING ADSORPTION EFFICIENCY

The pH of the solution is important in the determination of the adsorption efficiency of bionanomaterials in the removal of heavy metals because it determines the surface charge of the adsorbent as well as the speciation of the metal ions. Competition between protons (H +) and metal ions also inhibits adsorption at lower pH levels because of surface protonation, which causes a decline in the binding rates of cationic metals e.g. Pb2 +, Cd2 + and Cu2 + (Ho and McKay, 2000). The greater the pH the more the functional groups like the hydroxyl, carboxyl and amino groups are deprotonated resulting in a higher level of electrostatic attraction and complexation and better adsorption performance (Babel & Kurniawan, 2003). Nevertheless, high pH could cause precipitation of the metal and thus the distinction between adsorption and removal by precipitation could not be made easily (Fu and Wang, 2011). Therefore, maximization of pH is essential to maximize bionanomaterials-target metal ions interaction.

The other important aspect that affects the efficiency of adsorption is the surface properties of the bionanomaterials such as the surface area, pore size distribution and the presence of active functional groups. An increased specific surface area and well-developed porosity of nanomaterials enhance the quantity of active sites to bind to, thus increasing adsorption capacity and diffusion rates (Kumar et al., 2021). Chemical compositions and functionalization of bionanomaterials are also crucial parameters in defining their affinity towards a particular metals; amino-functionalized chitosan nanoparticles are highly selective towards Cr(VI) and Pb(II) as they develop a strong coordination bond (Vakili et al., 2019). Other surface modification methods like grafting, oxidation, and combination with metal oxides (e.g., Fe3O4, TiO2) also increase the surface reactivity and promote other mechanisms like ion exchange, chelation, and micro-precipitation (Bhattacharya and Gupta, 2008).

Other parameters like dosage of adsorbents, contact time, temperature and initial concentration of metals are also important parameters of operation that affect adsorption behavior. The increase in the adsorbent dosage usually leads to a higher efficiency in the metal removal due to the presence of additional active sites, but for some point, the aggregation of nanoparticles can decrease the effective surface area (Wang and Chen, 2016). The dynamics of adsorption depend on contact time, which in most cases displays rapid uptake in the beginning and slower diffusion controlled mechanisms (Ho and McKay, 2000). Adsorption thermodynamics is influenced by temperature in order to change the rate of reaction and interaction energies; endothermic adsorption systems tend to be better at higher temperatures (Foo & Hameed, 2010). Equally, increased concentration of initial metal ions forms greater force in mass transfer but can over-saturate the active sites faster (Babel & Kurniawan, 2003). These aspects should be optimally combined in order to realize the adsorption properties of bionanomaterials to achieve efficient wastewater purification.

VII. Regeneration and Reusability of Bionanoadsorbents

The parameters that are required to estimate the economic and environmental viability of bionanoadsorbents in heavy metal remediation are regeneration and reusability. Regeneration also makes sure that the adsorbent will be able to undergo multiple regenerations with much less adsorption capacity loss, leading to the lower cost of operation and reducing the waste to the environment (Vakili et al., 2019). Typical regeneration techniques are acidic and alkaline desorption, salt solutions and chelating agents which are determined by the type of metal used and the binding mechanism. The examples include, dilute acids, such as HCl and HNO3 are often used in desorbing cationic metals, including Pb2+ and Cd2+, and alkaline solutions, like NaOH are capable of desorbing anionic metals, including Cr(VI) (Fu & Wang, 2011). The chelating agents like EDTA are also prevalent since they have a high ability to complex but their effects on the environment should be taken into account (Babel & Kurniawan, 2003). The regeneration conditions should be chosen in such a manner that the structural integrity of bionanomaterials is preserved, particularly those that are made out of biopolymers, which can be destroyed by harsh chemical treatment.

Most bionanoadsorbents are highly reusable during several adsorption-desorption cycles because of their stable nanostructures and functionality group stability. As an example, magnetic bionanocomposites like Fe3O4-chitosan and Fe3O4-cellulose can be simply collected with the help of external magnets and reused over 5-10 cycles without losing their efficiency significantly (Kumar et al., 2021). In the same way, plant-mediated nanoparticles, such as nanoparticles produced as a result of the use of leaf and fruit extracts, show a high regeneration potential because of a strong surface chemistry and the lack of chemical leaching (Iravani, 2011). Nanomaterials based on microbial biomass (e.g., fungal or algal nanostructures) also can be successfully reused, but an overexposure to chemicals during the regeneration process can lead to the denaturation of proteins or polysaccharides on the surface (Singh et al., 2016). Therefore, the stability of the bionanomaterials is directly correlated to the stability of the functional groups and bonding interaction between the materials and metal ions.

One of the novel fields of investigation is the creation of regeneration strategies that are sustainable and friendly to the environment, which would enhance the process of using bionanoadsorbents in a circular manner. There are low-concentration organic acid, biosurfactants, biodegradable chelators, light thermal therapies, and other methods that are being tested to minimize ecological footprint of regeneration processes (Wang and Chen, 2016). Also, the combination of magnetic separation and membrane-based regeneration technology, results in increased efficiency of recovery and reduced losses of the materials (Bhattacharya & Gupta, 2008). More sophisticated regeneration methods such as electro-regeneration and desorption under ultrasound have also been found to enhance the rate of desorption and also functional groups can be restored without structural destruction (Foo & Hameed, 2010). In total, the regeneration and reusability of bionanoadsorbents require more attention in order to be used on a massive scale in the wastewater treatment plants, which will help in developing sustainable and cost-efficient heavy metal removal technologies.

VIII. Challenges and Research Gaps

Although bionanomaterials have the potential to be successfully used to remediate heavy metals, there are a number of challenges that hamper these efforts on the large scale production of the materials. The absence of scalable and reproducible synthesis strategies is one of the main constraints since the biological systems like plants, microbes and biopolymers have variable size, shape, and functional groups of nanoparticles (Iravani, 2011). This variability compromises the adsorption performance, adsorption reproducibility, and adsorption reliability in the actual wastewater environment. Moreover, the existence of opposing ions and variable pH in industrial effluents tends to decrease the adsorption capacity, and therefore, controlled laboratory findings are not easy to reproduce at industrial level (Fu and Wang, 2011). The complexity of biological extracts in green synthesis is also associated with the challenge of learning about the specific biomolecules that stabilize and bind metal which limits the clarity of the mechanisms.The other significant issue is stability, recovery and long term durability of bionanoadsorbents. Nanomaterials composed of the bio-polymer, including chitosan and alginate nanoparticles, are prone to swelling, dissolution, or degradation in extreme pH or high ionic strength conditions (Vakili et al., 2019). Moreover, the regeneration of the processes, in particular, the use of strong acids or bases, can cause harm to functional groups or the change of surface topography, which decreases adsorption efficiency with repetitive cycles (Wang and Chen, 2016). Magnetic nanocomposites have better recovery, and the problems of nanoparticle leaching, aggregation, and decay of magnetic response overtime remain to be challenged (Kumar et al., 2021). The ecotoxicological appraisals are also wanting since a potential of releasing nanoparticles into the waters during the use or reuse of the nanoparticles is also a concern to the environmental safety. Mechanistic understanding, process modeling, as well as field-scale applications of bionanomaterials are also not well researched areas. The majority of the research is based on batch research and little information has been explored on real wastewater matrices, continuous flow systems or pilot-scale reactor (Babel & Kurniewan, 2003). Moreover, the adsorption processes are not necessarily well characterized with the help of the complex analytical equipment, including XPS, FTIR mapping, and synchrotron-based spectroscopy (Bhattacharya and Gupta, 2008). The use of bionanomaterials in hybrid technologies, i.e., membrane systems, electrochemical reactors, and microbial fuel cells, is not adequately studied. Additionally, lifecycle assessment (LCA), cost-benefit analysis, and frameworks of the circular-economy are seldom implemented, leaving ambiguity as regards long-term sustainability and possibility of industry uptake (Foo & Hameed, 2010). To deal with these issues, it is necessary to employ interdisciplinary research in order to fill in the gaps in the optimal synthesis, material stability, mechanistic precision, and scale-up strategies of real-world wastewater treatment.

IX. Conclusion

Bionanomaterials are a relatively new but highly promising eco-friendly and efficient adsorbent, which can be utilized to detoxify the heavy metals of polluted water systems. Their distinct nanoscale characteristics, including large surface area, regulated porosity, and great concentration of functional groups of interest, play a major role in their ability to bind and immobilize toxic metal ions by mechanisms of electrostatic attraction, ion exchange, complexation, and redox reactions. Their attractiveness is enhanced further by the sustainable synthesis methods relying on plants, microbes and biopolymers which prevent the use of dangerous chemicals and decrease environmental effects. Many researches verify the high adsorption efficiency and selectivity of bionanoadsorbents in relation to the traditional materials, which has proven their effectiveness as a part of contemporary wastewater treatment technology. Nevertheless, the difficulty of large-scale production, structural stability, regeneration efficiency, and unpredictable performance in the real wastewater environment still hinder large-scale use. The gaps that still exist in the research are in the mechanistic characterization, ecotoxicity evaluation, cost evaluation, and full-scale validation. The future studies should therefore aim at fine tuning the green synthesis pathways, improve durability, come up with hybrid nanocomposites, and design scalable treatment systems. Altogether, bionanomaterials represent a promising avenue of heavy metal remediation and have high potential in promoting the principles of a circular economy in the field of water treatment, though only upon addressing existing drawbacks via the ongoing interdisciplinary development.

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