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Heavy Metal Bioremediation By Microalgae: A Review Of Removal Methods, By-Product Recovery, Obstacles, And Potential Future Applications

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Abstract: *Water pollution is a primary environmental concern on a global level due to the constant discharge of many pollutants into the aquatic environment. Treating heavy metals found in wastewater has attracted attention to novel technologies in recent years. The utilization of biological processes has been investigated because they are dependable, straightforward, and eco-friendly. Through this review, the researchers attempt to disseminate information regarding the environmental dangers of heavy metals, the function of heavy metal processing. Different microalgae use different external and internal processes microalgae species use different external and internal processes. An in-depth discussion is provided on the assessment of microalgae's processing potential and the usage of biochar generated from algae in the removal of heavy metals. Bioremediation of heavy metals alone is not a viable business plan. As a result, additional work is being done to create integrated treatment plans to make this procedure more affordable and long-lasting. This review describes recent developments in the use of microalgae for heavy metal therapy. Additionally, the challenges must be met to improve this process's efficiency, economy, sustainability, and cleanliness are covered. From the comments in this review, it can be inferred that bioremediation can be crucial to the sustainable processing of heavy metals and the development of the bio-economy*

***Keywords*: *Algae, Adsorption, Bioremediation, Biochar, Metals*.**

1.Introduction

Water pollution is a global environmental concern, as deteriorating water quality results from continuously releasing many pollutants into the aquatic environment [1]. It is known that pollution with heavy metals not only affects the environment but also causes toxic effects that harm human health [2].

As a result of the constant discharge of pollutants such as heavy metals, agricultural pesticides, industrial waste, and other pollutants, Water in a polluted environment contains numerous organic and inorganic pollutants [3]. Most pollutants may come from domestic, industrial, or agricultural effluents, and their physical and chemical compositions vary according to their source [4]. Subsequently, the degradation of water resources due to pollution with heavy metals and other metals became a source of concern for environmental organizations and governments around the world, as the accumulation and stability of heavy metals in the food chain increased the risk of their toxicity even when they were present in low concentrations in Water [5]. Because these heavy metals are distinguished by their resistance to breakdown and are particularly prone to accumulating in the bodies of living organisms, they are one of the most challenging types of environmental pollution to control [6].

In the past twenty years, the global interest in heavy metals has increased due to environmental pollution and the toxicity of some of these metals [Cd, Pb], even if they are found in low concentrations [7, 8]. Bioremediation alternative greener methods for removing heavy metals from liquid waste include bioaccumulation, bioabsorption, and physical treatments. Biotreatment is considered economical and environmentally friendly because it is readily available and occurs naturally when processing large amounts of heavy materials [9, 10]. Recently, microorganism-based biological treatment has attracted the attention of researchers worldwide because of its effectiveness, high efficiency, low cost, and environmental friendliness. Due to their high affinity and rapid adsorption kinetics, some microalgae and bacteria are potential biosorbents for inorganic compounds, including heavy metals [11, 12]. An inexpensive, green substance made of carbon is called biochar. The high carbon content, high cation exchange capacity, broad surface area, and stable structure of biochar are just a few of its unique benefits [13]. This review aims to disseminate information regarding the environmental dangers posed by heavy metals, the function of bioremediations employed in heavy metal processing, the many microalgae strains utilized for heavy metal removal, and their modes of action for remediation.

2. Heavy metals:

Due to their hazardous nature, heavy metals have drawn the most attention from researchers of all contaminants. It is possible to categorize them as elements having atomic densities of more than 5 g/cm [14]. Natural waterways typically include minim levels of heavy metals, but many are dangerous even at shallow doses [15]. Metals such as arsenic, cadmium, nickel, zinc, cobalt, chromium, copper, and lead are among the most common minerals in Water and cause significant health problems if they are released in large concentrations. They also cause environmental problems and may lead to higher costs for water treatment [16].

There are some necessary minerals for the growth of algae. These are called trace elements, such as Mn^{+2}, Ni^{+2}, Cu^{+2}, Mo^{+2}, and Fe^{+2}. They are used as micronutrients. In contrast, heavy metals such as Hg^{+2}, Sn^{+2}, Au^{+2}, Cd^{+2}, pb^{+2}, Sr^{+2}, and Ti^{+2} have no essential biological function and are toxic to algae [17]. The environment becomes contaminated with heavy metals due to direct or indirect human activity. Heavy metals are harmful and non-biodegradable, which is why they are still present in Water. On the other hand, when heavy metals build up in soft tissues without being digested by the body, they become poisonous [18].

Heavy metals have adverse effects on living organisms in general. Among the adverse effects they cause on plants are a decrease in seed germination and an effect on fat content. It is one of the damages caused by the cadmium element; the reduction in the activity of enzymes and plant growth caused by the chromium element; the inhibition of photosynthesis caused by the copper and mercury elements; and the element lead affects chlorophyll production and plant growth [19]. As for effects on animals, heavy metals cause cancer, organ damage, nervous system damage, effects on growth and development, and, in severe cases, death [20]. To prevent the adverse effects of heavy metal toxicity in the Water, adequate treatment of these wastes must occur before they are released into bodies of Water. The main goal of treatment is to eliminate any current or potential threat to human, animal, or environmental health, Bioremediation is classified into two categories: the treatment using plants and the treatment with microorganisms [21]. Microbiological treatment removes various pollutants using microorganisms [bacteria, fungi, and algae]. This technique relies on biological activity to reduce or destroy the toxicity of the pollutants [22].

- **Cadmium**

Cadmium and its compounds have been identified by the International Agency for Research on Cancer as being carcinogenic to humans [23]. Cadmium is a highly toxic element that accumulates in the kidneys in high concentrations. Cadmium can cause bone damage or kidney impairment. Studies conducted on humans and animals revealed that osteoporosis is a direct effect of exposure to cadmium, along with disturbances in calcium metabolism [24]. Another study conducted on freshwater fish showed that cadmium accumulates mainly [about 75%] in the kidneys, liver, and gills [25]. It can also be deposited in the heart and other tissues [26]. It causes pathological changes of varying severity in the mentioned organs [27]. Cadmium is highly soluble in Water compared to other metals. Inhaling high concentrations of cadmium can cause severe lung damage, so the researchers confirmed that smokers are more susceptible to cadmium poisoning than non-smokers because tobacco plants, like other plants, can absorb and accumulate cadmium from the soil [28]. According to the Agency for toxic Substances and Disease Registry [ATSDR], over 500,000 workers in the United States are exposed to hazardous cadmium annually [24, 29]. Cadmium has a lengthy half-life of roughly 25 to 30 years and accumulates in plants and mammals. Epidemiological evidence suggests that exposure to cadmium at work and in the environment may be linked to several-malignancies, including those of the breast, lung, prostate, nasopharynx, pancreas, and kidneys [27]. In trace amounts within the body, heavy metals are harmful to human health, even in low-level contaminated food and Water is one way to get exposed to contaminants. It has been demonstrated that lead and cadmium are absorbed by and accumulate in organs like the kidneys and liver. They have also been linked to various illnesses, including cardiovascular disease, kidney dysfunction, developmental problems, and neurological diseases [30].

- **Chromium**

Chromium occurs in several-oxidation states, but Cr [III] [chromium trivalent] and Cr [VI] [chromium hexavalent] are of paramount biological importance. There is a significant difference between chromium trivalent and chromium hexavalent about toxicological and environmental properties [31].

In amounts ranging from 50 to 200 g per day, trivalent chromium is necessary for humans. The metabolism of insulin depends on chromium. All plants contain the element; however, it is unknown if it is an essential nutrient. However, it is also necessary for animals [32]. The chromium's oxidation state affects its kinetics. Most of the trivalent form of chromium consumed daily is consumed with food. According to [33], the body only absorbs 0.5–3% of the total absorption of trivalent chromium. Contact with chromium-containing items, for instance, can lead to widespread skin exposure to the metal. Leather, preserved wood, or soil with vines. Chromium exposure at work may be considerably influenced by airborne particles [34].

Effects on humans from occupational exposure to high levels of chromium or its compounds, primarily Cr [VI], by inhalation may include psychotropic effects, potential hematologic effects, effects on the stomach and blood, effects on the liver and kidneys, and increased risks of lung cancer and death [35].

When both Cr [III] and Cr [VI] at high levels are parenterally injected into animals, effects on the fetus appear, with the hexavalent form accumulating in the fetuses to a much greater extent than the trivalent. Effects on the fetus from exposure to chromium have not been reported in humans. Chromosomal aberrations have been observed in some humans occupationally exposed to hexavalent chromium compounds and other substances [34]. In sensitive people, exposure to Cr [VI] and Cr [III] compounds has been linked to allergic reactions [such as asthma and dermatitis]. The general populace frequently has chromium eczema due to exposure to chromium in everyday items. Workers who frequently come into contact with high concentrations of chromium salts are less at risk than those who work with materials that contain traces of these salts [36]. Trivalent chromium is typically less hazardous to environmental species than hexavalent chromium. Hexavalent chromium in the environment is primarily a result of human activity. Chromium is reasonably stable in this oxidation state in pure air and Water, however it comes into contact with organic matter found in living things, soil, and Water, it is reduced to the trivalent state. [37]. According to numerous studies, chromium is a hazardous element that impairs plant metabolic processes, hinders crop growth and yield, and lowers the quality of vegetables and grains [38]. Chromite [Cr], especially Cr [VI], is a highly bioavailable HM that has not been shown to play any part in plant physiology. It has been discovered that chromium is highly harmful to plants. This toxicity is also determined by chemical speciation, which is regulated by other parameters, including soil pH, redox potential, organic matter, and microbial population [39].

- **Nickel**

Nickel is a metal that is widely distributed in the environment. It is a crucial component of approximately 100 different minerals, which have a wide range of industrial and commercial applications [40]. A minor portion of nickel's global usage is utilized in the jewelry sector for plating and alloying with gold and silver. However, it is widely utilized in a many other applications, including stainless steel and nickel hydride batteries in hybrid and electric automobiles, it has developed into a common substance in contemporary culture [41]. Nickel is linked to several environmental problems, including greenhouse gas emissions, habitat damage, and air, Water, and soil contamination. Because nickel deposits are frequently found in low-grade ores [containing only 1% to 2% nickel], the extraction and refining of the metal requires much energy. Due to the increased energy demand, mainly met by fossil fuels, greenhouse gas emissions into the environment have increased significantly [42].

Nickel is a ferromagnetic element naturally present in the earth's crust. Usually, oxygen, sulfur, and sulfur oxides and sulfides are involved. Nickel may be found in soil, meteorites, and volcanic emissions. The ocean contains around eight billion tons of nickel. Nickel is utilized in a wide range of industries, including the creation of alloys, electroplating, the creation of nickel-cadmium batteries, and as a catalyst in the chemical and food sectors, thanks to its unique physical and chemical qualities. The widespread use of products containing this metal causes nickel pollution of the environment. It has been determined that some microbes, plants, and animal species require nickel as an essential nutrient, although there is no evidence to support its nutritional significance for humans [43]. Human exposure to high nickel concentrations leads to several health problems, such as cancer, asthma, and heart disease [44]. Nickel-enriched enzymes are found in archaea, bacteria, algae, primitive eukaryotes, and plants [45 ,46, 47,48].

Nickel plays crucial roles in a wide range of physiological and morphological processes, including seed germination and productivity, and is necessary for the healthy growth and development of plants. However, nickel impacts plant metabolism, inhibits enzyme activity, and has an electron transfer effect on photosynthesis at high concentrations [49].

- **Arsenic**

The element arsenic is present in nature in various forms, including rocks, Water, air, vegetation, and wildlife. It can exist in both organic and inorganic forms as a mineral [50]. Most arsenic compounds have no taste or odor and are readily soluble in Water, which increases health hazards [51]. Mining operations, the processing of fossil fuels, and the burning of household and commercial garbage all require human resources. In sulfide ores, which also contain other metals including copper, lead, silver, and gold, arsenic can be found in natural sources. These natural sources are susceptible to arsenic release due to mineral degradation and rapid evaporation. Under reduction conditions, it can also result from the absorption of metal oxides and slow down the dissolving of iron and manganese oxides [52]. Because it is harmful and thought to be carcinogenic at doses as low as 0.01 g/ml, arsenic is regarded as a very toxic heavy metal. Arsenic enters the body primarily through breath, contact with the skin, and ingestion. After then, it has impacts the kidneys, bladder, skin, lungs, heart, and central nervous system. Arsenic dermatitis, leukocytosis, hyperkeratosis, hyperglycemia, miscarriage, and immune system changes Plant metabolism is impacted by it. disrupts the balance of carbon, amino acids, proteins, nitrogen, sulfur, and other metabolic pathways, which results in a phosphate imbalance in DNA [53]. According to a guideline by the US Environmental Protection Agency, arsenic is one of the most dangerous heavy metals. The oxidation state of arsenic—that is, arsenic, arsenic, and arsenic—determines its physical and chemical characteristics. The inorganic form of arsenic is the most dangerous. In physical therapy, microalgae are frequently seen attempting to detoxify arsenic by changing its inorganic form into an organic one. Chelated or functional groups, such as phosphates and nitrates, can convert them [54]. Arsenic has a close connection to human existence and is utilized extensively in more than 50 different industries, including the military, metallurgy, pesticides, the silicate industry, semiconductors, processing, feed, and cosmetics. In addition to extensively used rulers, arsenic-containing insecticides, male insecticides in hybrid rice, and arsenic-containing herbicides were also widely utilized in agricultural productivity. Arsenic is simultaneously the most harmful carcinogen that endangers people's health. Lung, skin, and bladder cancer can all be brought on by arsenic exposure in addition to acute and subacute arsenic poisoning [55,56, 57,58]. Investigating effective and inexpensive techniques to eliminate arsenic from the environment is necessary.

3. Bioremediation

Bioremediation is a technique used to remove environmental pollutants from an ecosystem based on microorganisms such as bacteria, fungi, and algae It also uses plants to eliminate hazardous pollutants and restore the ecosystem to its original state [59]. Alternatively it might be defined as a process that relies on biological mechanisms to reduce, break down, detoxify, or turn pollutants into a harmless state. In the past two decades, there have been recent developments in biological remediation techniques aimed at effectively treating polluted environments in an environmentally friendly manner at a meager cost compared to chemical or physical treatment methods [60]. The biological treatment process can be classified into two main types: in-situ and off-site. The processes that are in-situ include adding nutrients to the polluted environment to stimulate microorganisms to break down pollutants, adding new types of organisms, or modifying the original organisms to break down a specific pollutant using genetic engineering [61, 62]. Off-site treatment operations involve moving contaminated media from its original site to a different treatment site based on the type of contaminants present, the cost of treatment, the geographical location, or the geology of the contaminated site [63]. Bioremediation combines the methods used by numerous fields. Opportunities for novel bioremediation methods appear as each profession develops and as new cleanup requirements materialize. New methods for bioremediation will be available as novel, better known at the ecological, biochemical, and genetic levels [64]. So, Bioremediation is a remediation technology that is widely used and is constantly developing. Although many problems that initially restricted its usage have been resolved, some still need more research [65].

- **Phytoremediation by Algae**

Macroalgae and microalgae can be used to remove pollutants or convert them biologically, such as nutrients, heavy metals, hydrocarbons, and carbon dioxide from polluted air [66]. In general, microalgae have proven their efficiency in removing heavy metals. Algae absorb heavy metals through rapid absorption on the cell surface, which is called physical absorption, then these ions slowly move to the cytoplasm in the process of chemical absorption [67]. On the other hand, algae can use some elements in ctiyical biological processes, as iron is involved in photosynthesis and electron-transporting proteins [68]. In addition, microalgae produce oxygen as a by-product of photosynthesis, which aerobic bacteria can use to decompose organic pollutants in wastewater. As a result, microalgae can help reduce the need for mechanical ventilation during wastewater treatment [69]. Algae treatment is one of the most efficient advanced methods of removing pollutants in a safe and environmentally friendly manner due to its ability to proliferate, its resistance to the harsh conditions surrounding it, and its low cost [70]. Some metals are essential to algae, such as magnesium, which is also used to manufacture of chlorophyll and some enzymes such as Kinases and ATPases [71]. However if heavy metals are present in high concentrations, they can cause symptoms of toxicity and the effects of free radicals. In a study conducted on *Chlorella minutissima*, it proved efficient by removing 62%, 84%, 74%, and 84% of Cu^{+2}, Cd^{+2}, Mn^{+2}, and Zn^{+2} respectively, after planting it in sewage [72]. In Fez, Ante Kong, and New Delhi, India, arsenic was utterly removed from drinking water by the green algae Cladophora [73]. In a study used by Dominic et al.[74], Green algae like *Chlorella vulgaris* and two blue-green algae, *Synechocystic salina* and *Gloeocapsa gelatinosa* in the treatment of industrially contaminated Water, it was shown to be highly efficient in removing organic loads. Green algae such as Scendesmus sp., Chlorella sp., and blue-green algae like Nostoc sp have also been proven. High efficiency in removing nutrients, organic loads, and dissolved solids when used in the treatment of wastewater released after primary treatment [75]. Indicate [76] reference to the role of algae in the treatment of household waste water, as the removal rates of nutrients such as phosphate were high after three days of treatment. In a study in which two types of green algae were used, *Chlorella vulgaris* and *Chlorella reinhardtii*, for wastewater treatment, the results showed a decrease in the value of COD by 59% and 46%, respectively [77].

- **Mechanisms of Bioremediation by Algae**

During the biotreatment process, microalgae not only remove nitrogen and phosphorus, but can also remove and break down other toxic substances such as heavy metals, organic pollutants, and hydrocarbons. They can also convert low concentrations of heavy metals such as cadmium and mercury into sulfides and carbonates with low solubility and less toxicity. It was observed that when green algae *Chlamydomonas reinhardtii*, red moss *Cyanidioschyzon merolae* and the blue-green moss *Synechoccocus leopoliensis* are exposed to cadmium, these algae reduced the toxicity of the element by converting it to cadmium sulfide [78]. Another study showed that when red algae *Galdieria sulphuraria* are exposed to mercury Hg^{+2}, there was a 90% conversion of Hg^{+2} to beta-mercury sulfide [β-HgS] within 20 minutes [79]. Microalgae can form complexes with pollutants in wastewater thanks to their reactive clusters and active attachment sites. According to [80], this causes flocculation, which lowers the concentration of all of these total dissolved solids [TDS] and total suspended solids [TSS].

The bioaccumulation property carries out the mechanism of bioabsorption. Bioabsorption is one of the primary mechanisms by which algae absorb and destroy toxic pollutants relative to their large surface compared to their size, as they contain a large surface compared to their size and contain on the surfaces of their cells highly binding groups and effective systems [fig.1] for absorbing and storing polluting materials [81]. The cell wall in microalgae consists mainly of sugars [cellulose and alginate] and organic fats, providing many functional groups [such as amino and carboxyl, hydroxyl, imidazole, phosphate, sulfonate, thiol, etc.] capable of binding heavy metals [82]. In a study he conducted on the bluish-green *Lyngbya taylorii*, he showed its high ability to absorb many heavy metals [83].

As a property of bioaccumulation, it is a process by which algae accumulate toxic substances in the environment. This process occurs in two stages: the first is a rapid process similar to the process of bioabsorption, and the absorption of ions occurs in the cell, in contrast the second stage is slow and the ions are transferred into the cell by effective transport [84]. Heavy metals are efficiently transported through the cell membrane to the cytoplasm, where they are then bound by internal binding sites of proteins and peptides such as GSH metal transporters and oxidative stress-reducers [85,86]. For example, in a study of three types of green algae, *Oedogonium sp.*, Hydrodictyon, and Rhizoclonium, it was found to accumulate heavy metals such as vanadium and arsenic in the wastewater of coal power plants [87]. Another study conducted on Chlorella vulgaris showed that this alga can accumulate and reduce nickel oxide nanoparticles. NiO means algae can be used in the bioprocess of nanomaterials [88].

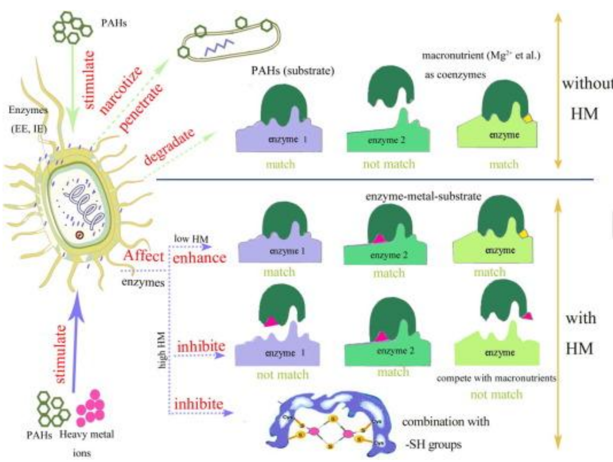

Fig.1: Process of enzymatic breakdown of PAHs by heavy metals [89]

- **Evaluation of various microalgae's potential for heavy metal remediation**

Eukaryotic bacteria known as microalgae are prevalent in watery environments. It controls metabolism by using sunlight to repair carbon dioxide from the environment [90,91]. Microalgae can treat wastewater to reduce its nutritional load [91]. Microalgae have been used to treat wastewater worldwide for the past three decades [92,93]. Several published studies have suggested that microalgae can process heavy metals [93], where Soeprobowati and Hariyati [94] examined the potential of microalgae such as *Chaetoceros sp.*, *Spirulina sp.*, *Chlorella sp*., and *Porphyridium sp*. to remove heavy metals such as cadmium, copper, and lead [at a concentration of < 0.5 mg l-1].

In addition, Shokri Khoubestani et al. [95] used a bio-sorbent derived from microalgae containing protein [43.5%], carbohydrates [20.3%], and fat [9.2%]. To remove chrome [III] and chrome [VI] in batch mode experiments and evaluate the pH effect, the results showed that at pH 6, the absorption of Cr [III] was 98.3%, and at pH 1, the absorption of Cr [VI] was 47.6%.

In another study, [96] studied Cd's bio-absorption and removal kinetics [II]. Using *C. vulgaris* live and dead, the results showed that the bacterium *C. vulgaris* has a high cadmium absorption efficiency in all dead cells [96.8%] and living cells [95.2%]. So, we conducted experiments with microalgae, *Scenedesmus incrassatulus*, to remove chrome [VI], cadmium [II], and copper [II]. The results showed that *Scenedesmus incrassatulus* eliminated 25–78% of heavy metals, with chromium [VI] being removed heavily.

Scenedesmus sp. ability for bioabsorption was investigated by [86]. The biomass of Scenedesmus sp. accumulated 92.89% of chromium according to the results of the solution biomass for chrome removal [VI]. The microalgae cell contains a variety of functional groups, including positively charged amides, aldehydes, carboxylic acids, halides, and phosphates that aid in bioabsorption, according to infrared spectroscopy [FTIR] by transforming Fourier. Lesson on the Mechanism of Lead [II] Removal Using Microalgae *S. obliquus*, Danouche et al. [97] The findings demonstrated that S. obliquus absorbed lead [II] by bioabsorption [85.5%] and bioaccumulation [14.5%] whether inside or outside of cells.

4. Adsorption

Adsorption is a separation process in which molecules condense on the adsorbent surface due to the van der Waals force between them. The adsorption susceptibility of a compound increases with the increase of its molecular weight; the number of functional groups, such as double bonds or halogen compounds, increases; and the polarizability of the molecules increases [98]. This method removes organic pollutants, toxic compounds, and dyes from water waste that conventional methods cannot remove [99].

These components can be removed largely by adsorption on the surfaces of many porous natural materials such as activated carbon and zeolite [100], aluminum oxide, animal charcoal, silica gel [101], fly ash, and porous clays [102]. The adsorption isotherms represent the change in the amount of adsorbent that is obtained by a certain amount of adsorbent liquid to a specific concentration limit at a specific temperature and pressure, through which the adsorption capacity of the adsorbent is determined [103]. The adsorption of pure liquids to the surface differs because the solution contains multiple substances, each interacting with the others to compete for active sites on the surface of the adsorbent. Thus, when any change occurs in the concentration of the solution, the components of the solution will replace each other. It is one of the properties of the solution that depends on the nature of the interactions between the solute and the solvent in the solution and the interactions that occur with the solid adsorbent surface [104]. A process similar to the adsorption process may occur, which is absorption, which is the penetration and spread of adsorbent particles on the surface of the adsorbent, and these particles are not collected on the surface of the adsorbent only, as happens in adsorption.

Many factors affect the adsorption process, including temperature, pH, ionic strength, amount of adsorbent, nature of the adsorbent, adsorption time, initial concentration, and the effect of the solvent [105]. Adsorption kinetics expresses the speed of withdrawal of adsorbent molecules from the solution and their adhesion to the adsorption surface, which requires overcoming the forces between molecules that impede the process of adsorption in the solution. [106]. Adsorption results from the bonding forces between the adsorbent and the adsorbent surface, regardless of the nature of the phases of the substance and the adsorbent element. Adsorption occurs between two phase: liquid-solid, liquid-gas, and gas-liquid [107]. Absorption methods are widely utilised to remove heavy metals from wastewater. Activated carbon is the most popular adsorbent and provides the best results, but its use is constrained by its high price. Its manufacturing and regeneration are costly [54].

5. Biochar

- **Biochar and Magnetic Biochar**

Biochar is a porous, carbon-based material made from the pyrolysis of organic matter. Biochar can be made from various ingredients, including plant materials and compost. The biomaterial consists mainly of cellulose, with some organic extracts and mineral components thrown in for good measure. The main elements present in biomass carbon are C, H, O, N, and S. The difference in the type of biomaterial results in the efficiency of the prepared biomass in terms of its adsorption capacity [108].

Different raw materials were used to synthesize biochar, which has different compositions. According to [109], microalgae-derived biochar comprises large aggregates that range in size from 10 to 100 m and has an uneven porosity of 1 m. Biochar produced from the pyrolysis of biomass and biochar formed from microalgae has different structural characteristics [110]. Various biomasses, including rice straw, bamboo cane, poplar leaves, waste from mangosteen shells, and gravel husk, are combined to create biochar. At temperatures between 300 and 700 °C, slow pyrolysis of microalgae yields 56.3-66.2% biochar. A temperature range of 350-950 °C produces 39-52% biochar from other biomass sources, such as sewage sludge. In the 400–1000 °C temperature range, olive skin biochar yields 9.4–44.5% by weight of the biochar output [109]. According to most research, magnetic biochar is an essential adsorbent for heavy metals from wastewater and even Water contaminated with nuclear waste [111].An adsorbent, biochar can absorb organic pollutants well. Nowadays, many researchers have studied biochar adsorption on organic matter in the soil, such as PAHs [43] and phthalate acid esters [112]. Some studies also showed that the treatment effect of a wastewater treatment system containing biochar on organic pollutants was significantly improved compared to that without biochar [113]. Algae-based biochar has a good adsorption capacity to remove organic and inorganic pollutants from wastewater compared to other carbonaceous materials. For example, the removal of heavy metals by microalgae [*Chlamydomonas sp.*] is 94% with a biosorption capacity of 152mg Cr[VI] g-1 [114]. Because magnetic biochar can be easily and quickly separated from aqueous media, magnetic separation is an ideal solution to the biochar problem. Magnetic biochar is made by combining biochar with magnetic materials, which is a great way to eliminate metallic contaminants in aqueous solutions [115].

Due to its ability to magnetically separate materials, magnetic biochar has recently attracted much attention. Magnetic biochar is an excellent soil amendment, making it a more and more desirable option for removing heavy metals from contaminated soils[116].

The use of biochar in treating of soil contaminated with abundant metals was investigated by [117]. Due to its numerous sources, high porosity rate, the presence of functional groups, and low price, biochar [BC], a carbon-based substance rich in pore structure, has become a promising adsorbent for the remediation of environmental contamination [118,57,119]. BC has undergone extensive research as a material for carbon sequestration and the stabilization of HM due to its full capacity to adsorb on the ion-exchange state of HM [120,121] .\

In a different study, biochar and magnetic biochar were used as effective, affordable, secure, and environmentally friendly methods for removing heavy metals like cadmium. The biochar was made from palm fronds and activated with sodium hydroxide before being treated with two concentrations of cadmium in the Water [5 ppm and 10 ppm]. The effectiveness of eliminating cadmium [II] was enhanced by the charcoal [BC]. When we added 0.5 g of biochar to the solution, cadmium was removed at a rate of 98 percent. However, when magnetite-biochar [MBC], which has the property of being magnetic, was added to the biochar prepared by adding Fe_3O_4, the adsorption performance of heavy metals was significantly improved, and the removal efficiency was increased up to 100%. This explains why MBC has such an excellent adsorption performance [122].

After preparing biochar, it must be characterized to determine its chemical make-up and form. Isotherms, such as nitrogen adsorption isotherms, X-ray diffraction [XRD], Fourier- transform infrared spectrometry [FTIR], and X-ray spectroscopy [XPS] are typical analytical procedures for biochar, according to an overview of the material. By calculating the multilayer adsorption capacity under various partial pressures of nitrogen, nitrogen adsorption isotherms are utilized to calculate the surface area of biochar. The Brunauer, Emmett, and Telle [BET] multilayer adsorption model can be used to calculate the biochar's surface area. Carbon crystals are analyzed using XRD by determining the direction and strength of the diffracted rays. Graphite and non-graphite carbon are the two types into which carbon crystals are typically categorized. The small, sharp reflection pattern indicates graphite, whereas non-graphite carbon is indicated by the broad reflection pattern [123]. Using the Fourier transform function, FTIR may be used to identify the chemical functional groups on biochar based on the wave in the frequency domain of the light intensity. Different function groups are represented by vibration at various locations in the IR spectrophotometer [124].

Figure 2 illustrates the impregnation-pyrolysis, chemical co-precipitation, solvothermal, and reductive co-precipitation processes used to successfully create magnetic biochar, as reported in the literature [125]. These biochar composites are demonstrated to offer efficient absorption, quick separation utilizing external magnets, and simple recycling [126]. However, the traditional magnetic medium loading procedure raises the sorbent's price[127]. Pyrolysis, co-precipitation, and the calcination process are three of the most often used methods reported by Thines *et al*. to create magnetic material [128]. A typical production technique was mentioned in the literature, such as traditional heating in an electrical furnace [129].

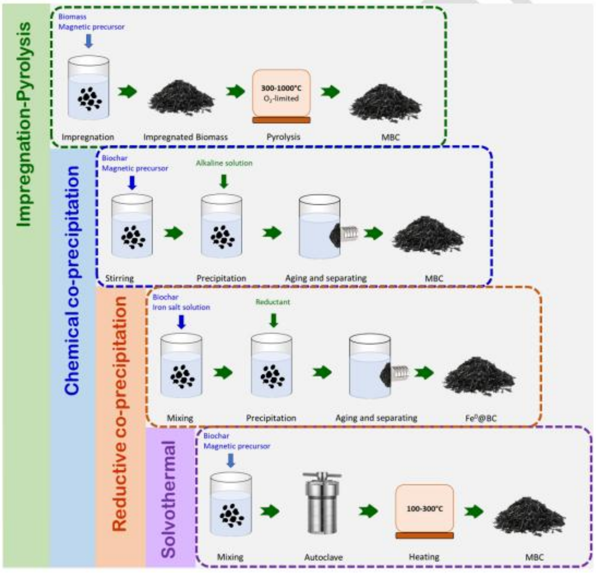

Figure 2: A schematic of typical techniques for making magnetic biochar [130].

- **Biochar applications:**

➢ **Application of biochar in heavy metal removal**

Over the past ten years, there has been an increase in interest in biochar because of its enormous potential for adsorbing minerals from aqueous solutions. Different heavy metals may co-exist with other pollutants in natural waterways, and as a result, other metals, ions, and organic contaminants compete for adsorption sites on the biochar surface. The competitive adsorption of heavy metals by biochar has only recently been examined in a few studies [131]. The mineral components of the biochar, which act as adsorption sites for heavy metals through sedimentation, are also crucial in the removal process. For example, the percentage of cadmium removal increased in the biochar of dairy manure due to the content of relatively soluble carbonates and phosphates and an increase in temperatures from 200 to 350 °C. The removal efficiency of cadmium was improved from 31.9 to 51.4 mg/g due to the increase in the proportion of metallic components in biochar, especially soluble ones such as carbonates [132]. Several studies revealed that biochar's ability to mitigate pollution includes micropore structure and surface physical adsorption and includes micropore structure and surface physical adsorption and relates to organic compounds and inorganic ions that may primarily affect mineral fixation [133,134].

Heavy metals are often removed using magnetized biochar through electrostatic adsorption and the formation of functional aggregates. Iron oxides play an essential role as buoyant heavy metal element pollutants are treated using a magnetic biochemical approach, where the most common buoyant heavy metal pollutants are dealt with. By using magnetized biochar, the activators improve the prepared materials' chemical and physical properties and thus increase pollutant removal efficiency [135]. Initially, biochar was employed to encourage carbon sequestration and agricultural advantages, However 2005 onward, the number of publications of indexed articles has grown exponentially due to the material's promising outcomes for pollution removal [136].

Due to its low production cost and distinct physicochemical characteristics, which are helpful for many applications, biochar has caught the scientific community's attention in recent years [137].

➢ **Organic pollutant treatment**

The increase in global population over the past two decades has resulted in a greater demand for Water for both human consumption and industrial use, which has increased the volume of wastewater dumped into the aquatic environment. Several pollutants, including carcinogenic heavy metals, have been identified in wastewater streams and described in the literature [138]. hydrocarbons from petroleum , polycyclic aromatic hydrocarbons [PAHs] [139], organic dyes [140], phenols, insecticides, medicines, and antibiotics for animals [141]. Organic pollutants have become one of the most critical environmental issues, along with heavy metals in Water, because they are rebellious and persistent in the environment [142]. Therefore, magnetic biochar is highly efficient in absorbing organic emissions, and the organic pollutants that are treated with magnetic biochar include phenols, pesticides, organic chlorine, antibiotics, and organic dyes [143]. Biochar prepared from natural materials shows a high ability to absorb organic materials. In general, electrostatic bonding and hydrogen bonding are the primary tools for absorbing organic materials by biochar, which varies according to biological materials' chemical and physical properties [144]. The presence of non-carbon materials makes their surfaces inhomogeneous, resulting in different adsorption mechanisms for the adsorption of organic compounds [145].

Designing the most effective, functional, and practical treatment approaches is still seen as problematic. The following processes were found to be the most promising among those that have been the research focus: chemical oxidation, electrocoagulation, membrane separation, reverse osmosis, filtering, adsorption, and biological treatment [146,147,148]. One of the most effective ways to remove various pollutants from wastewater and gaseous streams is adsorption [149,150].

Clays, zeolites, and active carbon are common adsorbents, with the latter being extensively employed for effective micropollutant removal, particularly in the potabilization of Water. In Europe, coal and biomass such as coco coir or coco shells that can be transported over large distances are typically utilized to manufacture the active carbon. The advantage of sustainably generated substrates, biochar, as an alternative to currently employed active carbon is made possible by local leftover biomass and well-regulated pyrolysis conditions [151]. While reducing greenhouse gas emissions and carbon sequestration are currently receiving much attention, the initial focus of interest in biochar was on improving agricultural productivity through the enhancement of soil fertility, increasing soil nutrient levels, and increasing soil water retention capacity [152, 153,154].

- **Treatment of inorganic pollutants**

Inorganic pollutants such as nitrates, phosphates, fluoride, and other inorganic pollutants are treated using magnetic biochar [143]. Among other pollutants, phosphorus is the most researched and the focus of attention among other inorganic pollutants, and the amount of magnetized biochar adsorbed ranges from 1.26 mg/g to 474.26 mg/g. Modified magnetic biochar has a higher ability to absorb phosphorus, as it was determined The adsorption powers of nitrate and fluoride on magnetic biochar were 15 mg/g and 9 mg/g, respectively. Removing inorganic anions includes surface complexes of adsorption, ion exchange, electrostatic interference, and co-precipitation [155]. Recently, British Columbia [BC] has emerged as a new sorbent due to its exceptional qualities, including eco-friendliness, abundance in functional groups and inorganic mineral species, containing micro and/or meso-porous structures, and high adsorption capacity, which were widely used to remove contaminants from wastewater [156,157]. However, biomass, reaction parameters, etc. correlated with BC and BC-based composite material performances. For instance, whereas BC manufactured at lower temperatures contained more harmful compounds such as polycyclic aromatic hydrocarbons [PAH], polychlorinated dibenzo dioxins [PCDD], and polychlorinated dibenzo furans [PCDF], BC prepared at higher temperatures had a comparatively high pH value. Moreover BC that came from animal manure was ash-rich. According to several studies, BC-based composites can significantly improve the efficacy of pollutants removal

[158]. Recently, Taha *et al*., [159] processed rice straw with phosphoric acid as biomass to produce TBC for eliminating pesticides from Water. Surprisingly, within 10 minutes, the residual pesticide concentration was below the legal limit for drinking water 0.1 g/L .

Furthermore, at pH 7.0, all pesticides [apart from oxamyl] could be eliminated in under two hours. According to [160], boosting TBC's aromaticity with phosphoric acid treatment can improve hydrophobic interactions and - interactions, which helps to increase the adsorption coefficient. The adsorption capabilities of atrazine by BC, Na2S modified BC [BS], and KOH-modified BC [BK] were further disclosed by [161] to be 1.94 mg/g, 2.69 mg/g, and 2.84 mg/g, respectively. Since BS and BK had relatively low H/C ratios, modified BC had abundant aromatic structure. More more aromatic surfaces and polyaromatic structures can provide electrons donor-acceptor interaction sites. The attraction between opposing quadrupoles can produce the - electron donor-acceptor interaction, which increases the removal rate, between the - electron-deficient molecule [atrazine] and the - electron-rich molecule [BK/BS].

6.Conclusion

Heavy metal pollution poses significant risks to both the environment and human health. Bioremediation, mainly using microorganisms and biochar, offers a promising and environmentally friendly approach to mitigate the impact of heavy metal contamination. Microalgae and bacteria can efficiently absorb and accumulate heavy metals, while biochar can adsorb and immobilize these contaminants.

Using microorganisms and biochar in heavy metal bioremediation has several advantages, including their effectiveness, cost-efficiency, and sustainability. However, further research is needed to optimize the application methods, understand the long-term effects, and ensure the safety of these techniques.

Implementing bioremediation strategies, such as phytoremediation using microalgae and modified biochar, can contribute to restoring polluted water bodies and contaminated soils. By utilizing these greener alternatives, we can work towards reducing the risks associated with heavy metal pollution and promoting a healthier environment for both ecosystems and human populations. However, further research at the molecular level is required to understand how algae resist heavy metals completely and to speed up cleanup and byproduct synthesis.

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