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Heavy Metal Adsorption from Wastewater Utilising Algae Developed Nanostructured Materials

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ABSTRACT: Numerous algae possess enormous potential to absorb metals, and there is a great deal of Promise for treating for using them to treat wastewaters. *Chlorella vulgaris* was used as Biosorbent to enhance the adsorption capacity. Heavy metals have harmful effects on ecosystems and human health, making their removal from wastewater a significant environmental concern. Because algae has special qualities, which include large surface area, tunable pore topologies and functionalizability, nanostructured materials have shown great promise as heavy metal ion adsorbents. The most recent developments in the creation and use of nanostructured materials for the adsorption of heavy metals from wastewater are reviewed in this work. Mesoporous silica, zeolites, magnetic nanoparticles, carbon-based nanomaterials, metal-organic frameworks and polymeric nanocomposites are some of the important materials that were covered. A thorough Examination is conducted of the mechanisms underlying adsorption ion exchange, surface complexation, electrostatic attraction, and precipitation. The study also addresses issues with cost, scalability, and environmental effect while highlighting the benefits of these materials, which include high adsorption efficiency, selectivity and regeneration potential. The promise of nanostructured materials to transform wastewater treatment systems is highlighted by recent advancements in hybrid nanomaterials, environmentally friendly production techniques and practical applications. In order to optimize these materials for industrial-scale applications and to guarantee their safe and sustainable usage in environmental remediation, this review emphasizes the necessity of ongoing research.

Keywords: Heavy metal Adsorption, Nanostructured materials, algae Wastewater treatment.

INTRODUCTION

Water is the main component of life on Earth. Urbanization, industry, and the growing world population have all contributed to a steady decline in the quantity and quality of water sources. Due to a variety of dangerous contaminants brought on by chemicals, industrial effluents, including inorganic and organic contaminants, and nuclear waste, more than 700 million people worldwide lack access to clean water (Punia *et al*., 2021, Naskaret *et al*., 2022 and Calzadilla *et al*., 2011). Pesticides, fertilizers, metal complex dyes, fixing agents (which promote the uptake of dye onto fibers), colorants', bleaching agents, heavy metals, and other substances are among the many ways that these compounds are released into the environment. On their cell surfaces, algae have a variety of functional groups that serve as active sites for metal ion binding, including hydroxyl, carboxyl, sulphate, phosphate, and amino groups. Heavy metals from wastewater have been successfully adsorbed by both macroalgae and microalgae. Furthermore, algal biomass may be readily grown from nutrient-rich effluent, supporting a circular bioeconomy that is sustainable. Nevertheless, despite their potential, low surface area, poor mechanical strength, and challenges with separation and regeneration following treatment can all restrict the natural biosorption efficacy of algae.

Green synthesis and cutting-edge nanotechnology are combined in the creation of nanostructured materials derived from algae. By using algae metabolites as natural reducing and stabilizing agents, these bio-nanomaterials are made in an environmentally responsible manner, eschewing the hazardous chemicals frequently employed in the production of conventional nanoparticles. This improves the biocompatibility and environmental safety of the final nanoparticles while also making the process sustainable.

Conventional heavy metal removal techniques, such as chemical precipitation, ion exchange, membrane filtration, and electrochemical treatment, frequently have drawbacks like high operating costs, secondary sludge production, and decreased effectiveness at low metal concentrations. These disadvantages have prompted the hunt for environmentally benign, economical, and sustainable substitutes. The natural capacity of algae to bind and remove metal ions through surface functional groups including hydroxyl (–OH), carboxyl (–COOH), sulphate (–SO_4H) and amino (–NH_2) has made algal-based biosorption one of the most promising biological techniques. Since both macroalgae and microalgae have shown high metal removal efficiencies, they are desirable options for extensive wastewater treatment projects.

Algal biomass and nanotechnology have been combined in recent years to create algae-derived nanostructured materials, which combine the benefits of biological systems with the special qualities of nanomaterials, like high surface area, increased reactivity, and adjustable functionality. The potential of these hybrid materials to increase adsorption efficiency, selectivity, and reusability is impressive.

The world's scientific community is starting to recognize that there is a water deficit and that immediate action is required to support sustainable development. This scarcity, exacerbated by climate change and rising demand even in regions with historically abundant water supplies, directly affects freshwater supply. There are also significant economic consequences.

Nearly 1.8 billion people, or two thirds of the world's population, are expected to live in water-stressed countries by 2025, with many of these countries experiencing acute water scarcity.

Between 1.7 and 2.4 billion urban residents worldwide are expected to be without access to water by 2050. Demand for water continually outpaces supply due to the intricate relationships between urbanization and climate change. All living things are at risk from heavy metal pollution of waterbodies caused by the careless disposal of household and industrial trash (De Filippis and Pallaghy 1994). Therefore, before releasing wastewater into rivers, it is imperative to reduce the heavy metal burden in the effluent. Chemical precipitation, ion exchange, adsorption, solvent extraction, membrane separation and other physicochemical methods have all been used to remove toxic metals from wastewater (Eccles, 1999).

However, these processes have a number of drawbacks, such as insufficient removal of metal, high energy or reagent requirements, costly equipment and monitoring system requirements, and the production of waste products that need to be disposed of, such as hazardous sludge. In addition to reducing some of the side effects of physical and chemical treatments, biological approaches offer an affordable way to remove metals from wastewaters that are higher in metals. The use of costly biomass, of all types, for the adsorption of heavy metals to be removed.

In this sense, it has been known for a few decades that microorganisms, particularly algae, can accumulate metals. However, it has only recently attracted increased attention due to its potential applications in environmental protection and the recovery of important or strategic metals (Malik and Dar 2024). The potential of algal biomass to accumulate metals is either greater than or equal to that of chemical sorbents. The term "biosorption" should really relate to the adsorption of metal ions on dead biomass, including metal ion binding on both extracellular and intracellular ligands, even though accumulation has become less frequent (Volesky and Holan 1995; Aksu, 1998). Algae absorb heavy metals through two distinct processes: a much slower active absorption and a quick passive uptake (Bates *et al.,* 1982). Wastewater has generated a lot of interest recently.

New approaches to wastewater remediation have been made possible by nanostructured materials made using algae or algal extracts to address these issues. By adding particular functional groups, increasing surface area, and improving porosity, the combination of nanotechnology with algal biosorbents improves adsorption effectiveness. Even at trace concentrations, algae-based nanomaterials such as metal oxide nanoparticles, magnetic nanocomposites, and biopolymer-based nanostructures have demonstrated exceptional effectiveness in binding and eliminating heavy metals. Additionally, magnetic nanoparticles make it simple to recover the adsorbent from treated water, improving process sustainability and efficiency.

2. Objectives of the Study

The study of heavy metal adsorption using algae derived nanostructured materials is shifting from laboratory scale feasibility to industrial grade sustainability. As of 2025, the future scope centers on three critical pillars: advanced engineering, circular economy integration and large scale deployment.

Advanced Molecular & genetic engineering. A promising method for heavy metal adsorption from wastewater is the combination of sophisticated molecular and genetic engineering with nanostructured materials made from algae. This technique efficiently eliminates hazardous heavy metals from contaminated water sources by utilising microalgae's inherent biosorption capacity, which is improved by nanotechnology.

Scability and industrial integration-A promising approach to environmental remediation is the adsorption of heavy metals from wastewater using nanostructured materials produced by algae. Recent developments in nanotechnology have produced effective nanoadsorbents that improve algae's adsorption capacity and qualify them for widespread industrial use.

Nanostructured materials and algal integrations-

Types of Nanomaterials: To increase the effectiveness of metal removal, algae like *Chlorella vulgaris* have been combined with a variety of nanomaterials, including magnetic nanoparticles and N-doped graphene oxide (Fóris *et al*., 2025 & Yokwana *et al*., 2025).

3. Circular economy & resource recovery

Algae combined with nanostructured materials offer a viable method for removing heavy metals from wastewater that is consistent with resource recovery and the circular economy. This technique provides an effective and long-lasting wastewater treatment solution by utilising the improved adsorption qualities of nanomaterials and the inherent biosorption capabilities of algae. In addition to increasing the effectiveness of heavy metal removal, the combination of these elements facilitates resource recovery and reuse, which promotes environmental sustainability.

4. Biosorption Process

In the middle of the 20th century, the first publications on biosorption were made. Since then, a lot of work has gone into describing and creating affordable, efficient biomaterials for biosorption, mostly for the treatment of wastewater. The application of diverse biomasses as sorbents has drawn interest from a variety of areas due to its shown capacity to remove harmful pollutants from aqueous solutions selectively at low concentrations and under a variety of settings. By defining the quantification techniques (kinetics and equilibrium) and identifying the influencing factors that determine efficiency and rate, progress has been made in comprehending the intricate mechanisms involved in biosorption (Michalak *et al*., 2013).

According to Gadd *et al.* (2009), adsorption is the physicochemical adherence of ions and molecules onto a solid material's surface. Van der Waals and electrostatic forces are involved in the physical interaction between metal and biosorbent, whereas ion exchange, proton shift, complexation, and metal chelation are related to the chemical foundation (Crist *et al*., 1999; Parmar *et al*., 1990). Independent of cellular metabolism, biosorption is a quick and reversible process in which ions from aqueous solutions attach to functional groups on biomass surfaces (Davis, *et al*., 2003).

Heavy metal adsorption by algae: In the context of biosorption, seaweed is mostly used in the wastewater treatment for reducing or removing toxic heavy metal contents (He *et al*., 2014). The removal of heavy metals from aquatic courses constitutes a relevant environmental challenge today due to the toxic nature of these elements for living organisms (Adamu, *et al*., 2015). Some heavy metals are toxic and carcinogenic, even in tiny concentrations, and they are non-biodegradable and can easily accumulate in living organisms. The heavy metal accumulation in soils and groundwaters is a growing concern; the main anthropogenic sources are mining operations, smelters, the paint industry, fertilizers, leather tanning, electroplating, alloy and battery manufacturing (Arumugam *et al*., 2018).

Algae use functional groups such as, carboxyl, hydroxyl and amino groups to bind heavy metals and increase their adsorption ability (Fan *et al*., 2023; Zeng *et al*., 2022). The ideal conditions for each metal vary, but factors like temperature, pH, and contact time all have an impact on the adsorption process (Yogeshwaran & Priya 2022; Zeng, *et al*., 2022).

Algal types and their effectiveness:

-*Tetradesmus obliquus* demonstrated high rates of lead, copper and cadmium removal, with maximum effectiveness at specific dosages (Fan *et al*., 2023).

-Under optimal conditions, *Microcystis aeruginosa* eliminated cadmium at a rate of 92.00% and copper at a rate of 83.24% (Zeng, *et al*., 2022).

-*Sargassum wightii's* ability to absorb zinc, lead and chromium was influenced by the pH and metal ion concentration (Akl *et al*., (2023).

5. Algae-caused metal accumulation

The concentration of metals in the surrounding environment determines how much metal can be accumulated by algae. The concentration factors of heavy metals in various algae species vary somewhat, but they generally increase when the amount of metals in the water decreases. The metal content of native algae may be used for biomonitoring of metal pollution in a water body since there is a correlation between the amount of metal in the water and the amount of metal acquired by algae (De Filippis and Pallaghy 1994). Additionally, the hazardous metal load can be decreased and precious metals like gold and silver can be recovered from wastewaters by taking use of algae's natural tendency to collect metals.

6. Methods for eliminating heavy metals from wastewater by employing algae

The process of biosorption

Biosorption is an inert method that uses biological materials as sorbents to efficiently mix and concentrate pollutants from wastewater. Through the phenomena of mass transfer, a material is moved from the liquid phase and sticks to a solid surface in this process. It includes a wide range of processes, including ion exchange electrostatic interaction, surface complexation, adsorption, and precipitation (Chia *et al.*, 2020).

The basic elements of biosorption consist of a solid-phase sorbent called a biosorbent and a target molecule that is present in the water in a dispersed state. The target sorbet, whether it consists of living or dead bacteria or their components, is drawn to this biomaterial, which also has a remarkable attraction for it. The quantity of sorbet molecules that can be absorbed depends on the biosorbent total capacity.

This process is repeated until the residual concentration in the liquid and the adsorbed substance reach equilibrium. It controls the distribution of the biosorbent affinity for a particular species in both the liquid and solid phases (Mantzorou *et al.*, 2018).

Adsorption of biological substances

Bioadsorption is a physical-chemical technique that directly removes heavy metals from wastewater by utilising the capacity of living organisms to absorb chemicals. Toxic substances attach to different biological elements of microalgal cells during this process, including the cell wall and extracellular polysaccharides (Saavedra *et al.*, 2018; Trinh *et al.*, 2020). Bhatt *et al.* (2022) revealed that pollutants and cell surfaces interact passively and non-metabolically to produce the behavior described.

Adsorption: a condition that sticks to metals

Adsorption is the method that is used most frequently for disposing of heavy metals. Adisasmito *et al.* 2023 and Abobakr & Abdo (2022) claim that metal ions adhere to the surfaces of adsorbent materials, efficiently trapping them and stopping their spread. This play about adsorption centres on the following characters.

Adsorbent Materials:

The abundance of functional groups and wide surface areas of these materials draw in metal ions. Zeolites, clays, activated carbon, and other nanomaterials are well-liked alternatives. Metal ions are positively charged metallic particles that are attracted to negatively charged areas on the adsorbent surface.

There are several ways to regulate the adsorption movement:

-Physical adsorption, also known as physisorption, occurs this week when the metal ion and the adsorbent surface form a transient bond, driven by the van der Waals force.

-Chemical adsorption, also known as chemisorption: More permanent metal ion attachment results from the creation of a stronger covalent or ionic connection.

-Ion exchange: To create selectivity for particular metals, metal ions are used as substitutes for other cations that are affixed to the adsorbent's surface.

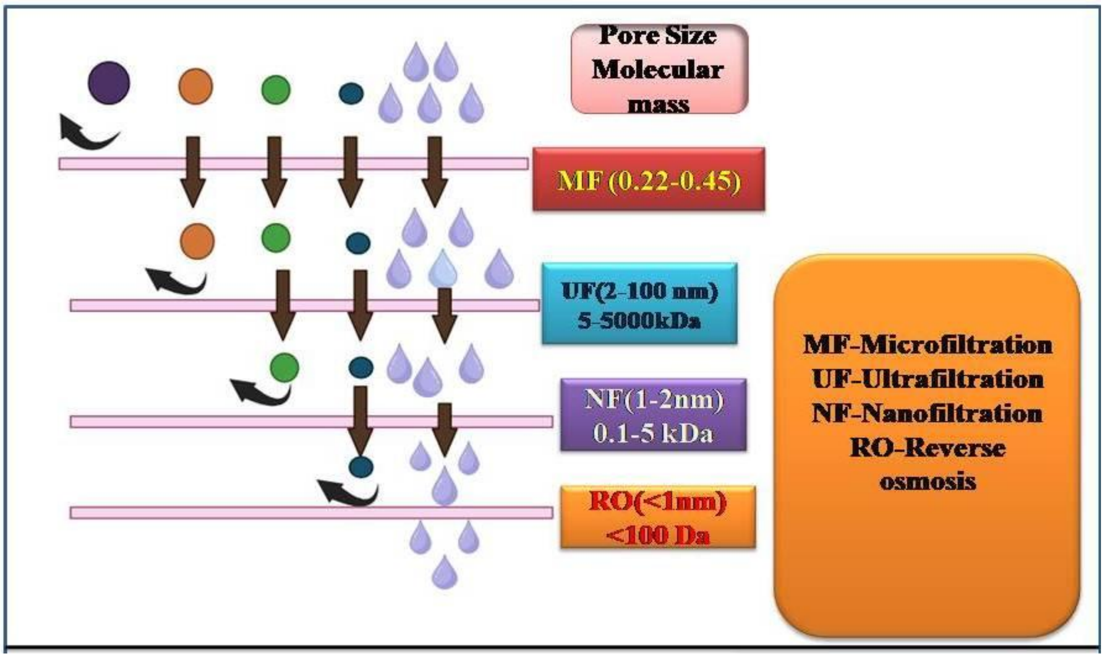

Fig. 1. Performance evaluation of four membranes in rejecting various heavy metal particles and ions (Karnwal & Malik 2024).

Table 1: The general benefits and concerns of common wastewater treatment techniques.

Waste treatment technique	**Advantages**	**Disadvantages**
Adsorption	Broad range of pH Low price Large capacity	Low selectivity Products of waste
Chemical precipitation	Low cost and easy to use	For trace ions, ineffective Waste materials
Ion exchange	Large capacity, easy to use	Regeneration of waste products Expensive
Separation of membranes	High effectiveness Superior selectivity	Regrowth Expensive high cost of running
Elimination by electrochemistry	High effectiveness Superior selectivity	Expensive High operating costs

7. The process of bioaccumulation

"Bioaccumulation" is the biologically dependent process by which metal ions actively enter living cells. Bioaccumulation, in contrast to biosorption, is dependent on the metabolic activities of living cells to actively transport metal ions across their membranes. Numerous chemical, physical and biological processes that take place both within and outside of cells depend heavily on live microbial cells. The majority of absorption occurs via energy-dependent transport channels that are fuelled by cellular energy, whereas passive diffusion only has a little impact on bioaccumulation (Fomina and Gadd 2014).

When selecting microorganisms for bioaccumulation, a few key traits must be present, such as the capacity to adjust to contaminated environments, resistance to elevated metal ion concentrations, and the existence of intracellular binding mechanisms (Bose *et al.*, 2021).

The initial temperature and concentration of metal ions also have an impact on the adsorption capacity; higher concentrations and suitable temperatures increase process efficiency (Gupta & Diwan 2017). The phenomena of bioaccumulation is then brought about by further interactions that occur within the cell by intracellular metal-binding proteins such metallothionein and phytochelatins (Dirbaz & Roosta 2018).

8. Adsorption of heavy metals using materials with nanostructures

Nanocomposites made of polymers

Since chitosan and cellulose are considered to be environmentally friendly cleaning agents, researchers are especially interested in nanoporous membranes constructed of these polymers (Yu *et al*., 2021). They are more able to absorb pollutants because of their large specific surface area, high gas permeability, and well-designed porous fibre network (Muthukumaran *et al.*, 2022).

Polymer-filled nano membranes exhibit exceptional selectivity and adsorption capacity due to unique functional moieties including NH_2, COOH and SO_3H (Karthik *et al.*, 2021). Categorized based on the substrate utilised, these micro adsorbents exhibit their adaptability in applications related to heavy metal removal. The distinct features and versatile activities of polymer-based nanoparticles have made them a promising solution for heavy metal pollution in water.

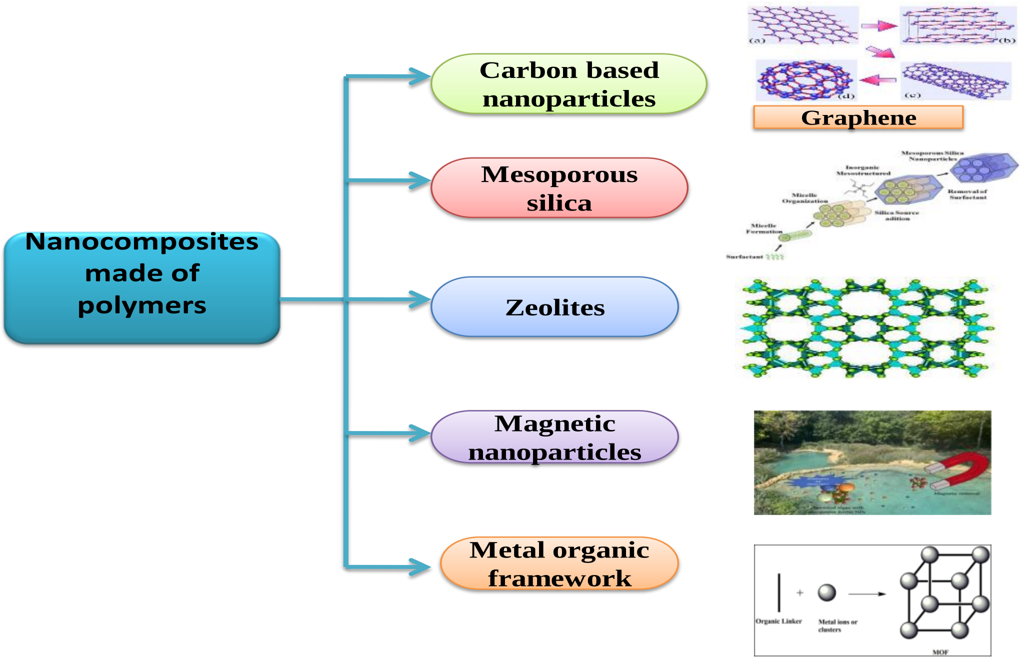

Fig. 2. Types of Polymeric nanocomposites.

Carbon-based nanoparticles:

Carbon-based nanomaterials, such as carbon nanotubes and graphene oxide membranes, can help cyanobacteria and algae bioremediate heavy metals in wastewater treatment. The broad family of carbon nanomaterials includes the following several carbon allotropes:

One-dimensional carbon nanotubes (CNTs), zero-dimensional fullerenes and quantum dots, three-dimensional nanodiamonds and nanohorns and two-dimensional graphene.

Because of its special chemical and physical properties, carbon nanostructures are used in many different sectors. The treatment and purification of water and wastewater, particularly heavy industrial and pharmaceutical wastes, have shown great potential for graphene and graphene oxide-based nanomaterials, as well as carbon and graphene quantum dot-derived nanomaterials. As adsorbents for the treatment and purification of wastewater, carbon nanomaterials, including activated carbon and single- and multi-walled carbon nanotubes, have been produced.

Mesoporous silica:

Due to its wide surface area, diverse surface properties, and typical pore diameter, a material based on nanostructured silica is being developed to adsorb metal ions. Furthermore, nano silica is a nontoxic, environmentally benign adsorbent due to its chemical inertness and lack of harmful health effects. Chemical nano silica changes, such as amino–thiol combinations, enable adsorption sensitivity and such significant limitations. Additionally, adding amino and thiol functional groups to the surface of nano silica improves its adsorption capacity and selectivity. Li *et al.* 2019, used nitrilotriacetic acid-modified silica gel (NTA silica gel).

Cu^{2+}, Pb^{2+}, and Cd^{2+} ions were removed from effluent. With relatively high adsorption capacities (53.14, 63.5, and 76.22 mg g^{-1} for Cd^{2+}, Cu^{2+}, and Pb^{2+} ions, respectively) and removal efficiencies ranging from

96% to 99%, the NTA silica gel showed quick removal of three metal ions: Pb^{2+}, Cu^{2+}, and Cd^{2+} ions. The effectiveness of NTA silica gel removal increased throughout a wide pH range (2–9) and held steady in the presence of competing metal ions (Na^{+}, Mg^{2+}, Cu^{2+}, and Al^{3+} ions) at different concentrations. Furthermore, the NTA silica gel had a high adsorption capacity since it was simple to regenerate and reuse for five cycles.

According to this study, Cu^{2+}, Cd^{2+}, and Pb^{2+} ions can be quickly, easily and effectively. Removed from contaminated aquatic environments using NTA silica gel, a reusable adsorbent.

Zeolites:

Biochar is a carbon-rich biomass byproduct that is produced via low-temperature thermal decomposition under oxygen-limited conditions. The quick development and widespread availability of goods made from algae biomass, including algal biochar, have recently sparked concerns. The latter carbon compounds have a larger nutritional content of N, ash and inorganic elements and a superior capacity for cation exchange than traditional lignocellulosic biochar. Moreover, algal biochar has a remarkable capacity for biosorption due to the abundance of polar functional groups on its surface.

This study investigated the production of macroporous ZSM-5 zeolite using algal bio charcoal as disposable templates. The impact of functional groups in the charcoal and inorganic elements on the final zeolites characteristics.

Magnetic nanoparticles:

Because of its simple manufacturing method, easy operation, time-saving nature, and reusability, magnetic nanoparticles (MNPs) have garnered increased attention recently as an alternative to hair gel (Hu *et al*., 2013).

In particular, magnetic nanoparticles have been researched because to their high specific surface area. Using a magnetic field, the MNPs could be readily removed from the growing media after adhering to algae (Safarik *et al.*, 2016).

The removal of Cr^{6+}, Co^{2+}, and Ni^{2+} from aqueous solutions by the microalgae in combination with NPs was able to do so at a rate that was both faster and more efficient than that of the metals when removed separately. This suggests that the algal cells and the nanomaterials worked in concert, with Bioadsorption and chemisorption acting as the primary mechanisms.

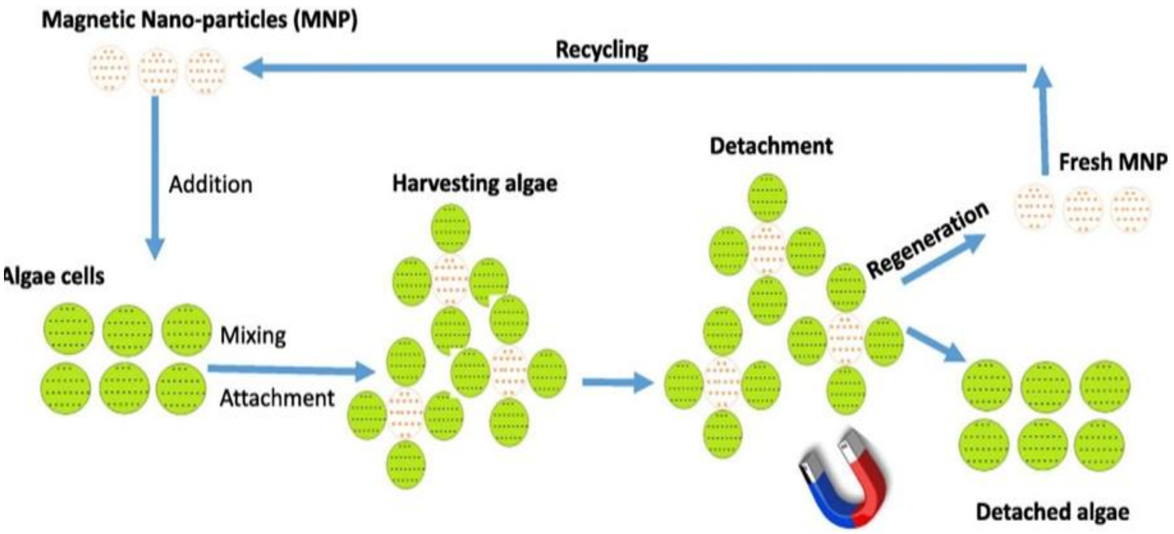

Fig. 3. Removal of heavy metal through Magnetic nanoparticles (Almomani, 2020).

Metal-organic frameworks:

Increasingly in demand as adsorbents and photo catalysts in the water treatment industry, metal-organic frameworks, or MOFs, are a new family of materials. However, not all of the environmental concerns associated with MOFs have been thoroughly investigated, including the underlying effects on aquatic creatures. Using a freshwater green alga (*Chlamydomonas reinhardtii*), Here, the toxicity of numerous typical MOFs was thoroughly assessed. Metal organic framework (MOF), which is made up of metal ions and multifunctional organic ligands, is one of the materials that have raised the most concerns. It has a regular, variable pore structure. Water stable MOFs are especially well-known in wastewater treatment (WWT) applications. MOFs have long demonstrated appealing advantages in membrane separation and adsorption technologies.

CONCLUSIONS

A revolutionary solution to the urgent problem of heavy metal contamination in wastewater is provided by the combination of nanostructured materials with algae-based biosorption. The trend of nanomaterials for water-pollutant treatment is rapidly increasing in this modern era, due to the limited water supply at the global level.

Together with the sophisticated capabilities of materials like mesoporous silica, zeolites and carbon-based nanomaterials, the special qualities of *Chlorella vulgaris*, *Tetradesmus obliquus*, *Sargassum wightii* and *Microcystis aeruginosa* hold great promise for effective, selective and regenerative metal ion removal.

The unique properties of *Chlorella vulgaris*, along with the advanced capabilities of materials such as mesoporous silica, zeolites and carbon-based nanomaterials, offer significant promise for efficient, selective, and regenerative metal ion removal. Despite the promising advancements, challenges related to cost, scalability and environmental impact must be carefully navigated to ensure that these technologies can be implemented on an industrial scale effectively.

Ongoing research and development are critical to optimizing these materials, ensuring their safe application and minimizing any potential negative effects on the environment. The potential to integrate sustainable production techniques and hybrid material designs further highlights the transformative potential of these approaches. As we move forward, these innovations are poised to play a vital role in the future of wastewater treatment, contributing to more sustainable and cleaner environments.

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