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Bio-based composites of alginate, cellulose, and *Moringa oleifera* for heavy metal removal in water purification: a comprehensive and critical review of mechanisms, fabrication, and performance

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The escalating prevalence of heavy metal contamination in aquatic ecosystems, driven by industrialisation, urbanisation, and population growth, has necessitated the development of sustainable and efficient water purification technologies. This review critically evaluates recent advances in developing and applying bio-based composites comprising sodium alginate, cellulose, and *Moringa oleifera* (*M. oleifera*) to remove heavy metals from aqueous systems. The review examines the physicochemical characteristics, adsorption mechanisms, and synergistic properties of these biopolymers, emphasising the role of the active compounds in each. The deduction from the comparative study of this review reveals cellulose-based composites demonstrating the highest overall adsorption performance, with several systems exceeding 1000 mg g⁻¹ across different heavy metals. Although alginate composites achieve the highest single reported capacity, 1742 mg g⁻¹ for Pb²⁺, their performance is more dependent on chemical or nanoparticle functionalisation. *M. oleifera* biosorbents show moderate adsorption capacities, with improvements mainly observed after chemical modification. Overall, cellulose composites exhibit the most consistent and versatile adsorption behaviour among the three materials. This review identifies potential applications, highlights key research gaps, and outlines future directions for advancing bio-based composite materials as viable solutions for sustainable water treatment.

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Environmental significance

This review highlights the potential of bio-based composites comprising alginate, cellulose, and *Moringa oleifera* as sustainable alternatives to conventional water treatment materials. These biopolymers, derived from renewable resources, offer low toxicity, biodegradability, and effective adsorption of toxic heavy metals from aqueous environments. Their application not only mitigates environmental pollution but also reduces dependency on synthetic, non-biodegradable materials that contribute to secondary waste generation. By valorising agricultural by-products and natural resources, such composites support circular economy principles and promote greener technologies for water purification, aligning with global efforts to address environmental sustainability and resource conservation.

1 Introduction

The rapid growth of the global population has significantly increased industrial activities, reducing the availability of clean water.^{1–3} Water is one of the most pressing environmental concerns, making obtaining safe and affordable clean water increasingly challenging. Heavy metal contamination in water is also a major concern, arising from both natural and human activities.^{4–6} Both industrial processes and natural phenomena,

such as the weathering of metal-rich rocks and geothermal activities, contribute to heavy metal pollution in water bodies.^{7–9} Drinking water is an invaluable resource for life, and ensuring access to water and sanitation by 2030 is a key objective outlined by the United Nations Sustainable Development Goals (UNSDGs).¹⁰

Water is an essential resource, and numerous statistics have been collected to assess various aspects of its usage, availability, and quality. Several international organisations actively gather and analyse water-related data, including the United Nations Educational, Scientific and Cultural Organisation (UNESCO),¹¹ the United Nations Children's Fund (UNICEF), and many others.¹² According to data from 57 countries in 2015, approximately 84 Litres of wastewater per capita were generated, yet only 29 Litres underwent treatment. By 2021, global household wastewater production had reached 271 billion cubic meters,

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with treatment rates improving to 55.5% based on data collected from 234 countries.^{13,14} Furthermore, studies indicate that approximately 70% of the Earth's surface is covered by water, of which only 2.5% consists of freshwater. A mere 1% of this freshwater is readily accessible for human use.¹⁵ The current global population of 7.6 billion people must share this limited resource. The United Nations projects that by 2050, the global population will reach 9.8 billion, with approximately 4 billion people expected to experience water scarcity. This will

exacerbate the existing crisis, as over two billion individuals already lack access to clean water.¹⁶ To address this challenge, efficient water treatment strategies must be developed to treat wastewater and natural water sources while ensuring sustainability through renewable energy sources.¹⁷⁻¹⁹

Various methods and materials have been proposed for tackling water contamination, with a growing emphasis on biopolymer-based solutions. Biopolymers, derived from natural sources such as cellulose, alginate (from brown algae), and chitosan (from crustacean shells), have gained considerable attention for water purification due to their biodegradability, eco-friendliness, and high adsorption capacity for heavy metals.²⁰⁻²² Their properties, such as high adsorption capacity and eco-friendliness, make them suitable materials for water purification applications and have been widely explored in recent studies.²³

Among these, cellulose is recognised as one of the most abundant polysaccharides on earth, characterised by its high mechanical strength, hydrophilicity, and ability to form stable composites.^{24,25} Alginate, extracted primarily from brown algae, is also rapidly gaining traction as a versatile biopolymer in different fields due to its unique gel-forming capabilities and non-toxic nature.^{26,27} The growing market for alginate reflects its increasing utilisation in water treatment, where it serves as an efficient medium for adsorbing heavy metal ions. Combining cellulose and alginate in composite forms presents a promising approach for enhancing adsorption efficiency and mechanical properties, making these biopolymers valuable for sustainable water treatment applications.^{21,24,28}

In addition to biopolymers, *M. oleifera* has been extensively investigated as a cost-effective, eco-friendly biosorbent for removing heavy metal ions from water.²⁹⁻³² These seeds contain



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natural cationic proteins and bioactive compounds that facilitate ion exchange and metal binding, improving water purification efficiency.³³ Studies have also demonstrated that *M. oleifera* seed pods can effectively remove mixtures of metals in wastewater, achieving optimal removal efficiency under specific conditions, such as a 60-minute contact time and a 1.0 gram sorbent dose.³⁴ The ability of *M. oleifera* to function as both a coagulant and an adsorbent positions it as a dual-function material for water treatment, enhancing its potential for integration with biopolymers like cellulose and alginate to develop advanced composite materials aimed at heavy metal ion contamination.^{27,35}

Although biopolymers and *M. oleifera* seed powders benefit water treatment, few studies have examined their hybrid composites. This presents a significant research gap in developing and characterising hybrid composites.³⁶ Few studies have been reported. Development of hybrid electrospun alginate-pulverised *M. oleifera* composites was done by Orisawayi *et al.*³⁷ In their studies, pulverised *M. oleifera* at a minimum dose suspension was incorporated into sodium alginate fibre using the electrospinning techniques.

Another study reported the development of effective biosorbents made from combining *M. oleifera* and alginate beads for uranium removal from aqueous solutions. Orisawayi *et al.*³² further developed sodium alginate fibres through wet-spinning. In contrast, more recent investigations have combined sodium alginate with polyethyleneimine and *M. oleifera* leaves–seed beads for uranium adsorption, including isotherm and kinetic analyses.³⁸ These composite systems have demonstrated improved adsorption capacity and favourable structural characteristics.

The selection of alginate, cellulose, and *M. oleifera* in this study stems from their complementary physicochemical and functional properties relevant to heavy-metal removal. Alginate offers a biocompatible, carboxyl-rich matrix with strong ion-binding capacity and efficient gel-forming behaviour, making it highly suitable for capturing multivalent metal ions.^{39–41} Cellulose, the most abundant natural polysaccharide, provides mechanical stability, a high surface area, and additional hydroxyl groups that boost adsorption.^{39,42–47} In contrast, *M. oleifera* seeds supply bioactive, cationic proteins and coagulant molecules capable of binding and aggregating dissolved metal ions.^{34,48,49} Although other biopolymers such as pectin, starch, and chitosan have been widely studied, they do not collectively offer this combination of mechanical robustness, adsorption efficiency, natural coagulation activity, and environmental sustainability.^{50–52}

Therefore, the novelty of this review arises from its focus on evaluating alginate, cellulose, and *M. oleifera* as distinct materials for heavy-metal removal, combined with an assessment of how their complementary traits could be strategically melded to improve adsorptive performance. While many studies and reviews have examined these materials separately or with other biopolymers, none have explored their combined potential within a single analytical framework, offering a new perspective for designing more effective and sustainable adsorbent systems.

The study first outlines heavy metal contamination as a significant environmental concern, summarising key pollutants and regulatory limits set by the United States Environmental Protection Agency (EPA), World Health Organisation (WHO) and European Union (EU), including the origin or sources of the heavy metals. It then evaluates the limitations of conventional treatment methods, such as chemical precipitation, ion exchange, and membrane filtration, emphasising the need for sustainable alternatives. The focus then shifts to biopolymers, particularly sodium alginate and cellulose, exploring their adsorption mechanisms, composite formulations, and integration with *M. oleifera* to enhance performance. Fabrication techniques such as electrospinning and wet spinning are also reviewed for their role in optimising material properties. Having established the urgency of water pollution and the potential of biopolymer-based solutions, it is crucial first to understand the nature, sources, and health implications of the primary contaminants and heavy metals that threaten aquatic systems.

2 Background on heavy metals

Heavy metal ions such as lead (Pb^{2+}), cadmium (Cd^{2+}), cobalt (Co^{2+}), nickel (Ni^{2+}), barium (Ba^{2+}), copper (Cu^{2+}), chromium in both trivalent and hexavalent states ($\text{Cr}^{3+}/\text{Cr}^{6+}$), zinc (Zn^{2+}), mercury (Hg^{2+}), and arsenic in trivalent and pentavalent forms (As^{3+} , As^{5+}) constitute major contaminants in aquatic ecosystems. Their elevated toxicity and persistence in natural waters make them a significant environmental concern.^{53,54} There are several primary sources of heavy metal ions. Fig. 1 illustrates the different sources of environmental pollution caused by heavy metals and the adverse effects of the metals on pollution by heavy metal ions.^{50,55,56} Fig. 1a shows the primary industrial sources, such as the mining industries,⁵⁷ textile industries,^{58,59} thermal and nuclear plants associated with the cement industry,⁶⁰ the manufacturing and conservation of wood, dye production,⁶¹ metal plating and those associated with the steel manufacturing industries,⁶² energy and water cooling processes,³⁰ the production of photographic materials,⁶³ the manufacturing of various corrosive paints,⁶⁴ and other industrial activities in the global oil and gas industries.^{65–67}

However, heavy metal contamination is not limited to industrial activities alone. Fig. 1b shows a broader perspective, incorporating additional sources such as urban solid waste, wastewater effluents, e-waste, biosolids, fertilisers, pesticides, corrosion, pharmaceutical products, and natural occurrences, including volcanic eruptions. These diverse contamination sources contribute significantly to environmental pollution, making the development of sustainable remediation strategies imperative. Heavy metal ions are often described as metallic forms of elements that are mostly denser than water and have a large atomic radius.⁶⁸ Heavy metal ions are dangerous and more prevalent, resulting from the persistent half-life.^{69,70} The common organic compounds found in most water bodies can be degraded over time. Still, when polluted into water bodies, the heavy metals remain an environmental issue as most of them are difficult to decompose in the water.



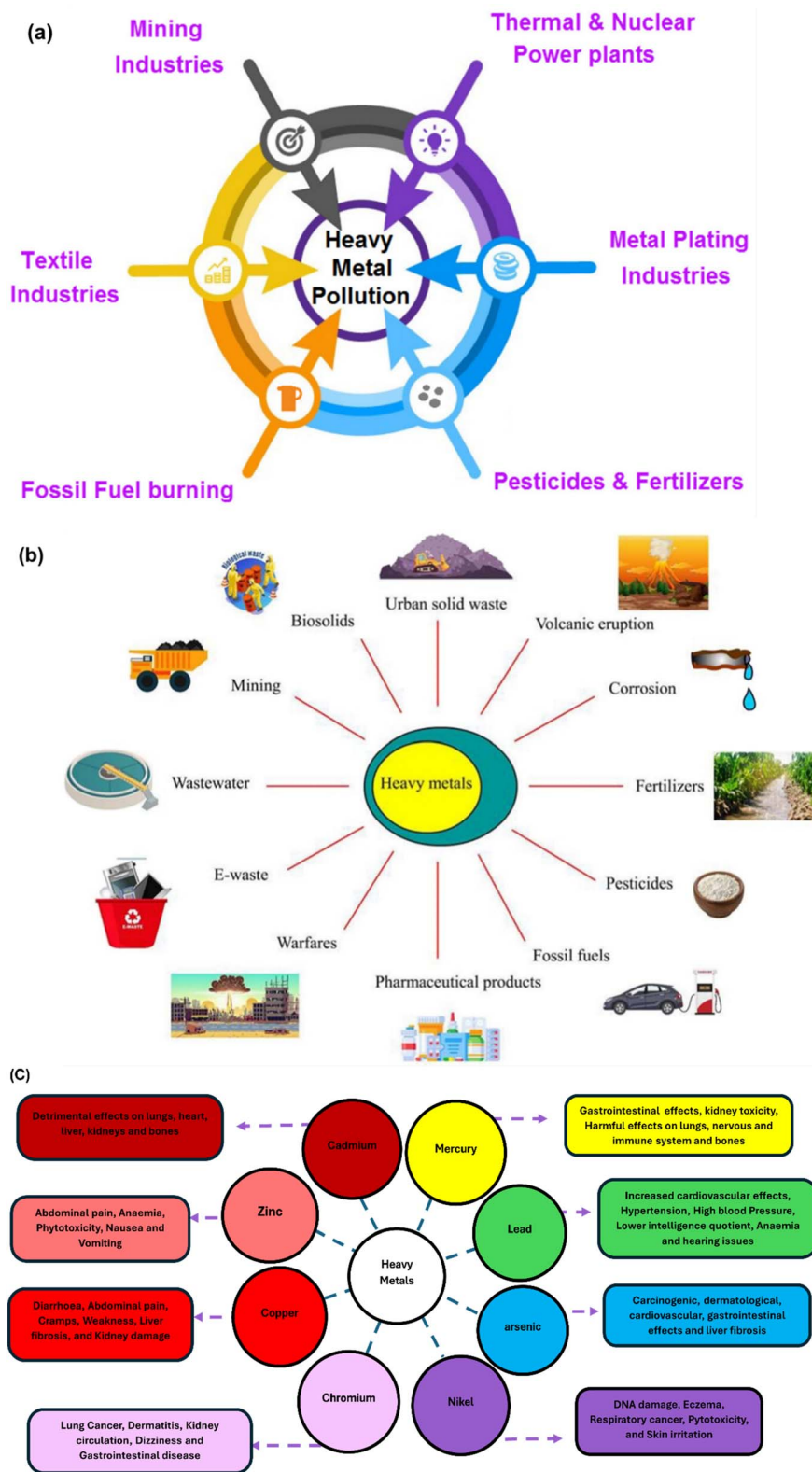


Fig. 1 (a and b) are the different sources of environmental pollution caused by heavy metals, and (c) the adverse effects of commonly encountered heavy metals on other human organs (all figures are adapted and (c) was modified with permission, Licensed under Elsevier's terms).^{50,55,56}



**Table 1** Regulatory standards, health effects, and sources and in industrial origins of heavy metal contaminants in drinking water (EPA, WHO, and EU)

Heavy metals ^{68,71-74}	Potential health effects from long-term exposure above the MCL (unless specified as short-term) ^{68,71-74}	EPA (drinking water MCL) ^{71,72} (mg L ⁻¹)	WHO guideline value (MPL) ⁷⁴ (mg L ⁻¹)	EU drinking water standard (MPL) ⁷³ (mg L ⁻¹)	Sources of contaminants in drinking water ^{68,71-74}	Industrial origins for the heavy metals
Lead (Pb)	Neurodevelopmental effects, cardiovascular, renal, and reproductive issues, children could show slight deficits in attention span	Action level = 0.010	0.01	0.01	Corrosion of household plumbing systems; erosion of natural deposits	Battery manufacturing, metal smelting and refining, paint and pigment industries, ammunition production, plumbing and soldering waste
Cadmium (Cd)	Kidney damage, gastrointestinal toxicity, carcinogenic effects	0.005	0.003	0.005	Corrosion of galvanised pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints	Electroplating industries, Ni-Cd battery production, PVC and plastic stabilisers, mining and smelting operations, pigment manufacturing
Cobalt (Co)	Allergic reactions, cardiovascular effects, and potential carcinogenicity	Not established	Not established	Not established	Industrial sources, mining activities, alloy production	Battery manufacturing (especially Li-ion and rechargeable batteries), superalloy and aerospace component production, mining and ore smelting of copper and nickel, chemical catalyst manufacturing, pigments, ceramics, and glass colouring industries, electroplating and metal finishing, cement and steel production waste
Nickel (Ni)	Respiratory issues, carcinogenic effects, microbial toxicity	Not established	0.07	0.02	Industrial discharges; erosion of natural deposits; nickel plating and battery industries	Electroplating and surface finishing, stainless steel manufacturing, mining and refinery effluents, catalyst production
Barium (Ba)	Hypertension or increase in blood pressure, muscle weakness, neurological disorders	2	0.7	Not established	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits	Oil and gas drilling operations (example: barite-based drilling muds), paints, pigments, and ceramics manufacturing, glass and electronic component production, metal refining and alloy processing, rubber and plastic additives industries, fireworks and pyrotechnics, waste from chemical manufacturing processes



Table 1 (Contd.)

Heavy metals ^{68,71-74}	Potential health effects from long-term exposure above the MCL (unless specified as short-term) ^{68,71-74}	EPA (drinking water MCL) ^{71,72} (mg L ⁻¹)	WHO guideline value (MPL) ⁷⁴ (mg L ⁻¹)	EU drinking water standard (MPL) ⁷³ (mg L ⁻¹)	Sources of contaminants in drinking water ^{68,71-74}	Industrial origins for the heavy metals
Copper (Cu)	Liver, kidney, neurological damage, bioaccumulation in aquatic species	Action level = 1.3	2.0	2.0	Corrosion of household plumbing systems; erosion of natural deposits	Mining and smelting, electrical and electronics industries, metal pipe corrosion, pesticide formulation
Chromium (Cr)	Carcinogenic, severe respiratory effects, industrial exposure risk	0.1	0.05	0.05	Discharge from steel and pulp mills; erosion of natural deposits	Leather tanning, stainless steel and alloy production, electroplating, dye and pigment industries, wood preservation processes
Zinc (Zn)	Immune suppression, developmental issues, metabolic disorders	5	Not established	Not established	Corrosion of galvanised pipes; industrial discharges; erosion of natural deposits	Galvanisation industries, rubber and tyre manufacturing, pigment and paint industries, brass alloy production
Mercury (Hg)	Neurotoxin, kidney damage, bioaccumulates in marine organisms	0.002	0.006	0.001	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands	Chlor-alkali plants, thermometer and lamp manufacturing, gold and silver mining, dental amalgam waste, chemical production processes
Arsenic (As)	Skin damage or problems with the circulatory system may have increased the risk of getting cancer	0.010 as of 01/23/06	0.01	0.01	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes	Mining and ore processing, pesticide and herbicide manufacturing, semiconductor and microelectronics industries, and coal combustion effluents

The United States Environmental Protection Agency (EPA) with Maximum Contaminant Levels (MCLs),^{71,72} The World Health Organisation (WHO), and the European Union (EU), with the maximum permissible level,^{73,74} have established regulatory limits for these contaminants to protect water quality and public health.^{68,75} Lead has been extensively studied as one of the metals causing environmental pollution, resulting from its high level of toxicity and often widespread presence.^{76,77} Contamination from lead is common and is primarily due to its use in many plumbing infrastructures, resulting from the erosion of natural deposits and its presence in most automobile batteries.⁷⁸ The presence of lead, even at low blood concentrations of 1–2 $\mu\text{g dL}^{-1}$, lead exposure may lead to severe health effects, including neurodevelopmental, cardiovascular, renal, and reproductive issues, and in children, could show slight deficits in attention span.⁷⁹ The EPA MCL is 0.01 mg L^{-1} , with WHO and EU also maintaining a 0.01 mg L^{-1} limit.

In addition, metal ions such as cadmium are another frequently encountered heavy metal pollutant because they are primarily released in most industrial processes. The EPA MCL is 0.005 mg L^{-1} , while WHO and EU enforce limits of 0.003 mg (ref. 80) chromium is well-documented as an environmental contaminant and primarily originates from most industrial activities and processes, such as electroplating, textile manufacturing, and the stainless steel industry. In most research, this metal has been highlighted as its toxic and carcinogenic, therefore causing concern. The EPA sets an MCL of 0.1 mg L^{-1} , whereas the WHO and the EU impose stricter limits of 0.05 mg L^{-1} .⁸¹

Mercury is also a highly toxic heavy metal introduced into the environment through various industrial activities, and processed are often contain mercury and waste in water bodies and can cause challenges for aquatic ecosystems; reports show that mercury can transform into methylmercury, known as a bioavailable form, that is accumulated in marine bodies and therefore affecting the aquatic organisms. This poses a serious Neurotoxin, as kidney damage bioaccumulates in aquatic organisms and is a health threat to humans consuming contaminated seafood. The EPA enforces an MCL of 0.002 mg L^{-1} , the WHO sets 0.006 mg L^{-1} , while the EU has a more stringent limit of 0.001 mg L^{-1} .^{82,83}

Arsenic, a naturally occurring metalloid, poses serious health risks. Arsenic can cause severe health conditions in the skin, causing skin damage or problems with the circulatory system, cancer, and cardiovascular diseases.^{7,84} It is a significant contaminant in the groundwater; due to its high toxicity, the EPA, WHO, and EU all impose a maximum limit of 0.01 mg L^{-1} , particularly in regions where mainly agricultural activities have historically involved arsenic-based pesticides.^{82,84}

Other metals, such as nickel, barium, copper, and zinc, pose significant environmental and health risks due to their persistence in water bodies. These metals also enter aquatic ecosystems through industrial discharge, mining, and improper waste disposal, contaminating drinking water sources and affecting marine life. Nickel exposure can lead to allergic reactions, respiratory issues, and carcinogenic effects, disrupting aquatic microbial activity. Nickel is commonly found in metal alloys,

including mining waste and industrial effluents. Barium contamination originates from the oil drilling, glass, and paint industries. Soluble barium compounds pose health risks, causing hypertension, muscle weakness, and neurological disorders.^{84–86}

Copper and zinc are essential metals but become toxic in excess, leaching from plumbing, mining, and fertilisers. Copper bioaccumulates in fish and amphibians, disrupting metabolism and causing liver, kidney, and neurological issues in humans. Zinc pollution can lead to immune suppression, developmental problems, and metabolic disorders, ultimately affecting fish growth and disrupting the balance of phytoplankton. The presence of these metals in water demands effective pollution control, water treatment, and stricter regulations to mitigate their toxic effects on human health and ecosystems.^{87–89}

Table 1 provides a comparative overview of major heavy metal contaminants, their potential health risks, and their regulatory limits established by the EPA, WHO, and EU. Fig. 1c shows a retrieved study from a previous study retrieved from the literature, which shows the adverse effects of commonly encountered heavy metals on different human organs.⁸⁶ Furthermore, these standards are crucial for maintaining water safety, and exposure to heavy metals can have severe biological consequences, affecting multiple human organs. This illustration complements the regulatory data presented in Table 1 by emphasising the physiological risks associated with prolonged exposure to heavy metals.

The legally enforceable Maximum Contaminant Levels (MCLs) ensure the safety of drinking water. The World Health Organisation (WHO) provides guidelines, values, and Maximum Permissible Levels (MPLs) based on health risk assessments. The European Union (EU) sets strict regulatory limits on drinking water quality that are mandatory for all EU member states.^{69–72}

Several treatment technologies have been developed to address the environmental challenge posed by heavy metal contamination due to their hazardous effects and regulatory significance in water systems. The following section critically examines these technologies for the removal of heavy metals from water.

3 Water treatment technologies for removing heavy metals

3.1 Chemical precipitation

Chemical precipitation has been used and described as an effective method for removing heavy metals, primarily from wastewater. Chemical precipitation is widely used in industrial wastewater treatment due to its simplicity, cost-effectiveness, and established technology.^{90,91} This method uses chemical reagents that react with most metal ions to form an insoluble precipitate.⁹² Studies show that the primary precipitation mechanisms include hydroxide and sulphide precipitation, which facilitate the removal of these metal ions during the process. However, the main limitations of this method involve difficulties in removing mixed metals due to pH levels that may



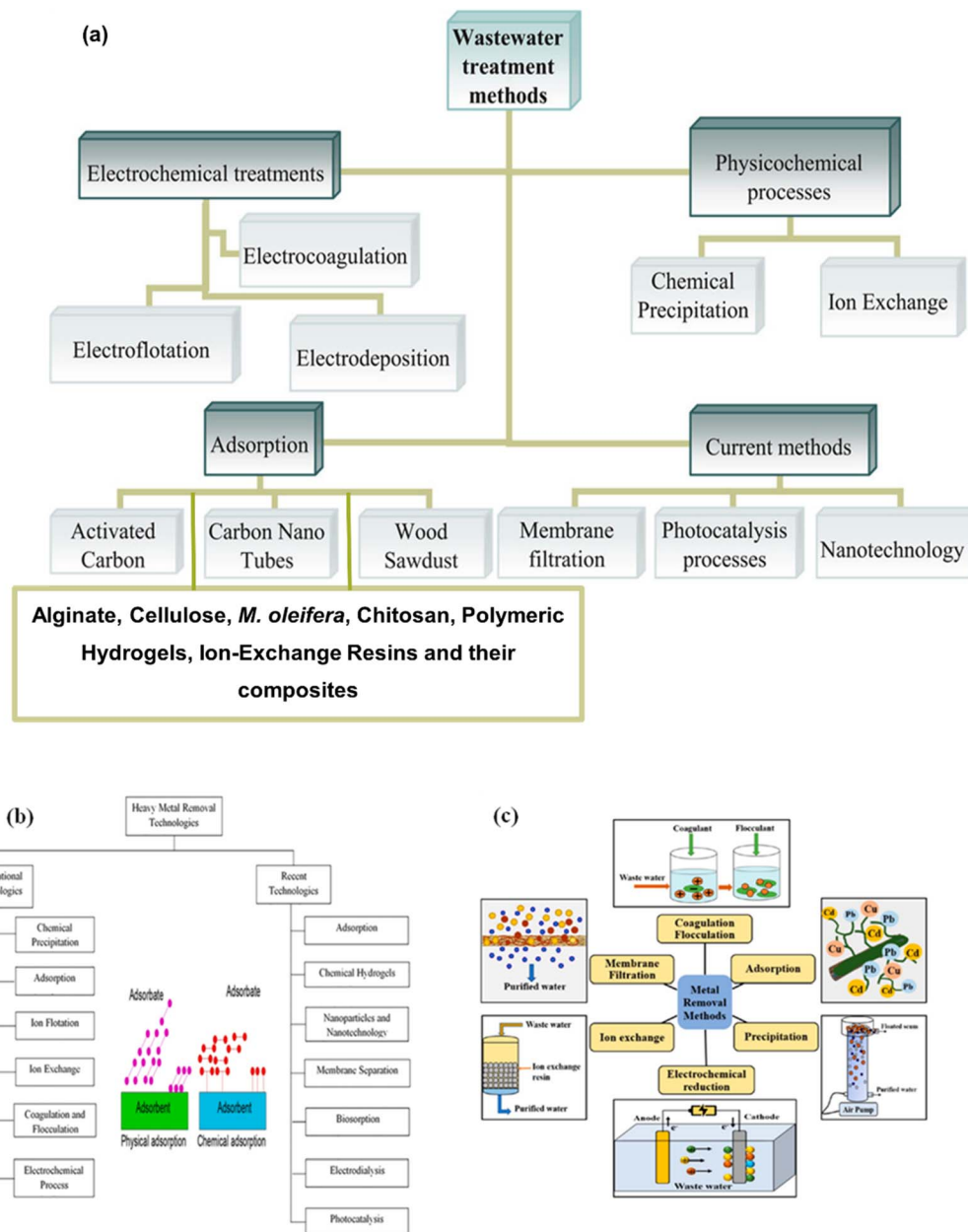


Fig. 2 (a) Water treatment of remediation methods, including electrochemical, physicochemical, and adsorption-based processes (modified with permission, Licensed under Wiley's terms) (b), (modified with permission, Licensed under Elsevier's terms) and (c) heavy metal removal technologies, comparing conventional and advanced techniques, (adapted with permission, Licensed under ACS publication's terms).^{90,91,114}

be difficult to control when hydroxide precipitation is used.^{93,94} In addition, there is also a risk of secondary contamination, particularly from sulphide precipitation, which can sometimes lead to the formation of toxic hydrogen sulphide (H_2S) gas, as reported.⁹⁵

3.2 Ion exchange

Another widely used method is ion exchange, which is often applied in water purification technologies, as this method relies on ion exchange to remove metal ions. During the process, ion exchange media include zeolite resins and synthetic organic

polymers.⁹⁶ These methods have been proven effective for eliminating cations and anions from freshwater, ensuring high removal efficiency. However, this method has several drawbacks, including the requirement for pretreatment and chemical regeneration, which can lead to secondary pollution due to the materials used. Therefore, ion exchange leaves some secondary pollution after water treatment.⁹⁷ Studies suggest that this method is less effective for highly concentrated mixed-metal wastewater, making it more suitable for applications involving mixed heavy-metal solutions from aqueous solutions.^{97,98}



3.3 Membrane separation

Membrane separation technologies are emerging methods employed for pressure-driven processes such as ultrafiltration, nanofiltration, reverse osmosis, concentration, and removing some heavy metal ions.^{99,100} This method is advantageous due to its simple operation, low energy consumption, and absence of significant phase changes, making it an environmentally friendly alternative. However, challenges associated with this method include the high cost of membrane materials and their susceptibility to fouling and degradation, which may reduce the long-term efficiency of the process.¹⁰¹ Despite these limitations, membrane separation remains a valuable technology for water treatment, particularly in removing low-concentration contaminants or pollutants from water.^{101,102}

3.4 Electrochemical technologies

Electrochemical methods, including electrocoagulation, electrodeposition, electrooxidation, and electrolotation, have been extensively explored for heavy metal removal. These techniques involve the application of electrical currents to induce coagulation, charge neutralisation, and precipitation of heavy metal ions.¹⁰³ Electrochemical processes are known for their high removal efficiency, ease of operation, and minimal sludge production, reducing the need for additional conditioning treatments. However, their applicability is often limited by energy consumption, electrode material degradation, and the potential formation of secondary contaminants.^{104,105}

3.5 Bioremediation

The bioremediation technique is another method that utilises biological processes for water treatment. This approach includes microbial remediation and phytoremediation, which involve using microorganisms or plants to degrade, immobilise, or remove heavy metals from water bodies.¹⁰⁶ Studies have shown that this method has been proven to be an environmentally sustainable method. It is also cost-effective and has been successfully applied for the restoration of the most polluted sites. However, bioremediation has significant limitations, including overdependence on low metal concentrations and long remediation cycles, making it challenging to scale up the process for industrial applications.^{107–109}

3.6 Adsorption

Over the decades, adsorption has emerged as one of the most efficient and widely used methods for removing heavy metals from contaminated water.⁵⁵ The process has emerged as a promising alternative for water treatment. Adsorption is the process in which ions, atoms, or molecules adhere to the surface of a solid material. It differs from absorption, which involves the penetration of molecules into the interior of a solid.^{110,111} Based on the forces governing this phenomenon, adsorption is categorised as physisorption or chemisorption.¹¹² This method relies on interfacial interactions between metal ions (adsorbate) and the materials used for their removal (adsorbent). Various media can be utilised to facilitate

contaminant removal through mechanisms such as pore filling, surface binding, and chemical interactions.¹¹³ Some of the materials reported for use include activated carbon, carbon nanotubes, wood sawdust, alginate, cellulose, *M. oleifera*, chitosan, polymeric hydrogels, ion-exchange resins, and their composites. As illustrated in Fig. 2a, wastewater treatment methods are categorised into electrochemical treatments, physicochemical processes, and adsorption-based processes, highlighting their applications in contaminant removal.^{90,91}

Fig. 2(b and c) provide a comparative overview of heavy metal removal technologies, distinguishing between conventional methods, such as chemical precipitation, ion exchange, and electrochemical processes, and advanced techniques, including nanotechnology, membrane filtration, and photocatalysis. The inset in Fig. 2a further illustrates the physical and chemical adsorption mechanisms of different adsorbate–adsorbent interactions, demonstrating their effectiveness in pollutant removal.⁹¹ Unfortunately, most reported methods or techniques are associated with high costs, operational complications, low efficiency, excessive chemical use, and secondary pollutants, which restrict their applications. With the development of highly flexible, easy-to-operate, and efficient adsorbent designs, adsorption has emerged as a promising alternative for water treatment. Adsorption is highly advantageous due to its simplicity, cost-effectiveness, high selectivity, and ability to treat dilute wastewater. The ability to recycle adsorbents has been reported to minimise secondary pollution, making adsorption a preferred choice for water treatment applications.

While conventional technologies demonstrate varying degrees of effectiveness, many are limited by high costs, secondary pollution, or low selectivity. These limitations have spurred the exploration of sustainable alternatives, particularly those derived from bio-based materials, as discussed in the next section.

4 Bio-based biodegradable composites and blends for water purification

4.1 Overview of sustainable biopolymer composites

Biopolymers are naturally occurring polymers produced by living organisms. Biological resources, including plants, animals, agricultural residues, and microorganisms, are viable feedstocks for synthesising biopolymers. Fig. 3 shows a typical classification and characteristics of biopolymers that have been reported.²⁹ Among the primary sources derived from agriculture and plants are corn stalks, maize, wheat, potatoes, and barley.

Biopolymers consist of monomeric units such as nucleotides, saccharides, or amino acids that form nucleic acids, carbohydrates, and proteins.^{112–114} Biopolymers are known to be renewable and eco-friendly alternatives to most synthetic polymers derived from fossil fuels.^{115–120} Biopolymers have gained significant attention due to their biodegradability and potential to address environmental challenges.^{121–124} The projections indicate that global plastic production is expected to surpass 1800 million metric tons annually by 2050. The focus on





Fig. 3 Classification and properties of biopolymers (adapted with permission, Licensed under Elsevier's terms).²⁹

biopolymers, primarily cellulose and alginate, for water treatment is well-justified due to their abundant functional groups, which facilitate the efficient adsorption of heavy metal ions and other pollutants. Over the decades, several studies have highlighted the environmental issues associated with synthetic polymers, emphasising the need for biodegradable alternatives. Kogje *et al.*¹²⁵ found that biopolymers derived from natural sources minimise plastic waste and have higher biodegradability than standard plastics. Similarly, Emre *et al.*¹²⁶ also demonstrated the potential of polysaccharide-based biopolymers to reduce environmental pollution through improved adsorption. Researchers have documented the efficiency of biopolymers such as cellulose, alginate, and chitosan in adsorbing heavy metals from aqueous solutions.^{82,83,127,128}

Moreover, alginate has emerged as a promising biopolymer, which also contains carboxyl groups that play a crucial role in the ion exchange process, making it an effective adsorbent for heavy metals like cadmium, chromium, and other metal ions.^{129,130} Several studies have also demonstrated the effectiveness of cellulose–alginate hydrogels in contaminant removal. In particular, the hydrogels have been shown to substantially enhance the adsorption efficiency of both dyes and heavy metal ions, achieving up to approximately 85% removal of methylene blue, which is associated with metal ions.^{131,132} The tensile strength and durability of cellulose, combined with the gel-forming ability of alginate, ensure the formation of stable and effective adsorbent composites. The environmental sustainability and cost-effectiveness of cellulose and alginate instead of synthetic polymers align with the increasing demand for eco-friendly water treatment materials. The interaction between the hydroxyl groups in cellulose and

the carboxyl groups in alginate enhances the ion-exchange interactions and adsorption capacity of these hydrogels, making them practical for water purification.^{133,134} Fig. 4 presents a detailed schematic representation of the sources and structures of cellulose and alginate, along with their physical and chemical modification methods to enhance their performance in water purification applications. Additionally, it categorises the significant approaches for modifying these biopolymers to improve their functionality. These modifications, categorised into physical and chemical, encompass blending, ultrasonic treatment, cross-linking, focusing on the use of crosslinking agents such as Ethylenediaminetetraacetic Acid (EDTA), Gamma-Linolenic Acid (GLA), Ethylene Glycol Monobutyl Ether (EGBE), Epichlorohydrin (ECH), and Polyethylene Glycol (PEG), including grafting to enhance the material's adsorption efficiency, mechanical stability, and chemical resistance in water remediation applications. These modification techniques are essential in tailoring cellulose–alginate composites for optimised performance in environmental applications.

The adsorption and regeneration mechanisms of biopolymeric composites are very crucial. These have been extensively studied for their effectiveness in removing heavy metals. Understanding these mechanisms is essential for optimising their performance in water treatment applications. Fig. 5(a) presents a reported adsorption mechanism illustrating the interaction of metal ions (M^+) with active functional groups in biopolymeric composites. The process involves electrostatic attraction, ion exchange, and surface complexation, facilitated by hydroxyl ($-OH$), carboxyl ($-COO^-$), and amine ($-NH_2$) groups.¹³⁵ Adsorption efficiency is influenced by pH, where ion



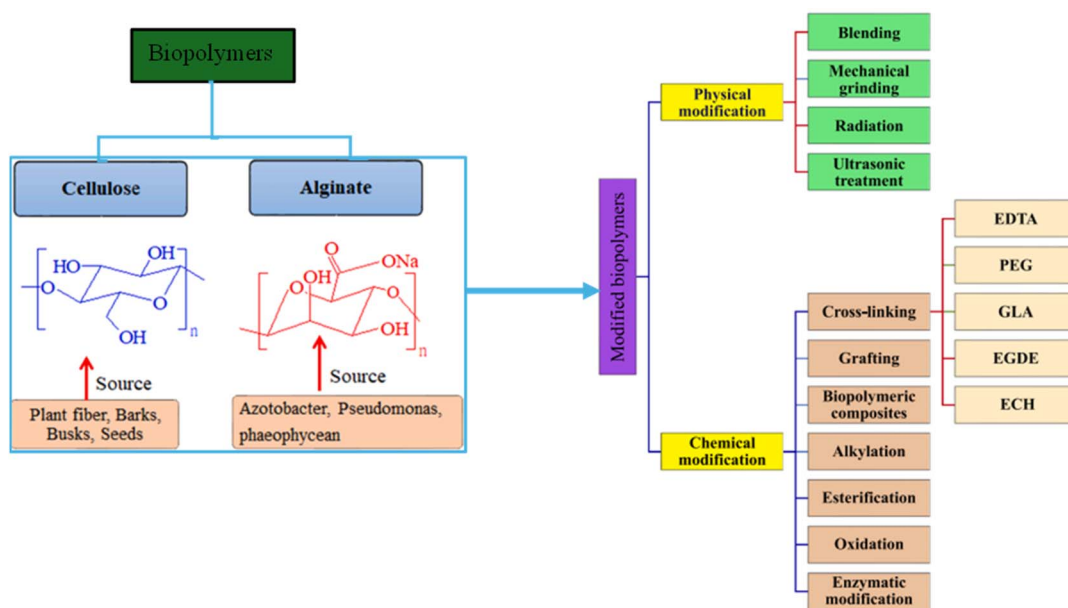


Fig. 4 Schematic representation of the sources and structures of cellulose and alginate, along with their physical and chemical modification methods aimed at enhancing their performance in water purification applications (modified with permission, Licensed under Elsevier's terms).²¹

exchange dominates at lower pH levels. At the same time, electrostatic and surface complexation mechanisms become more prominent at higher pH values, as observed in several studies.^{136,137} The adsorption performance of cellulose–alginate composites has been well-documented, with removal efficiencies varying depending on the composite structure, porosity, and availability of functional groups. Furthermore, Fig. 5(b) highlights various regeneration strategies for restoring adsorption capacity. These include chemical regeneration using eluents such as Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Ethylenediaminetetraacetic acid (EDTA), and Sulfuric acid (H₂SO₄), as well as physical and biological treatments like oxidation, ultrasound, and thermal degradation. Integrating effective regeneration methods ensures the long-term usability of biopolymeric adsorbents, making them viable options for sustainable water purification.

4.2 Sodium alginate and its composites

4.2.1 Alginate extraction and structure.

Alginates are biopolymers derived from natural sources, widely recognised for their versatility and diverse applications across various fields.^{27,138} The abundance of algae in water bodies has been estimated, with the production of industrial alginate amounting to approximately 30 000 tons, representing less than 10% of biosynthesised alginate. Therefore, there is considerable potential for alginate to be utilised in the design of sustainable composite materials. Primarily, alginate is extracted from brown seaweed algae such as (*Ascophyllum* spp., *Laminaria* spp., *Macrocystis pyrifera*, *Sargassum* spp, *Alario*, *Ecklonia*, *Eisenia*, *Nercocystis*, *Sargassum*, *Cystoseira*, *Fucus*, and several others).¹³⁹ Studies show that seaweed-derived alginate is the most commercially utilised form, as bacterial alginate presents an

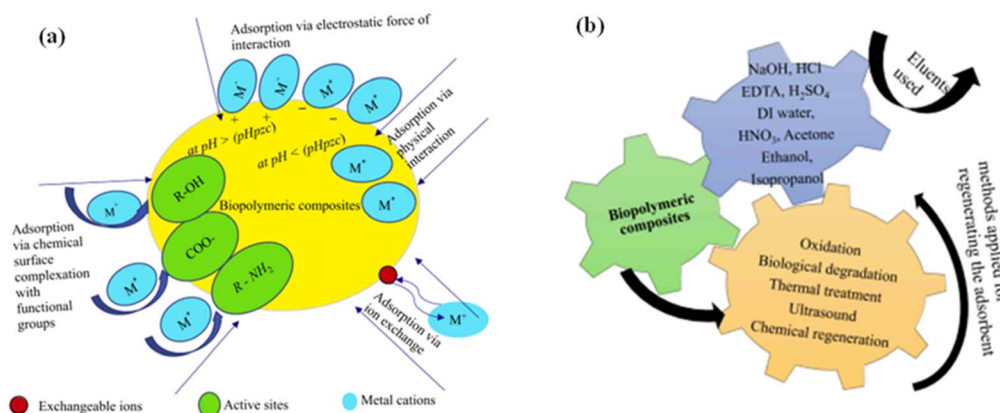


Fig. 5 (a) Proposed adsorption mechanism of biopolymeric composites for heavy metal removal, and (b) regeneration methods and chemicals used for biopolymeric composites during the adsorption–desorption process (adapted with permission, Licensed under Elsevier's terms).²¹



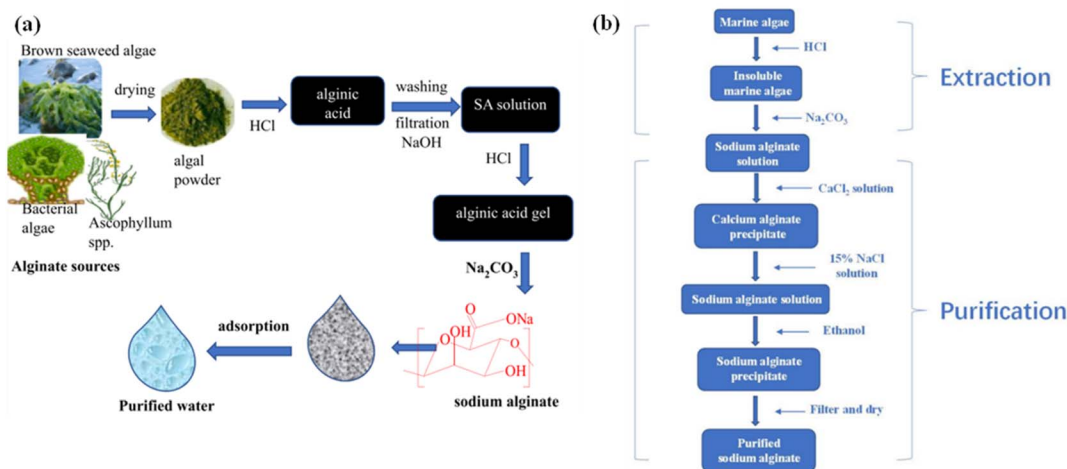


Fig. 6 (a) Extraction and preparation of alginate from the raw sources and their application toward heavy metal removal, (adapted with permission, Licensed under Elsevier's terms) and (b) typical industrial process of sodium alginate extraction *via* calcium precipitation (Creative Commons Attribution (CC BY 4.0) from MDPI).^{21,142}

alternative source with distinct advantages for several applications.^{140,141} Typically, alginate extracted from brown algae is treated with various chemicals at different synthesis stages. Briefly, the production process of sodium alginate begins with the harvesting and drying of seaweed, after which it undergoes mechanical processing to be converted into algal powder.¹⁴² This powder will be treated with hydrochloric acid (HCl) to extract the alginic acid, which serves as the precursor for sodium alginate including sodium carbonate (Na₂CO₃) as part of the extraction process. The extracted alginic acid will be washed, filtered, and treated with sodium hydroxide (NaOH) to form a sodium alginate (SA) solution.¹⁴³ The solution is then further treated with HCl to enhance the purity and produce an alginic acid gel. The samples will then be neutralised with alkali agents such as sodium hydroxide and/or sodium carbonate, converting them into sodium alginate, a water-soluble polymer widely used across various industries.¹⁴⁴ The purification of the extracted alginate was conducted through a chemically assisted process before filtration and drying. Specifically, the crude alginate was subjected to sequential treatments using calcium chloride (CaCl₂), sodium chloride (NaCl), or further treated with ethanol to remove residual impurities, enhance polymer purity, and improve the physicochemical characteristics of the final biopolymer. The extraction process of alginate is illustrated in Fig. 6a, showing the key steps involved in alginate preparation from raw seaweed sources and its subsequent transformation into sodium alginate and its applications in the adsorption process, retrieved from the literature. In contrast, other literature shown in Fig. 6b explains the Industry process of sodium alginate extraction *via* calcium precipitation.

Alginate has been invaluable because it is helpful in water purification applications due to the presence of hydroxyl (-OH) and carboxyl (-COO⁻) functional groups present in its polymer backbone.¹⁴⁵ SA can effectively interact with heavy metal ions and other pollutants in aqueous environments. SA can also undergo an adsorption mechanism that allows contaminants to bind to the polymer surface, facilitating the removal of

impurities and contributing to environmental remediation efforts.¹⁴⁶ This property has positioned alginate as a promising material in sustainable water treatment technologies.

Structurally, alginates are linear block copolymer polysaccharides composed of two fundamental monomeric units: β-D-mannuronic acid (M-block) and α-L-guluronic acid (G-block), the latter being the C-5 epimer of the former.¹⁴⁷ C-5 epimer of the former.¹⁴⁷ These monomers are linked through β-(1-4) glycosidic bonds, forming an unbranched, water-soluble polymer chain. Additionally, alginate polymers can exhibit various sequential forms or arrangements of these monomeric units, including homopolymer M- or G-blocks, alternating MG-blocks, and more complex configurations such as GM-blocks and interspersed MG/GM sequences of varying lengths, with different interchangeable possibilities as shown in Fig. 7a-c, allowing for structural versatility and structurally modified model describing the interactions between alginate G-blocks and divalent cations, primarily Ca²⁺ illustrates their strong affinity for metal ions and other pollutants through ionic-displacement mechanisms. These interactions facilitate efficient regeneration *via* simple filtration and contribute to the formation of stable ionic gels, thereby making alginate-based systems excellent candidates for water-pollution remediation.¹⁴⁷ A distinctive property of alginates is their ability to undergo reversible sol-gel transitions upon interaction with divalent and trivalent metal ions. Calcium chloride (CaCl₂) is commonly used to induce gelation, particularly through interactions with the GG-block regions, facilitating the formation of a rigid, three-dimensional network often described using the "egg-box" model.¹⁴⁸ This structural transformation occurs as calcium ions (Ca²⁺) form ionic cross-links between the G-block residues, forming a hydrogel. The schematic representation of this process, as depicted in Fig. 1c, is adapted from work.¹⁴⁹ illustrates how calcium ions mediate the cross-linking of alginate chains, resulting in a stable gel network. The binding capacity with divalent metal cations reported is Pb²⁺ > Cu²⁺ > Cd²⁺ > Ba²⁺ > Sr²⁺ > Ca²⁺ > Co²⁺, Ni²⁺, Zn²⁺ > Mn²⁺.¹⁵⁰ Beyond



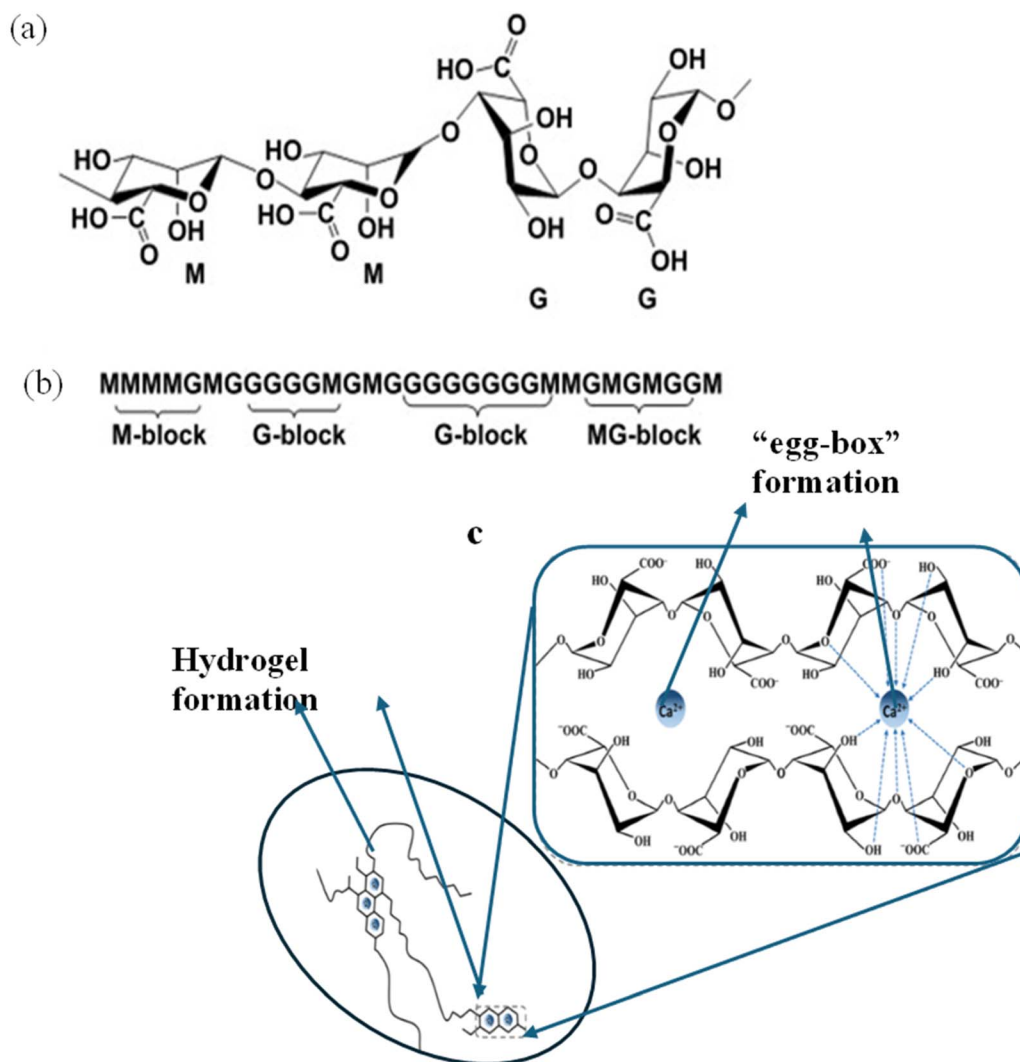


Fig. 7 Schematic of alginate structure: structure of alginate showing (a) chain conformation (b) block distribution, and (adapted with permission, Licensed under Elsevier's terms) (c) a structurally modified model describing the interactions between alginate G-blocks and divalent cations (Ca^{2+}) (Creative Commons Attribution (CC BY 4.0) from MDPI).^{147,149}

their gelation properties, alginates are extensively studied for their capacity to adsorb heavy metal ions from aqueous environments. The presence of abundant hydroxyl and carboxyl functional groups in the polymer backbone enables strong interactions with metal ions, making alginates a promising material for water purification and environmental remediation applications.^{38,151}

4.2.2 Functional modifications in alginate-based adsorbents. Various functional modifications have been explored to enhance the adsorption performance of alginate-based materials for removing heavy metal ions from aqueous environments.^{134,152,153} These modifications aim to improve key parameters, including selectivity, mechanical stability, and regeneration capacity. Fig. 8 illustrate an example of fabricating alginate-based composites, as reported in a previous study.¹⁵³ Studies have categorised alginate composite materials into several groups, including polymeric blends and graft

copolymers, biopolymer-based composites, alginate-inorganic nanohybrids, magnetic nanocomposites, and structurally engineered forms such as electrospun fibres, wet-spun fibres, and 3D-printed structures. Each class offers distinct physico-chemical advantages that contribute to improved efficiency in heavy metal ion adsorption.²⁷

4.2.2.1 Polymeric blends and graft copolymers. The formation of alginate-based polymeric blends and graft copolymers has been extensively employed to enhance adsorption selectivity and reusability. Studies have shown that surface grafting with functional groups such as thiol ($-\text{SH}$) and amine ($-\text{NH}_2$) enhances the selective affinity for metal ions. Thiolated alginates exhibit strong binding to metal ions, while aminated variants demonstrate high adsorption of Cd^{2+} .^{39,152} Cross-linking alginate, particularly with calcium ions, yields mechanically robust hydrogel beads that resist dissolution in aqueous media and maintain stable adsorption capacities



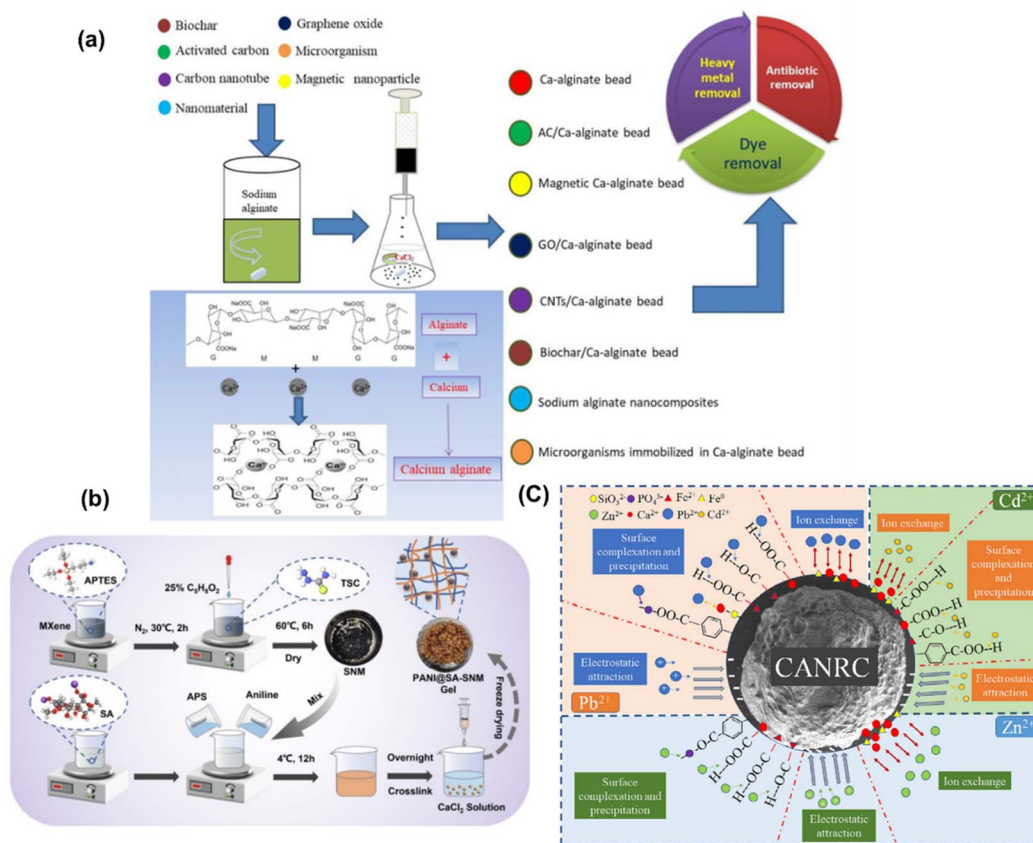


Fig. 8 Examples of (a) fabrication of alginate-based composites, (b) adsorption mechanisms of alginate composites (adapted with permission, Licensed under Elsevier's terms), and (c) preparation of PANI@SA-SNM gel adsorbent using calcium alginate to encapsulate nZVI-rice straw composite (CANRC) for Pb²⁺, Zn²⁺, and Cd²⁺ removal (adapted with permission, Licensed under Elsevier's terms).^{41,153,159}

across multiple use cycles.^{152,154} For instance, hydrogels are often based on ionic or covalent crosslinking without specific fillers or advanced frameworks. Calcium-cross-linked sodium alginate beads have demonstrated capacities ranging from 54.9 to 82.8 and 135.5 mg g⁻¹ for Cu²⁺, Ag⁺, Fe²⁺, and Fe³⁺, respectively.¹⁵⁴ The polyaniline–sodium alginate–MXene nanomaterial composite (PANI@SA-SNM) integrates MXene nanosheets and polyaniline within a sodium alginate hydrogel matrix, significantly enhancing the adsorption of Cu²⁺ and Hg²⁺ ions when used for their removal from aqueous solution. The interaction between polyaniline's redox-active nitrogen sites, MXene's layered surface functionalities, and alginate's carboxyl groups facilitates high metal uptake (up to 352.76 mg g⁻¹), confirming the efficacy of multifunctional polymeric blends in adsorptive remediation.⁴¹ Modified alginate-based biocomposite hydrogel microsphere, effectively adsorbing Pb²⁺ and Cu²⁺ ions, has 369.6 mg g⁻¹ and 124.1 mg g⁻¹, and some studies also reported the potential cellulose–alginate sponges that exhibit high water permeability and excellent reusability properties. Studies have further demonstrated the effectiveness of alginate-based hybrid materials. Notably, mesoporous alginate/ β -cyclodextrin beads exhibit remarkable adsorption capacities for Pb²⁺, Cu²⁺, Cd²⁺, and Ni²⁺ 21.09, 15.54, 2.47, and 2.68 mg g⁻¹, respectively, highlighting the enhanced performance of alginate–polymer

composites for heavy-metal removal.^{46,142} Moreover, sodium alginate-based carboxymethyl cellulose (CMC) hydrogel beads Pb²⁺ uptake (>600 mg g⁻¹), demonstrating the benefits of combining carboxyl-rich alginate matrices with amine-rich copolymers. Similarly, the sodium alginate-g-poly(acrylic acid-co-acrylamide) nanocomposite hydrogel absorbed Pb²⁺, Cd²⁺, Ni²⁺, and Cu²⁺ at concentrations of 231.88, 235.62, 67.52, and 76.35 mg g⁻¹, respectively.

4.2.2.2 Inorganic fillers and nanomaterials. Incorporating inorganic fillers, such as metal oxides and salts, into alginate matrices enhances ion exchange capabilities and structural rigidity while increasing the surface area. These additives interact physically or chemically with alginate to form functional hybrid structures. For instance, alginate-caged magnesium sulphate nanoparticle microbeads demonstrated an adsorption capacity of 84.7 mg g⁻¹ for Pb²⁺.¹⁴² The inclusion of magnesium sulfate (MgSO₄) likely provides ionic sites for selective lead interaction while boosting the mechanical robustness of the hydrogel structure. The carbonised composite manganese-crosslinked sodium alginate showed excellent removal of As³⁺ (189.29 mg g⁻¹), As⁵⁺ (193.29 mg g⁻¹), and Cr⁶⁺ (104.5 mg g⁻¹).¹⁴³ Manganese enhances redox activity, reducing toxic ions and subsequent immobilisation. This composite benefits from electrostatic and surface complexation



mechanisms enabled by the manganese-carbon interface. The calcium alginate-nanoscale zero-valent iron (nZVI)-biochar composite reportedly adsorbs Pb^{2+} , Zn^{2+} , and Cd^{2+} with capacities of 47.99, 71.77, and 47.27 mg g^{-1} , respectively,¹⁴⁵ combining the adsorptive nature of biochar with the magnetic and reductive properties of nanoscale zero-valent iron (nZVI). The cross-linked alginate-rice husk ash-graphene oxide-chitosan nanoparticles (CL-ARCG-CNP) composite combines alginate with silica-rich rice husk ash, reduced graphene oxide, and chitosan nanoparticles, forming a cross-linked hybrid with a high Pb^{2+} adsorption capacity of 242.5 mg g^{-1} . This multifunctional system leverages the high surface area of GO, the amine-rich functionality of chitosan, and the reactive silanol groups from rice husk ash, collectively enhancing Pb^{2+} chelation and stability in aqueous environments.⁴⁰ The calcium carbonate on alginate/chitosan biocomposite (CSAX_Ca) was also reported to have an affinity for the pollutants Cu^{2+} and Pb^{2+} at the adsorption capacities 429, 1742 mg g^{-1} . This performance is attributed to the ionic exchange properties of CaCO_3 , combined with the carboxyl groups of alginates and the amine groups of chitosan, respectively.¹⁵⁵ Such materials serve dual functions: adsorbing metal ions and reducing them to less toxic or immobilised

forms while being easily recoverable due to their magnetic properties. These composites demonstrate the effectiveness of hybrid materials that combine inorganic fillers with alginate to produce multifunctional adsorbents. Their efficacy is further enhanced by the synergistic role of metal oxides in charge exchange, redox transformations, and maintaining structural integrity.^{156,157}

4.2.2.3 Magnetic nanocomposites. Magnetic nanocomposites offer the dual benefits of effective heavy metal removal and straightforward post-treatment separation utilising external magnetic fields. These materials are essential in scalable water treatment technologies.¹⁵⁸ The calcium alginate-nZVI-biochar composite for removing Pb, Zn, and Cd from water: insights into governing mechanisms and performance. This category is exemplified by calcium alginate-nZVI-biochar, as nZVI provides magnetic properties and facilitates the reductive precipitation of metal ions. The removal capacities for Pb^{2+} , Zn^{2+} , and Cd^{2+} with adsorption capacities of 47.99, 71.77, and 47.27.¹⁵⁹ Demonstrate the synergistic role of nZVI with alginate's ion exchange capability. While no other strictly magnetic composites are explicitly mentioned in the dataset, this entry emphasises a growing research interest in merging magnetic

Table 2 Adsorption capacities of alginate-based composites for heavy metal removal

S. no.	Alginate-based adsorbents	Pollution/target heavy metal ion(s)	Adsorption capacity (mg g^{-1})	References
1	Modified alginate-based biocomposite hydrogel microsphere	Pb^{2+} and Cu^{2+}	369.6 (Pb^{2+}) and 124.1 (Cu^{2+})	164
2	Mesoporous alginate/ β -cyclodextrin polymeric beads	Pb^{2+} , Cu^{2+} and Cd^{2+} , Ni^{2+}	21.09 (Pb^{2+}), 15.54 (Cu^{2+}), 2.47 (Cd^{2+}) and 2.68 (Ni^{2+})	46
3	Alginate-caged magnesium sulfate nanoparticle microbeads	Pb^{2+}	84.7 for Pb^{2+}	165
4	Carbonised composite manganese crosslinked sodium alginate	As^{3+} , As^{5+} and Cr^{6+}	189.29 (As^{3+}), 193.29 (As^{5+}) and 104.50 (Cr^{6+})	166
5	Amino-functionalised sodium alginate aerogel	Cr^{6+} and Cd^{2+}	678.67 (Cr^{6+}) and 464.23 (Cd^{2+})	167
6	Calcium alginate-nZVI-biochar	Pb^{2+} , Zn^{2+} and Cd^{2+}	47.99 (Pb^{2+}), 71.77 (Zn^{2+}) and 47.27 (Cd^{2+})	159
7	Sodium alginate-based carboxymethyl cellulose hydrogel beads	Pb^{2+}	—	168
8	Sodium alginate-g-poly(acrylic acid-co-acrylamide) nanocomposite hydrogel	Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+}	231.88 (Pb^{2+}), 235.62 (Cd^{2+}), 67.52 (Ni^{2+}) and 76.35 (Cu^{2+})	169
9	Alginate/reduced graphene double-network and single-network hydrogel beads	Cu^{2+} , $\text{Cr}_2\text{O}_7^{2-}$	169.5 (Cu^{2+}) and 72.5 ($\text{Cr}_2\text{O}_7^{2-}$)	154
10	Tetrasodium thiacalixarenetetrasulfonate-sodium alginate nanocomposite hydrogel	Pb^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} and Cr^{3+}	99.8 (Pb^{2+}), 67.4 (Ni^{2+}), 90.56 (Cu^{2+}), 94.5, 74.9 (Co^{2+}) and 79.2 (Cr^{3+})	170
11	Sodium alginate hydrogel beads by post-crosslinking	Cu^{2+} , Ag^+ and Fe^{3+}	54.9 (Cu^{2+}), 82.8 (Ag^+) and 135.5 (Fe^{3+})	154
12	Sodium alginate-functionalised <i>M. oleifera</i> seed wet-spinning	Cu^{2+} , Cd^{2+} and Ni^{2+}	17113	MXene/polyaniline/sodium alginate (PANI@SA-SNM)
13	Orange peels/alginate (OAF)	Cr^{3+}	224.3 (Cr^{3+})	—
14	Orange peels/alginate (OAF)	Cr^{3+}	224.3 (Cr^{3+})	—
15	Cross-linked alginate-rice husk ash-graphene oxide-chitosan nanoparticles (CL-ARCG-CNP)	Pb^{2+}	242.5 (Pb^{2+})	40
16	Calcium carbonate on alginate/chitosan biocomposite (CSAX_Ca)	Cu^{2+} and Pb^{2+}	429 (Cu^{2+}) and 1742 (Pb^{2+})	155
17	Alginate + encapsulated <i>M. oleifera</i>	Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Mn^{2+}	5.8 (Co^{2+}), 4.78 (Ni^{2+}), 4.6 (Cu^{2+}), 1.3 (Zn^{2+}), and 1.02 (Mn^{2+})	48



responsiveness with adsorption functionalities. The advancement of magnetically recoverable alginate-based adsorbents represents a practical approach for real-time and reusable water purification applications.

4.2.2.4 Metal-organic frameworks (MOFs) and graphene-based composites (GBC). Advanced nanostructures such as reduced graphene oxide (rGO), thiacalixarene derivatives, and metal-organic frameworks (MOFs) significantly enhance alginate performance due to their high surface areas, π - π interactions, and diverse coordination environments.¹⁶⁰⁻¹⁶³ The alginate/reduced graphene double-network hydrogel beads and their single-network counterparts exhibited 169.5 and 72.5 mg g⁻¹ capacities for Cu²⁺ and Cr₂O₇²⁻, respectively.^{63,163} The double-

network structure offers improved mechanical stability and a higher density of adsorption sites. Meanwhile, rGO sheets promote π -electron-rich regions, facilitating cation- π interactions and electrostatic attractions. The tetrasodium thiacalixarene tetra sulfonate-sodium alginate nanocomposite hydrogel achieved broad-spectrum metal ion adsorption: Pb²⁺ (99.8 mg g⁻¹), Ni²⁺ (67.4 mg g⁻¹), Cu²⁺ (90.56 mg g⁻¹), Cd²⁺ (94.5 mg g⁻¹), Co²⁺ (74.9 mg g⁻¹), and Cr³⁺ (79.2 mg g⁻¹).¹⁴⁴ As macrocyclic ligands, thiacalixarene derivatives provide tailored cavities that selectively complex metal ions. Their integration into alginate matrices substantially enhances binding specificity and capacity through host-guest chemistry. These advanced composites demonstrate the potential of incorporating MOFs,

Table 3 Adsorption capacities of cellulose, regenerated cellulose and cellulose-based hydrogels

S. no.	Cellulose-based composite	Pollution/target heavy metal ion(s)	Adsorption capacity (mg g ⁻¹)	References
1	Carboxymethyl cellulose/gelatin composite hydrogel	Cd ²⁺ , Hg ²⁺ and Pb ²⁺	147.7 (Cd ²⁺), 88.62 (Hg ²⁺) and 163.89 (Pb ²⁺)	198
2	CuMOF on sodium alginate/chitosan/cellulose nanofibril composite hydrogel	Pb ²⁺	531.38 for Pb ²⁺	187
3	Sodium alginate/cellulose nanofibre composite hydrogel	Pb ²⁺	544.66 for Pb ²⁺	188
4	Porous kappa-carrageenan/cellulose hydrogels	Pb ²⁺	486 ± 28.5 for Pb ²⁺	199
5	Cellulose hydrogels (G50)	UO ₂ ²⁺	572.3 for UO ₂ ²⁺	193
6	Carboxymethyl cellulose/chitosan/alginate acid hydrogels	Cr ⁶⁺ , Ni ²⁺ and Cu ²⁺	>750 for (Cr ⁶⁺ , Ni ²⁺ and Cu ²⁺)	133
7	Chitosan/cellulose phosphonate composite hydrogel	Pb ²⁺ and Cu ²⁺	211.42 (Pb ²⁺) and 74.29 (Cu ²⁺)	51
8	Cellulose (37%)-chitosan (63%)	Cu ²⁺	94.3 for Cu ²⁺	52
9	Cellulose/chitosan/PVA/nano-Fe ₂ O ₃	Cu ²⁺	15.95 for Cu ²⁺	200
10	Oxidised carboxymethyl cellulose hydrogel	Ag ⁺ , Pb ²⁺ , Cu ²⁺	407 (Ag ⁺), 1250 (Pb ²⁺) and 1111 (Cu ²⁺)	201
11	Wheat straw cellulose-g-poly (acrylic acid)/poly(vinyl alcohol)	Cu ²⁺	142.7 for Cu ²⁺	201
12	Carboxymethyl cellulose-based cryogels	Pb ²⁺ , Ni ²⁺ , Co ²⁺	550 (Pb ²⁺), 620 (Ni ²⁺) and 760 (Co ²⁺)	202
13	Cellulose grafted with acrylonitrile (CelEnEs)	Cr ⁵⁺	—	203
14	Collagen/cellulose hydrogel beads (M-CS/PVA/CCNFs)	Cu ²⁺	67.36 mg g ⁻¹ for (Cu ²⁺)	204
15	Mercurized cellulose	Cu ²⁺ , Cd ²⁺ and Pb ²⁺	30.4 (Cu ²⁺), 86.0 (Cd ²⁺) and 205.9 (Pb ²⁺)	205
16	Cellulose/ZrO ₂	Ni ²⁺	79.0 for Ni ²⁺	206
17	Cellulosic graft polymerisation of glycidyl methacrylate-co-methacrylic	Co ²⁺	11.5 and 11 for Co ²⁺	207
18	Poly(ethylene imine)-modified cellulose	Cu ²⁺	102	208
19	Welan gum-modified cellulose	Cd ²⁺ , Pb ²⁺ and Cu ²⁺	83.6 (Cd ²⁺), 77.0 (Pb ²⁺) and 67.4 (Cu ²⁺)	43
20	Cellulose acetate (CA)/silica composite	Cr ⁵⁺	19.46 for (Cr ⁵⁺)	45
21	Oxidised cellulose-based materials	Hg ²⁺	258.75 for (Hg ²⁺)	182
22	Cellulose-based composite hydrogel microsphere	Co ²⁺ and Ni ²⁺	358 (Co ²⁺) and 373 (Ni ²⁺)	180
23	Cellulose-based hydrogel-modified kaolin	Pb ²⁺ and Cu ²⁺	879.84 (Pb ²⁺) and 543.50 (Cu ²⁺)	209
24	Carboxymethyl cellulose hydrogel-pectin-based	Cd ²⁺ , Pb ²⁺ and Cu ²⁺	84.4 (Cd ²⁺), 159.4 (Pb ²⁺), and 125.6 (Cu ²⁺)	210



graphene derivatives, and supramolecular chemistries into alginate-based platforms to create highly selective and high-capacity adsorbents. Their tunable architectures and multi-functional binding sites facilitate the simultaneous removal of various metal ions from aqueous environments.

4.2.2.5 Bio-based/biowaste-derived alginate composites. Bio-based and biowaste materials are gaining popularity, as studies have shown that alginate composites derived from orange and nectarine peels (OAF and NAF) exhibit high adsorption capacities for Cr^{5+} ions. These agro-waste materials provide additional hydroxyl and phenolic functionalities that enhance hexavalent chromium's chelation and electrostatic attraction. Table 2 shows the adsorption capacities of alginate-based composites for heavy metal removal. Integrating alginate improves structural integrity and water dispersibility, demonstrating a green valorisation strategy for effective Cr^{5+} removal, with adsorption capacities of 224.3 and 256.5 mg g^{-1} .⁶⁴ A multi-metal adsorption study using *M. oleifera* extract encapsulated in sodium alginate matrices reported modest adsorption capacities for Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , manganese ion (Mn^{2+}) and sometimes uranyl ion (UO_2^{2+}). Although the uptake values (1.02–5.8 mg g^{-1}) are relatively low, the system uses plant-derived bioactives to introduce additional binding functionalities into alginate networks. The biosorption mechanism is likely driven by phytochemical interactions combined with the carboxyl groups of alginates. Pollutants: Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} ; adsorption capacities: 5.8, 4.78, 4.6, 1.3, 1.02 mg g^{-1} .⁴⁸ In another study, Sodium alginate was functionalised with *M. oleifera* seed powder and fabricated *via* wet spinning to explore its use for removing heavy metals, particularly Cu^{2+} , Cd^{2+} , and Ni^{2+} , as investigated by Orisawayi *et al.*²⁷ Although the adsorption capacity was not reported, future work was discussed to investigate this further. The study primarily aimed to investigate the natural bioactive compounds in *M. oleifera* that enhance metal binding. At the same time, the alginate matrix provides ionic carboxyl for additional sorption. This combination illustrates a sustainable approach for producing biodegradable, fibre-based adsorbents with a selective affinity for the metal. The electrospinning process fabricates a hybrid of pulverised *M. oleifera* seed powder embedded within a sodium alginate matrix, with polyethylene oxide (PEO) as a co-spinning agent.³⁷ The process was successful, as investigated, aiming to explore the feasibility of producing fibrous biosorbents that harness the natural adsorptive capacity of *M. oleifera*, the ion-exchange potential of alginate, and the fibre-forming capability of PEO. While the complete adsorption properties of these composites have not yet been evaluated, the conceptual integration of these materials through electrospinning could serve as a baseline for a potential method for generating nanostructured materials with improved surface area, porosity, and enhanced alginate mechanical properties, thereby facilitating improved interaction with heavy metal ions in aqueous solutions.

In addition to alginate, cellulose, another abundant, renewable, and functional biopolymer, has demonstrated considerable promise in heavy metal ion adsorption, as detailed in other sections.

4.3 Cellulose-based adsorbents

Cellulose is the most abundant natural biopolymer on Earth, consisting of a long-chain polysaccharide composed of β -D-glucose units, which are often covalently linked by acetal functionalities between the equatorial (OH) groups on the carbon atoms, known as (C4) and (C1), *via* β -1,4-glycosidic bonds.^{173,174} Its unique molecular structure contributes to its exceptional physicochemical stability, particularly its insolubility in water, which arises from the extensive hydrogen bonding and crystallinity imparted by its glycosidic linkages.^{175–177} The long polymer chains are organised into two distinct regions: highly ordered crystalline domains confer mechanical strength and stability, and amorphous regions enhance chemical reactivity and biological interactions.^{178–180} Cellulose is predominantly obtained from plant cell walls, although microbial sources produce bacterial cellulose with unique nanostructures.^{178,179,181} Increasingly, agricultural residues are being explored as low-cost, renewable sources of cellulose for developing sustainable materials. Due to its intrinsic properties, renewability, biodegradability, chemical stability, non-toxicity, and the abundance of reactive hydroxyl groups, cellulose is an excellent platform for fabricating advanced functional materials. Among various cellulose-based materials, cellulose hydrogels and their regenerated counterparts have emerged as a prominent class of water purification media.^{45,176,182}

4.3.1 Cellulose composite hydrogels. Cellulose composite hydrogels are synthesised by blending native or modified cellulose with other biopolymers, such as chitosan, gelatine, alginate, nanomaterials, and other biosorbents.^{183,184} This creates an interpenetrating network of several polymer networks that enhances the surface area and activity for adsorption.¹⁸⁵ These composites offer promising results in removing toxic heavy metals due to their high swelling capacity, porous structure, and the synergistic effect of the combined components.^{52,185–187} Several works have been developed to incorporate different cellulose hydrogels into the composite; however, only a few will be discussed in this section on cellulose hydrogels for adsorption, as detailed in Table 3 comparing the varying adsorption capacities of cellulose, regenerated cellulose, and cellulose-based hydrogels for heavy metal removal. Copper-based Metal–Organic Framework (CuMOF) immobilised on sodium alginate/chitosan/cellulose nanofibril hydrogel composite was developed and demonstrated an adsorption capacity of 531.38 mg g^{-1} for Pb^{2+} .¹⁸⁷ Similarly, the sodium alginate/cellulose nanofibre composite hydrogel achieved a higher adsorption capacity of 544.66 mg g^{-1} for Pb^{2+} .¹⁸⁸ Multi-ion removal was also demonstrated by carboxymethyl cellulose/chitosan/alginate hydrogels, which exhibited exceptional uptake ($>750 \text{ mg g}^{-1}$) for Cr^{6+} , Ni^{2+} , and Cu^{2+} .¹³⁰ Furthermore, oxidised carboxymethyl cellulose hydrogels demonstrated outstanding adsorption capacities of 1250 mg g^{-1} for Pb^{2+} , 1111 mg g^{-1} for Cu^{2+} , and 407 mg g^{-1} for Ag^+ , revealing the critical role of oxidation in enhancing metal ion binding.¹⁸⁹

4.3.2 Regenerated cellulose composites. In addition to hydrogels, regenerated cellulose-based composites are another



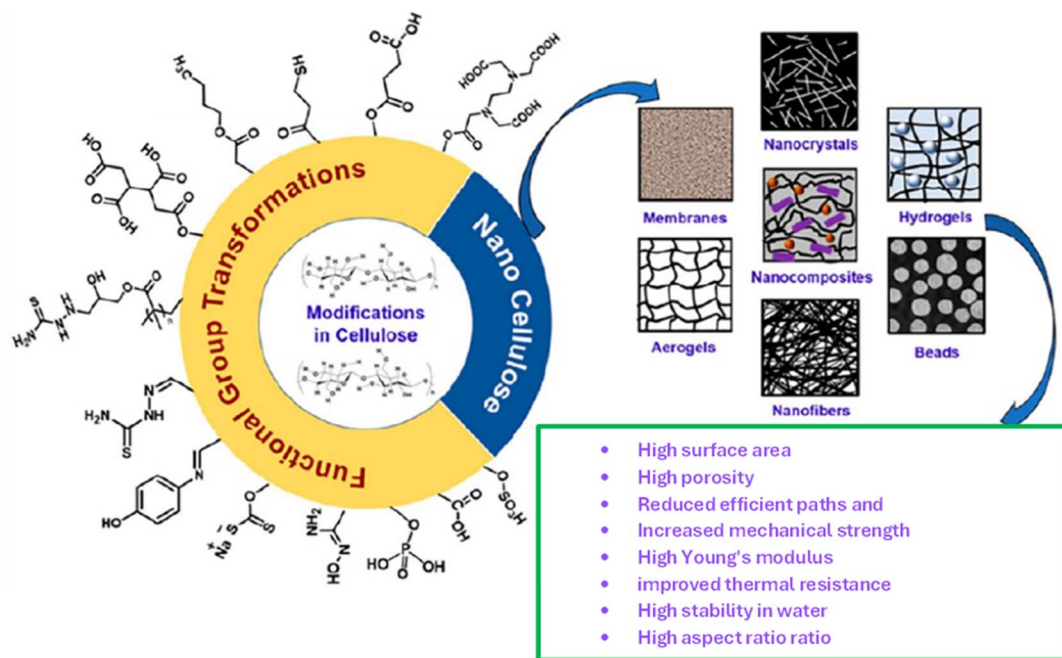


Fig. 9 Emerging nanocellulose-based modifications of cellulose for enhanced removal of heavy metal ions from water (modified with permission, Licensed under ACS Publication's terms).¹¹⁴

significant category of adsorbents for removing heavy metal ions from aqueous solutions.^{190,191} These materials are typically produced by dissolving native cellulose in eco-friendly solvents such as ionic liquids or alkali-urea systems, then reconstituting them into films, fibres, or beads through controlled regeneration.¹⁹² Although these structures do not exhibit the water-swollen matrix typical of hydrogels, they retain high crystallinity and mechanical strength. Cellulose-based hydrogel microspheres exhibited high removal capacities of 373 mg g^{-1} for Ni^{2+} and 358 mg g^{-1} for Co^{2+} ,¹⁸⁰ facilitated by the increased surface area and the formation of micro spherical morphologies, which provide rapid diffusion pathways and more active sites for metal binding, carboxymethyl cellulose hydrogel-pectin-based system demonstrated adsorption capacities of 84.4 mg g^{-1} for Cd^{2+} , 159.4 mg g^{-1} for Pb^{2+} , and 125.6 mg g^{-1} for Cu^{2+} .¹⁹³ Despite lower capacities in some systems, such as mercerised cellulose with 30.4 mg g^{-1} for Cu^{2+} , Cd^{2+} and Pb^{2+} adsorption capacity of 30.4 mg g^{-1} , 86.0 and $205.9 \text{ mg per g Pb}^{2+}$, respectively and that of cellulose acetate/silica composite, which was 19.46 mg g^{-1} for Cr^{5+} . In addition, Regenerated cellulose can also be blended with other biopolymers or inorganic materials to improve surface reactivity and adsorption capacity, and the applications have shown that regenerated cellulose composites are suitable for dynamic filtration systems and can be engineered for high reusability and targeted removal of heavy metals.^{114,194,195} Together, cellulose hydrogels and regenerated cellulose composites offer complementary pathways for creating efficient and sustainable adsorbents.¹⁹⁶ Table 3 presents the adsorption capacities of cellulose, regenerated cellulose, and cellulose-based hydrogel composites for non-targeted heavy metal ions, as reported in the literature. This

highlights the potential limitations of cellulose as a suitable water treatment material. Their physicochemical diversity and tunable surface functionality make cellulose-based systems crucial in pursuing greener water treatment technologies.¹⁹⁷

Recently, advancements in functional materials science have positioned cellulose, particularly in its nanoform known as nanocellulose.^{114,211} These materials are emerging sustainable biopolymers for various water treatment applications. Fig. 9 illustrates the functionalisation of cellulose through chemical modification.¹¹⁴ The abundant hydroxyl groups enable the introduction of various reactive moieties, such as carboxyl, amine, thiol, and sulfonate groups, as reported.^{212,213} This has been studied to significantly enhance the material's affinity for heavy metal ions in aqueous solutions, with the functional group transformations altering the surface charge, coordination capacity, and hydrophilicity.^{91,194} These nanocellulose-based systems exhibit a high surface area, increased porosity, enhanced mechanical strength, and aqueous stability, all of which are desirable characteristics for adsorbents specifically targeting the removal of divalent heavy metal contaminants such as Pb^{2+} , Cd^{2+} , Cr^{6+} , and Cu^{2+} from wastewater.^{114,214} Furthermore, nanocellulose's high aspect ratio and tunable functional surfaces facilitate efficient diffusion, rapid ion exchange, and chelation processes, improving adsorption kinetics and capacity.^{214,215} Consequently, modified cellulose and its nanostructured derivatives serve as renewable, biodegradable, and highly effective materials for the adsorption and removal of toxic metal ions in water purification systems.^{216,217}

While alginate, cellulose derivatives, and their composites have shown considerable promise as eco-friendly adsorbents in water purification, their performance can be significantly





Fig. 10 Photographs and modified images of the (a) unpeeled seeds (MOU), (b) shelled seeds (MOS), (c) seed powder (MoP), (d) husk (MOH), (e) husk powder (MOHP), (f) dried leaves (MODL), (g) leaves powder (MODLPL), (h) bark pieces (MP), (i) bark powder (BPD).²³⁶

enhanced through hybridisation with plant-derived materials that offer active biosorption properties. One such material, *M. oleifera* seed powder, has garnered attention for its rich bioactive compounds and ability to adsorb heavy metal ions effectively. The following section explores the potential of *M. oleifera* as a natural biosorbent in sustainable water treatment. Beyond structural biopolymers like alginate and cellulose, plant-based biosorbents such as *M. oleifera* offer complementary adsorption mechanisms and bioactive functionalities, enriching the development of multifunctional composite systems for water purification.

5 *M. oleifera*-based adsorbents

The *M. oleifera* tree thrives in tropical and subtropical regions worldwide. It is often called the “miracle tree” or “drumstick” in

English. Nowadays, *M. oleifera* has naturalised throughout the tropics, including regions in Africa, Central and South America, and Southeast Asia. *M. oleifera* has been introduced and cultivated across Europe for research purposes, enhancing its accessibility.^{218–220}

5.1 Biosorption mechanisms and functional components of *M. oleifera*

Research has shown that *M. oleifera* seeds are primarily protein-rich and exhibit active functions known for binding with pollutants. The tree is also reported to have been a preferred source of nutrition and second-generation biodiesel, and its components can be used as drugs. They have reportedly demonstrated an affinity for absorbing carbon dioxide from the atmosphere.^{219,221} Fig. 10 displays the various *M. oleifera* biomass samples used in this study, including *M. oleifera*



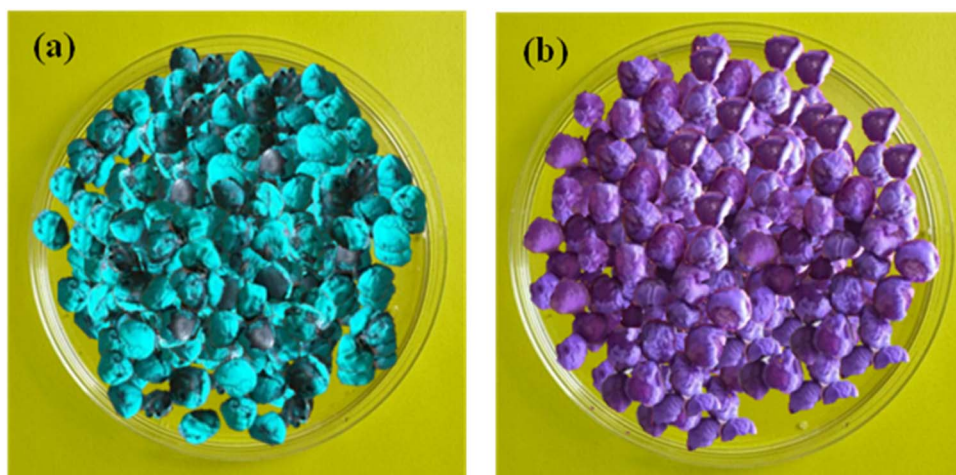


Fig. 11 Illustration of the nature of *M. oleifera* seeds after 24 hours of the sorption process for heavy metal ions from an aqueous solution: (a) Brilliant Green (BG) and (b) Crystal Violet (CV) sorption.²³⁷

unpeeled seeds (MOU), *M. oleifera* shelled seeds (MOS), *M. oleifera* seed powder (MoP), *M. oleifera* husk (MOH), *M. oleifera* husk powder (MOHP), *M. oleifera* dried leaves (MODL), *M. oleifera* dried Leaves powder (MODLP), *M. oleifera* bark pieces (MOB), *M. oleifera* and bark powder (MOBP). These components represent the diverse functional fractions of *M. oleifera* investigated for coagulant and adsorbent applications in water purification. Studies suggest that each part contains a protein that can be used as an antimicrobial flocculant to remove wastewater impurities through electrostatic interactions between the cationic protein and colloids.²²² Some studies have also shown that *M. oleifera*, known for its high content of bioactive compounds, shows promise in various water

treatment applications due to its availability, biodegradability, and non-toxicity. Therefore, the coagulating properties make them a potential additive for alginate in water purification applications, presenting a promising alternative to alginate, as it has been previously used in the manufacture and functionalisation of alginate.²²³ However, only a few studies have explored the combination of *M. oleifera* with most biopolymers, such as alginate and cellulose. In the case of heavy metal ions, *M. oleifera* has been reported to remove heavy metals such as copper, cadmium, chromium, and lead at rates of 95%, 76%, 70%, and 93%, respectively.^{224,225} In a study on using *M. oleifera* seed for water treatment, the final concentration of copper was below the desirable limit for drinking water (less than

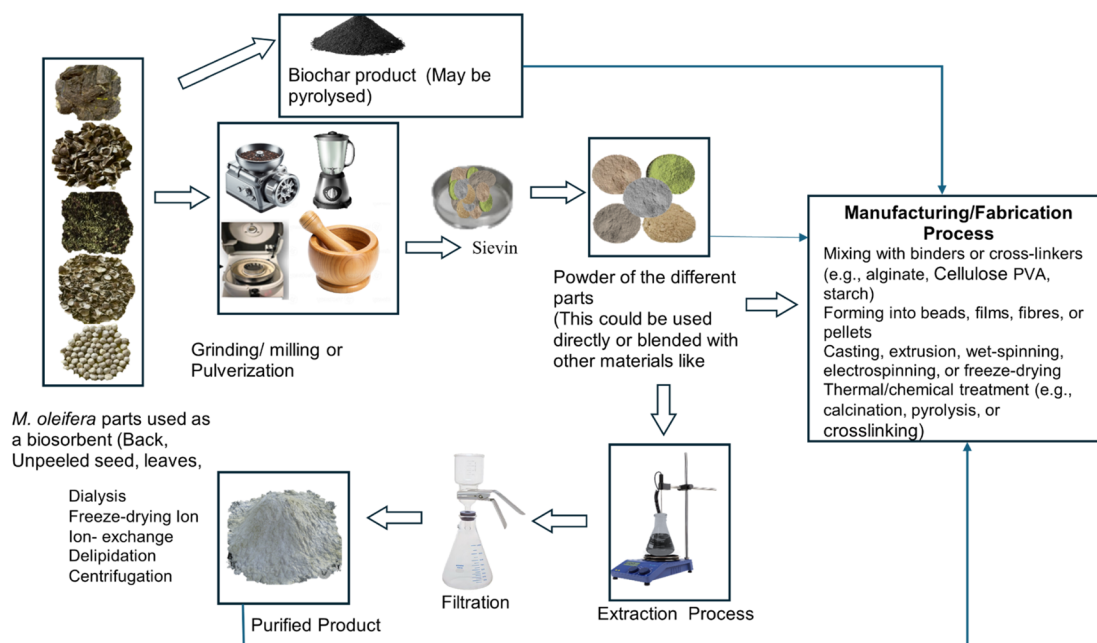


Fig. 12 A typical illustration step of processing *M. oleifera* parts for water treatment application.



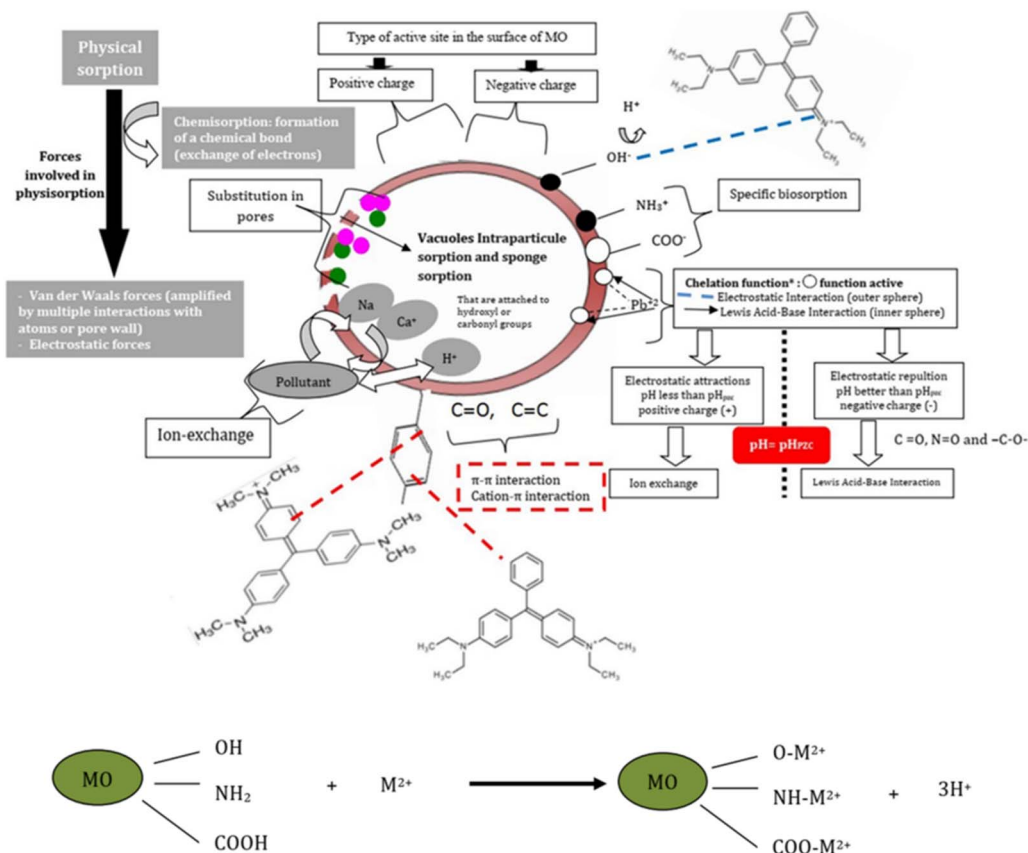


Fig. 13 Schematic illustration of the various mechanisms involved in *M. oleifera* biosorption for removing toxic contaminants from aqueous solutions, such as Cr^{5+} , V^{5+} , and Pb^{2+} . Probable mechanism ion-exchange mechanism between *M. oleifera* and metal ions (M^{2+}) (Open access).²³⁷

1 mg L^{-1}).^{226,227} However, the removal of cadmium, chromium, and lead after coagulation with *M. oleifera* seed cake coagulant did not meet the limits of drinking water standards.

This inconsistency is closely related to the underlying mechanisms governing its removal efficiency was also observed in studies carried out by Orisawayi *et al.*,²⁵ and study on the purification of river water using *M. oleifera* seed for copper removal for point-of-use household application discussed that the cationic proteins and bioactive compounds present in *M. oleifera* could function primarily as a natural coagulant.²²⁸

Several recent studies also discussed that the mechanisms are highly effective for metal ions such as Cu^{2+} , which exhibit favourable interactions with the functional groups in the extract.²²⁹⁻²³¹ However, ions such as Cd^{2+} , Pb^{2+} , and Cr^{3+} and Cr^{5+} possess lower charge densities, weaker binding affinities, or distinct hydrolysis behaviours, which could result in less efficient coagulation and adsorption. This possibly suggests reason *M. oleifera* is an excellent coagulant; its capacity as a high-affinity adsorbent is limited for specific metal species, and therefore, its performance may require enhancement through composite formulation or integration with other biopolymers.^{232,233} Therefore, additional treatments may be required to meet the standards of the EPA, WHO, EU, and some indigenous bureau standards, such as those of the indigenous peoples. The study's findings indicate that *M. oleifera* seed cake

is suitable as a coagulant and is effective for pre-treatment applications for removing heavy metals from water systems.²²⁵

Fig. 11 presents an example of MOS biosorption comparison before and after 24 hours of brilliant green (BG) and biosorption of crystal violet (CV) of typical *M. oleifera* seed obtained from literature as when used, it was reported that adsorb heavy metal ions, these functions provide selective and effective absorption for various metal ions which belong to Class B, including Hg^{2+} , Ag^{3+} , Pd^{2+} , Pt^{5+} , Pt^{3+} , Au^{3+} , and Cs^{+} . For instance, Benettayeb *et al.* observed an enhancement in sorption for the ions Pb^{2+} , Cd^{2+} , and Cu^{2+} .²²⁶ Nwagbara *et al.*²²⁵ also demonstrated that adsorbents with amine groups possess unique properties, enabling them to adsorb compounds with cationic or anionic charges at different pH values, which are present in the *M. oleifera* seed and capable of removing these heavy metals from an aqueous solution.²³⁴ By using composite coagulants, drinking water standards can be met, and in many cases, heavy metals are not detected in the treated water. Polymers possess numerous functional groups, including carboxylic, amine, hydroxyl, and sulfonic. They can be used as complexing agents for the adsorptive removal of metal ions from aqueous solutions.^{40,235}

5.1.1 Processing pathways and fabrication. The schematic flow illustrated in Fig. 12 provides a comprehensive overview of the sequential processing stages and functional applications of



Table 4 Biosorbents for heavy metal adsorption of various toxic heavy metal pollutants (*M. oleifera* parts used for heavy metal adsorption)

S. no.	Biosorbent part of <i>M. oleifera</i> with or without modification	Pollution/target heavy metal ion(s)	Adsorption capacity (mg g ⁻¹)	References	
1	Pure seed/leaves	Pb ²⁺ , Cd ²⁺ , Co ²⁺ and Ni ²⁺	Seed 13.29 (Pb ²⁺), 4.97 (Cd ²⁺), 5.80 (Co ²⁺) and 3.61 (Ni ²⁺)	Leaves 49.50 (Pb ²⁺), 16.13 (Cd ²⁺), 10.94 (Co ²⁺) and 10.16 (Ni ²⁺)	30
3	Pods modified HNO ₃ 0.3 M	Pb ²⁺ and Cd ²⁺	35.97 (Pb ²⁺) and 18.24 (Cd ²⁺)		256
4	Pure seed	Pb ²⁺	For 5.6 (Pb ²⁺)		257
5	Leaves modified diethylamine functionalisation	Cr ⁵⁺	60.6061 for (Cr ⁵⁺)		258
6	Pure leaves	Pb ²⁺	45.83 for (Pb ²⁺)		222
7	Pure seed	Cd ²⁺	357.14 for (Cd ²⁺)		259
9	Gum-modified acryloylation reaction	Hg ²⁺	840.34 for (Hg ²⁺)		260
10	Pure seed pods	Cr ⁵⁺	119.02 for (Cr ⁵⁺)		261
11	Pure seed and pure husk	Cu ²⁺ and Cd ²⁺	13.089 (Cu ²⁺) and 13.123 (Cd ²⁺)		262
12	Seed modified with oil extraction to obtain <i>M. oleifera</i> cake (byproduct)	Pb ²⁺	12.24 (Pb ²⁺)		263
13	Leaves modified with activated carbon	As ⁵⁺	6.23 (As ⁵⁺)		264
14	Pure seed-modified oil extraction to obtain <i>M. oleifera</i> cake (byproduct)	Cd ²⁺	7.864 (Cd ²⁺)		265
15	Seed oil extraction to obtain <i>M. oleifera</i> cake (byproduct)	Cr ³⁺	3.191 (Cr ³⁺)		266
16	Leaves esterification with NaOH followed by citric acid treatment	Cd ²⁺ , Cu ²⁺ and Ni ²⁺	171.37 (Cd ²⁺), 167.90 (Cu ²⁺) and 163.88 (Ni ²⁺)		267
17	<i>M. oleifera</i> bark (MOB)	Cd ²⁺ and Cu ²⁺	39.41 (Cd ²⁺) and 36.59 (Cu ²⁺)		236
18	<i>M. oleifera</i> bark (MOB)	Ni ²⁺	30.38 for (Ni ²⁺)		268
19	Wood	Cu ²⁺ , Ni ²⁺ and Zn ²⁺	11.53 (Cu ²⁺), 19.08 (Ni ²⁺) and 17.67 (Zn ²⁺)		269
20	Leaves citric acid treatment	Pb ²⁺	209.54 for (Pb ²⁺)		269
21	Bark	Pb ²⁺	34.6 for (Pb ²⁺)		270

various *M. oleifera* seed components, including whole seeds, shelled seeds, unshelled seeds, husk, bark, and gum, for preparing natural coagulants and bio-adsorbents intended for heavy metal ion removal in water purification systems.²³⁸ *M. oleifera* is a multipurpose tree whose biomass contains several valuable fractions.²³⁹ The whole seed comprises both the kernel and the seed coat. In contrast, shelled seeds specifically refer to the kernel, which is the nutrient-rich part, and the unshelled seeds and husks are more fibrous. The bark contains lignocellulosic compounds suitable for thermal activation.²⁴⁰ Additionally, *M. oleifera* gum, a natural exudate from the bark, is a polysaccharide-based biopolymer with potential flocculant and stabilising properties. Each part possesses distinct physicochemical features that dictate its suitability for either coagulation or adsorption applications.^{240–242}

The initial processing step involves mechanical disintegration using grinders, blenders, or a traditional mortar and pestle. This process reduces particle size, increases surface area, and facilitates further downstream applications. A sieving stage follows to ensure particle homogeneity for consistent application. The protein-rich shelled seeds and gum exudates undergo aqueous or solvent-based extraction. The cationic proteins from the kernel interact with negatively charged colloids in water, promoting coagulation and flocculation. *M. oleifera* gum, due to its polysaccharide backbone and high molecular weight, enhances coagulation through bridging mechanisms and aids in viscosity control during composite synthesis.^{243,244} This process is particularly relevant in systems where organic turbidity or microbial contamination is a concern. The fibrous seed husks, bark, and other lignocellulosic fractions are



subjected to pyrolysis or chemical activation to produce biochar or activated carbon. These materials exhibit a high surface area and porosity, essential for effective adsorption of heavy metal ions.^{245,246}

Surface functional groups such as hydroxyl, carboxyl, and phenolic moieties facilitate metal binding through ion exchange, surface complexation, and electrostatic attraction. The performance of bio-based composites derived from *M. oleifera*, alginate, and cellulose is subsequently enhanced through systematic material modification techniques to improve structural integrity, processability, and adsorption efficiency in water purification systems.^{246–248} These modifications typically begin by mixing the primary biopolymers with binders or cross-linking agents, such as poly(vinyl alcohol) (PVA), starch, or modified cellulose derivatives, and the process seeks to strengthen the network structure, enhance the dispersion of *M. oleifera* components, and improve compatibility within the matrix materials.^{242,249,250}

The modified blends can be fabricated into functional forms, such as beads, films, fibres, or pellets, each offering distinct surface area and porosity advantages for water treatment.²⁴⁹ Depending on the desired morphology and end-use application, various fabrication techniques, including casting, extrusion, wet spinning, electrospinning, and freeze-drying, are utilised.^{37,242,251}

5.2 Heavy metal biosorption mechanism of *M. oleifera* in aqueous systems

Fig. 13. Schematic illustration of the various mechanisms involved in the biosorption of *M. oleifera* for removing toxic contaminants, such as Cr^{5+} , V^{5+} , and Pb^{2+} ; this was explained by Benettayeb *et al.*²³⁶ In a critical review of the emphasis, recent pieces of evidence study *M. oleifera* as a biosorbent for water and

wastewater treatment. The primary biosorption mechanisms by which *M. oleifera* interacts with toxic heavy metal ions. The ion-exchange mechanism is central, whereby native ions (*e.g.*, Na^+ , H^+ , Ca^{2+}) present on the biosorbent surface are replaced by heavy metal ions (M^{2+}), such as Pb^{2+} , Cr^{5+} , and V^{5+} . The functional groups that facilitate this process reported that are peculiar to *M. oleifera* include hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), carbonyl ($\text{C}=\text{O}$), and amine ($-\text{NH}_2$) that are present in *M. oleifera*.^{151,252,253} The adsorption mechanisms encompass electrostatic attraction between negatively charged functional groups and metal cations, surface complexation, chemisorption, and intraparticle diffusion within the porous matrix. The overall biosorption performance is further influenced by the solution pH, the surface charge of the adsorbent, and the specific interaction modes governing metal–ligand binding. These interactive mechanisms collectively highlight *M. oleifera*'s efficiency as a multifunctional biosorbent for remediating metal-contaminated water.^{254,255} Table 4 also presents the biosorbents for heavy metal biosorption of various toxic heavy metal pollutants (main *M. oleifera* parts used for heavy metal adsorption).

An evaluation of the biosorption capacities reported from the table reveals clear differences in performance among various *M. oleifera* plant parts. The gum-derived materials, particularly those modified *via* acryloylation, exhibit exceptionally high adsorption capacities, reaching 840.34 mg g^{-1} for Hg^{2+} , indicating a high density of reactive functional groups. Modified leaves consistently show superior performance, achieving values above 150 mg g^{-1} for Cd^{2+} , Cu^{2+} , and Ni^{2+} , especially when treated with NaOH –citric acid or activated carbon, suggesting that surface functionalisation significantly enhances metal-binding affinity. Seed-based materials, including seed cake by-products, also demonstrate promising performance, with adsorption capacities up to 357.14 mg g^{-1} for Cd^{2+} ,

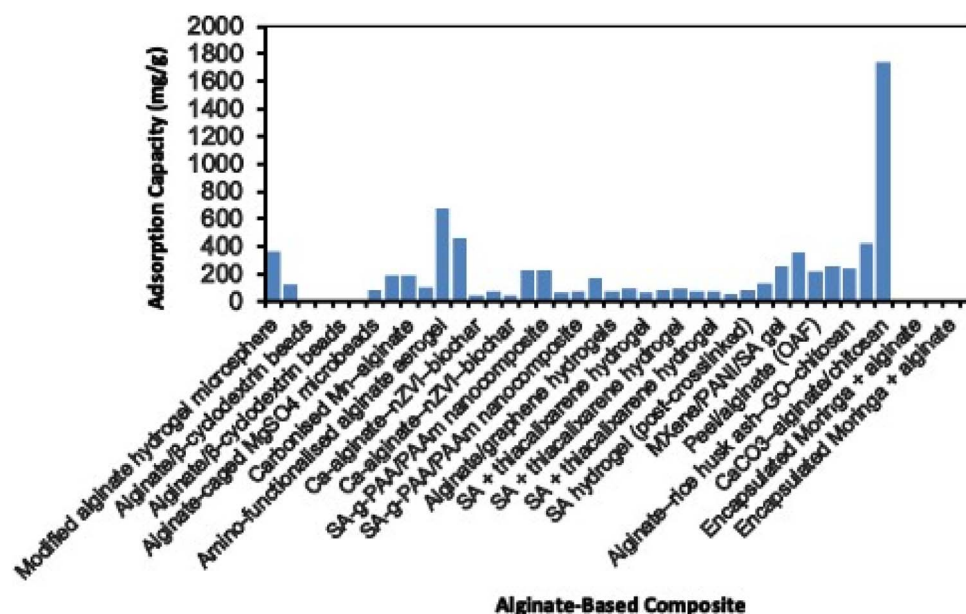


Fig. 14 Comparison of adsorption capacities of alginate-based composites.



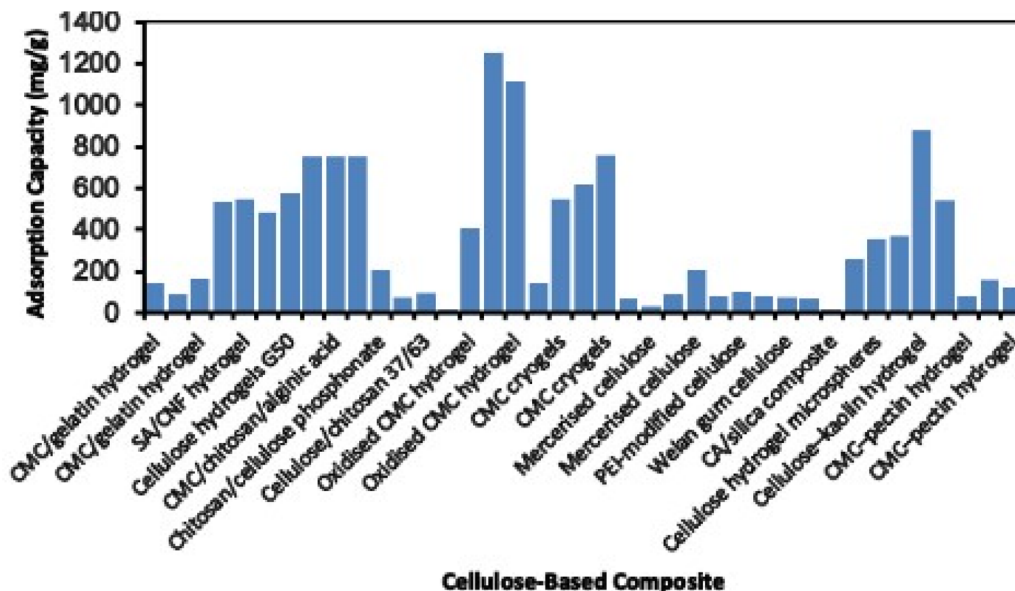


Fig. 15 Comparison of adsorption capacities of cellulose-based composites.

reflecting their favourable protein and lipid composition. By contrast, bark, wood, and unmodified seed or pod materials tend to exhibit lower uptake values. Based on these findings, there is a clear indication that leaves, gums, and chemically modified seed-derived materials are the most promising bio-sorbent components for heavy-metal remediation.

Various fabrication techniques have been employed to enhance bio-based composites' adsorption efficiency and stability, including electrospinning, wet spinning, hydrogel formation, and hybrid processing. These methods enable the formation of fibres or gels with high surface area, tunable porosity, and enhanced stability, all of which are critical for water treatment applications. While numerous studies have demonstrated the promising capabilities of *M. oleifera*, alginate,

and cellulose, significant research gaps remain in integrating these materials effectively for real-world applications. The following section identifies these gaps and proposes future research pathways.

6 Comparative evaluation of sodium alginate, cellulose composited and the *M. oleifera* parts biosorbent

A systematic comparison of sodium alginate, cellulose, and *M. oleifera* composites is essential to establish their relative adsorption performance and identify the most efficient bio-based materials for heavy metal removal.^{114,271} Although each of these biopolymers exhibits distinctive structural features and

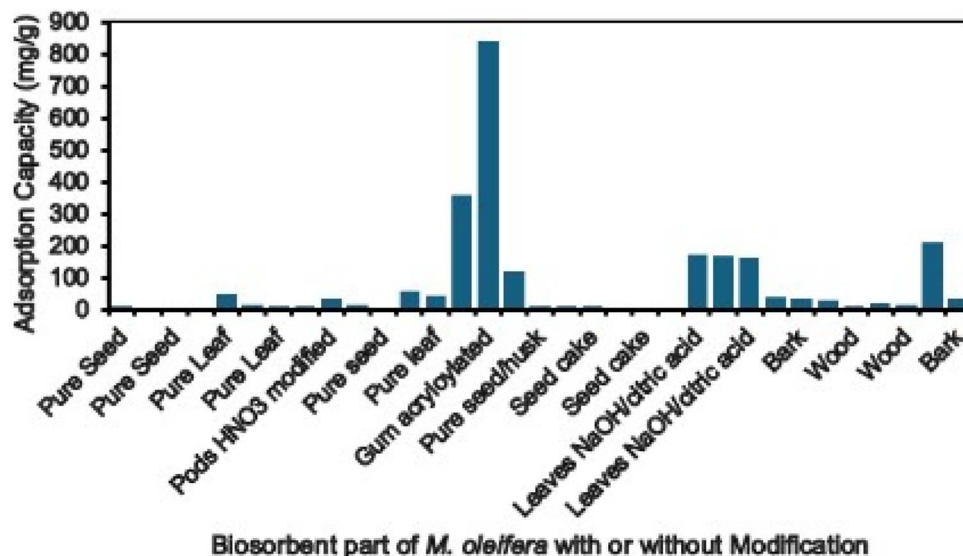


Fig. 16 Comparison of the adsorption capacities of parts of *M. oleifera* with or without modifications.



Table 5 Comparative findings from the study on electrospun and wet-spun fibre processing and properties

S. no.	Parameter	Electrospinning (alginate-based)	Wet-spinning (alginate-based)	Wet-spinning (cellulose-based)	References
(1) Processing comparison					
1	Solubility	Water-soluble, requires blending with polyethene oxide (PEO) for electrospinning and crosslinking for stability	Water-soluble, requires ionic crosslinking for stability	Water-insoluble retains stability in water	36
2	Processing method	Electrospinning <i>via</i> high voltage application onto a collector plate	Water-soluble, requires ionic crosslinking for stability	Wet-spinning using ionic liquid (EMIM DEP), then water coagulation	32 and 276
3	Crosslinking mechanism	Post-processing electrospinning crosslinking using CaCl ₂	Ionic crosslinking <i>via</i> divalent Ca ²⁺ (egg-box model)	Hydrogen bonding-based structural regeneration	27 and 36
4	Fibre morphology	Nanofibrous structure with a high surface area after spinning	Soft polymeric network fibres	Dense, well-packed fibres with strong interchain interactions	27 and 36
5	Spinnability	Requires precise control of viscosity and voltage	Easier to spin but prone to swelling	Challenging to spin due to high viscosity	27, 32 and 36
(2) Mechanical properties comparison					
1	Tensile strength	Not reported	With different concentrations of <i>M. oleifera</i> seed, but best at 1% MoP (lower)	With different concentrations of <i>M. oleifera</i> seed, but best at 2% MoP (higher)	27 and 32
2	Young's modulus	Not reported	Lower dependent on hydration state	Higher improved stiffness due to dense hydrogen bonding	27 and 32
3	Elongation at break	Not reported	Moderate, decreases with <i>M. oleifera</i> seed due to embrittlement	Higher retains flexibility at higher <i>M. oleifera</i> content	27, 32 and 36
4	Structural rigidity	Not reported	Soft and flexible, but weaker than cellulose-based fibres	Rigid and mechanically stable	277
5	Fracture behavior	Not reported	Soft and flexible, but weaker than cellulose-based fibres	Ductile failure can elongate before breaking	27, 32 and 36
(3) Microstructure and porosity					
1	Microstructure morphology	Highly porous nanostructure	Open pore structure, good for ion diffusion	Dense, compact structure	27, 32 and 36
2	Pore interconnectivity	Excellent, ideal for diffusion-based applications	Moderate, interconnected pores improve diffusion	Lower interconnectivity reduces diffusion efficiency	27, 32 and 36



Table 5 (Contd.)

S. no.	Parameter	Electrospinning (alginate-based)	Wet-spinning (alginate-based)	Wet-spinning (cellulose-based)	References
Water interaction & adsorption properties					
3	Water interaction	Moderate hydrophilicity, tunable <i>via</i> crosslinking	Highly hydrophilic, swells in aqueous conditions	Water-stable, resistant to degradation	27, 32 and 36
4	Possible resistance to ion leaching	Less prone to ion leaching with possible Ca ²⁺ ion compared to wet-spun alginate	Prone to Ca ²⁺ ion leaching, impacting stability	Highly resistant to leaching	27, 32 and 36
5	Adsorption efficiency	Potential is higher due to nanofibre morphology, but adsorption was not conducted for these studies	Potential high, suitable for multiple metal ions	Moderate, selective for Cu ²⁺	27, 32 and 36
6	Heavy metal selectivity (based on the SEM-EDX characterisation)	Expected more selective adsorption due to surface functionalisation (recommended for future studies)	Broad-spectrum adsorption (Cu ²⁺ , Ni ²⁺ , Cd ²⁺)	Selective adsorption, primarily Cu ²⁺	27, 32 and 36
(4) Industrial suitability and economic perspectives					
1	Industrial suitability	Best for high surface area applications (<i>e.g.</i> , nanofiltration)	Best for filtration membranes requiring mechanical strength	Best for water treatment systems	27, 32 and 36
2	Recyclability potential	Moderate recyclability: crosslinking affects reusability	Possible limited recyclability due to ionic crosslinking	Possibility of more recyclable materials due to hydrogen bonding regeneration	27, 32 and 36
3	Cost-effectiveness	Higher cost due to high-voltage equipment and polymer additives	Low-cost, simple processing, widely available materials	Moderate cost, ionic liquid processing is expensive	27, 32 and 36
4	Sustainability factor	Sustainable but requires additional processing for stability due to the addition of PEO	Highly sustainable, from seaweed and plant-based sources	Sustainable, but depends on ionic liquid recycling	278 and 279
5	Processing challenges	Requires strict control (voltage, viscosity, humidity)	Crosslinking control is essential for stability	Complex ionic liquid handling limits the feasibility during the dissolution and wet-spinning process	280 and 281
6					



Table 5 (Contd.)

S. no.	Parameter	Electrospinning (alginate-based)	Wet-spinning (alginate-based)	Wet-spinning (cellulose-based)	References
	Scalability for mass production	Scalable but requires advanced electrospinning setups	Scalable but requires precise crosslinking control	Scalable but ionic liquid recycling is a challenge	32, 36 and 282
(5) Industrial suitability and economic perspectives					
1	Industrial suitability	Best for high surface area applications (e.g., nanofiltration)	Best for filtration membranes requiring mechanical strength	Best for water treatment systems	27, 32, 36 and 283
2	Recyclability potential	Moderate recyclability: crosslinking affects reusability	Possible limited recyclability due to ionic crosslinking	Possibility of more recyclable materials due to hydrogen bonding regeneration	27, 32, 36 and 283
3	Cost-effectiveness	Higher cost due to high-voltage equipment and polymer additives	Low-cost, simple processing, widely available materials	Moderate cost, ionic liquid processing is expensive	27, 32, 36 and 284
4	Sustainability factor	Sustainable but requires additional processing for stability due to the addition of PEO	Highly sustainable, from seaweed and plant-based sources	Sustainable, but depends on ionic liquid recycling	27, 32 and 36
5	Processing challenges	Requires strict control (voltage, viscosity, humidity)	Crosslinking control is essential for stability	Complex ionic liquid handling limits the feasibility during the dissolution and wet-spinning process	27, 32 and 36
6	Scalability for mass production	Scalable but requires advanced electrospinning setups	Scalable but requires precise crosslinking control	Scalable but ionic liquid recycling is a challenge	27, 32, 36 and 280–282

functional groups that support metal ion binding, their adsorption efficiencies differ considerably depending on the degree of chemical modification, composite formulation, and the physicochemical characteristics of the target ions.¹⁸⁵ This systematic comparison is based on the data retrieved from Tables 2–4 of this study. Fig. 14 shows the comparison of the adsorption capacities of alginate-based composites. Alginate composites show very high adsorption efficiencies, particularly when hybridised with metal oxides, nano-additives, or functional groups. Notable peak capacities include all metal ions Pb^{2+} at 1742 mg g^{-1} for CaCO_3 -alginate/chitosan composite,¹⁵⁵ Cr^{6+} with 678.67 mg per g amino-functionalised alginate aerogel

and Cd^{2+} with 464.23 mg g^{-1} .²⁷² The deduction from these findings shows an extraordinary adsorption capacity after chemical/nano-based functionalisation.

In addition, Fig. 15 presents the comparison of adsorption capacities of cellulose-based composites extracted the study shows the peak values of capacities retrieved from the cellulose-based composites for metal ions with the highest adsorption are Pb^{2+} at 1250 mg g^{-1} , with an oxidised CMC hydrogel with affinity with for Cu^{2+} at 1111 mg g^{-1} , Co^{2+} with 760 mg g^{-1} and the CMC cryogel Ni^{2+} at 620 mg g^{-1} .^{201,202} The findings show the strength of sustained high adsorption across multiple metal ions, broad selectivity, and stability in aqueous environments.



Furthermore, Fig. 14 also shows the comparison of the adsorption capacities of parts of *M. oleifera* with or without modification. The *M. oleifera*-based adsorbent study was limited to pure *M. oleifera* parts and modified treatment. Our findings show high adsorption capacities, particularly when chemically modified. Peak capacities include Hg^{2+} 840.34 mg g^{-1} for acryloylated *M. oleifera* gum,²⁶⁰ Cd^{2+} with 357.14 mg g^{-1} of the pure seed, and Pb^{2+} with capacities of 209.54 mg g^{-1} for citric-acid-modified leaves.^{259,269} Overall, the key findings from the comparative evaluation indicate a clear performance hierarchy among the three biopolymer systems. Cellulose-based composites show the highest overall efficiency, with several materials achieving capacities above 1000 mg g^{-1} for metals such as Pb^{2+} and Cu^{2+} . Alginate composites display very high peak capacities, including the highest value reported (1742 mg g^{-1} for Pb^{2+}), but this performance is strongly dependent on functionalisation. In contrast, *M. oleifera* biosorbents generally exhibit moderate adsorption, with higher capacities achieved only after chemical modification. Overall, cellulose demonstrates the most stable and versatile adsorption behaviour (Fig. 16).

7 Consolidated comparative discussion of electrospinning and wet spinning

Building upon the comparative evaluation presented in the preceding section, it is essential to examine how the choice of fabrication technique further shapes the structural and functional attributes of these biopolymer-based adsorbents using the specific biopolymers and the biosorbent *M. oleifera* composites. The following discussion, therefore, consolidates the key features of electrospinning and wet spinning, highlighting how each method distinctly influences fibre morphology, active-site accessibility, and overall adsorption performance.

Electrospinning and wet spinning have been identified as the key fabrication techniques for biopolymer-based and adsorbent materials. However, consolidated information on the comparison of these techniques for these specific biopolymers on how these methods distinctly influence the final adsorbent's properties of the materials, such as general processing parameters, mechanical properties, microstructure and porosity, water interaction and adsorption properties and industrial suitability and economic perspectives. This section combines the findings of this study with relevant literature on biopolymer-based fibres for wastewater purification. The results align with previous studies on electrospinning wet-spinning alginate, cellulose and *M. oleifera*. The development of bio-based fibre materials for water treatment addressed in this research is very crucial in addressing the increasing contamination of both domestic and industrial wastewater, such as oil and gas, mining, chemical processing, and textile wastewater, among others, with heavy metal ions such as Cu^{2+} , Ni^{2+} , Pb^{2+} , Cr^{6+} , and Cd^{2+} . These contaminants, common in effluents from the oil and gas, mining, chemical processing, and textile sectors, pose

critical risks to human health and ecological integrity and several metals which could pose serious risks to human health, aquatic ecosystems, and environmental sustainability.²⁷³

This comparative analysis could serve as a guideline for researchers and industries currently working in water treatment, particularly those related to wastewater treatment and management.²⁷⁴ Table 5 shows several comparisons, like the selected fabrication technique, which might be tailored to specific treatment goals, whether for heavy metal adsorption, mechanical durability, or large-scale industrial filtration.

The comparative assessment demonstrates that each fibre system offers distinct strengths relevant to water purification. Electrospun alginate fibres offer the highest porosity and surface area, making them theoretically ideal for adsorption-based applications; however, experimental data on their mechanical and adsorption performance remain limited. Wet-spun fibre, specifically those fabricated from alginate fibres, is the most cost-effective and sustainable; yet, their tendency to swell and leach Ca^{2+} compromises long-term structural stability. Wet-spun cellulose fibres deliver superior mechanical strength and water stability due to dense hydrogen bonding when ionic liquid was used,²⁸⁵ but their compact microstructure restricts diffusion and adsorption efficiency.

Overall, no single fabrication method is universally optimal. Instead, the results suggest that hybrid structures integrating the high surface area of electrospun alginate with the mechanical robustness of cellulose wet-spun fibres may offer the most balanced performance for advanced heavy-metal removal in water purification. Future studies can build on this analysis by modifying fibre compositions used in our study or related literature by integrating nanomaterials for enhanced selectivity to scale up the fibre for production in real-world applications.

To bridge the gap between scientific research and industrial adoption, a study has ensured that the development of bio-based water purification materials, including those incorporating *M. oleifera*, aligns with sustainability goals, regulatory compliance, and practical feasibility.²⁷⁵ Furthermore, we believe that countries such as developing nations, where low-cost and locally sourced materials are essential for clean water access, can use *M. oleifera*-based fibre composites to provide a viable, sustainable, and highly effective solution for addressing heavy metal contamination in drinking water and industrial wastewater.

8 Research gaps and future directions

Despite significant progress in developing biopolymer-based adsorbents for heavy metal remediation, key research gaps persist in the current literature. Many existing systems depend heavily on synthetic or chemically modified materials, raising concerns about sustainability, cost, and potential secondary pollution. Natural biopolymers like sodium alginate and cellulose are gaining increased attention due to their abundance, biodegradability, and functional groups suitable for metal ion binding. However, their full potential is yet to be realised, particularly in hybrid forms incorporating low-cost biosorbents



such as *M. oleifera*. While seed extracts have been extensively studied as biosorbents because of their cationic proteins and bioactive components, limited research has been conducted on their integration with alginate and cellulose using advanced fabrication techniques like wet spinning and electrospinning. Despite the rising demand for biodegradable and renewable alternatives, several studies have focused on synthetic polymers and unsustainable materials. Integrating alginate, cellulose, and *M. oleifera* within engineered fibres marks an emerging research frontier. These materials can be utilised to develop adsorbents with tunable adsorption capacities based on optimised parameters such as pH, dosage, and contact time. However, the experimental frameworks for selecting and fine-tuning these parameters have not been fully developed. Furthermore, although the seed has been the most studied part of *M. oleifera*, other parts of the plant, such as the bark, husk, and leaves, contain functional bioactive compounds and should be comparatively assessed for their adsorption efficacy.

Therefore, future studies should aim to:

(I) Explore underutilised parts of *M. oleifera* in combination with alginate, cellulose or their combinations.

(II) Optimise electrospinning and wet spinning methods to fabricate advanced biopolymeric adsorbents.

(III) Establish application-relevant parameters for enhanced adsorption capacities.

(IV) Validate composite performance in real water matrices and assess their regeneration, reusability potential and detailed assessment of adsorption performance.

These gaps highlight the need for systematic investigations that bridge materials science and environmental engineering. The insights gained from this review provide a foundational basis for selecting suitable material combinations, fabrication strategies, and operational parameters for improved heavy metal adsorption.

9 Conclusion

This review critically evaluates the potential of alginate, cellulose, and *M. oleifera*-based composites for heavy metal removal from aqueous systems. These bio-based materials offer environmentally friendly, low-cost alternatives to conventional synthetic adsorbents and align with the goals of sustainable water treatment. Sodium alginate and cellulose provide the necessary functional groups for efficient adsorption, while *M. oleifera* contributes additional bioactive compounds that enhance adsorption performance. Although significant progress has been made in their utilisation, a lack of integrated systems developed using advanced fabrication techniques such as electrospinning and wet spinning remains. The novelty of this study lies in its emphasis on the potential interactions among these bio-based components and the emerging fabrication strategies that can enhance their adsorption properties. Based on the systematic comparison of sodium alginate, cellulose, and *M. oleifera* composites, alginate-based systems consistently show that cellulose-based composites offer the most consistent and broadly effective adsorption performance. Alginate-based systems can reach exceptionally high capacities,

though largely when modified. *M. oleifera* adsorbents remain effective and sustainable but generally show lower capacities unless chemically enhanced. Taken together, cellulose emerges as the most reliable high-performance bio-adsorbent, followed by alginate and *M. oleifera*. Notably, the review highlights how adsorption performance can be tuned through parameter optimisation rather than solely relying on mechanical strength or structural modifications. The major gaps remain in developing sustainable, high-performance bio-based adsorbents. The combined use of alginate, cellulose, and *M. oleifera*, especially within engineered fibres, remains underexplored, and optimisation frameworks for adsorption parameters are still limited. Furthermore, most work focuses only on the seed, leaving other functional plant parts insufficiently investigated. The findings herein contribute to the body of knowledge by outlining the suitability of these biopolymers as viable adsorbents for water purification and by identifying clear directions for material selection, design, and implementation. Ultimately, this review provides a basis for designing future studies to improve adsorption capacities through the development of tailored composites using sustainable materials and processes.

Author contributions

Orisawayi Abimbola: conceptualisation, literature search, literature funding acquisition, analysis, visualisation, software, project administration, methodology, investigation, formal analysis, conceptualisation, writing – review & editing, writing – original draft. Krzysztof K. Koziol & Sameer S. Rahatekar: supervision.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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Federal Government of Nigeria, through its relevant ministries, investigate and promote the utilisation of abundant natural resources such as *M. oleifera*, seaweeds (for alginate extraction), and cellulose-rich agro-residues. Furthermore, establishing accessible electrospinning and wet-spinning facilities for researchers working in this area would significantly enhance national research capacity and foster innovation in sustainable water treatment technologies. Harnessing these bioresources for sustainable water treatment technologies could enhance national environmental strategies and contribute to achieving the UN Sustainable Development Goals (SDGs).

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