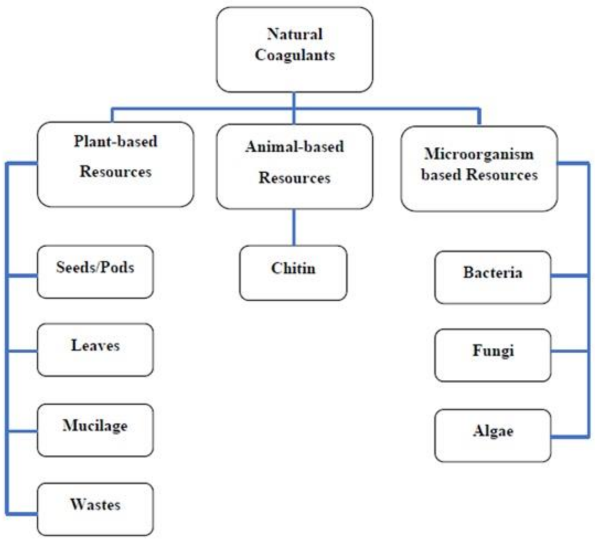
Global NEST Journal, Vol 24, No 4, pp 594-606

Role of natural coagulants in the removal of heavy metals from different wastewaters: principal mechanisms, applications, challenges, and prospects

Alazaiza M.Y.D.[1]*, Albahnasawi A.[2], Al Maskari O.[1], Al Maskari T.[1], Abujazar M.S.S.[3], Abu Amr S.S.[4], Nassani D.E.[5]
[1]Department of Civil and Environmental Engineering, College of Engineering, A'Sharqiyah University, 400, Ibra, Oman
[2]Department of Environmental Engineering, Gebze Technical University, 41400 Kocaeli, Turkey
[3]Al-aqsa Community Intermediate college, Al-aqsa University, Gaza - Palestine - P.B.4051
[4]International College of Engineering and Management, P.O. Box 2511, C.P.O Seeb, P.C. 111, Sultanate of Oman
[5]Department of Civil Engineering, Hasan Kalyoncu University, 27500 Gaziantep, Turkey
Received: 08/09/2022, Accepted: 03/10/2022, Available online: 09/10/2022
*to whom all correspondence should be addressed: e-mail: my.azaiza@gmail.com
https://doi.org/10.30955/gnj.004478

Graphical abstract



Abstract

Industrial wastewater has become a great concern due to high concentrations of several hazardous contaminants, particularly heavy metals. Heavy metal contamination and its consequences for human health and the environment have gained interest in developing low-cost, long-term cleanup technologies. Biologically based wastewater treatment approaches being more effective than conventional treatment methods are getting more attention recently. Applying natural coagulants in wastewater treatments has progressively improved the coagulation-flocculation process efficiency. The main mechanism for heavy metals removal by coagulation is adsorption; therefore, natural coagulants perform better than chemical coagulants in heavy metals removal as natural coagulants contain biopolymers with active sites for heavy metals adsorption. This systematic review focuses on applying nature coagulants for heavy metals removal from different environmental systems. A systematic and comprehensive search for related articles on Web of Science, PubMed, and Scopus on the use of natural coagulant for heavy metal removal from wastewater was conducted up to May 2022. After examining, extracting and deleting duplicate records, 81 relevant articles containing data on types of natural coagulants, extraction methods of active compounds, mechanisms of metal removal by coagulation process, and the performance of natural coagulants for the removal of heavy metals have been reviewed. Their major findings with technical gaps and possible solutions are summarized. The review is novel as it summarizes the main findings of a series of previously published articles on the role of natural coagulants, particularly the removal of heavy metals. The review also identified gaps and research questions and suggested possible solutions for the successful practical application of natural coagulants in wastewater treatment.

Keywords

Heavy metals, wastewater, natural coagulants, sources, applications, mechanisms.

1. Introduction

Water is vital for good quality of life and global socio-economic growth since water resources (surface water, groundwater, and water reserves) are integral to various industrial and agricultural sectors (Iber *et al.*, 2021). The several different functions (food production, industrial, mining and drinking water supply) attributed to the utilization of water resources show the importance of water quality management and the need to implement it. Furthermore, proper water resource treatment favors reducing contaminants in the water supply and the safety of the population (Gomes *et al.*, 2022). Water pollution has long been a global problem that has worsened due to rapid industrialization and population development (Cho *et al.*, 2020). Heavy metals, dyes, toxic anions, and organic compounds have infiltrated waterways due to anthropogenic and natural weathering processes (Dao *et al.*, 2021). Water pollution has caused widespread concern in developing countries, particularly industrial wastewater pollution, which poses a major threat to the environment and human health (Tang *et al.*, 2020). Sedimentation/settling of colloidal particles is vital in primary and sometimes secondary treatment of water and wastewater of various origins and compositions. For this purpose, various physio-chemical methods, including centrifugation and the use of different organic and inorganic chemicals, have been in practice to improve the performance and settling efficiency of multiple pollutants like organic contaminants and heavy metals. Coagulation/flocculation is an effective and cost-effective way to settle/sedimentation of colloidal particles (organic and inorganic) in water treatment processes. It effectively decreases water contaminants such as COD, turbidity, colour, suspended solids (SS), heavy metals, oil, and organic matter. The terms "Coagulation" and "Flocculation" describe procedures that cause particles to clump or bind together to speed up the rate at which they settle. The clump is also known as aggregation, agglomeration, or floc. These terms are used interchangeably; flocculation refers to adding long-chain polymers that bind the particles together, while coagulation is more related to altering the surface charge of the particles to produce aggregation. During chemical coagulation/flocculation, various chemicals (such as Alum and Poly Aluminum Chloride) are used to remove undesired particles from water. At the same time, the process results in the formation of a large amount of extra waste, which has severe environmental effects and a high cost (Abujazar *et al.*, 2022; Vega Andrade *et al.*, 2021).

Hence, exploring natural coagulants and their role in dewatering, settling/sedimentation of colloidal particles, and in broader perspectives is now getting greater attention to make the treatment process cost-effective, efficient and environmentally friendly. Numerous studies indicate the usefulness and efficiency of natural coagulants such as *Ocimum basilicum*, Cactus (*Opuntia ficusindica*), *Orchis mascula* tuber starch, Chitosan, Alyssum seed, and *C. obtusifolia* seed gum in the removal of different contaminants such as heavy metals, dye, turbidity, oil, and other organic components from various types of wastewaters (Dao *et al.*, 2021; Deepa *et al.*, 2022; Lamaming *et al.*, 2022; Wagh *et al.*, 2022). When natural coagulants are used, coagulation results primarily from interactions between charged/ionogenic sites of polymers that can adsorb or coat colloidal contaminant species. This process is known as adsorption/charge neutralization. Crucial process variables for optimal coagulation include coagulant dosage, solution pH, and mixing. To our present state of knowledge, no systematic review has discussed the role of natural coagulants in removing heavy metals from different environmental systems. This review aims to discuss and present the main findings of the latest studies type, extraction methods and the performance of natural coagulants to remove heavy metals. Furthermore, a comprehensive comparison between natural coagulation and chemical coagulation based on different wastewater treatments is also presented in this review. Finally, this review discusses the challenges, limitations, and prospects of using natural coagulants for heavy metals removal.

2. Materials and methods

This systematic review adopted the methodology of collection and screening to summarize the main findings in recent years (from 2018 to 2022) from literature considering the use of natural coagulants for heavy metals removal, identifying gaps, challenges and suggesting solutions.

2.1. Information sources

Searches were performed using keywords and MESH phrases, as well as a review of article references and consultation with specialists. The inclusion criteria for articles were published or presented in English, with contribution technique results specified as variables, efficiency, and a full-text publication available electronically through our institution's subscription. The last search was carried out on May 20, 2022. To complete the search process, we the references of publications that met the entry criteria. The procedure did not include studies such as the letter to the editor, editorials, books, or chapters. Using natural coagulants for heavy metal removal was considered an additional input parameter for the next investigation stage. To assure the study's accuracy, all steps of the search and selection of publications were carried out independently by two people. Following the criteria for systematic review studies, a comprehensive examination using three electronic databases, including Scopus, PubMed, and Web of Science, was performed for all publications published up to May 2022, as well as the reference lists of the selected articles (natural coagulation) AND (heavy metals).

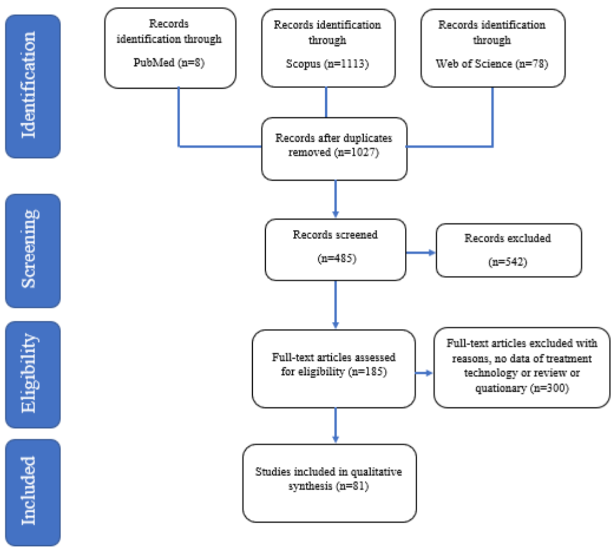


Figure 1. The employed standard protocol (P.R.I.S.M.A.) for a literature review.

2.2. Search strategy

The title and abstract of the articles were carefully checked after the first stage of systematic review, and the articles that met the entrance requirements were selected. In contrast, the remaining were rejected. Full texts were reviewed for searches that did not fit the title and abstract categories. All publications citations were entered into Mendeley software (version 1.19.8, Mendeley, U.K.), and inclusion and exclusion criteria were checked. A conventional four-step approach was used for the investigation, which is explained in the following sections and summarized in Figure 1.

2.2.1. Identification

The systematic review was conducted on publications from the PubMed, Scopus, and Web of Science databases and the Wily Online Library, Ovid, and Springer databases using the P.R.I.S.M.A. checklist. Google Scholar was also used as a complementary to complete the results. "Natural coagulants," "heavy metals elimination, "plant-based coagulant," "animal-based," and "microorganism-based coagulant' were among the search terms used in all databases. Additional publications were found by checking the references of the article bibliographies. Until May 20, 2022, all studies were reviewed.

2.2.2. Screening

The articles extracted and retrieved from the initial search were first screened in terms of titles and abstracts to determine which ones were the most pertinent. Duplicate results were eliminated by collecting and sorting the results of all keyword combination searches, which were then subjected to human screening by two authors based on the inclusion/exclusion criteria. Duplicates were eliminated, as were those that did not fulfill the eligibility criteria. Additionally, all citations from publications were reviewed for additional relevant articles and collected for inclusion using the same standards.

2.2.3. Eligibility

The full texts of selected articles (n = 185) were obtained at this stage, and their eligibility was assessed using the same exclusion criteria used in the abstract selection stage.

2.2.4. Inclusion

Information on heavy metals, as well as extraction procedures. Heavy metal information, as well as extraction procedures, were included among the eligible data.

2.3. Data extraction process

The author's name, place of origin, year of publication, category of contaminant, and results were collected for each study.

3. Results and discussions

The articles included in the studies were published between 2018 and 2022. Three hundred publications were rejected in the first phase because of a lack of entry requirements among 485 articles extracted from databases and other sources. After further review and evaluation, the full text of the selected articles (185 articles) was eliminated, with 104 articles being removed due to the lack of a specific type of coagulant or use for removing another pollutant. Finally, 81 publications were used in the research.

3.1. Natural coagulants mechanisms and types

The increasing attention to health risks and the environmental issue has stimulated interest in using green technologies for wastewater treatment (Nath *et al.*, 2019). One competitive alternative is natural coagulants that can replace chemical coagulants in wastewater treatment (Shafiq *et al.*, 2018). Natural coagulants are abundant, locally available, renewable, less influenced by water pH, and produce environmentally friendly sludge. Based on the functional groups, natural coagulants consist of proteins, polysaccharides, and polyphenols (Figure 2). These active compounds can be ionic or non-ionic (Kristianto, 2021).

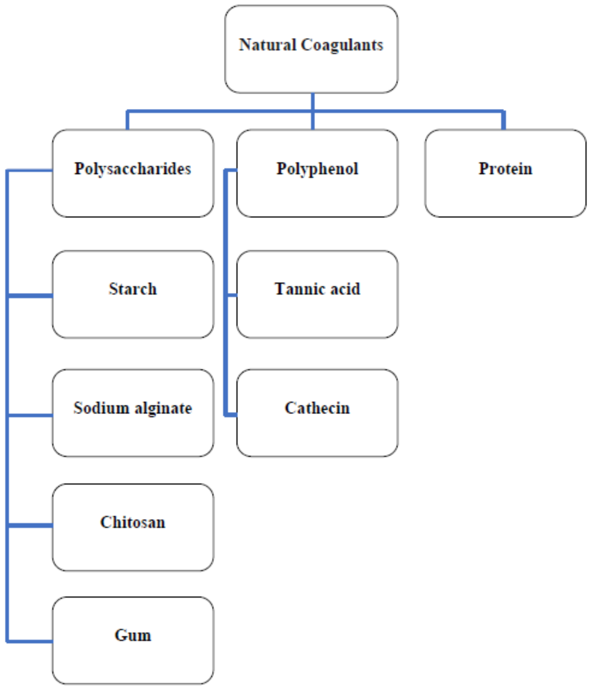


Figure 2. Active compounds found in natural coagulants.

There are four coagulation mechanisms: namely, charge neutralization, double-layer compression, sweep flocculation, and inter-particle bridging (Figure 3) (Saleem and Bachmann, 2019). The active compounds in natural coagulants stimulate the main coagulation mechanisms: 1) charge neutralization where two oppositely charged ions/particles undergo sorption, 2) Sweep flocculation: colloidal particles are trapped by the sweep flocculation coagulant, which causes them to settle to the bottom (Nimesha *et al.*, 2022). The hydrolysis process that results in the precipitation of amorphous metal hydroxide produces a lattice-like structure. 3) polymer bridging: where long-chain polymers destabilize colloid particles by binding them together, making them more stable (Sun *et al.*, 2020).

The source of active compounds in natural coagulants could be extracted from plants, animals, and microbes

(Figure 4). Polysaccharides-based coagulants generally stimulate polymer bridging mechanisms, while charge neutralization mechanisms are found in natural protein-based coagulants (Qasem *et al.*, 2021).

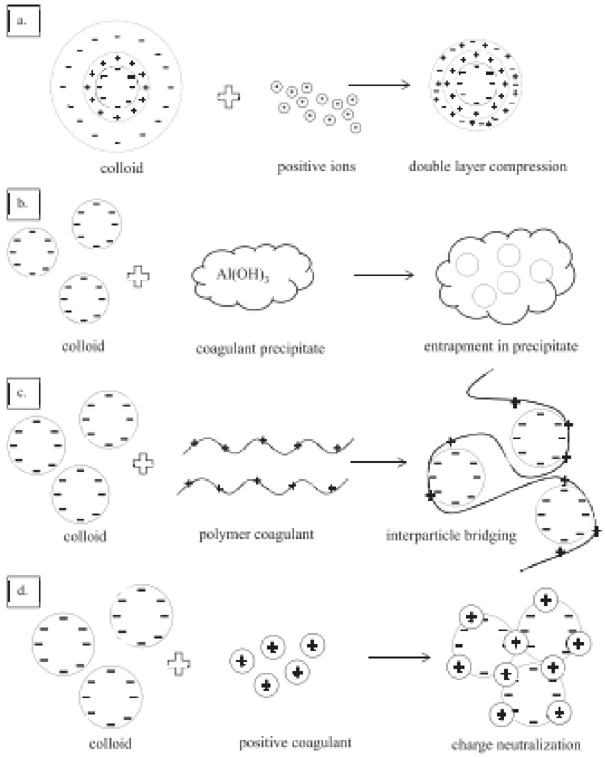


Figure 3. Coagulation/flocculation main mechanisms (adopted from Saleem & Bachmann, 2019).

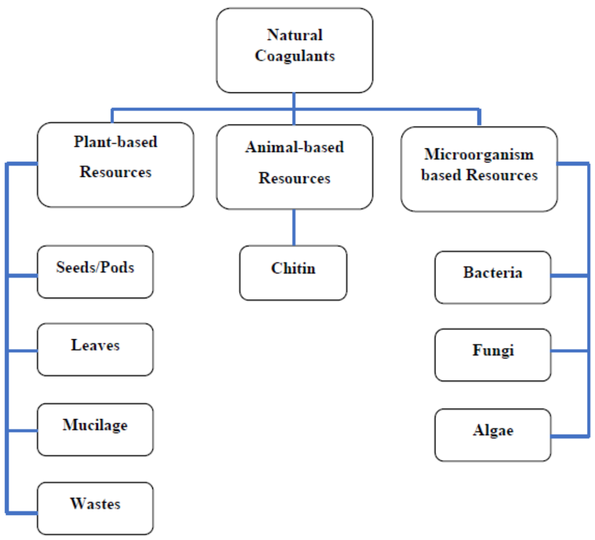


Figure 4. Source of natural coagulants.

3.1.1. Plant-based natural coagulants

Plant-based coagulants are natural and organic water-soluble coagulants extracted/derived from different parts and types of plants. Seeds, pods, peels, leaves, and fruit wastes are the parts of the plant that could be used to produce coagulants (Ahmad *et al.*, 2022). Plant-based coagulants with different active parts have been studied for water purification since the 1970s. Most of the examined coagulants refer to the *Fabaceae* family, and the main parts extracted are seeds. The seeds of *M. oleifera* are the most studied plant-based coagulants (Saleem and Bachmann, 2019). The performance of plant-based coagulants can undoubtedly replace chemical coagulants. It has proven to be a competitive alternative to chemical coagulants in the wastewater treatment industry due to its superiority over chemical coagulation (Ibrahim *et al.*, 2021). The active compounds present in plant-based coagulants differ according to the species of the plant. For example, *M. oleifera* contains 34% proteins, 15.5% lipids, and 15% carbohydrates, while *O. ficusindica* contains 12.7% galacturonic acid and 30% L-arabinose, 22% D-xylose and 21% D-galactose R (Owodunni and Ismail, 2021).

3.1.2. Animal-based

Chitosan is the most widely used coagulant of animal origin in wastewater treatment and the second polysaccharide available after cellulose (Bahrodin *et al.*, 2021). Marine invertebrates, such as crabs, crustaceans, insects, and shrimps, are the main sources of chitosan. Chitosan is a deacetylated derivative of chitin, and its non-toxic, biodegradable compound contains a high molecular weight cationic polymer. Primary hydroxyl, secondary hydroxyl, and amino are functional groups found in chitosan. Chitosan and chitin contain about 7% additional nitrogen, which is considered low by other polysaccharides. The low nitrogen content makes chitosan an attractive, natural coagulant that can be used without increasing the nitrogen load (Yu and Fu, 2020). Adsorption is the main mechanism used by chitosan to remove heavy metals. Furthermore, chitosan from crustacean shells contains 30-50% calcium carbonate, 30-40% proteins and 20-30% chitin. These active compounds can be used effectively in the coagulation process to eliminate colloidal organic and inorganic effluents from wastewater (El-Gaayda *et al.*, 2021).

3.1.3. Microorganism based

In addition to natural coagulants from plants and animals, some natural coagulants are synthesized by microorganisms, such as fungi and bacteria (Wang *et al.*, 2019). The coagulant produced depends on the species of microorganism. For instance, proteoglycan coagulants can be produced from *Bacillus mojavensis* strain 32Ais effective for flocculation as it contains 98% polysaccharide and 1.6% protein (Das *et al.*, 2021). Therefore, the selection of bacterial strain is crucial for producing highly efficient natural coagulants. The production of microbial coagulant includes four steps: 1) identification of bacteria strain, 2) bacterial screening, 3) optimization of the culture conditions, and 4) determination of flocculating activity (Tomasi *et al.*, 2022). The growth of microorganisms requires the addition of essential nutrients such as nitrogen, phosphor, and carbon. Using nutrient-rich environments as growing media, such as wastewater and sludge, can lower the cost of microorganism-produced coagulants. Polysaccharides-rich wastes such as sugarcane, oil effluent, starch, sago molasses, soybean juice, and corn steep are optimal media for microorganism cultivation (Ahmad *et al.*, 2022).

3.2. Process of extracting natural coagulents from plants

Plant-based coagulants need preparation process to be a ready product for the coagulation treatment method (Figure 5). The preparation process includes three steps : 1) griding (primary), 2) extraction (secondary), and purification (tertiary) (Okolo *et al.*, 2021; Vardhan *et al.*, 2019). The most important step in the primary stage is screening usable parts. The selection depends on the plant species. For instance, for the cactus, the usable part can be extracted from the vascular tissue by eliminating the skin and spine; for the Aloe vera, the active compounds can be produced from the peripheral spine and mature leaves (Omer *et al.*, 2022). Washing by chemical pretreatment (acid-alkaline) or distilled water is conducted to remove all impurities from the grain, contaminants, and sand/soil to prevent yeast and fungi. After washing and drying, the plant parts were ground into a fine powder containing plant tissue and active compounds.

In some cases, the plant powder can be used directly for water purification; however, the researchers indicated that further extraction steps are required to achieve a high yield (El-Gaayda *et al.*, 2021). The second step includes extracting the active compounds from the fine powder by excluding unwanted components. Saline solution, organic solution, alcoholic solution, and water can be used for extraction. Oil removal is desirable before the extraction process since the oil can increase the organic load of the treated water. Therefore, a solvent such as alcohol removes the oil from the plant parts. After extraction, the mixture is filtered to remove suspended solids and collect the natural coagulant (Kanmani *et al.*, 2017). The collected supernatants after extraction can be used directly for the coagulation process.

Preparing the coagulant freshly before the experiment is recommended to prevent aging and/or degradation, which can affect the coagulant (Mehdinejad and Bina, 2018). The third step (purification) is barely imposed due to the high cost needed to produce the purified product. Purification can be done by many methods, such as dialysis, ion exchange, and lyophilization. The ion exchange method uses charge phenomena to isolate the cationic coagulant from non-ionic and anionic contaminants. At the same time, the lyophilization technique involves attaining the crude extract and drying the supernatant using a vacuum and low temperature (Nimesha *et al.*, 2022).

3.3. Fundamentals of heavy metals removal process by the natural coagulants

The main mechanisms of heavy metal removal by coagulation are adsorption, co-precipitation and complexation (Tang *et al.*, 2016). The enthalpy of adsorption determines the elemiation of heavy metals by coagulation processes. Many factors affect heavy metal removal through the coagulation process (Razzak *et al.*, 2022). This section discusses the effect of valence state and initial concentration of heavy metals, pH and temperature impacts, and the interaction between heavy metals and organic substance.

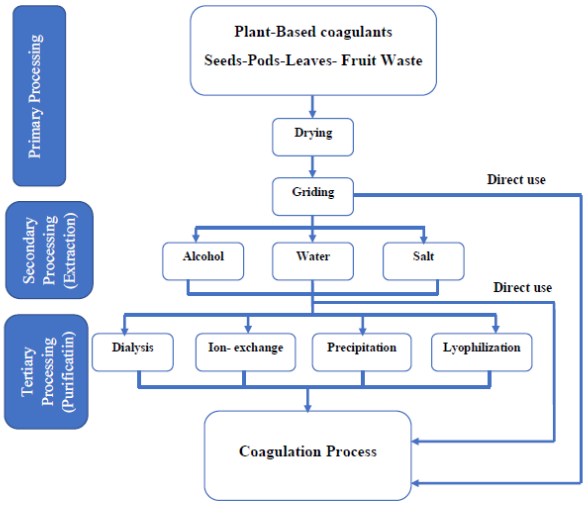


Figure 5. Extraction process for plant-based coagulant.

3.3.1. Effect of valence state and initial concentration of heavy metals

Higher valence heavy metals are highly favourably adsorbed on the active sites of the coagulant. Therefore, it is recommended to pre-oxidize heavy meals before the coagulation process to reduce the use of chemicals (Saleh *et al.*, 2022). However, lower valence heavy metals work better than the higher ones. For example, the removal of Sb (III) is higher than that of Sb(V) as the latter is more soluble in water. A lower concentration of heavy metals leads to lower removal efficiency because the flocs produced are few, low in density and large in size (Tang *et al.*, 2016).

3.3.2. Effect of pH

pH is an important factor affecting heavy metal removal during coagulation (El-Gaayda *et al.*, 2021). To be precise, the effect of pH is complex and depends on the type of coagulant. Generally, heavy metal precipitation occurs when the pH is high; however, alkaline conditions do not mean higher heavy metal removal, as the optimum pH range is different when using an inorganic coagulant (Rajoria *et al.*, 2022).

3.3.3. Effect of other inorganic substances

The co-excitation of some inorganic substances such as S^{2-} and Ca^{2+} could enhance the elimination of heavy metals. S^{2-} can react with heavy metals and produce precipitation that increases the removal efficiency (Vardhan *et al.*, 2019). The presence of Ca^{2+} can enhance heavy metal removal by the following mechanisms: 1) Ca^{2+} compresses the thickness of the double layer, which decreases charge exclusion; 2) reduces the negative charge of the flocs; 3) increases precipitation; 4) When the pH is high (alkaline condition), the formation of $CaCO_3$ enhances the co-precipitation, adsorption and entanglement of heavy metals. On the other hand, some inorganic substances, such as silica and phosphate, compete with heavy metals for adsorption sites. As a result, the heavy metal removal efficiency is lower than expected (Vidu *et al.*, 2020).

3.3.4. Effect of organic substances

Organic matter can react with heavy metals to form an insoluble substance, a colloidal or soluble complex (Shrestha *et al.*, 2021). The characteristics of the coagulant and organic substance determine the form of the products, and the dominant form influences the heavy removal of heavy metals. Humic acid (HA) at high pH considerably enhances the removal of heavy metals. However, the presence of antimony ions beside HA significantly reduces the heavy metal removal efficiency as HA is a supermolecule that competes with heavy metals and occupies adsorption sites on the formed oxyhydroxide. Furthermore, HA adsorbs part of the antimony ions, increasing the complex's solubility (Qasem *et al.*, 2021). With a low coagulant dosage, competition for adsorption sites is strong, leading to low removal of heavy metals. The competition effect is negligible at high coagulant doses because organic and inorganic contaminants are removed simultaneously. As mentioned above, the heavy metal removal by coagulation is complex. The presence of colloidal particles in water affects the entire process because these particles can adsorb heavy metals and end up in a co-precipitation mechanism (Sun *et al.*, 2020).

3.4. Performance of natural coagulants in the removal of heavy metals

Chitosan has been recently studied as a natural coagulant due to its high ability to adsorb metals in a wide range. In a study, Sun *et al.* (2019) investigated the performance of chitosan in the treatment of electroplating wastewater containing Ni(II). The effects of chitosan dose, pH, and reaction time were examined to find the optimal operation condition. The results showed that the concentration of Ni(II) was reduced to 0.61 mg/L where the optimal operating conditions were found: pH of 9, chitosan dose of 40 mg/L and reaction G value of 300 S^{-1}.

In a recent study, Lu *et al.* (2022) applied a machine learning approach to predict the efficiency of chitosan-based flocculation for heavy metals removal. The results indicated that the molecular weight and pH of the solution were the most dominant parameters controlling the heavy metals removal process. In addition, the result of the experiment indicated that operating conditions of pH greater than 7 and dosage (50-150 mg/L) are optimal for high removal efficiency. In another study, López-Maldonado *et al.* (2017) prepared a novel natural coagulant using chitosan extract to separate heavy metals from wastewater of the metal finishing industry. The results indicate the effectiveness of the new agent in separating heavy metals.

Many studies have focused on the performance of *Moringa oleifera,* a plant-based coagulant for removing heavy metals from different types of wastewater because it is remarkably efficient as a coagulant. In a study conducted by Tanko *et al.* (2020), who investigated the removal of heavy metals from the tannery wastewater by extracting *Moringa oleifera* seed. The results revealed that the removal efficiencies for chromium, cadmium, and iron were around 99%, while those for cobalt, copper, manganese, lead and zinc were around 91%. The results suggest that using *Moringa oleifera* seeds as a coagulant is an economical, easy-to-use and environmentally friendly method for the removal of heavy metals removal from tannery wastewater.

In another study, Aziz *et al.* (2021) studied the removal potential of nickel, lead, and cadmium from synthetic groundwater using plant-based coagulant extracted from *Moringa oleifera* seeds and *Musa cavendish* peel biomass. The active compound was extracted using NaOH (0.1M) and HNO_3 (1N). The result showed that the main mechanism for heavy metal removal was adsorption and chemo-sorption. Furthermore, the results revealed that the total cost was 0.17 USD per 50 L, which was considered useful for low-income, remote communities.

Abiyu *et al.* (2018) investigated the performance of two species of Moringa, *stenopetala* and *olifera*, as natural coagulants for removing heavy metals from wastewater. They found that water treatment *stenopetala* was more effective than with *oleifeara* seed. Similarly, Marzougui *et al.* (2021) studied the performance of three different types of *Morinaga oleifera* (Egyptian, Indian, and Mornag) for urban wastewater treatment. The different concentrations (0-150 mg/L) were used. The results showed that the Egyptian *Morinaga oleifeara*, at a dose of 150 mg/L, has the highest performance in terms of Cd removal.

Ravikumar and Udayakumar (2020) investigated the performance of the Moringa seed coagulation process followed by bentonite clay adsorption for heavy metal removal from drinking water. The results pointed that the removal efficiency of Cr, Pb, and Cd was higher than 98% in the pH range of 2 to 8, indicating that the natural coagulant could work in a wide pH range. In a study, (Ali and Seng (2018) investigated the removal of heavy metals from river water samples using *Moringa oleifeara* press cake. The results indicated that the removal efficiency of Cr, Cu and Fe was 93.73, 88.86 and 66.99%, respectively.

Soumaoro *et al.* (2021) investigated the accumulation of heavy metals in chickens drinking water treated with *Moringa oleifeara*. The results indicated that the bioaccumulation of As, Cd, Cr, Cu, Ni and Pb was lower in chickens drinking water treated with *Moringa oleifeara*. The results suggest that *Moringa oleifera* seeds are a natural coagulant that may treat water containing the unwanted concentration of heavy metals and ensure poultry meat is safe for consumption. Interestingly, Hassanein *et al.* (2017) investigated the remediation of chromium-contaminated soil for agricultural purposes by adding (1 g/Kg) of *Moringa oleifera*. The results showed that powdered Moringa seeds protected the wheat crop against cadmium toxicity.

In a later study, Mehdinejad and Bina (2018) examined the removal of heavy metals from raw water using

Moringa oleifera as a coagulation aid with Alum. The results suggest that metal ions are removed more efficiently with increasing turbidity, possibly due to coagulant efficiency and adsorption of metal ions to solids at high turbidity. However, most studies in the literature have focused on the performance of *Moringa oleifera* as a plant-based coagulant for water and wastewater purification. Other studies also highlight the performance of other plants such as henna, tannin and *opuntia ficus*. In a recent study, Mehrmand *et al.* (2022) studied the removal of Pb, Cu and Ni using z functionalized henna powder. The results showed that the main mechanism was adsorption. The adsorption isotherm for Pb and Cu was Langmuir, whereas Ni corresponds to the Freundlich isotherm.

In another study, Banch *et al.* (2019) examined the performance of a natural tannin-based coagulant to remediate stabilized leachate. The removal efficiency of heavy metals (Fe, Zn, Cu, Cr, Cd, Pb, As and Co) was also examined. The results suggest that organic molecules and heavy metals can be effectively removed from stabilized landfill leachate using a tannin-based natural coagulant. In a later study, Righetto *et al.* (2021) evaluated the performance of tannin coagulating products to treat leachate. Heavy metal removal was also examined. The results reported high removal of Fe (92%), Cr (68%), Ba (48%), Ti (91%), Al (51%), and vanadium (V) 44%, while other elements were removed in small amounts: Mn (33%), Ni (14%), B (15%), Si (4%), and Sr (8%). The results indicated that the main mechanism of removal was the complexion with tannin.

Apandi *et al.* (2019) indirectly used natural coagulant to remove heavy metals from wet market wastewater. Firstly, the phycoremediation method was used to remove heavy metals by cultivating *Scenedesmus* species. In the next step, two natural coagulants (*Cajanus cajan* and *Cicer arietinum*) were used to harvest microalgae. The results showed that Cd, Cr, and Fe removal efficiency was 87.24, 85.55, and 90.35%, respectively, while the harvesting capacity was higher than 85% for the two natural coagulants.

Wan *et al.* (2019) studied the performance of *Opuntia ficus* as a natural coagulant for the treatment of tailings pond water. The results showed that *Opuntia ficus* exhibited higher Arsenic (As) removal than chemical coagulants such as ferric chloride and Alum. In a recent study, Solano *et al.* (2022) investigated the performance of *Opuntia ficus* as a natural coagulant for heavy metals removal from river water samples. The results showed that the heavy metals removal efficiency was Fe (90%), Mn (90%) and more than 60% for Cr and As, while the removal efficiency of Cd, Pb, and Ni was less than 40%. The results revealed that the percentages of heavy metals removed are determined by the appropriate initial pH conditions, the initial heavy metal concentrations in the water samples, and the mucilage content.

In another study, Abrha *et al.* (2019) examined the performance of chemically treated (HCl and NaOH) *Opuntia ficus* to remove Zn and Mn from synthetic aqueous solution. The results showed that *Opuntia ficus* treated with NaOH exhibited a significant increase in removal efficiency for Zn (from 36 to 95.9%) and Mn (from 33.2 to 88.6%). The removal efficiency increased due to increased oxygen and decreased carbon content after NaOH treatment. Since adsorption is the main mechanism for removing heavy metals from wastewater using plants/animal parts, many studies have reported the adsorption capacity of natural coagulants. In a study, Ridzwan *et al.* (2022) studied the performance of dried cockle shells as natural coagulants to remove Cu and Mn from Synthetic wastewater. The results indicated that Mn was adsorbed on the Cockleshell due to monolayer adsorption (monolayer adsorption is usually completed by binding the solute molecule onto the dried cockle shell adsorbent surface through chemisorption reaction), where the Gaussian energy distribution onto the heterogeneous surface was responsible for Cu adsorption. Cu and Mn removal efficiency were 88.9% and 77,8%, respectively, at an optimal dose of 150 g/L and a contact time of 105 minutes.

El-Chaghaby *et al.* (2020) used the dried leaves of *Bougainvillea glapra* to Pb remove from wastewater. The results indicated that the maximum removal efficiency was 84.65% when the initial concentration of Pb was 25 mg/L. The presence of various active surface groups capable of binding adsorbate ions. The study showed that the dried leaves of *Bougainvillea glapra* could be used as environmentally friendly bio-sorbents to remove lead ions from synthetic wastewater. In another study, Ravikumar and Udayakumar (2021) studied the coagulo-adsorbents process's performance for removing heavy metals from drinking water. The composite process used *Moringa oleifera* gum with bentonite clay. The findings suggest that clay-polymer composites of *Moringa oleifera* gum and bentonite clay have a higher metal ion removal capacity (up to 100 percent reduction).

Halysh *et al.* (2020) examined the performance of Walnut shells for heavy metals removal from low-waste water demineralization systems. Orthophosphoric acid was used to treat the shells before the biosorption experiment. The results showed that the pretreatment of Walnut shells with inorganic acid plays an important role in the adsorption capacity of the shells. The increased concentration of treated acid leads to the enhancement of shells' adsorption properties. The use of algae-based natural coagulant/bio-adsorbent has not been well studied in the literature; however, there are few attempts to use algae-based natural material for the removal of heavy metals removal from wastewater. In a study, Pham *et al.* (2021) investigated the role of modified *H. fusiformis* algae (pretreated with NaOH and HCl) to produce a bio-adsorbent material to remove Cd, Ni, Cu, and Pb from synthetic wastewater. The results showed that pretreatment with NaOH significantly improved the biosorption efficiency of algae.

In contrast, the HCl modification did not improve the biosorption capability of algal cells. Moreover, heavy metal biosorption onto the algal cell surface was enhanced when the pH of the solution increased. These results suggest that *H. fusiformis* could be a better metal biosorption option.

In another study, Badr *et al.* (2020) used an experimental factorial method to optimize Se adsorption on *Cyperus laevigatus* cell surface from an aqueous solution. The operating conditions were studied, such as pH, initial Se concentration, contact time, and algae dosage. Results showed that pH and initial Se concentration significantly affected Se adsorption. Low pH 2 was considered optimal for Se removal, whereas the increased initial concentration of Se decreased the removal efficiency.

Agunbiade *et al.* (2019) studied the flocculation capability of a biopolymeric flocculant produced by *Terrabacter* sp. to remove heavy metals from dairy wastewater. The results showed a high removal efficiency for Fe (77.7%), Al (74.8%), Mn (61.9%) and Zn (57.6%). According to Fourier transform infrared spectroscopy (FTIR), the pure bioflocculant contained carboxyl, hydroxyl and amino groups, which may be responsible for flocculation. The results demonstrated that the Bioflocculant might be an alternative candidate for wastewater treatment and heavy metal remediation. Many studies have compared the performance of natural coagulants with chemical coagulants to assess the visibility of alternative chemicals with biocoagulents. In a study, Nyström *et al.* (2020) studied the efficiency of five coagulants (Chitosan, Iron chloride, Alum, and two pre-hydrolyzed aluminum coagulants) for the treatment of semi-synthetic stormwater. Results showed that all coagulants performed well (average 90% removal) in terms of metals removal. However, the chitosan-based coagulant removed more than 72% of Cu, while the Alum only removed 55 %. In addition, dissolved Zn was only reduced when chitosan was used. These results reveal that natural coagulants like chitosan may perform better than chemical coagulants.

In another study, (Wan *et al.* (2019) compared the performance of *Opuntia ficus-indica*, Alum, and ferric chloride for tailings pond water treatment. Interestingly, *Opuntia ficus*-based coagulants showed higher removal of As (64%) than Alum and ferric chloride. The increased As removal by *Opuntia ficus* could be attributed to the proton in the O.H. group in the mucilage polymer (polymer containing *Opuntia ficus*) that attracted the O atom in the arsenate anions resulting from the binding between polymers and As, whereby a coagulation effect occurs. In a subsequent study, Jagaba *et al.* (2021) investigated the performance of five coagulants: Alum, ferric chloride, zeolite, chitosan, and *Moringa oleifera* seed extract for the removal of heavy metals from wastewater. The results indicated that chitosan as a biopolymer and natural coagulant exhibited the highest removal efficiency for Pb, Cd, Mn and Fe, followed by *Moringa oleifera* and least for zeolite coagulants. The study suggests that natural coagulants such as *Moringa oleifera* and chitosan could replace chemical coagulants as they require less dosage and are less harmful to the environment (Table 1).

Table 1.: Application of natural coagulant for removing heavy metals from different wastewater types

Coagulants	Properties	Contaminants	Conditions	Findings	Reference
Chitosan	Animal-Based	Cu, Cr, and Ni	• Cu, Cr, and Ni initial concentration 20.0 mg/L • Coagulant dosage 2.0 mg/L	• According to the Zeta potential detection, chelation, charge neutralization, adsorption bridging, and seep flocculation are the key mechanisms for eliminating heavy metals.	(Sun *et al.*, 2019)
Chitosan	Animal-Based	Ca, Cr, Cu, Pb, Ni, Zn, and Cd	• Coagulant dosage (150–180 mg/L)	• The strong relationship between the electrokinetic properties of heavy metals hydroxides and the physicochemical characteristics (charge and size) of coagulants and metals removal efficiency suggests that coagulants perform complementary functions such as chemical affinity electrostatic interaction and particle entrapment under the conditions used.	(López-Maldonado *et al.*, 2017)

Moringa oleifera	Plant-based	Cd, Cr, Fe, Cu, Co, Pb. Mn and Zn	• Coagulant dosage (125, 250, 375, 500, 625, 750) mg/L	• Heavy metals may be efficiently removed from tannery wastewater using *Moringa oleifera* seed extract. • The study found a significant reduction in physicochemical and heavy metal parameters when tannery effluent was treated using *Moringa oleifera* seed extract.	(Tanko *et al.*, 2020)
Moringa oleifera sand Musa cavendish.	Plant-Based	Ni, Pb, and Cd	• The initial concentrations of heavy metals; Pb (0.024–0.483) µmol/L; • Ni (0.170-1.704) µmol/L; • Cd (0.009–0.098) µmol/L) • Coagulant dosage 200 mg/L • pH 7	• The efficiency of the bio-coagulant is attributable to the existence of functional groups with a high capacity for adsorbing heavy metal ions.	(Aziz *et al.*, 2021)
Moringa oleifera	Plant-Based	Cd and Fe	• Coagulant dosage (50, 100, 150) mg/L	• Moringa-treated urban wastewater has a high T.K.N. content, making it suitable for agricultural irrigation because it eliminates the need for chemical nitrogen fertilizers. As a result, urban wastewater treated with *M. oleifera* coagulants can be used for irrigation without causing harm to crops, soil, animals, or humans.	(Marzougui *et al.*, 2021)
Moringa oleifera	Plant-based	Fe, Cu, and Cr	• Heavy metals initial concentration (1,2,4) mg/L • Coagulant dosage (1000-20000) ppm	• *Moringa oleifera* is an excellent heavy metal remover. The heavy metal removal percentage was increased as the coagulant concentration rose until the optimum concentration was reached.	(Ali and Tien Seng, 2018)
Henna powder	Plant-based	Cu, Pb, and Ni	• Heavy metals initial concentration (10-50) mg/L • Henna powder concentration (1000-5000) mg/L • Temperature (15, 25, 40, 60) ^{0}C	• Because henna is employed solely to synthetized the adsorbent (without being washed with water), the adsorbent contains various chemical components,	Mehrmand *et al.*, 2022)

			• pH 2-8	resulting in excellent metal adsorption efficiency in both acidic and basic conditions.	
Tannin-based product	Plant-Based	Fe, Ti, Cr, Al, Ba and V	•Coagulant dosage (5-20) mL/L •pH 6-8	• Tannin was shown to create sludge of comparable or superior quality to that produced by conventional coagulants.	(Righetto *et al.*, 2021b)
Opuntia ficus	Plant-Based	Fe, Mn, Cr, Ar, Cd, Ni, and Pb	•pH (6-8.5) • coagulant dosage (87.5, 175, 350) mg/L • heavy metals concentration (0.05-1.5) mg/L	• The appropriate initial pH conditions determine the varying percentages of heavy metals removed, initial heavy metal concentrations in Yautepec River water samples, and mucilage concentration.	(Vargas-Solano *et al.*, 2022)
Five different coagulants		Cd, Cr, Cu, Ni, Pb, and Zn	• Stormwater samples were collected and analyzed in terms of heavy metals, organic, and inorganic contents.	• The removal of dissolved copper differed among the coagulants studied, with chitosan having a 72 percent higher removal impact than the other coagulants. Chitosan was the sole coagulant that appeared to remove the dissolved fraction of zinc (51 percent).	(Nyström *et al.*, 2020)

4. Recommendation and future directions

Despite the advantages of using natural coagulants over chemical coagulants, there are many disadvantages of using natural coagulants in water and wastewater treatment that raise issues for future research. Current process of extracting coagulants from animal and plants are complicated; therefore, a novel, reliable, and simple extraction process should be developed to use natural coagulants easily. In some studies, Chemical coagulants have been shown to have higher removal efficiency than natural coagulants. Nevertheless, improving natural coagulant extraction procedures may enhance the removal efficincy of these green coagulants, requiring further investigations in this area. Since the water and wastewater sector uses so many of these coagulants, finding new sources for producing natural coagulants is an important task. More research is needed to find new sources of natural coagulants, such as non-edible plants or novel medicinal plants, and the best parameters for a green coagulation mehods for different wastewaters. Further investigatuins should be conducted to explore the effectiveness of natural coagulants in removing heavy metals from water and wastewater.

5. Conclusion

Heavy metals are difficult to remove from water and wastewater because of their low concentration and susceptibility to biodegradation. Many studies have shown that natural coagulants can be used to remediate water and wastewater. Adsorption and polymer bridging are the two main mechanisms natural coagulants use to remove heavy metals from water and wastewater. Plant-based coagulants are cheaper than animal-based coagulants. While the research using natural coagulants to remove heavy metals from various environmental systems is limited, the available data shows that this bio-coagulation has a bright future in wastewater treatment. Natural coagulants are preferable to chemical coagulants because they require less dosage, produce less sludge, and have low/no toxicity. Further research is needed in areas such as developing effecinetn extraction process, evaluating the effect of environmental parameters on process performance to complete the transition from chemical coagulant to a natural coagulant, discovering new sources for natural coaulents, and optimize the coagulation process optimal for heavy metals removal.

Acknowledgement

The research leading to these results has received funding from Ministry of Higher Education, Research, and Innovation (MoHERI) of the Sultanate of Oman under the Block Funding Program, MoHERI Block Funding Agreement No. MoHERI/BFP/ASU/01/2021.

References

Abiyu A., Yan D., Girma A., Song X., and Wang H. (2018). Wastewater treatment potential of Moringa stenopetala over Moringa olifera as a natural coagulant, antimicrobial agent and heavy metal removals. *Cogent Environmental Science,* **4**. https://doi.org/10.1080/23311843.2018.1433507.

Abrha Y.W., Kye H., and Kang J.W. (2019). Chemically treated cactus (Opuntia) as a sustainable biosorbent for the removal of heavy metals from aqueous solution: Characterization and adsorption capacity. *Desalin. Water Treat,* **144**, 345–354. https://doi.org/10.5004/dwt.2019.23580.

Abujazar M.S.S., Karaağaç S.U., Abu Amr S.S., Alazaiza M.Y.D., and Bashir M.J. (2022). Recent advancement in the application of hybrid coagulants in coagulation-flocculation of wastewater: A review. *Journal of Cleaner Production,* **345**. https://doi.org/10.1016/j.jclepro.2022.131133.

Agunbiade M.O., Pohl C., Heerden E. Van, Oyekola O., and Ashafa A. (2019). Evaluation of fresh water actinomycete bioflocculant and its biotechnological applications in wastewaters treatment and removal of heavy metals. *Journal of Environmental Research and Public Health,* **16,** 1–15. https://doi.org/10.3390/ijerph16183337.

Ahmad A., Kurniawan S.B., Abdullah S.R.S., Othman A.R., and Hasan H.A. (2022). Exploring the extraction methods for plant-based coagulants and their future approaches. *Science of the Total Environment,* **818**, 151668. https://doi.org/10.1016/j.scitotenv.2021.151668.

Ali E.N., Tien Seng H. (2018). Heavy Metals (Fe, Cu, and Cr) Removal from Wastewater by Moringa Oleifera Press Cake. *MATEC Web of Conferences,* **150**, 1–5. https://doi.org/10.1051/matecconf/201815002008.

Apandi N.M., Sunar N.M., Maya R., and Radin S. (2019). Scenedesmus sp . harvesting by using natural coagulant after phycoremediation of heavy metals in different concentration of wet market wastewater for potential fish feeds*,* 1–23.

Azi N.A.A., Jayasuriya N., Fan L., and Al-Gheethi A. (2021). A low-cost treatment system for underground water using Moringa oleifera seeds and Musa cavendish peels for remote communities. *Journal of Chemical Technology and Biotechnology,* **96,** 680–696. https://doi.org/10.1002/jctb.6581.

Badr N.B.E., Al-Qahtani K.M., and Mahmoud A.E.D. (2020). Factorial experimental design for optimizing selenium sorption on Cyperus laevigatus biomass and green-synthesized nano-silver. *Alexandria Engineering Journal,* **59**, 5219–5229. https://doi.org/10.1016/j.aej.2020.09.051.

Bahrodin M.B., Zaidi N.S., Hussein N., Sillanpää M., Prasetyo, D.D., and Syafiuddin, A. (2021). Recent Advances on Coagulation-Based Treatment of Wastewater: Transition from Chemical to Natural Coagulant. *Current Pollution Reports*, **7**, 379–391. https://doi.org/10.1007/s40726-021-00191-7.

Banch T., Hanafiah M., Alkarkhi A., Abu S. (2019). Factorial Design and Optimization of Landfill. *Polymers* (Basel).

Cho Y.W., Yun J.H., Kwon S.H., Eom Y.J., and Kim W.J. (2020). Aggregate removal of particulate matter by selective protein-rich fraction of Moringa oleifera extract. *Journal of Industrial and Engineering Chemistry,* **81**, 161–166. https://doi.org/10.1016/j.jiec.2019.09.004.

Dao M.T., Nguyen V.C.N., Tran T.N., Nguyen X. Du, Vo D.T., Nguyen V.K., Hoang L.T.T.T. (2021). Pilot-Scale Study of Real Domestic Textile Wastewater Treatment Using Cassia fistula Seed-Derived. *coagulant Journal of Chemistry*. https://doi.org/10.1155/2021/7608856.

Das N., Ojha N., Mandal S.K. (2021). Wastewater treatment using plant-derived bioflocculants: Green chemistry approach for safe environment. Water. *Science and Technology,* **83**, 1797–1812. https://doi.org/10.2166/wst.2021.100.

Deepa D., Keerthana R., Pratheep Kumar R., and Suryaprakash R. (2022). Primary treatment of dairy wastewater using bio based natural coagualnts. *Materials Today: Proceedings*. https://doi.org/10.1016/j.matpr.2022.02.125.

El-Chaghaby G.A., Rashad S., and Abd El-Kader S.F. (2020). Dried leaves of bougainvillea glabra plant for the removal of lead ions from aqueous solution by adsorption. *Egyptian Journal of Botany,* **60**, 707–718. https://doi.org/10.21608/ejbo.2020.26449.1476.

El-Gaayda J., Titchou F.E., Oukhrib R., Yap P.S., Liu T., Hamdani M., and Ait Akbour R. (2021). Natural flocculants for the treatment of wastewaters containing dyes or heavy metals: a state-of-the-art review. *Journal of Environmental Chemical Engineering,* **9**, 106060. https://doi.org/10.1016/j.jece.2021.106060.

Gomes H.de O., Freire P. de T.C., do Nascimento R.F., and Pereira Teixeira R.N. (2022). Removal of contaminants from water using Moringa oleifera Lam. as biosorbent: An overview of the last decade. *Journal of Water Process Engineering,* **46**, 102576. https://doi.org/10.1016/j.jwpe.2022.102576.

Halysh V., Trus I., Gomelya M., Trembus I., Pasalskiy B., Chykun N., Trokhymenko G., and Remeshevska I. (2020). Utilization of modified biosorbents based on walnut shells in the processes of wastewater treatment from heavy metal ions. *Journal of Ecological Engineering,* **21***,* 128–133. https://doi.org/10.12911/22998993/119809.

Hassanein R.A., Abdelkader A.F., and Faramawy H.M. (2017). Defatted coagulant seeds of moringa oleifera and moringa peregrena mediate alleviation of cadmium toxicity in wheat (triticum aestivum L.) plant. *Plant Omics,* **10**, 127–133. https://doi.org/10.21475/poj.10.03.17.pne423.

Iber B.T., Okomoda V.T., Rozaimah S.A., Kasan N.A. (2021). Eco-friendly approaches to aquaculture wastewater treatment: assessment of natural coagulants vis-a-vis chitosan. *Bioresource Technology Reports,* **15**, 100702. https://doi.org/10.1016/j.biteb.2021.100702.

Ibrahim A., Yaser A.Z., Lamaming J. (2021). Synthesising tannin-based coagulants for water and wastewater application: A review. *Journal of Environmental Chemical Engineering,* **9**, 105007. https://doi.org/10.1016/j.jece.2020.105007.

Jagaba A.H., Kutty S.R.M., Hayder G., Baloo L., Ghaleb A.A.S., Lawal I.M., Abubakar S., Al-dhawi B.N.S., Almahbashi N.M.Y. and Umaru I. (2021). Degradation of Cd, Cu, Fe, Mn, Pb and Zn by Moringa-oleifera, zeolite, ferric-chloride, chitosan and alum in an industrial effluent. *Ain Shams Engineering Journal,* **12**, 57–64. https://doi.org/10.1016/j.asej.2020.06.016.

Kanmani P., Aravind J., Kamaraj M., Sureshbabu P. and Karthikeyan S. (2017). Environmental applications of chitosan and cellulosic biopolymers: A comprehensive outlook. *Bioresource Technology,* **242**, 295–303. https://doi.org/10.1016/j.biortech.2017.03.119.

Kristianto H. (2021). Recent advances on magnetic natural coagulant: a mini review. *Environmental Technology Reviews,* **10**, 254–269. https://doi.org/10.1080/21622515.2021.1986576.

Lamaming J., Saalah S., Rajin M., Ismail N.M., Yaser A.Z. (2022). A Review on Bamboo as an Adsorbent for Removal of Pollutants for Wastewater Treatment. *International Journal of Chemical Engineering*. https://doi.org/10.1155/2022/7218759.

López-Maldonado E.A., Zavala García O.G., Escobedo K.C., and Oropeza-Guzman M.T. (2017). Evaluation of the chelating performance of biopolyelectrolyte green complexes (NIBPEGCs) for wastewater treatment from the metal finishing industry. *Journal of Hazardous Materials,* **335**, 18–27. https://doi.org/10.1016/j.jhazmat.2017.04.020.

Lu C., Xu Z., Dong B., Zhang Y., Wang M., Zeng Y., and Zhang C. (2022). Machine learning for the prediction of heavy metal removal by chitosan-based flocculants. *carbohydrate polymers,* **285**, 119240. https://doi.org/10.1016/j.carbpol.2022.119240.

Marzougui N., Guasmi F., Dhouioui S., Bouhlel M., Hachicha M., Berndtsson R., and Sleimi N. (2021). Efficiency of different moringa oleifera (Lam.) varieties as natural coagulants for urban wastewater treatment. *Sustainability,* **13***,* 1–14. https://doi.org/10.3390/su132313500.

Mehdinejad M.H., and Bina B. (2018). Application of moringa oleifera coagulant protein as natural coagulant aid with alum for removal of heavy metals from raw water. *Desalination Water Treatment,* **116**, 187–194. https://doi.org/10.5004/dwt.2018.22546.

Mehrmand N., Moraveji M.K., and Parvareh A. (2022). Adsorption of Pb(II), Cu(II) and Ni(II) ions from aqueous solutions by functionalised henna powder (Lawsonia Inermis); isotherm, kinetic and thermodynamic studies. *International Journal of Environmental Analytical Chemistry*, **102**, 1–22. https://doi.org/10.1080/03067319.2020.1715376.

Nath A., Mishra A., Pande P.P. (2019). A review natural polymeric coagulants in wastewater treatment. *Materials Today: Proceedings*, **46**, 6113–6117. https://doi.org/10.1016/j.matpr.2020.03.551.

Nimesha S., Hewawasam C., Jayasanka D.J., Murakami Y., Araki N., and Maharjan N. (2022). Effectiveness of natural coagulants in water and wastewater treatment. *Global Journal of Environmental Science and Management*, **8**, 101–116. https://doi.org/10.22034/gjesm.2022.01.08.

Nyström F., Nordqvist K., Herrmann I., Hedström A., and Viklander, M. (2020). Removal of metals and hydrocarbons from stormwater using coagulation and flocculation. *Water Research*, **182**. https://doi.org/10.1016/j.watres.2020.115919.

Okolo B.I., Adeyi O., Oke E.O., Agu C.M., Nnaji P.C., Akatobi K.N.,and Onukwuli, D.O. (2021). Coagulation kinetic study and optimization using response surface methodology for effective removal of turbidity from paint wastewater using natural coagulants. *Science Africa*, **14,** e00959. https://doi.org/10.1016/j.sciaf.2021.e00959.

Omer A.M., Dey R., Eltaweil A.S., Abd El-Monaem E.M., Ziora, Z.M. (2022). Insights into recent advances of chitosan-based adsorbents for sustainable removal of heavy metals and anions. *Arabian Journal of Chemistry*, **15,** 103543. https://doi.org/10.1016/j.arabjc.2021.103543

Owodunni A.A., Ismail S. (2021). Revolutionary technique for sustainable plant-based green coagulants in industrial wastewater treatment—A review. *Journal of Water Process Engineering*, **42**, 102096. https://doi.org/10.1016/j.jwpe.2021.102096.

Pham B.N., Kang J., Lee C., and Park S. (2021). applied sciences Solution Using Hizikia fusiformis as an Algae-Based Bioadsorbent, **11**, 1–13.

Qasem N.A.A., Mohammed R.H., and Lawal D.U. (2021). Removal of heavy metal ions from wastewater: a comprehensive and critical review. *npj Clean Water*, **4**. https://doi.org/10.1038/s41545-021-00127-0.

Rajoria S., Vashishtha M., and Sangal V.K. (2022). Treatment of electroplating industry wastewater: a review on the various techniques. *Environmental Science and Pollution Research*. Springer Berlin Heidelberg. https://doi.org/10.1007/s11356-022-18643-y.

Ravikumar K., and Udayakumar J. (2021). Moringa oleifera gum composite a novel material for heavy metals removal. *International Journal of Environmental Analytical Chemistry*, **101**, 1513–1553. https://doi.org/10.1080/03067319.2019.1686142.

Ravikumar K., Udayakumar J. (2020). Moringa oleifera biopolymer coagulation and bentonite clay adsorption for hazardous heavy metals removal from aqueous systems. *Geosystem Engineering*, **23**, 265–275. https://doi.org/10.1080/12269328.2020.1778544

Razzak S.A., Faruque M.O., Alsheikh Z., Alsheikhmohamad L., Alkuroud D., Alfayez A., Hossain S.M.Z., and Hossain M.M. (2022). A comprehensive review on conventional and biological-driven heavy metals removal from industrial wastewater. *Environmental Advances*, **7**, 100168. https://doi.org/10.1016/j.envadv.2022.100168.

Ridzwan N.F.A.A., Aziz N.A., Akbar N.A., Ghani Z.A., Hamzah N., Zin N.S.M. (2022). Removal of Mn and Cu Ions in Synthetic Wastewater Using Dried Cockle Shell. *Environment and Ecology Research*, **10**, 31–43. https://doi.org/10.13189/eer.2022.100104.

Righetto I., Al-Juboori R.A., Kaljunen J.U., and Mikola A. (2021)a. Multipurpose treatment of landfill leachate using natural coagulants - Pretreatment for nutrient recovery and removal of heavy metals and micropollutants. *Journal of Environmental Chemical Engineering*, **9**. https://doi.org/10.1016/j.jece.2021.105213.

Righetto I., Al-Juboori R.A., Kaljunen J.U., Mikola A. (2021)b. Multipurpose treatment of landfill leachate using natural coagulants - Pretreatment for nutrient recovery and removal of heavy metals and micropollutants. *Journal of Environmental Chemical Engineering*, **9**, 105213. https://doi.org/10.1016/j.jece.2021.105213.

Saleem M., Bachmann R.T. (2019). A contemporary review on plant-based coagulants for applications in water treatment. *Journal of Industrial and Engineering Chemistry*, **72**, 281–297. https://doi.org/10.1016/j.jiec.2018.12.029.

Saleh T.A., Mustaqeem M., Khaled M. (2022). Water treatment technologies in removing heavy metal ions from wastewater:

A review. Environ. *Nanotechnology,monitoring and management*, **17**, 100617. https://doi.org/10.1016/j.enmm.2021.100617.

Shafiq M., Alazba A.A., Amin M.T. (2018). Removal of heavy metals from wastewater using date palm as a biosorbent: A comparative review. *Sains Malaysiana*, **47**, 35–49. https://doi.org/10.17576/jsm-2018-4701-05.

Shrestha R., Ban S., Devkota S., Sharma S., Joshi R., Tiwari A.P., Kim H.Y., and Joshi M.K. (2021). Technological trends in heavy metals removal from industrial wastewater: A review. *Journal of Environmental Chemical Engineering*, **9**, 105688. https://doi.org/10.1016/j.jece.2021.105688.

Soumaoro I., Pitala W., Gnandi K., and Kokou T. (2021). Health Risk Assessment of Heavy Metal Accumulation in Broiler Chickens and Heavy Metal Removal in Drinking Water using Moringa Oleifera Seeds in Lomé, Togo. *journal of health and pollution*, **11**, 1–15. https://doi.org/10.5696/2156-9614-11.31.210911.

Sun Y., Shah K.J., Sun W., and Zheng H. (2019). Performance evaluation of chitosan-based flocculants with good pH resistance and high heavy metals removal capacity. *Separation and Purification Technology*, **215**, 208–216. https://doi.org/10.1016/j.seppur.2019.01.017.

Sun Y., Zhou S., Pan S.Y., Zhu S., Yu Y., and Zheng H. (2020). Performance evaluation and optimization of flocculation process for removing heavy metal. *Chemical Engineering Journal*, **385**, 123911. https://doi.org/10.1016/j.cej.2019.123911.

Tang X., Huang T., Zhang S., Wang W., and Zheng H. (2020). The role of sulfonated chitosan-based flocculant in the treatment of hematite wastewater containing heavy metals. Colloids Surfaces A *Physicochemical and Engineering Aspects*, **585**, 124070. https://doi.org/10.1016/j.colsurfa.2019.124070.

Tang X., Zheng H., Teng H., Sun Y., Guo J., Xie W., Yang Q., and Chen, W. (2016). Chemical coagulation process for the removal of heavy metals from water: a review. *Desalination. water treatment*, **57**, 1733–1748. https://doi.org/10.1080/19443994.2014.977959.

Tanko M.A., Sanda B.Y., and Bichi M.H. (2020). Application of moringa oleifera seed extract (Mose) in the removal of heavy metals from tannery wastewater. Niger. *Journal Technology Development*, **17**, 70–78. https://doi.org/10.4314/njtd.v17i2.1.

Tomasi I.T., Machado C.A., Boaventura R.A.R., Botelho C.M.S., and Santos S.C.R. (2022). Tannin-based coagulants: Current development and prospects on synthesis and uses. *Science of The Total Environment*, **822**. https://doi.org/10.1016/j.scitotenv.2022.153454.

Vardhan K.H., Kumar P.S., and Panda R.C. (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *Journal of Molecular Liquids*, **290**, 111197. https://doi.org/10.1016/j.molliq.2019.111197.

Vargas-Solano S.V., Rodríguez-González F., Martínez-Velarde R., Morales-García S.S., Jonathan M.P. (2022). Removal of heavy metals present in water from the Yautepec River Morelos México, using Opuntia ficus-indica mucilage. *Environmental Advances*, **7**. https://doi.org/10.1016/j.envadv.2021.100160.

Vega Andrade P., Palanca C.F., de Oliveira M.A.C., Ito C.Y.K., and dos Reis A.G. (2021). Use of Moringa oleifera seed as a natural coagulant in domestic wastewater tertiary treatment: Physicochemical, cytotoxicity and bacterial load evaluation. *Journal of Water Process Engineering*, **40**. https://doi.org/10.1016/j.jwpe.2020.101859.

Vidu R., Matei E., Predescu A.M., Alhalaili B., Pantilimon C., Tarcea C., *et al.* (2020). Removal of heavy metals from wastewaters: A challenge from current treatment methods to nanotechnology applications. *Toxics*, **8**, 1–37. https://doi.org/10.3390/toxics8040101

Wagh M.P., Aher Y., Mandalik A. (2022). Potential of Moringa Oleifera Seed as a Natural Adsorbent for Wastewater Treatment. *Trends Science*, **19**, 1–11. https://doi.org/10.48048/tis.2022.2019.

Wan J., Chakraborty T., Xu C. (Charles), Ray M.B. (2019). Treatment train for tailings pond water using Opuntia ficus-indica as coagulant. *Separation and Purification Technology*, **211**, 448–455. https://doi.org/10.1016/j.seppur.2018.09.083.

Wang R., Liang R., Dai T., Chen J., Shuai X., Liu C. (2019). Pectin-based adsorbents for heavy metal ions: A review. *Trends Food Science and Technology*, **91**, 319–329. https://doi.org/10.1016/j.tifs.2019.07.033.

Yu X., and Fu Y. (2020). Progress in research and application of natural polymer coagulants. *E3S Web Conference*, **143**, 0–3. https://doi.org/10.1051/e3sconf/202014302042.