

REMOVAL OF MERCURY AND LEAD BY BIOADSORBENTS. AN OVERVIEW

FRANCISCA L. ARANDA AND BERNABÉ L. RIVAS*

Polymers Department, Faculty of Chemistry, University of Concepcion, Casilla 3 C, Concepcion, Chile.

ABSTRACT

Humanity and industrialization have led to ecosystems, in all their matrices, being compromised in terms of pollution generated by different metals. Among them we find mercury and lead, both correspond to metals highly dangerous for all ecosystems and their trophic chains. In this review we will look at the dangers of these metals and the ways in which they can be removed, ranging from more traditional processes to adsorption processes with materials derived from natural sources and how they can be an effective source of heavy metal removal.

Keywords: Heavy metals, contaminants, polymers, removal, bioadsorbent.

1. INTRODUCTION

The great increase in the human population and with it industrialization [1-3] have caused different ecosystems to be severely affected by different types of pollution. Currently, heavy metal pollution in water bodies is a growing and constant concern due to the serious problems generated around the world. These inorganic pollutants affect both surface and groundwater [4] directly affecting aquatic ecosystems and human health. Having the ability to bioaccumulate [5-7] in organisms, generate different types of adverse effects and can lead to death. This type of pollution is mainly associated with mining companies, petroleum refining, textiles, production of pesticides, paints, pigments, among others [8, 9]. Some authors [8] mention that unlike organic compounds, these are not biodegradable to any degree, making them more dangerous. Due to the significant threat to environmental and human health [10], this problem not only occurs in different bodies of water but also includes all matrices: Air pollution substantially affects the quality of both soil and water [11]. In the case of soil pollution, this is generated due to the indiscriminate release of different types of pollutants, among which are hydrocarbons, metals, pesticides, etc. Although these heavy metals are naturally in the Earth's crust, each of the human activities related to these inorganic compounds have led to a strong biochemical and biogeochemical imbalance [3, 12, 13]. Thus, in the case of water pollution, it occurs due to direct factors, such as discharges from industrialists, and indirect factors such as rainfall, or water runoff through the soil [10, 11, 14, 15]. To treat this problem, a number of removal methods have been suggested including chemical precipitation [16], electrodialysis, MOFs [17], flotation [18],

membrane filtration [19], photocatalysis [20], nanofiltration [21] and adsorption [22-25]. However, this article will detail the different methods of adsorption, emphasizing removal using environmentally friendly materials.

1.1 Heavy metals

Metals have a wide variety of applications and that is why their importance is great. They are present in different metabolic and biochemical functions, however, serious problems can be caused if there is a deficit or excess of them. However, due to the great industrialization, large amounts of organic and inorganic pollutants have been released. The latter correspond largely to heavy metals that, due to their high molecular weights and densities above 5 g cm^{-3} [26, 27], it becomes more difficult to remove them. As mentioned above, these types of elements generate many non-beneficial impacts for the environment, accumulating in all food webs and seriously threatening the health of all organisms [11, 28-32]. Among the most researched and relevant heavy metals in the environmental sector are As, Cd, Cr, Hg, Pb, Ni, and Zn [33, 34], metals that when in contact with different ligands can influence characteristics such as toxicity and their environmental fate. There are records in which an increase in cell mortality is determined due to EDTA-Cu complexes [35], damage to the lungs and kidneys due to cadmium [23, 36] and other diseases associated with different heavy metals as detailed in Table 1.

Table 1. General aspects of different heavy metals.

Metal	Toxicity	Main sources	Permitted levels (domestic water) (mg L^{-1})*	Reference
Arsenic	Dangers to the circulatory system and skin, can cause cancer	Agricultural, electronic waste, metal smelting	0.01	[27]
Cadmium	Damage to lungs, kidneys and osteoporosis	Batteries, natural sources, mining and/or metal working	0.003 - 0.005	[23, 36]
Mercury	Damage to the heart, brain, delayed mental development	Mining	0.002	[36]
Lead	Arthritis, renal dysfunction, fatigue, hallucinations, hypertension.	Mining	0.01	[37]
Cinc	Severe intoxications	Industrial emissions	5	[38]
Copper	Damage, in proteins, lipids, DNA, production of free radicals.	Agriculture, mining	1.3	[39]
Chromium	DNA damage, cancer development	Metal fabrication, energy production	0.05	[40]

This review will look at the general and chemical aspects of the metals mercury (Hg) and lead (Pb), as well as their effective removal.

1.2 Mercury (Hg)

Although different geological processes, such as magmatic intrusion and hydrothermal cycles can be important sources of Hg[41], this is one of the heavy metals that is mostly emitted in different ways into the environment by industries in which the burning of fossil fuels occurs [42] such as coal, production of nuclear fuel corresponding to the purification of uranium and separation of the isotopes U235 and U238 [43] and in addition to the incomplete burning of waste that has mercury [44]. Metal that at room temperature is liquid and where its different forms in which mercury exists, whether elemental, organic and

inorganic, causes it to present different types of toxicity to the environment [44-46]. As for inorganic mercury, it can be found in the form of mercury chloride (HgCl_2), which being a highly volatile compound exists in the form of atmospheric gas, mercury oxide (HgO), mercury hydroxide ($\text{Hg}(\text{OH})_2$), and mercury sulfide (HgS). It has the organic form of mercury when it combines with carbon and forms methylmercury compounds such as CH_3HgCl and CH_3HgOH . This is how mercury species with an oxidation state +2 correspond to a highly toxic form that, as has been exposed, is released into the environment by different anthropogenic and natural sources [19].

Organic mercury species such as methylmercury (MeHg), ethylmercury (EtHg), dimethylmercury (Me₂Hg), phenylmercury (PhHg) [47] and their inorganic forms are extremely important because they are used as parameters for the quality of the environment because, as already mentioned, they accumulate at different levels of the trophic chain being absorbed by plants where they then go to higher organisms generating serious problems [48] (see Figure 1).

1.2.1 Methylmercury

It corresponds to one of the organic and highly toxic forms of mercury, contained mainly in fish where it is predominantly found and where records point to a value greater than 80%. Although this species is associated with neuromuscular disorders [49], visual deficit, problems with speech, hearing [50], liver and heart [51], the mechanism by which methyl mercury triggers its toxicity is not fully known [49]

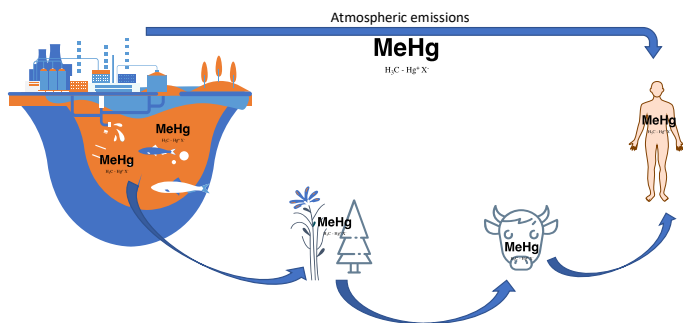


Figure 1. Methyl mercury and its transport in the different trophic plots.

Recently it was discovered that rice is also an important source of MeHg [52] however, the main sources correspond to mining processes [49], specifically gold mining [52] and where its high persistence and biomagnification, make this species, the neurotoxin that seriously threatens human and wildlife [53].

1.2.2 Ethylmercury.

As well as methylmercury, ethylmercury is one of the common species of mercury [54]

and that its greater presence in the environment is due to anthropogenic factors [55]. Exposure to this substance can usually occur at very young ages because ethylmercury is present in some vaccines as a preservative [56, 57] and although it accumulates in different tissues, its half-life is shorter in mammals [49].

1.3 Lead (Pb)

Heavy metal whose main source is given to anthropogenic sources such as lead smelting and extraction [58], lead-based gasoline [59] battery processing and the burning of fossil fuels [58, 60] and that corresponds to one of the metals that at high concentrations turns out to be toxic [61], so like mercury it brings severe consequences for the kidneys [62], liver [63], brain development inducing apoptosis in the tissues of different organs [46]. The damage produced by Pb is such that over time its use in paints [64], gasolines [60, 65], welds [66], etc., where there has been a significant reduction in Pb exposure [59]. However, this element can cause effects that are not only harmful to humans, but also to plants and animals through soil, food, water, dust, etc. (see figure 2) being one of the most toxic due to the destructive influence on different metabolic processes [67]. The toxic nature of lead occurs by coming into contact with the cell and changing the biochemical cycle of life [68].

In addition, there are records where lead, as well as other heavy metals passes through

the blood-brain barrier and leads to a high risk factor for diseases such as senile Alzheimer's [69] and dementia, decreasing IQ, kidney damage, reduced bone growth, carcinogenic problems, ataxia, central nervous system damage and epilepsy [70, 71].

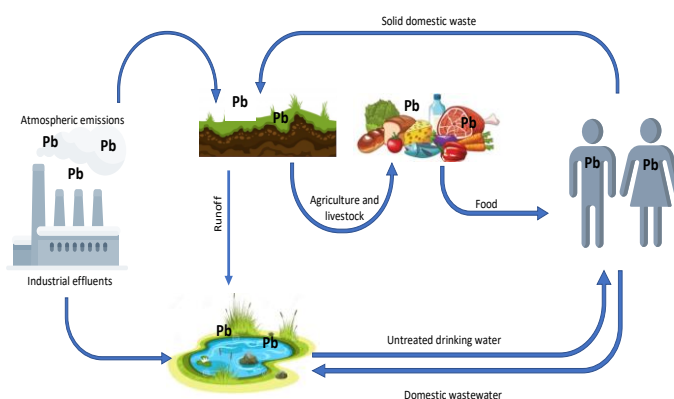


Figure 2. Transport of lead through all matrices

2. REMOVAL OF HEAVY METALS

As already described, heavy metals have a great influence on all ecosystem matrices, affecting at the cellular level the different organisms that are in contact even in small quantities. That is why over the years we have been working on new technologies that are efficient and friendly to the environment so that the removal of metals is as efficient as possible. For this, a wide variety of removal methods have been reported, however, this time we will detail in 2 adsorption methods and in the removal by polymers and some derivatives. As already described, heavy metals have a great influence on all ecosystem matrices, affecting at the cellular level the different organisms that are in contact even in small quantities. That is why over the years we have been working on new technologies that are efficient and friendly to the environment so that the removal of metals is as efficient as possible. For this, a wide variety of removal methods have been reported, however, this time we will detail in 2 adsorption methods and in the removal by polymers and some derivatives.

2.1 Removal by adsorption processes.

A number of adsorption-based remediation techniques have been reported for the effective removal of heavy metals [72]. The efficiency of these techniques is mainly based on the surface of the adsorbent, since the generated system, adsorbate-adsorbent, is the one that will determine the type of interactions: if they are physical they will be Van der Waals forces, or chemical ones such as metallic or covalent forces [73].

2.1.1 Biochar

We well know that mercury and lead are two of the most dangerous heavy metals for

both human and animal health [74], as well as for the ecosystem and all its environmental matrices [75, 76]. In addition, there is a record where both metals mentioned are neurotoxins [77, 78] highly dangerous and that its greatest emissions to the environment are produced by anthropogenic activities and that they are extremely difficult to eliminate due to the high volatility and low solubility in water [79]. Currently, activated carbon is one of the most studied mercury adsorbents but has the disadvantages of being a low yield material and high cost of capital [80], factors that hinder its practical application. Thus, biochar is a good alternative due to its characteristics: porous material, contains various functional groups such as phenol, carboxyl and hydroxyl [81] and are usually made from agricultural, animal and wood residues.

For the elimination of mercury by biochar, a series of methods can be considered, among which electrostatic interactions, ion exchange, precipitation, complexation and physical adsorption stand out [82-84]. There are a number of authors who detail the elimination of mercury, among which is the impregnation of mercury in biochar particles and accumulates on sulfurized biochar surfaces [83]; use of phosphorus-doped biochar as active sites for proper disposal [85]; development of magnetic biochar with tea residues to efficiently and environmentally friendly control the removal of elemental mercury [79]. In addition to mercury, biochar is highly efficient in terms of lead removal, where there is an extensive record in which modified biochar is used for lead removal in aqueous solutions [86-88] and that seems to be a rather promising technique

[89]; it is also argued that biochar modified with cotton stalks are highly efficient in terms of lead removal [90], where their results yielded six different adsorption mechanisms in which we find precipitation, ion exchange, complexation, among others [91]; other authors mention that the biochar of poplar powder [92] provides a good form of adsorption of metals such as Pb^{+2} of wastewater, there are also biochar of straw from crops [93], biochar doped with nitrogen and phosphorus in order to increase and improve its adsorption capacity [94], other Biochar modified with MgO derived from crofton herbs where the author registers high efficiency and low cost for the elimination of Pb^{+2} [95], among other methods using biochar.

2.1.2 Clays

In general, clays can present a high level of environmental protection due to structural properties, where we find octahedral to tetrahedral structures of 1:1 such as kaolinite and 2:1 such as montmorillonite [96]. Because of their structures, they have been extensively studied for metal removal [97, 98], dyes [99] and other organic compounds [100] and inorganic. While modified clays and clays can remove a number of contaminants, there are some of them that are mostly used for the removal of heavy metals, such as montmorillonite [101], bentonite, kaolinite, vermiculite, and illite [102, 103]. Clays have been recorded to very effectively adsorb heavy metals such as lead and mercury [96]. In general, clay minerals behave as if they were chelating ion exchange absorbers for heavy metals [104], which is why clays can be good elements for the removal of metals and even more so modified clays [103] (see figure 3).

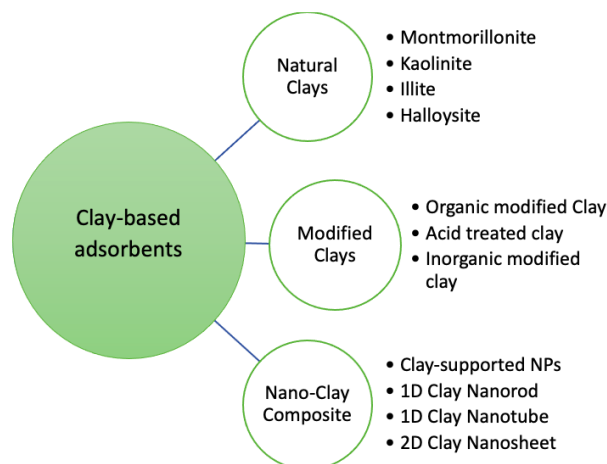


Figure 3. Classification of the different types of clays. Image adapted [103].

This is why there is a series of works where many types of clays are detailed and their importance in terms of the elimination of heavy metals [96-98, 105-110]. Work is reported in which bentonite grafted with poly(N-acrylylglycinemide) (PNAGA – BNT) is used as a new clay-polymer material for the removal of mercury(II) [111] other works mention the montmorillonite processed with acid where they obtain a reduction of lead toxicity 75% [112]; there is also a mining residue that has developed into a new adsorbent, this by modifying copper bromide. This modification is based on tonstein and copper bromide (CuBr₂-TCS) and allowed a removal efficiency ranging between 78.3 and 92.1% [113], other clay modifications are based on halloysite nanotubes, HNT, and where their modification with magnetic microsphericals [CuCl₂ – HNTs (SiO₂-Fe₃O₄)] allowed the removal of mercury HgO, HgO, and HgCl₂ [114].

2.2 Removal by polymer materials

As we have seen so far, there are several effective methods for the removal of different contaminants, traditionally there are the processes of advanced oxidation [115], ion exchange [116], coagulation / flocculation [117] and photocatalysis [118]. In addition to these methods, adsorption methods are one of the methods with high yields due to their characteristics in terms of simplicity, effectiveness and design [73, 119, 120]. However, in recent times the use of polymers as methods of removing contaminants has begun to be widespread, since there are many natural polymers available and synthetic [121] that fulfill this function (see figure 4).

Over time, the appearance of trace metals and other contaminants in the different environmental, food and biological matrices [122] has begun to have greater attention, so the use of polymers for the removal of these contaminants has been a new focus of study. There is extensive literature reporting the use of different types of polymers for the removal of heavy metals and other contaminants [36, 38, 123-134], that is why we will detail in the removal via polymeric hydrogels and chitosan.

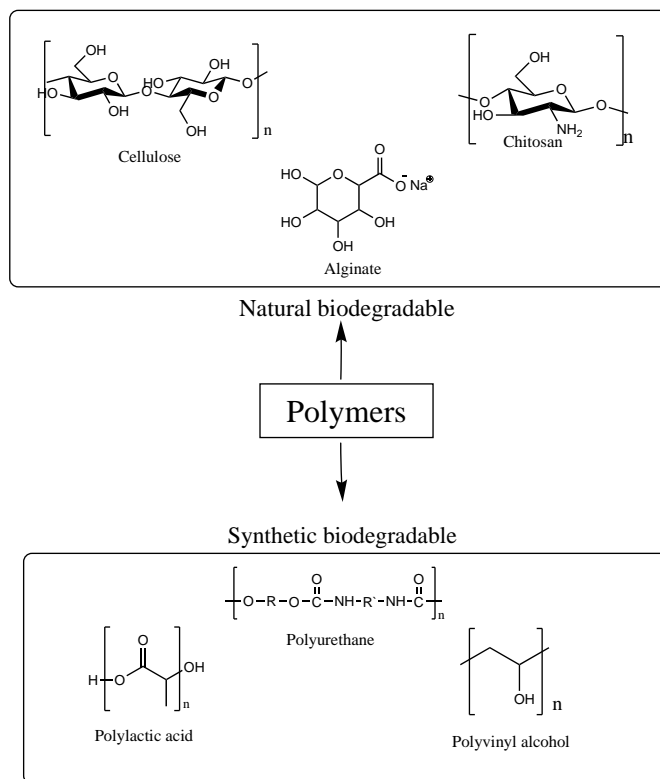


Figure 4. Classification of some natural and synthetic biodegradable polymers.

Hydrogels

Hydrogels are considered three-dimensional cross-linked hydrophilic structures [135-138], are usually polymers, and have as their main characteristic to contain large amounts of water [139]. The swelling to which hydrogels are subjected occurs in 3 steps:

- Diffusion of water in the three-dimensional network of the hydrogel
- The polymer chains are loosened and
- Occurs the expansion of the structure of the hydrogel

The networks of these hydrogels are established through covalent bonds [140] or interactions that are usually physical, such as hydrogen bonds [141], hydrophobic interactions [142], coordination [143], electrostatic [144] and supramolecular [145]. Over the years, a number of natural polymers have been studied such as polypeptides [146], polysaccharides [139], chitosan [147], alginates [148] and synthetic polymers such as acrylamide [149] and polyvinyl alcohol [150] to be able to synthesize hydrogels that have attractive properties [151] and efficient for use in different areas. The advance in the study of removal of contaminants with hydrogels arises from the complete non-efficiency of adsorbent materials, which despite being accessible, fast and having relatively good removal percentages, the lack of active sites [152, 153] for the adsorption of highly toxic heavy metals [154] causes their adsorption capacity to be decreased. Hydrogels, among many good characteristics they possess, have a particularity that bulk and porous structures [148] can increase their characteristics as an improvement in water separation and recovery while maintaining a good adsorption performance [155], this capacity increases in metal cations [156] so it makes it an excellent material for the removal of heavy metals. Currently, there is a large number of hydrogels with different functionalities in order to provide improvements in terms of their efficiency.

Recently it has been explored in asymmetric hydrogels, these manage to generate spontaneously incorporated potentials due to the diffusion of counterions [157]. In this way, hydrogels have been developed that contain chemical gradients with forces that drive the transfer of mass and thereby achieve the elimination of heavy metals. This is how active sites are exposed inside hydrogels and polluting ions being permeable within hydrogels facilitate their removal [158].

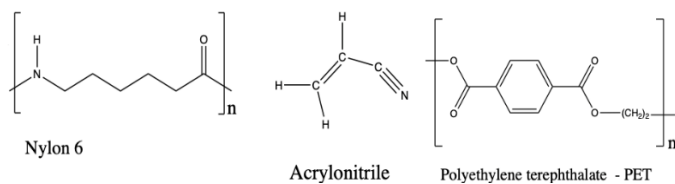


Figure 5. Common synthetic fibers. Nylon 6, Acrylonitrile, and Polyethylene terephthalate.

Currently, there is a lot of literature associated with the synthesis and application of this type of fibers and the application as chelators of heavy metals [159]: in one of the works the preparation of polymeric adsorbents functionalized by the amination of acrylonitrile-ethylene glycol-dimethacrylate is presented, this functionalized polymer obtained quite promising results in terms of the adsorption of lead ions in aqueous systems [160]. Other authors [161] have prepared polyacrylonitrile-based fibers with chelated Ag ions (Ag-SH-PANF) by chemical modification in order to obtain materials with highly efficient antibacterial capabilities. Other hydrogels for the removal of heavy metals are those based on cellulose [162-164], which seems to be quite good if we consider that cellulose production is between 75,000 and 100,000 million tons [162] and characteristics such as a high specific surface that allows to have more active sites and that their hydroxyl groups allow to have an easier graft of functionalities [165] of amine, ester and sulfate groups [166]. Although there is a series of cellulose-based hydrogels that allows the elimination of organic compounds such as methylene blue [167, 168] and phenol, is also extremely effective in terms of inorganic contaminants and heavy metal ions such as lead (Pb^{2+}) where 98% removal percentages have been obtained with cellulose-based hydrogels from multiple active sites where the raw material corresponds to microcrystalline cellulose [169], and lead removal (Pb^{2+}) corresponding to 44mg g^{-1} from cellulose/diatomite bead hydrogels modified with maleic anhydride [170].

In other cases, lead removal percentages of 70% have been obtained in 6 min, this is based on a porous keratin/polyacrylic acid hydrogel (keratin-PAA). The synthesized hydrogel had a specific surface area of $49.35\text{m}^2\text{ g}^{-1}$ with pore distribution of 6.20 nm, which led it to have a maximum lead adsorption of 234.6 mg g^{-1} [171]. As for lead, hydrogels are highly efficient in mercury removal [172, 173]. To see the ways in which mercury can be removed by hydrogels, it must be taken into account that there must be functional groups related to mercury to obtain effective removals. For example, hydrogels containing amide groups are quite good for the removal of Cu^{2+} and Ni^{2+} ; amidoxime groups ($R-C(NH_2)=N-O$) form complexes with heavy metals such as Co^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} [174], in addition to showing affinity for uranium [175]. Likewise, compound hydrogels such as poly(2-hydroxyethyl methacrylate-co-acrylamide) cross-linked rubber tragacanth (GT-Cl-(HEMA-co-AAm)) and another hydrogel compound poly(2-hydroxyethylmethacrylate-co-acrylamide/zinc oxide) reticulated rubber tragacanth (GT-Cl-(HEMA-co-AAm/ZnO) hydrogel are also recorded, however, the latter is the one who presents a better mercury adsorption capacity [176]. Another of the hydrogels that allow the removal of heavy metals is the ligand of metabenzoporphodimethene (meta-BPDM) immobilized in guar rubber hydrogel of polyacrylamide / carboxymethyl (PAM / CMG) where removal percentages of 78.8% were recorded for zinc, 67.6% for cadmium and 80.4% for mercury [177]. Maximum mercury removal refers to and proves the base principle of hard soft acid [178-180]. In general, hydrogels correspond to highly efficient structures in terms of heavy metal removal [153, 158, 181], however, it is necessary to detail in other elements that are equally or mostly efficient and of natural matrices

2.2.2 Chitosan

Chitosan is a biopolymer generated from the deacetylation (see Figure 5) of chitin that is derived from the exoskeleton of crustaceans [15, 182, 183] corresponds to the most abundant biopolymer after cellulose [184, 185].

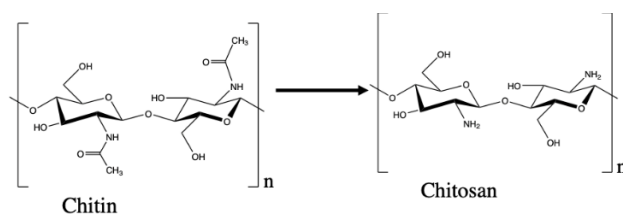


Figure 5. Desacetylation of chitin

Among the properties it has, in addition to being biodegradable [186], non-toxic, biocompatible [187] and economical, it has high adsorption capacities due to the functional groups amine ($-NH_2$) and hydroxyl ($-OH$) that it has as active sites for the adsorption of different metal ions [188], so it corresponds to a copolymer consisting of 2-amino-2-deoxy-b-D-glucose linked to β -1,4-(deacetylated D-glucosamine) and N-acetyl-D-glucosamine with less molecular weight (MW) than chitin possessing a molecular weight greater than 100kDa [189, 190].

2.2.2.1 Physicochemical properties of Chitosan.

Chitosan, increasingly attractive for use, has extremely important characteristics such as chelation, viscosity, solubility, among others. While the unbranched, linear form of chitosan has been reported to possess excellent viscosity, it is also known that this property can be modified by altering deacetylation conditions. One of the most important characteristics of chitosan is its high degree of deacetylation, since it enhances it in areas such as pharmacy and biotechnology, so the physicochemical characteristics of chitosan are affected by different factors among which we find crystallinity, MW, degradation methods and its degree of deacetylation (DD). If we detail in parameters such as MW and DD, we can find 2 types of chitosan: a) chitosan of high molecular weight, ranging between 190 and 375 kDa, with a $DD > 75\%$ and b) chitosan of low molecular weight, ranging between 20 and 190 kDa, with a $DD < 75\%$ and (b) low molecular weight chitosan, ranging from 20 to 190 kDa, with a $DD < 75\%$.

Authors have reported an inversely proportional relationship between the rate of degradation and DD, which also depends on the distribution of acetyl groups [187]. If you have a higher DD you will see a much lower degradation rate, and on the contrary, if we have a lower DD, we will have a degradation rate, we will have a faster rate of degradation [191, 192]. There is also a relationship between MW and the solubility of chitosan; authors report that there is a biological relationship between these two parameters and that is that the lower the MW, the greater the solubility that the molecule will have [193, 194]. In general, solubility will depend largely on the positioning of the acetyl groups that are throughout the chain, the methods of deacetylation, ionic strength and pH. For this last parameter we can see it through its three reactive positions, an amino group and two hydroxyl groups, where the amino group corresponds to the most sensitive to pH changes and is responsible for the cationic nature of chitosan [195-197]. It is recorded that at pH above 6, the amino group deprotonates and chitosan becomes insoluble [187, 198], however modified chitosan products have higher solubility in water over wider pH ranges [193].

2.2.2.2 Chitosan as material to remove heavy metals

Due to the extensive properties of chitosan, a large number of works related to the removal of heavy metals based on modified chitosan and chitosan have been reported. However, due to properties such as solubility in acid medium, low thermal stability, low mechanical strength and low surface area [199] it is that the use of modified chitosan [15] has been preferred to facilitate the removal of metals. Among these modifications are cross-linkers such as glutaraldehyde (GLU) [200, 201], ethylene glycol ether diglicidil (EGDE) [202, 203], epichlorohydrin (ECH) [204, 205], among others. These allow to provide a greater capacity of adsorption (among other characteristics) to the chitosan; for example, there are studies where cross-linked chitosan beads with GLU, EGDE and ECH are used for the removal of Cu(II) obtaining results of 59.67, 62.47, and 45.94 mg g^{-1} respectively [206]. Other modifications are those of grafted chitosan, which are based on the grafting of active functional groups that allow a better elimination of heavy metals [15], among them we find polyanilines [207], polyethylene glycol [208], acrylonitrile [209], acrylamide [210], among others.

One of the most recent modifications are those related to magnetic chitosan which, although its industrial application is very challenging, including paramagnetic nanoparticles in the design of chitosan-based nanoadsorbents gives it quite promising magnetic properties in terms of metal removal [15]. Based on magnetic chitosan, a series of investigations have been reported detailing the removal of metals such as Cd(II), Cu(II), Zn (II) [211], Cr(VI) [212], Pb(II) [213], among other metals.

2.2.2.3 Removal of mercury by chitosan

Different forms of chitosan have been recorded for the removal of many heavy metals. It is not the exception for the case of mercury since there are fluorescent hydrogels based on chitosan for the adsorption of Hg^{2+} and Hg^+ , for which the authors prepared NH₂-BODIPY [214] with reduction of NO₂ to NH₂ in order to be able to introduce it into chitosan through a Schiff base formation reaction. As seen in Figure 6, mercury is combined with the C=N action site and adsorption capacities of 121 mg·g⁻¹ were obtained, which, according to the authors, corresponds to seven times more than the original chitosan [215].

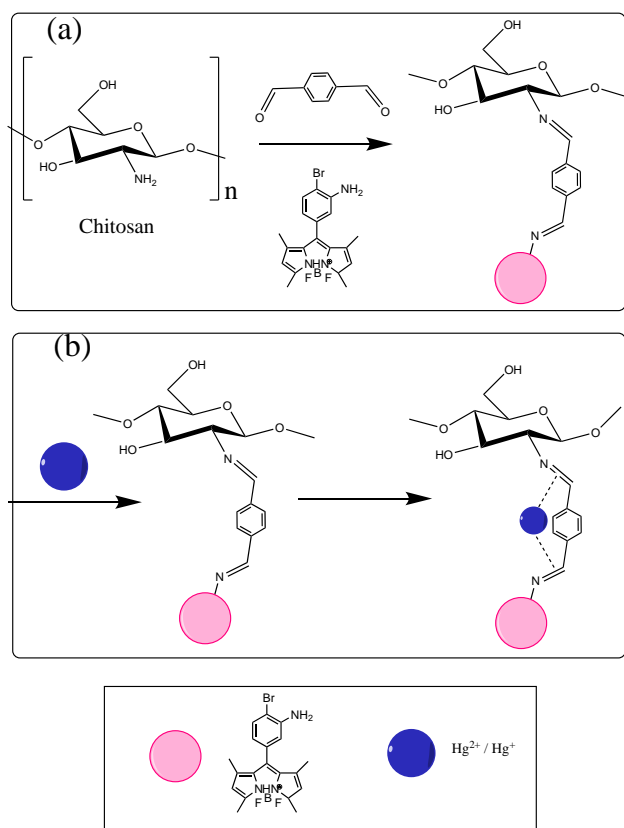


Figure 6. (a) Chitosan modified with -NH₂ BODIPY and (b) chitosan – BODIPY with mercury. Image adapted [215].

In other studies, ionic printing was performed by manufacturing sorbents printed with mercury ions derived from modified chitosan. It has been considered that functionalized chelating materials with electron donor ligands have the high capacity to form extremely stable complexes when they manage to coordinate with metal ions. For that the authors point out the use of the Schiff base ligand that was derived from the acid-4-amino-3-hydroxybenzoic acid and the 2-pyridinecarboxaldehyde (HPB) to then incorporate it into the chitosan through the amide bonds. Thus, the modified chitosan polymeric ligand that was obtained was combined with the Hg(II) ions to achieve the polymeric complex, achieving the impression in the crosslinking with glutaraldehyde, eliminating the Hg(II) ions and reaching a maximum capacity of 315 mg·g⁻¹ [216].

The use of a compound of *Ulva lactuca*/chitosan is another of the methods used that allow a good removal of heavy metals such as mercury. The authors used *Ulva lactuca* (also known by the common name sea lettuce) due to its low economic cost, it is an excellent bioindicator material [217] that allows to evaluate water contaminants, however, despite the fact that mercury removal is

quite efficient, the preparation of hybrid materials from natural polymers such as chitosan [218, 219], allows you to have greater and greater adsorption/removal capacities of Hg²⁺. In this study, the authors report a sorption capacity of 189, 144 mg·g⁻¹ of Hg²⁺, at a rate 93% faster than the utilization of *Ulva lactuca* alone.

2.2.2.4 Removal of lead by chitosan.

As for mercury and all other heavy metals mentioned in this article, there are a number of methods in which chitosan, mostly modified, is used to remove/remove lead (Pb²⁺). A rather attractive technique is based on the use of chitosan with microbial adsorbents [220, 221] in which the separate or combined use of chitosan with *Bifidobacterium longum* and *Saccharomyces cerevisiae* allowed effective removal of lead (II) in aqueous solutions [222]. However, despite the fact that the elimination was effective, it was recorded that the chitosan/*B. longum* adsorbent presented a higher percentage of adsorption than the other materials [223]. The study analyzed variables such as initial concentration, contact time, temperature and pH, where the maximum percentage of lead (II) adsorption was 97.6% [221]. Other studies suggest yeast biomass modified with ethylenediamine coated with magnetic microparticles of chitosan, a material that allows the adsorption of lead ions at high capacities. The preparation of these materials was carried out at temperatures of 20, 30, and 40°C with maximum adsorption capacities of 121.26, 127.37, and 134.90 mg·g⁻¹ respectively [206]. Heavy metal removal studies, specifically lead, are reported with magnetic silica nanoparticles coated with chitosan modified with diethylenetriaminopentaacetic acid (DTPA), a chelating molecule with three nitrogen atoms corresponding to tertiary amine and five carboxylic groups that are as a semi-flexible ligand [224], to improve the adsorption of lead from wastewater. In this lead removal system, methyl blue (MB) was used with the aim of improving the removal capacity due to its sulfonic acid groups in the molecules, creating new specific active sites for lead adsorption [213].

CONCLUSIONS

As already mentioned, over time a wide variety of techniques have been used for the removal of heavy metals (reverse osmosis, membrane filters, ion exchange, clays, biochar, hydrogels, etc.) from wastewater, however the need to have efficient and low-cost materials has been increasing. In general, the removal of heavy metals such as lead and mercury, with adsorbent materials is considered a fairly economically viable, sustainable, efficient and highly replicable technique that allows the elimination of about 97% for the case of lead and about 93% for mercury, so continuing with research of this type could allow in the future, the removal of 100% of these metal ions that today are a serious problem for the environment and humanity.

References

1. Umesha MK, Venkatesh S, Seshagiri S. Nanomaterials and Biopolymers for the Remediation of Polluted Sites. *Biotechnology for Zero Waste: Emerging Waste Management Techniques*. 2022:329-41.
2. Yang F, Yang P. Biopolymer-Based Membrane Adsorber for Removing Contaminants from Aqueous Solution: Progress and Prospects. *Macromolecular Rapid Communications*. 2022;43(3):2100669.
3. Razzak SA, Faruque MO, Alsheikh Z, Alsheikhmohamad L, Alkuroud D, Alfayez A, et al. A comprehensive review on conventional and biological-driven heavy metals removal from industrial wastewater. *Environmental Advances*. 2022;7:100168.
4. Lee S, Lingamdinne LP, Yang J-K, Koduru JR, Chang Y-Y, Naushad M. Biopolymer mixture-entrapped modified graphene oxide for sustainable treatment of heavy metal contaminated real surface water. *Journal of Water Process Engineering*. 2022;46:102631.
5. Barakat M. New trends in removing heavy metals from industrial wastewater. *Arabian journal of chemistry*. 2011;4(4):361-77.
6. Choque-Quipe D, Ramos-Pacheco BS, Ligarda-Samanez CA, Barboza-Palomino GI, Kari-Ferro A, Taipei-Pardo F, et al. Heavy metal removal by biopolymers-based formulations with native potato starch/nopal mucilage. *Revista Facultad de Ingeniería Universidad de Antioquia*. 2020(103):44-50.
7. Hoang AT, Pham XD. An investigation of remediation and recovery of oil spill and toxic heavy metal from maritime pollution by a new adsorbent material. *Journal of Marine Engineering & Technology*. 2021;20(3):159-69.
8. Hoang AT, Nizetić S, Cheng CK, Luque R, Thomas S, Banh TL, et al. Heavy metal removal by biomass-derived carbon nanotubes as a greener environmental remediation: A comprehensive review. *Chemosphere*. 2022;287:131959.

9. Jia Y, Wang L, Qu Z, Yang Z. Distribution, contamination and accumulation of heavy metals in water, sediments, and freshwater shellfish from Liuyang River, Southern China. *Environmental Science and Pollution Research*. 2018;25(7):7012-20.
10. R J, Gurunathan B, K S, Varjani S, Ngo HH, Gnansounou E. Advancements in heavy metals removal from effluents employing nano-adsorbents: Way towards cleaner production. *Environmental Research*. 2022;203:111815.
11. Rajendran S, Priya TAK, Khoo KS, Hoang TKA, Ng H-S, Munawaroh HSH, et al. A critical review on various remediation approaches for heavy metal contaminants removal from contaminated soils. *Chemosphere*. 2022;287:132369.
12. Siddeeg SM. A novel synthesis of TiO₂/GO nanocomposite for the uptake of Pb²⁺ and Cd²⁺ from wastewater. *Materials Research Express*. 2020;7(2):025038.
13. Yan X, Liu M, Zhong J, Guo J, Wu W. How human activities affect heavy metal contamination of soil and sediment in a long-term reclaimed area of the Liaohe River Delta, North China. *Sustainability*. 2018;10(2):338.
14. Lu Y, Song S, Wang R, Liu Z, Meng J, Sweetman AJ, et al. Impacts of soil and water pollution on food safety and health risks in China. *Environment international*. 2015;77:5-15.
15. Haripriyan U, Gopinath KP, Arun J. Chitosan based nano adsorbents and its types for heavy metal removal: A mini review. *Materials Letters*. 2022;312:131670.
16. Zheng J, Li Y, Xu D, Zhao R, Liu Y, Li G, et al. Facile fabrication of a positively charged nanofiltration membrane for heavy metal and dye removal. *Separation and Purification Technology*. 2022;282:120155.
17. Qasem NAA, Mohammed RH, Lawal DU. Removal of heavy metal ions from wastewater: a comprehensive and critical review. *npj Clean Water*. 2021;4(1):36.
18. Pooja G, Kumar PS, Indraganti S. Recent advancements in the removal/recovery of toxic metals from aquatic system using flotation techniques. *Chemosphere*. 2022;287:132231.
19. Chakraborty R, Asthana A, Singh AK, Jain B, Susan ABH. Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*. 2022;102(2):342-79.
20. Shoneye A, Sen Chang J, Chong MN, Tang J. Recent progress in photocatalytic degradation of chlorinated phenols and reduction of heavy metal ions in water by TiO₂-based catalysts. *International Materials Reviews*. 2022;67(1):47-64.
21. Li P, Lan H, Chen K, Ma X, Wei B, Wang M, et al. Novel high-flux positively charged aliphatic polyamide nanofiltration membrane for selective removal of heavy metals. *Separation and Purification Technology*. 2022;280:119949.
22. Aranda FL, Gayoso A, Palma-Onetto V, Rivas BL. REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS BY USING RESINS FROM PINUS RADIATA BARK RESINS. *Journal of the Chilean Chemical Society*. 2022;67(1):5403-7.
23. Feng X, Long R, Wang L, Liu C, Bai Z, Liu X. A review on heavy metal ions adsorption from water by layered double hydroxide and its composites. *Separation and Purification Technology*. 2022;284:120099.
24. Rasheed T, Kausar F, Rizwan K, Adeel M, Sher F, Alwadai N, et al. Two dimensional MXenes as emerging paradigm for adsorptive removal of toxic metallic pollutants from wastewater. *Chemosphere*. 2022;287:132319.
25. Zheng X, Ni C, Xiao W, Liang Y, Li Y. Ionic liquid grafted polyethersulfone nanofibrous membrane as recyclable adsorbent with simultaneous dye, heavy metal removal and antibacterial property. *Chemical Engineering Journal*. 2022;428:132111.
26. Briffa J, Sinagra E, Blundell R. Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon*. 2020;6(9):e04691.
27. De Beni E, Giurlani W, Fabbri L, Emanuele R, Santini S, Sarti C, et al. Graphene-based nanomaterials in the electroplating industry: A suitable choice for heavy metal removal from wastewater. *Chemosphere*. 2022;292:133448.
28. de Almeida Rodrigues P, Ferrari RG, Dos Santos LN, Junior CAC. Mercury in aquatic fauna contamination: a systematic review on its dynamics and potential health risks. *Journal of Environmental Sciences*. 2019;84:205-18.
29. Li J, Cai C, Li J, Li J, Li J, Sun T, et al. Chitosan-Based Nanomaterials for Drug Delivery. *Molecules*. 2018;23(10):2661.
30. Rivas BL, Ovando P, Villegas S. High-retention properties for Hg (II) ions of a resin containing ammonium and pyridine groups. *Journal of applied polymer science*. 2002;83(12):2595-9.
31. Rivas BL, Pooley SA, Muñoz C, Leiton L. Heavy metal ions removal through poly (acrylamide-co-methacrylic acid) resin. *Polymer bulletin*. 2010;64(1):41-52.
32. Rivas BL, Pooley SA, Aceitón E, Geckeler KE. Synthesis, characterization and properties of a selective adsorbent to mercury (II) ions. *Journal of applied polymer science*. 2002;85(12):2559-63.
33. Ali H, Khan E, Ilahi I. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *Journal of Chemistry*. 2019;2019:6730305.
34. Khan T, Muhammad S, Khan B, Khan H. Investigating the levels of selected heavy metals in surface water of Shah Alam River (A tributary of River Kabul, Khyber Pakhtunkhwa). *Journal of Himalayan Earth Sciences*. 2011;44(2):71-9.
35. Wang Y, Liu Y, Wu B, Rui M, Liu J, Lu G. Comparison of toxicity induced by EDTA-Cu after UV/H₂O₂ and UV/persulfate treatment: Species-specific and technology-dependent toxicity. *Chemosphere*. 2020;240:124942.
36. Yan C, Qu Z, Wang J, Cao L, Han Q. Microalgal bioremediation of heavy metal pollution in water: Recent advances, challenges, and prospects. *Chemosphere*. 2022;286:131870.
37. Zaynab M, Al-Yahyai R, Ameen A, Sharif Y, Ali L, Fatima M, et al. Health and environmental effects of heavy metals. *Journal of King Saud University - Science*. 2022;34(1):101653.
38. Miao F, Zhang Y, Li Y, Lin Q. A synthetic health risk assessment based on geochemical equilibrium simulation and grid spatial interpolation for zinc (II) species. *Journal of Environmental Management*. 2022;304:114207.
39. Shahane SP, Kumar A. Estimation of health risks due to copper-based nanoagrochemicals. *Environmental Science and Pollution Research*. 2022;29(17):25046-59.
40. Tumolo M, Ancona V, De Paola D, Losacco D, Campanale C, Massarelli C, et al. Chromium Pollution in European Water, Sources, Health Risk, and Remediation Strategies: An Overview. *International Journal of Environmental Research and Public Health*. 2020;17(15):5438.
41. Zheng L, Sun R, Hintelmann H, Zhu J, Wang R, Sonke JE. Mercury stable isotope compositions in magmatic-affected coal deposits: New insights to mercury sources, migration and enrichment. *Chemical Geology*. 2018;479:86-101.
42. Li C, Wang H, Liao X, Xiao R, Liu K, Bai J, et al. Heavy metal pollution in coastal wetlands: A systematic review of studies globally over the past three decades. *Journal of Hazardous Materials*. 2022;424:127312.
43. Hassan SSM, Awwad NS, Aboterika AHA. Removal of mercury(II) from wastewater using camel bone charcoal. *Journal of Hazardous Materials*. 2008;154(1):992-7.
44. Hu X, Chen C, Zhang D, Xue Y. Kinetics, isotherm and chemical speciation analysis of Hg(II) adsorption over oxygen-containing MXene adsorbent. *Chemosphere*. 2021;278:130206.
45. Luo H, Cheng Q, Pan X. Photochemical behaviors of mercury (Hg) species in aquatic systems: A systematic review on reaction process, mechanism, and influencing factor. *Science of The Total Environment*. 2020;720:137540.
46. Mani M, Kabekkodu S, Joshi M, Dsouza H. Ecogenetics of lead toxicity and its influence on risk assessment. *Human & Experimental Toxicology*. 2019;38(9):1031-59.
47. da Silva Cunha FA, de Oliveira MJ, Florez-Rodriguez PP, Santos JCC. Mercury speciation in estuarine water using dithiol-based magnetic solid-phase extraction and cold vapor atomic fluorescence spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 2022;192:106412.
48. Yu H, Li J, Luan Y. Meta-analysis of soil mercury accumulation by vegetables. *Scientific Reports*. 2018;8(1):1-10.
49. Wildner G, Loreto JS, de Almeida P, Claro MT, Ferreira SA, Barbosa NV. Short exposure to ethyl and methylmercury prompts similar toxic responses in *Drosophila melanogaster*. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*. 2022;252:109216.
50. Farina M, Rocha JB, Aschner M. Mechanisms of methylmercury-induced neurotoxicity: evidence from experimental studies. *Life sciences*. 2011;89(15-16):555-63.
51. Clarkson TW, Magos L. The toxicology of mercury and its chemical compounds. *Critical reviews in toxicology*. 2006;36(8):609-62.
52. Kodamatani H, Shigetomi A, Akama J, Kanzaki R, Tomiyasu T. Distribution, alkylation, and migration of mercury in soil discharged from the Itomuka mercury mine. *Science of The Total Environment*. 2022;815:152492.
53. Huang Y, Gong Y, Tang J, Xia S. Effective removal of inorganic mercury and methylmercury from aqueous solution using novel thiol-functionalized graphene oxide/Fe-Mn composite. *Journal of Hazardous Materials*. 2019;366:130-9.
54. Wang Y, Zhu A, Fang Y, Fan C, Guo Y, Tan Z, et al. Dithizon-functionalized C18 online solid-phase extraction-HPLC-ICP-MS for speciation of ultra-trace organic and inorganic mercury in cereals and environmental samples. *Journal of Environmental Sciences*. 2022;115:403-10.
55. Nogara PA, Farina M, Aschner M, Rocha JB. Mercury in our food. *ACS Publications*; 2019. p. 1459-61.

56. Dórea JG. Integrating experimental (in vitro and in vivo) neurotoxicity studies of low-dose thimerosal relevant to vaccines. *Neurochemical research*. 2011;36(6):927-38.
57. Dórea JG. Low-dose Thimerosal (ethyl-mercury) is still used in infants vaccines: Should we be concerned with this form of exposure? *Journal of Trace Elements in Medicine and Biology*. 2018;49:134-9.
58. Zhang H, Yan J, Niu J, Wang H, Li X. Association between lead and cadmium co-exposure and systemic immune inflammation in residents living near a mining and smelting area in NW China. *Chemosphere*. 2022;287:132190.
59. Nag R, Cummins E. Human health risk assessment of lead (Pb) through the environmental-food pathway. *Science of The Total Environment*. 2022;810:151168.
60. Seleznev A, Yarmoshenko I, Malinovsky G, Ilgasheva E, Chervyakovskaya M, Streletskaia M, et al. Lead isotope ratios in urban surface deposited sediments as an indicator of urban geochemical transformation: Example of Russian cities. *Applied Geochemistry*. 2022;137:105184.
61. Li Y, Cummins E. Hazard characterization of silver nanoparticles for human exposure routes. *Journal of Environmental Science and Health, Part A*. 2020;55(6):704-25.
62. Guo G, Lei M, Wang Y, Song B, Yang J. Accumulation of As, Cd, and Pb in sixteen wheat cultivars grown in contaminated soils and associated health risk assessment. *International journal of environmental research and public health*. 2018;15(11):2601.
63. Zwolak A, Sarzyńska M, Szpyrka E, Stawarczyk K. Sources of soil pollution by heavy metals and their accumulation in vegetables: A review. *Water, air, & soil pollution*. 2019;230(7):1-9.
64. Namungu L, Mburu C, Were F. Evaluation of Occupational Lead Exposure in Informal Work Environment in Kenya.
65. Das R. Chapter 23 - Sources of lead (Pb) in atmosphere over Indian cities and health impacts. In: Singh RP, editor. *Asian Atmospheric Pollution*: Elsevier; 2022. p. 435-52.
66. Singh P, Mitra P, Goyal T, Sharma S, Purohit P, Sharma P. Levels of lead, aluminum, and zinc in occupationally exposed workers of North-Western India. *Journal of Basic and Clinical Physiology and Pharmacology*. 2022;33(2):191-7.
67. Jagirani MS, Balouch A, Mahesar SA, Alveroglu E, Kumar A, Tunio A, et al. Selective and sensitive detoxification of toxic lead ions from drinking water using lead (II) ion-imprinted interpenetrating polymer linkage. *Polymer Bulletin*. 2022;79(3):1887-909.
68. Turdean GL. Design and Development of Biosensors for the Detection of Heavy Metal Toxicity. *International Journal of Electrochemistry*. 2011;2011:343125.
69. Verheijen MCT, Krauskopf J, Caiment F, Nazaruk M, Wen QF, van Herwijnen MHM, et al. iPSC-derived cortical neurons to study sporadic Alzheimer disease: A transcriptome comparison with post-mortem brain samples. *Toxicology Letters*. 2022;356:89-99.
70. Kumar A, MMS C-P, Chaturvedi AK, Shabnam AA, Subrahmanyam G, Mondal R, et al. Lead toxicity: health hazards, influence on food chain, and sustainable remediation approaches. *International journal of environmental research and public health*. 2020;17(7):2179.
71. Sun Q, Li Y, Shi L, Hussain R, Mehmood K, Tang Z, et al. Heavy metals induced mitochondrial dysfunction in animals: Molecular mechanism of toxicity. *Toxicology*. 2022;469:153136.
72. Chen Y, Zhang Z, Deng W, Wang Z, Gao M, Gao C, et al. Mechanistic insight into the electrochemical adsorption behaviour of Cd²⁺ and Na⁺ on MnO₂ in a deionization supercapacitor. *Desalination*. 2022;521:115384.
73. Ahmad K. Study of different polymer nanocomposites and their pollutant removal efficiency. *Polymer*. 2021;217:123453.
74. Wang A, Zheng Z, Li R, Hu D, Lu Y, Luo H, et al. Biomass-derived porous carbon highly efficient for removal of Pb (II) and Cd (II). *Green Energy & Environment*. 2019;4(4):414-23.
75. Liu Y, Dai L, Ke X, Ding J, Wu X, Chen R, et al. Arsenic and cation metal removal from copper slag using a bipolar membrane electro dialysis system. *Journal of Cleaner Production*. 2022;338:130662.
76. Qiu Z, Tang J, Chen J, Zhang Q. Remediation of cadmium-contaminated soil with biochar simultaneously improves biochar's recalcitrance. *Environmental Pollution*. 2020;256:113436.
77. Ashraf I, Ahmad F, Sharif A, Altaf AR, Teng H. Heavy metals assessment in water, soil, vegetables and their associated health risks via consumption of vegetables, District Kasur, Pakistan. *SN Applied Sciences*. 2021;3(5):1-16.
78. Raza Altaf A, Teng H, Saleem M, Raza Ahmad H, Adil M, Shahzad K. Associative interplay of *Pseudomonas gessardii* BLP141 and pressmud ameliorated growth, physiology, yield, and Pb-toxicity in sunflower. *Bioremediation Journal*. 2021;25(2):178-88.
79. Altaf AR, Adewuyi YG, Teng H, Gang L, Abid F. Elemental mercury (Hg₀) removal from coal syngas using magnetic tea-biochar: Experimental and theoretical insights. *Journal of Environmental Sciences*. 2022;122:150-61.
80. Liu D, Yang L, Wu J, Li B. Molten salt shielded preparation of rice straw biochars doped by copper sulfide for elemental mercury capture. *Journal of the Energy Institute*. 2022;102:176-83.
81. Qasim HM, Abudi ZN, Alzubaidi LA. Cobalt ion removal using magnetic biochar obtained from *Conocarpus erectus* leaves. *Biomass Conversion and Biorefinery*. 2022.
82. Liu P, Ptacek CJ, Blowes DW, Landis RC. Mechanisms of mercury removal by biochars produced from different feedstocks determined using X-ray absorption spectroscopy. *Journal of Hazardous Materials*. 2016;308:233-42.
83. Tang J, Ptacek CJ, Blowes DW, Liu Y, Feng Y, Finckel YZ, et al. Mercury adsorption kinetics on sulfurized biochar and solid-phase digestion using aqua regia: A synchrotron-based study. *Chemical Engineering Journal*. 2022;428:131362.
84. Xu X, Schierz A, Xu N, Cao X. Comparison of the characteristics and mechanisms of Hg (II) sorption by biochars and activated carbon. *Journal of colloid and interface science*. 2016;463:55-60.
85. Zhou M, Xu Y, Luo G, Zhang Q, Du L, Cui X, et al. Facile synthesis of phosphorus-doped porous biochars for efficient removal of elemental mercury from coal combustion flue gas. *Chemical Engineering Journal*. 2022;432:134440.
86. Khan ZH, Gao M, Qiu W, Song Z. Mechanism of novel MoS₂-modified biochar composites for removal of cadmium (II) from aqueous solutions. *Environmental Science and Pollution Research*. 2021;28(26):34979-89.
87. Yogeshwaran V, Priya A. Adsorption of lead ion concentration from the aqueous solution using tobacco leaves. *Materials Today: Proceedings*. 2021;37:489-96.
88. Zamora-Ledeza C, Negrete-Bolagay D, Figueroa F, Zamora-Ledeza E, Ni M, Alexis F, et al. Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods. *Environmental Technology & Innovation*. 2021;22:101504.
89. Liu T, Lawluy Y, Shi Y, Ighalo JO, He Y, Zhang Y, et al. Adsorption of cadmium and lead from aqueous solution using modified biochar: A review. *Journal of Environmental Chemical Engineering*. 2022;10(1):106502.
90. Ifthikar J, Wang J, Wang Q, Wang T, Wang H, Khan A, et al. Highly efficient lead distribution by magnetic sewage sludge biochar: sorption mechanisms and bench applications. *Bioresource technology*. 2017;238:399-406.
91. Gao L, Li Z, Yi W, Li Y, Zhang P, Zhang A, et al. Impacts of pyrolysis temperature on lead adsorption by cotton stalk-derived biochar and related mechanisms. *Journal of Environmental Chemical Engineering*. 2021;9(4):105602.
92. Cheng S, Liu Y, Xing B, Qin X, Zhang C, Xia H. Lead and cadmium clean removal from wastewater by sustainable biochar derived from poplar saw dust. *Journal of Cleaner Production*. 2021;314:128074.
93. Yang K, Wang X, Cheng H, Tao S. Enhanced immobilization of cadmium and lead adsorbed on crop straw biochars by simulated aging processes. *Environmental Pollution*. 2022;302:119064.
94. Pan J, Deng H, Du Z, Tian K, Zhang J. Design of nitrogen-phosphorus-doped biochar and its lead adsorption performance. *Environmental Science and Pollution Research*. 2022;29(19):28984-94.
95. Cheng S, Zhao S, Guo H, Xing B, Liu Y, Zhang C, et al. High-efficiency removal of lead/cadmium from wastewater by MgO modified biochar derived from crofton weed. *Bioresource Technology*. 2022;343:126081.
96. Novikau R, Lujanienė G. Adsorption behaviour of pollutants: Heavy metals, radionuclides, organic pollutants, on clays and their minerals (raw, modified and treated): A review. *Journal of Environmental Management*. 2022;309:114685.
97. Es-sahbany H, Berradi M, Nkhili S, Hsissou R, Allaoui M, Loutfi M, et al. Removal of heavy metals (nickel) contained in wastewater-models by the adsorption technique on natural clay. *Materials Today: Proceedings*. 2019;13:866-75.
98. Gu S, Kang X, Wang L, Lichtfouse E, Wang C. Clay mineral adsorbents for heavy metal removal from wastewater: a review. *Environmental Chemistry Letters*. 2019;17(2):629-54.
99. Chaari I, Medhioub M, Jamoussi F, Hamzaoui AH. Acid-treated clay materials (Southwestern Tunisia) for removing sodium leuco-vat dye: Characterization, adsorption study and activation mechanism. *Journal of Molecular Structure*. 2021;1223:128944.
100. Baigorria E, Fraceto LF. Novel nanostructured materials based on polymer/organic-clay composite networks for the removal of carbendazim from waters. *Journal of Cleaner Production*. 2022;331:129867.
101. Lee H, Rukmanikrishnan B, Lee J. Rheological, morphological, mechanical, and water-barrier properties of agar/gellan gum/montmorillonite clay composite films. *International journal of biological macromolecules*. 2019;141:538-44.

102. Awad AM, Shaikh SM, Jalab R, Gulied MH, Nasser MS, Benamor A, et al. Adsorption of organic pollutants by natural and modified clays: a comprehensive review. *Separation and Purification Technology*. 2019;228:115719.
103. Zhang T, Wang W, Zhao Y, Bai H, Wen T, Kang S, et al. Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. *Chemical Engineering Journal*. 2021;420:127574.
104. Hizal J, Yilmazoglu M. Montmorillonite Clay Composite for Heavy Metal Removal from Water. In: Inamuddin, Ahamed MI, Lichtfouse E, Asiri AM, editors. *Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water*. Cham: Springer International Publishing; 2021. p. 93-112.
105. Dim PE, Termtanun M. Treated Clay Mineral as Adsorbent for the Removal of Heavy Metals from Aqueous Solution. *Applied Science and Engineering Progress*. 2021;14(3):511-24.
106. Esmaili A, Mobini M, Eslami H. Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies. *Applied Water Science*. 2019;9(4):97.
107. Hussain ST, Ali SAK. Removal of heavy metal by ion exchange using bentonite clay. *Journal of Ecological Engineering*. 2021;22(1).
108. Mnasri-Ghnimi S, Frini-Srasra N. Removal of heavy metals from aqueous solutions by adsorption using single and mixed pillared clays. *Applied Clay Science*. 2019;179:105151.
109. Otunola BO, Olofade OO. A review on the application of clay minerals as heavy metal adsorbents for remediation purposes. *Environmental Technology & Innovation*. 2020;18:100692.
110. Yadav VB, Gadi R, Kalra S. Clay based nanocomposites for removal of heavy metals from water: A review. *Journal of Environmental Management*. 2019;232:803-17.
111. Yilmaz Ş, Zengin A, Şahan T. Bentonite grafted with poly(N-acryloyl glycineamide) brush: A novel clay-polymer brush hybrid material for the effective removal of Hg(II) and As(V) from aqueous environments. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2021;612:125979.
112. Wang M, Bera G, Mitra K, Wade TL, Knap AH, Phillips TD. Tight sorption of arsenic, cadmium, mercury, and lead by edible activated carbon and acid-processed montmorillonite clay. *Environmental Science and Pollution Research*. 2021;28(6):6758-70.
113. Liu J, Ren S, Cao J, Tsang DC, Beiyuan J, Peng Y, et al. Highly efficient removal of thallium in wastewater by MnFe₂O₄-biochar composite. *Journal of Hazardous Materials*. 2021;401:123311.
114. Duan X-L, Yuan C-G, Guo Q, Niu S-L, He K-Q, Xia G-W. Preparation of halloysite nanotubes-encapsulated magnetic microspheres for elemental mercury removal from coal-fired flue gas. *Journal of Hazardous Materials*. 2021;406:124683.
115. Al-Bsoul A, Al-Shannag M, Tawalbeh M, Al-Taani AA, Lafi WK, Al-Othman A, et al. Optimal conditions for olive mill wastewater treatment using ultrasound and advanced oxidation processes. *Science of The Total Environment*. 2020;700:134576.
116. Fiorenza R, Farina RA, Malannata EM, Lo Presti F, Balsamo SA. VOCs Photothermo-Catalytic Removal on MnOx-ZrO₂ Catalysts. *Catalysts*. 2022;12(1):85.
117. Al-Qodah Z, Tawalbeh M, Al-Shannag M, Al-Anber Z, Bani-Melhem K. Combined electrocoagulation processes as a novel approach for enhanced pollutants removal: A state-of-the-art review. *Science of The Total Environment*. 2020;744:140806.
118. Almomani F, Al Ketife A, Judd S, Shurair M, Bhosale RR, Znad H, et al. Impact of CO₂ concentration and ambient conditions on microalgal growth and nutrient removal from wastewater by a photobioreactor. *Science of The Total Environment*. 2019;662:662-71.
119. Kubra KT, Salman MS, Hasan MN. Enhanced toxic dye removal from wastewater using biodegradable polymeric natural adsorbent. *Journal of Molecular Liquids*. 2021;328:115468.
120. Munjur HM, Hasan MN, Awwal MR, Islam MM, Shenashen M, Iqbal J. Biodegradable natural carbohydrate polymeric sustainable adsorbents for efficient toxic dye removal from wastewater. *Journal of Molecular Liquids*. 2020;319:114356.
121. Al Sharabati M, Abokwiek R, Al-Othman A, Tawalbeh M, Karaman C, Orooji Y, et al. Biodegradable polymers and their nano-composites for the removal of endocrine-disrupting chemicals (EDCs) from wastewater: A review. *Environmental Research*. 2021;202:111694.
122. Jakavula S, Biata NR, Dimpe KM, Pakade VE, Nomngongo PN. A Critical Review on the Synthesis and Application of Ion-Imprinted Polymers for Selective Preconcentration, Speciation, Removal and Determination of Trace and Essential Metals from Different Matrices. *Critical Reviews in Analytical Chemistry*. 2022;52(2):314-26.
123. Goyal S, Jacob J. 2, 2'-Bipyridine containing chelating polymers for sequestration of heavy metal ions from organic solvents. *Journal of Applied Polymer Science*. 2022:52121.
124. Hargreaves AJ, Vale P, Whelan J, Alibardi L, Constantino C, Dotro G, et al. Coagulation-flocculation process with metal salts, synthetic polymers and biopolymers for the removal of trace metals (Cu, Pb, Ni, Zn) from municipal wastewater. *Clean Technologies and Environmental Policy*. 2018;20(2):393-402.
125. He M, Wang R-D, Wu T, Wang S, Zhang W-Q, Du L, et al. Two novel coordination polymers for Hg (II) removal in water. *Inorganic Chemistry Communications*. 2022:109426.
126. Huang L, Liu R, Yang J, Shuai Q, Yuliarto B, Kaneti YV, et al. Nanoarchitected porous organic polymers and their environmental applications for removal of toxic metal ions. *Chemical Engineering Journal*. 2021;408:127991.
127. Karmakar A, Paul A, Santos IsR, Santos PM, Sabatini EP, Gurbanov AV, et al. Highly Efficient Adsorptive Removal of Organic Dyes from Aqueous Solutions Using Polyaromatic Group-Containing Zn (II)-Based Coordination Polymers. *Crystal Growth & Design*. 2022.
128. Liu J, Ma Y, Zhang Y, Shao G. Novel negatively charged hybrids. 3. Removal of Pb²⁺ from aqueous solution using zwitterionic hybrid polymers as adsorbent. *Journal of Hazardous Materials*. 2010;173(1):438-44.
129. Mohseni M, Akbari S, Pajootan E, Mazaheri F. Amine-terminated dendritic polymers as a multifunctional chelating agent for heavy metal ion removals. *Environmental Science and Pollution Research*. 2019;26(13):12689-97.
130. Phan D-N, Khan MQ, Nguyen N-T, Phan T-T, Ullah A, Khatri M, et al. A review on the fabrication of several carbohydrate polymers into nanofibrous structures using electrospinning for removal of metal ions and dyes. *Carbohydrate Polymers*. 2021;252:117175.
131. Sheng X, Shi H, You D, Ding X, Peng M, Shao P, et al. Specific πδ⁺-πδ⁻ interaction enables conjugated microporous polymers for highly selective capture of Pd (II). *Chemical Engineering Journal*. 2022;437:135367.
132. Skorjanc T, Shetty D, Trabolsi A. Pollutant removal with organic macrocycle-based covalent organic polymers and frameworks. *Chem*. 2021;7(4):882-918.
133. Waheed A, Baig N, Ullah N, Falath W. Removal of hazardous dyes, toxic metal ions and organic pollutants from wastewater by using porous hyper-cross-linked polymeric materials: A review of recent advances. *Journal of Environmental Management*. 2021;287:112360.
134. Moreno-Villoslada I, Rivas BL. Retention of metal ions in ultrafiltration of mixtures of divalent metal ions and water-soluble polymers at constant ionic strength based on Freundlich and Langmuir isotherms. *Journal of Membrane Science*. 2003;215(1):195-202.
135. Pei X, Zhang H, Zhou Y, Zhou L, Fu J. Stretchable, self-healing and tissue-adhesive zwitterionic hydrogels as strain sensors for wireless monitoring of organ motions. *Materials Horizons*. 2020;7(7):1872-82.
136. Shalla AH, Yaseen Z, Bhat MA, Rangreez TA, Maswal M. Recent review for removal of metal ions by hydrogels. *Separation Science and Technology*. 2019;54(1):89-100.
137. Torres-García R, Flores-Estrada J, Cauich-Rodríguez JV, Flores-Reyes M, Flores-Merino MV. Design of a polyacrylamide and gelatin hydrogel as a synthetic extracellular matrix. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 2022;71(4):266-77.
138. Zhu QL, Dai CF, Wagner D, Daab M, Hong W, Breu J, et al. Distributed electric field induces orientations of nanosheets to prepare hydrogels with elaborate ordered structures and programmed deformations. *Advanced Materials*. 2020;32(47):2005567.
139. Yang Q, Peng J, Xiao H, Xu X, Qian Z. Polysaccharide hydrogels: Functionalization, construction and served as scaffold for tissue engineering. *Carbohydrate Polymers*. 2022;278:118952.
140. Shahi S, Roghani-Mamaqani H, Talebi S, Mardani H. Stimuli-responsive destructible polymeric hydrogels based on irreversible covalent bond dissociation. *Polymer Chemistry*. 2022;13(2):161-92.
141. Qiao L, Liu C, Liu C, Zong L, Gu H, Wang C, et al. Self-healing, pH-sensitive and shape memory hydrogels based on acylhydrazone and hydrogen bonds. *European Polymer Journal*. 2022;162:110838.
142. Panja S, Dietrich B, Adams DJ. Controlling syneresis of hydrogels using organic salts. *Angewandte Chemie International Edition*. 2022;61(4):e202115021.
143. Sun W, Xue B, Fan Q, Tao R, Wang C, Wang X, et al. Molecular engineering of metal coordination interactions for strong, tough, and fast-recovery hydrogels. *Science Advances*. 2020;6(16):eaaz9531.
144. Yang T, Xu C, Liu C, Ye Y, Sun Z, Wang B, et al. Conductive polymer hydrogels crosslinked by electrostatic interaction with PEDOT:PSS dopant for bioelectronics application. *Chemical Engineering Journal*. 2022;429:132430.

145. Hashmi S, GhavamiNejad A, Obiweluozor FO, Vatankhah-Varmoosfaderani M, Stadler FJ. Supramolecular Interaction Controlled Diffusion Mechanism and Improved Mechanical Behavior of Hybrid Diffusion Systems of Zwitterions and CNT. *Macromolecules*. 2012;45(24):9804-15.
146. Li Z, Xu W, Yang J, Wang J, Wang J, Zhu G, et al. A Tumor Microenvironments-Adapted Polypeptide Hydrogel/Nanogel Composite Boosts Antitumor Molecularly Targeted Inhibition and Immunoactivation. *Advanced Materials*. 2022;2200449.
147. Peers S, Montembault A, Ladavière C. Chitosan hydrogels incorporating colloids for sustained drug delivery. *Carbohydrate Polymers*. 2022;235:118689.
148. Zhang W, Ou J, Wang B, Wang H, He Q, Song J, et al. Efficient heavy metal removal from water by alginate-based porous nanocomposite hydrogels: The enhanced removal mechanism and influencing factor insight. *Journal of Hazardous Materials*. 2021;418:126358.
149. Wang Y, Desroches GJ, Macfarlane RJ. Ordered polymer composite materials: challenges and opportunities. *Nanoscale*. 2021;13(2):426-43.
150. Meireles Gouvêa Boggione D, Boggione Santos IJ, Menezes de Souza S, Santos Mendonça RC. Preparation of polyvinyl alcohol hydrogel containing bacteriophage and its evaluation for potential use in the healing of skin wounds. *Journal of Drug Delivery Science and Technology*. 2021;63:102484.
151. Yang D. Recent Advances in Hydrogels. *Chemistry of Materials*. 2022;34(5):1987-9.
152. Gu Y, Ye M, Wang Y, Li H, Zhang H, Wang G, et al. Lignosulfonate functionalized gC 3 N 4/carbonized wood sponge for highly efficient heavy metal ion scavenging. *Journal of Materials Chemistry A*. 2020;8(25):12687-98.
153. Jiao G-J, Ma J, Li Y, Jin D, Zhou J, Sun R. Removed heavy metal ions from wastewater reuse for chemiluminescence: Successive application of lignin-based composite hydrogels. *Journal of Hazardous Materials*. 2022;421:126722.
154. Feng Y, Wang H, Xu J, Du X, Cheng X, Du Z, et al. Fabrication of MXene/PEI functionalized sodium alginate aerogel and its excellent adsorption behavior for Cr (VI) and Congo Red from aqueous solution. *Journal of Hazardous Materials*. 2021;416:125777.
155. Zhou G, Luo J, Liu C, Chu L, Crittenden J. Efficient heavy metal removal from industrial melting effluent using fixed-bed process based on porous hydrogel adsorbents. *Water research*. 2018;131:246-54.
156. Wang B, Wan Y, Zheng Y, Lee X, Liu T, Yu Z, et al. Alginate-based composites for environmental applications: a critical review. *Critical reviews in environmental science and technology*. 2019;49(4):318-56.
157. Wang H, Sun Y, He T, Huang Y, Cheng H, Li C, et al. Bilayer of polyelectrolyte films for spontaneous power generation in air up to an integrated 1,000 V output. *Nature Nanotechnology*. 2021;16(7):811-9.
158. Qi S, Lin M, Qi P, Shi J, Song G, Fan W, et al. Interfacial and build-in electric fields rooting in gradient polyelectrolyte hydrogel boosted heavy metal removal. *Chemical Engineering Journal*. 2022;444:136541.
159. Stone C, Windsor FM, Munday M, Durance I. Natural or synthetic—how global trends in textile usage threaten freshwater environments. *Science of the Total Environment*. 2020;718:134689.
160. Gupta A. Preparation of ethyleneamine functionalized crosslinked poly (acrylonitrile-ethylene glycol-dimethacrylate) chelating resins for adsorption of lead ions. *Separation Science and Technology*. 2017;52(3):447-55.
161. Chang L, Duan W, Chen A, Li J, Huang S, Tang H, et al. Preparation of polyacrylonitrile-based fibres with chelated Ag ions for antibacterial applications. *Royal Society open science*. 2020;7(7):200324.
162. Thakur S, Verma A, Kumar V, Jin Yang X, Krishnamurthy S, Coulon F, et al. Cellulosic biomass-based sustainable hydrogels for wastewater remediation: Chemistry and prospective. *Fuel*. 2022;309:122114.
163. Wang Y, Gong Y, Lin N, Jiang H, Wei X, Liu N, et al. Cellulose hydrogel coated nanometer zero-valent iron intercalated montmorillonite (CH-MMT-nFe0) for enhanced reductive removal of Cr(VI): Characterization, performance, and mechanisms. *Journal of Molecular Liquids*. 2022;347:118355.
164. Zhu J-L, Wang M-L, Shi S-C, Ren J-X, Huang H-D, Lin W, et al. In-situ constructing robust cellulose nanocomposite hydrogel network with well-dispersed dual catalysts for the efficient, stable and recyclable photo-Fenton degradation. *Cellulose*. 2022;29(3):1929-42.
165. Zhou A, Chen W, Liao L, Xie P, Zhang TC, Wu X, et al. Comparative adsorption of emerging contaminants in water by functional designed magnetic poly (N-isopropylacrylamide)/chitosan hydrogels. *Science of the Total Environment*. 2019;671:377-87.
166. Thakur S, Verma A, Sharma B, Chaudhary J, Tamulevicius S, Thakur VK. Recent developments in recycling of polystyrene based plastics. *Current Opinion in Green and Sustainable Chemistry*. 2018;13:32-8.
167. Salama A. Preparation of CMC-gP (SPMA) super adsorbent hydrogels: Exploring their capacity for MB removal from waste water. *International journal of biological macromolecules*. 2018;106:940-6.
168. Yu Z, Hu C, Dichiaro AB, Jiang W, Gu J. Cellulose nanofibril/carbon nanomaterial hybrid aerogels for adsorption removal of cationic and anionic organic dyes. *Nanomaterials*. 2020;10(1):169.
169. Wu Q, He H, Zhou H, Xue F, Zhu H, Zhou S, et al. Multiple active sites cellulose-based adsorbent for the removal of low-level Cu (II), Pb (II) and Cr (VI) via multiple cooperative mechanisms. *Carbohydrate Polymers*. 2020;233:115860.
170. Li Y, Chen M, Wan X, Zhang L, Wang X, Xiao H. Solvent-free synthesis of the cellulose-based hybrid beads for adsorption of lead ions in aqueous solutions. *RSC advances*. 2017;7(85):53899-906.
171. Cao H, Ma X, Wei Z, Tan Y, Chen S, Ye T, et al. Behavior and mechanism of the adsorption of lead by an eco-friendly porous double-network hydrogel derived from keratin. *Chemosphere*. 2022;289:133086.
172. Darban Z, Shahabuddin S, Gaur R, Ahmad I, Sridewi N. Hydrogel-Based Adsorbent Material for the Effective Removal of Heavy Metals from Wastewater: A Comprehensive Review. *Gels*. 2022;8(5):263.
173. Zhao C, Liu Q, Tan Q, Gao M, Chen G, Huang X, et al. Polysaccharide-based biopolymer hydrogels for heavy metal detection and adsorption. *Journal of Advanced Research*. 2022.
174. Zeng L, Liu Q, Xu W, Wang G, Xu Y, Liang E. Graft copolymerization of crosslinked polyvinyl alcohol with acrylonitrile and its amidoxime modification as a heavy metal ion adsorbent. *Journal of Polymers and the Environment*. 2020;28(1):116-22.
175. Bai J, Chu J, Yin X, Wang J, Tian W, Huang Q, et al. Synthesis of amidoximated polyacrylonitrile nanoparticle/graphene composite hydrogel for selective uranium sorption from saline lake brine. *Chemical Engineering Journal*. 2020;391:123553.
176. Thakur S, Sharma B, Thakur A, Kumar Gupta V, Alsanie WF, Makatsoris C, et al. Synthesis and characterisation of zinc oxide modified biorenewable polysaccharides based sustainable hydrogel nanocomposite for Hg2+ ion removal: Towards a circular bioeconomy. *Bioresource Technology*. 2022;348:126708.
177. Chauhan D, Kumar A, Warkar SG. An efficient adsorbent for the removal of Zn2+ Cd2+ and Hg2+ from the real industrial effluents. *International Journal of Environmental Science and Technology*. 2022;19(3):1483-94.
178. Choi C, de Izarra A, Han I, Jeon W, Lansac Y, Jang YH. Hard-Cation-Soft-Anion Ionic Liquids for PEDOT: PSS Treatment. *The Journal of Physical Chemistry B*. 2022;126(7):1615-24.
179. Ayers PW, Mohamed M, Heidar-Zadeh F. The Hard/Soft Acid/Base Rule: A Perspective from Conceptual Density-Functional Theory. *Conceptual Density Functional Theory: Towards a New Chemical Reactivity Theory*. 2022;1:263-79.
180. Li B, Guo L, Ge L, Kwok HF. Pearson's principle-inspired hollow metal sulfide for amplified photoelectrochemical immunoassay for disease-related protein. *Biosensors and Bioelectronics*. 2022:114210.
181. Perumal S, Atchudan R, Thirukumaran P, Yoon DH, Lee YR, Cheong IW. Simultaneous removal of heavy metal ions using carbon dots-doped hydrogel particles. *Chemosphere*. 2022;286:131760.
182. Begum S, Yuhana NY, Md Saleh N, Kamarudin NHN, Sulong AB. Review of chitosan composite as a heavy metal adsorbent: Material preparation and properties. *Carbohydrate Polymers*. 2021;259:117613.
183. Luna R, Touhami F, Uddin MJ, Touhami A. Effect of temperature and pH on nanostructural and nanomechanical properties of chitosan films. *Surfaces and Interfaces*. 2022;29:101706.
184. Ahmed S, Ikram S. Chitosan: derivatives, composites and applications: John Wiley & Sons; 2017.
185. Kou S, Peters LM, Mucalo MR. Chitosan: A review of sources and preparation methods. *International Journal of Biological Macromolecules*. 2021;169:85-94.
186. Ke C-L, Deng F-S, Chuang C-Y, Lin C-H. Antimicrobial Actions and Applications of Chitosan. *Polymers*. 2021;13(6):904.
187. Azmana M, Mahmood S, Hilles AR, Rahman A, Arifin MAB, Ahmed S. A review on chitosan and chitosan-based bionanocomposites: Promising material for combatting global issues and its applications. *International Journal of Biological Macromolecules*. 2021;185:832-48.
188. Upadhyay U, Sreedhar I, Singh SA, Patel CM, Anitha KL. Recent advances in heavy metal removal by chitosan based adsorbents. *Carbohydrate Polymers*. 2021;251:117000.
189. Cavallaro G, Micciulla S, Chiappisi L, Lazzara G. Chitosan-based smart hybrid materials: a physico-chemical perspective. *Journal of Materials Chemistry B*. 2021;9(3):594-611.

190. Moreno JAS, Mendes AC, Stephansen K, Engwer C, Goycoolea FM, Boisen A, et al. Development of electrosprayed mucoadhesive chitosan microparticles. *Carbohydrate polymers*. 2018;190:240-7.
191. Nilsen-Nygaard J, Strand SP, Vårum KM, Draget KI, Nordgård CT. Chitosan: Gels and interfacial properties. *Polymers*. 2015;7(3):552-79.
192. Sarmento B, das Neves J. Chitosan-based systems for biopharmaceuticals: delivery, targeting and polymer therapeutics: John Wiley & Sons; 2012.
193. Panda PK, Dash P, Chang Y-H, Yang J-M. Improvement of chitosan water solubility by fumaric acid modification. *Materials Letters*. 2022;316:132046.
194. Younes I, Rinaudo M. Chitin and chitosan preparation from marine sources. Structure, properties and applications. *Marine drugs*. 2015;13(3):1133-74.
195. Ali A, Ahmed S. A review on chitosan and its nanocomposites in drug delivery. *International Journal of Biological Macromolecules*. 2018;109:273-86.
196. Detsi A, Kavetsou E, Kostopoulou I, Pitterou I, Pontillo ARN, Tzani A, et al. Nanosystems for the encapsulation of natural products: The case of chitosan biopolymer as a matrix. *Pharmaceutics*. 2020;12(7):669.
197. Fakhri E, Eslami H, Maroufi P, Pakdel F, Taghizadeh S, Ganbarov K, et al. Chitosan biomaterials application in dentistry. *International journal of biological macromolecules*. 2020;162:956-74.
198. Kumirska J, Weinhold MX, Thöming J, Stepnowski P. Biomedical activity of chitin/chitosan based materials—influence of physicochemical properties apart from molecular weight and degree of N-acetylation. *Polymers*. 2011;3(4):1875-901.
199. Denkbaş EB, Kilicay E, Birlikseven C, Öztürk E. Magnetic chitosan microspheres: preparation and characterization. *Reactive and Functional Polymers*. 2002;50(3):225-32.
200. Machado TS, Crestani L, Marchezi G, Melara F, de Mello JR, Dotto GL, et al. Synthesis of glutaraldehyde-modified silica/chitosan composites for the removal of water-soluble diclofenac sodium. *Carbohydrate Polymers*. 2022;277:118868.
201. Torres-Badajoz SG, Rodríguez-Núñez JR, López-Ramírez E, Peña-Caballero V, Villa-Lerma AG, Madera-Santana TJ, et al. Kinetic and Equilibrium Studies of Cr (VI) Adsorption Using Glutaraldehyde-Crosslinked Chitosan Beads. *Iranian Journal of Science and Technology, Transactions A: Science*. 2022:1-14.
202. Jawad AH, Abdulhameed AS, Selvasembian R, AlOthman ZA, Wilson LD. Magnetic biohybrid chitosan-ethylene glycol diglycidyl ether/magnesium oxide/Fe₃O₄ nanocomposite for textile dye removal: Box-Behnken design optimization and mechanism study. *Journal of Polymer Research*. 2022;29(5):1-15.
203. Rosales GG, Ávila-Pérez P, Reza-García J, Cabral-Prieto A, Pérez-Gómez E. Nanoparticle Beads of Chitosan-Ethylene Glycol Diglycidyl Ether/Fe for the Removal of Aldrin. *Journal of Chemistry*. 2021;2021.
204. Dumont VC, Carvalho IC, Andrade VB, de Sá MA, Ferreira AJ, Carvalho SM, et al. Nanohydroxyapatite reinforced chitosan and carboxymethyl-chitosan biocomposites chemically crosslinked with epichlorohydrin for potential bone tissue repair. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 2022;71(10):740-55.
205. Lee SJ, Hwang K-J, Youn Y, Kim S-C, Yoon S-D, Shim W-G. Synthesis and Characteristic Properties of Crosslinked Chitosan with Epichlorohydrin for Nitrate Removal from Water. *Journal of Nanoscience and Nanotechnology*. 2021;21(9):4974-9.
206. Li T-t, Liu Y-g, Peng Q-q, Hu X-j, Liao T, Wang H, et al. Removal of lead (II) from aqueous solution with ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles: Kinetic and equilibrium modeling. *Chemical Engineering Journal*. 2013;214:189-97.
207. Gabris MA, Rezanian S, Rafieizonooz M, Khankhaje E, Devanesan S, AlSalhi MS, et al. Chitosan magnetic graphene grafted polyaniline doped with cobalt oxide for removal of arsenic (V) from water. *Environmental research*. 2022;207:112209.
208. Mahatmanti F, Kusumastuti E, Rengga W, Siswanta D. Chitosan-silica-polyethylene Glycol (Ch/Si/P) Solid Membrane for Removal of Cu (II), Zn (II) and Cd (II) Ions from Aqueous Solutions. *Challenges and Advances in Chemical Science Vol 1*. 2021:54-72.
209. Sabaa MW, Elzanaty AM, Abdel-Gawad OF, Arafa EG. Synthesis, characterization and antimicrobial activity of Schiff bases modified chitosan-graft-poly (acrylonitrile). *International journal of biological macromolecules*. 2018;109:1280-91.
210. Eliza E, Desneli D, Mara A, Riyanti F. Study of Effect of Weight Ratio on Copolymerization of Chitosan and Acrylamide. *IJFAC (Indonesian Journal of Fundamental and Applied Chemistry)*. 2021;6(3):96-102.
211. Karimi F, Ayati A, Tanhaei B, Sanati AL, Afshar S, Kardan A, et al. Removal of metal ions using a new magnetic chitosan nano-bio-adsorbent: A powerful approach in water treatment. *Environmental Research*. 2022;203:111753.
212. Hamza MF, Hamad DM, Hamad NA, Abdel-Rahman AAH, Fouda A, Wei Y, et al. Functionalization of magnetic chitosan microparticles for high-performance removal of chromate from aqueous solutions and tannery effluent. *Chemical Engineering Journal*. 2022;428:131775.
213. Huang Y, Zheng H, Hu X, Wu Y, Tang X, He Q, et al. Enhanced selective adsorption of lead(II) from complex wastewater by DTPA functionalized chitosan-coated magnetic silica nanoparticles based on anion-synergism. *Journal of Hazardous Materials*. 2022;422:126856.
214. Li C, Marin L, Cheng X. Chitosan based macromolecular probes for the selective detection and removal of Fe³⁺ ion. *International Journal of Biological Macromolecules*. 2021;186:303-13.
215. Li C, Duan L, Cheng X. Facile method to synthesize fluorescent chitosan hydrogels for selective detection and adsorption of Hg²⁺/Hg⁺. *Carbohydrate Polymers*. 2022;288:119417.
216. Hajri AK, Jamoussi B, Albalawi AE, Alhawiti OHN, Alsharif AA. Designing of modified ion-imprinted chitosan particles for selective removal of mercury (II) ions. *Carbohydrate Polymers*. 2022;286:119207.
217. Pereira L. Seaweed flora of the european north atlantic and mediterranean. *Springer handbook of marine biotechnology*: Springer; 2015. p. 65-178.
218. Metin AÜ, Alver E. Fibrous polymer-grafted chitosan/clay composite beads as a carrier for immobilization of papain and its usability for mercury elimination. *Bioprocess and biosystems engineering*. 2016;39(7):1137-49.
219. Negm NA, Hefni HH, Abd-Elalaa AA, Badr EA, Abou Kana MT. Advancement on modification of chitosan biopolymer and its potential applications. *International journal of biological macromolecules*. 2020;152:681-702.
220. do Nascimento JM, de Oliveira JD, Rizzo AC, Leite SG. Biosorption Cu (II) by the yeast *Saccharomyces cerevisiae*. *Biotechnology Reports*. 2019;21:e00315.
221. Khanniri E, Yousefi M, Mortazavian AM, Khorshidian N, Sohrabvandi S, Arab M, et al. Effective removal of lead (II) using chitosan and microbial adsorbents: Response surface methodology (RSM). *International Journal of Biological Macromolecules*. 2021;178:53-62.
222. Awwal MR, Hasan MM. Novel conjugate adsorbent for visual detection and removal of toxic lead (II) ions from water. *Microporous and mesoporous materials*. 2014;196:261-9.
223. Lin D, Ji R, Wang D, Xiao M, Zhao J, Zou J, et al. The research progress in mechanism and influence of biosorption between lactic acid bacteria and Pb (II): a review. *Critical reviews in food science and nutrition*. 2019;59(3):395-410.
224. Huang Y, Wu H, Shao T, Zhao X, Peng H, Gong Y, et al. Enhanced copper adsorption by DTPA-chitosan/alginate composite beads: mechanism and application in simulated electroplating wastewater. *Chemical Engineering Journal*. 2018;339:322-33.