



Review

Hg(II) removal from water by chitosan and chitosan derivatives: A review

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ABSTRACT

Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment. Its toxicity is related to the capacity of its compounds to bioconcentrate in organisms and to biomagnify through food chain. A wide range of adsorbents has been used for removing Hg(II) from contaminated water. Chitosan is obtained by alkaline deacetylation of chitin. The adsorption capacity of chitosan depends on the origin of the polysaccharide, and on the experimental conditions in the preparation, that determine the degree of deacetylation. A great number of chitosan derivatives have been obtained by crosslinking with glutaraldehyde or epichlorohydrin among others or by grafting new functional groups on the chitosan backbone with the aim of adsorbing Hg(II). The new functional groups are incorporated to change the pH range for Hg(II) sorption and/or to change the sorption sites in order to increase sorption selectivity. The chemical modification affords a wide range of derivatives with modified properties for specific applications. Hg(II) adsorption on chitosan or chitosan derivatives is now assumed to occur through several single or mixed interactions: chelation or coordination on amino groups in a pendant fashion or in combination with vicinal hydroxyl groups, electrostatic attraction in acidic media or ion exchange with protonated amino groups. This review reports the recent developments in the Hg(II) removal in waste water treatment, using chitosan and its derivatives in order to provide useful information about the different technologies. When possibly the adsorption capacity of chitosan and chitosan derivatives under different experimental conditions is reported to help to compare the efficacy of the Hg(II) removal process. A comparison with the adsorption capacity of other low-cost adsorbents is also tabled.

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1. Introduction

Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment including lithosphere, hydrosphere, atmosphere and biosphere and its toxic nature has been known for centuries. Mercury persists in the environment and often creates long-term contamination problems. There is general agreement on the following six points: (1) the element mercury and its compounds have no known normal metabolic function and its presence in living organisms represents contamination from natural and anthropogenic sources (2) forms of mercury with relatively low toxicity can be transformed into forms with very high toxicity through biological and other processes; (3) methylmercury can be bioconcentrated in organisms and biomagnified through food chains, returning mercury directly to man and other upper trophic level consumers in concentrated form; (4) mercury is a mutagen, teratogen, and carcinogen, and causes embryocidal, cytochemical, and histopathological effects; (5) high mercury content in some species of fish and wildlife from remote locations emphasize the complexity of natural mercury cycles and human impacts on these cycles and (6) the anthropogenic use of mercury should be reduced, because the difference between tolerable natural background levels of mercury and harmful effects in the environment is exceptionally small [1].

The toxicity of mercury depends strongly on its redox state [2]. The most toxic form of mercury is the highly reactive Hg^{2+} , which binds to the amino acid cysteinein proteins. In contrast, the danger of elemental mercury (Hg^0) and organo-mercury compounds lies in their transport routes. Mercury vapor is easily inhaled, enters the blood stream in the lungs and is thus distributed throughout the body. Within cells, it is oxidized to reactive Hg^{2+} . The toxicity of monomethylmercury (MeHg^+) or dimethylmercury (Me_2Hg) is caused by its ability to penetrate membranes within seconds and also to cross the blood–brain barrier. Symptoms of mercury poisoning are mainly neuronal disorders but also damage to the cardiovascular system, kidney, bones, etc. [2,3].

The three major sources of Hg emissions are natural, anthropogenic and re-emitted sources [4]. Urban discharges, agricultural materials, mining and combustion and industrial discharges are the principal anthropogenic sources of Hg pollution in the environment. The most important ore of mercury, cinnabar (HgS), has been mined continuously since 415 BC. In the period before the industrial revolution, Hg was used extensively in gold extraction; in the 1800s, it was used in the chloralkali industry, in the manufacture of electrical instruments, and as a medical antiseptic; and since 1900, it has been used in pharmaceuticals, in agricultural fungicides, in the pulp and paper industry and in the production of plastics [5].

Mercury undergoes complex physical, chemical and biological transformations in the environment, being the principal ones: (a) the transport of Hg^0 through the atmosphere, its photochemical oxidation to reactive Hg^{2+} and subsequent deposition on soils, lakes, rivers and the sea; (b) the methylation of Hg^{2+} by reducing bacteria in anoxic habitats, its uptake by aquatic organisms and accumulation in the food web, resulting in high mercury concentrations in fish and chronic low level exposure of humans [6]. Hg contamination can be much more widespread than that observed for other metals, due to atmospheric transport [7,8] or to biomagnification through the food chain, reaching fish and humans [9].

From the above considerations, it is evident that removal of mercury ions from water and wastewater is very important. Different technologies are available: chemical precipitation, coagulation, ion exchange, membrane technologies, adsorption, etc. The latter is by far the most versatile and widely used, and activated carbon is the most commonly used sorbent. However, the use of activated carbon is expensive, so there has been increased interest in the last years in

the use of other adsorbent materials, particularly low-cost adsorbents [10,11]. The use of adsorbents containing natural polymers has received great attention, in particular polysaccharides such as chitin and its derivate chitosan. Excellent reviews on metal complexation by chitosan are those of Varma et al., Crini and Kurita [12–14]. Chitin is the second most abundant natural biopolymer after cellulose and the most abundant amino polysaccharide. It is found in the shells of crustaceans, shells and skeletons of mollusks and krill, on the exoskeletons of some arthropods and in the cell walls of some fungi [15,16]. Chitin exists in nature as ordered crystalline microfibrils. Depending on its source, three different crystalline polymorphic forms of chitin have been identified: α -chitin, the most abundant (shrimp and crab shells), β -chitin (squid pen), and γ -chitin (stomach cuticles of cephalopoda) corresponding to parallel, anti-parallel and alternated arrangements of polymer chains, respectively [17].

Chitosan, a copolymer that is primarily composed of β (1 \rightarrow 4) linked 2-amino-2-deoxy-D-glucopyranose units, and residual 2-acetamido-2-deoxy-D-glucopyranose units, is a chemical derivative obtained by alkaline deacetylation of chitin and also it is found naturally in some fungal cell walls. Since it is harmless to humans and presents excellent biological properties such as biodegradation in the human body, immunological, antibacterial, and wound-healing activity [18,19], chitosan has been widely used in food and pharmaceutical processes and in medical and agricultural drugs [20–24].

Chitosan is well known as an excellent biosorbent for metal cation removal in near-neutral solutions because the large number of NH_2 groups. The excellent adsorption characteristics of chitosan for heavy metals can be attributed to (1) high hydrophilicity due to large number of hydroxyl groups of glucose units, (2) presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups) (3) high chemical reactivity of these groups and (4) flexible structure of the polymer chain [13]. The reactive amino group selectively binds to virtually all group III transition metal ions but does not bind to groups I and II (alkali and alkaline-earth metal ions) [25]. Also, due to its cationic behavior, in acidic media, the protonation of amine groups leads to adsorption of metal anions by ion exchange [26,27].

Several methods have been used to modify natural chitosan either physically or chemically in order to improve the adsorption capacity [28,29]. Crosslinking with glutaraldehyde (GLA) or epichlorohydrin (EPI) can be cited as examples of chitosan chemical modifications. These reactions are done in order to prevent its dissolution in acidic solutions or to improve metal sorption properties (to increase sorption capacity and/or to enhance sorption selectivity) [26]. It must be taken into account that crosslinking can reduce the adsorption capacity as it diminishes the quantities of free amino groups, but this loss of capacity may be necessary to ensure stability of the polymer [10]. The adsorption capacity of chitosan varies with porosity, crystallinity, affinity for water, percent deacetylation and the related amino group content [30].

Chitosan can be molded in several shapes, membranes, microspheres; gel beads and films, and is able to provide a ratio: surface area/mass that maximizes the adsorption capacity and minimizes the hydrodynamic limitation effects, such as column clogging and friction loss [31].

The aim of this study is to review the literature in order to provide useful information about the different technologies for Hg removal from solution using chitosan and its derivatives and when possibly to report the adsorption capacity under different experimental conditions.

1.1. Physicochemical characteristics of chitosan

Chitosan, poly- β (1-4)-2-amino-2-deoxy-D-glucopyranose is a polysaccharide obtained by partial or total N-deacetylation of chitin

poly- β (1-4)-2-acetamide-2-deoxy-D-glucopyranose. The difference between chitin and chitosan is the deacetylation degree and their respective solubility in dilute acidic media. Chitosan is the only derivative soluble at a degree of deacetylation above 40% [32]. Although the polymer backbone consists of hydrophilic functional groups and is hydrophobic in nature, chitosan is normally insoluble in water at near neutral pH and most common organic solvents (e.g. DMSO, DMF, NMP, organic alcohols, pyridine). The insolubility of chitosan in aqueous and organic solvents is a result of its crystalline structure, which is attributed to extensive intramolecular and intermolecular hydrogen bonding between the chains and sheets, respectively [33].

The degree of deacetylation depends on the raw material from which chitin was obtained and the experimental procedure, and controls the fraction of free amino groups that will be available for interactions with metals ions [26]. When the degree of deacetylation of chitin is larger than 40–50%, chitosan becomes soluble in acidic media. The solubilization occurs by protonation of the NH_2 groups on the C2 position of the D-glucosamine unit, although the distribution of acetyl groups along the chain may modify solubility [30,34]. The presence of amino groups makes chitosan a cationic polyelectrolyte ($\text{pK}_a = 6.5$), one of the few found in nature.

The adsorption capacity of chitosan depends on the origin of the polysaccharide, and on the experimental conditions in the preparation, that determine the degree of acetylation, molecular weight, crystallinity, hydrophilicity, etc. [35]. Metal adsorption on chitosan or chitosan derivatives is now assumed to occur through several single or mixed interactions: chelation or coordination on amino groups in a pendant fashion or in combination with vicinal hydroxyl groups, electrostatic attraction in acidic media or ion exchange with protonated amino groups through proton exchange or anion exchange, the counter ion being exchanged with the metal ion [13]. It is important to note, that different kind of interactions can act simultaneously and that hydrogen bonding due to the amino groups can also be involved in the sorption process.

1.2. Modified chitosan

Chitosan can be modified by chemical or physical processes in order to improve the mechanical and chemical properties.

1.2.1. Physical modification

The efficiency of adsorption depends on physicochemical properties, mainly surface area, porosity and particle size of adsorbents. Chitosan has a very low specific area ranging between 2 and $30 \text{ m}^2 \text{ g}^{-1}$ whereas most commercial activated carbons range between 800 and $1500 \text{ m}^2 \text{ g}^{-1}$ [13]. Chitosan based material are used in different fields of application in the form of powder, flakes and foremost as gels: beads, membranes, sponge, fibers, hollow fibers, etc. [36–39]. Flake and power forms of chitosan are not suitable to be used as adsorbents due to their low surface area and no porosity [12]. Chitosan flakes modified into beads are essential for the enhancement of adsorption performance [26]. There are many studies describing the preparation of chitosan gels [39–44]. Manufacturing of gel beads allows an expansion of the polymer network improving access to internal sorption sites and enhancing diffusion mechanisms [43].

Despite the high performance of chitosan beads, there have been difficulties in transferring the process to industrial applications, probably because they are fragile in nature in terms of mechanical strength and they present low stability in acidic media [45].

The solvent evaporation method is mainly used for the preparation of chitosan membranes and films. Solid chitosan is obtained when an acidic chitosan solution is mixed with alkali. This method is used also to produce chitosan membranes, fibers, but foremost spherical beads of different sizes and porosities [26,46].

Furthermore, porous three-dimensional sponges can be prepared by freeze-drying, where chitosan solutions or gels are frozen followed by lyophilisation. The porosity and morphology of the material produced depends on the chitosan molecular weight and on the composition and concentration of the starting solution, and most importantly on the freezing temperature and freezing rate [42].

Porosity and related characteristics can be manipulated using cryogenic phase separation, by cross-linking agents, incorporating spacer metals that can be later removed, by adjusting of the base in the casting bath, by the inclusion of hydrocarbons such as nonanyl chloride to reduce hydrophobic effect, and by the grafting of compounds containing functional groups to chitosan [47].

An increase in intraparticle diffusion can be obtained by reducing crystallinity by dissolution of chitosan (in acid solution) followed by a coagulation process for the preparation of gel beads [43] or by direct freeze-drying of the polymer solution [48].

1.2.2. Chemical modification

The chemical modification of chitosan is of interest as the modification would not change the fundamental skeleton of chitosan but bring new or improved properties. A great number of chitosan derivatives have been obtained with the aim of adsorbing metal ions by grafting new functional groups on the chitosan backbone. The new functional groups are incorporated to increase the density of sorption sites, to change the pH range for metal sorption and to change the sorption sites in order to increase sorption selectivity for the target metal [14]. The chemical modification affords a wide range of derivatives with modified properties for specific and use applications in diversified areas mainly of pharmaceutical, biomedical and biotechnological fields [49].

There is a lot of literature concerning chitosan derivatives. Excellent reviews are those of Varma et al., Crini, Kurita, Sashiwa and Aiba, Mourya and Inamdar, Rinaudo [12–14,24,49,50].

Chemical modification of chitosan has two main aims: (a) to improve the metal adsorption properties, and (b) to change the solubility properties of chitosan in water or acidic medium. The substitution chemical reactions involve the NH_2 group in the C2 position or the OH groups in the C3 and C6 positions of acetylated and deacetylated units. The main reaction easily performed involving the NH_2 group is the quaternization of the amino group or the reductive amination in which an aldehydic function reacts with the NH_2 group [50]. Grafting of chitosan allows the formation of functional derivatives by covalent binding of a molecule, the graft, onto the chitosan backbone [19]. The properties of the resulting graft copolymers are controlled by the characteristics of the side chains, including molecular structure, length and number [49].

Cross-linking agents are generally composed by functional groups separated by some spaced molecules that can be structured in various forms (rings, straight chains, branched chains). The crosslinking agents can be of varying length and contain other functional groups than those involved in cross linking [47]. Partial crosslinking by di/polyfunctional reagents enables the use of chitosan for metal adsorption in acidic medium. In a general way, the adsorption capacity decreases with the extent of crosslinking as it diminishes the reactive sites on the chitosan polymer [51] but also, it can improve the adsorption capacity, depending on the functional groups in the crosslinking agent [52]. Several bi- or polyfunctional cross-linking agents have been used, such as glutaraldehyde (GLA) [29,45,53–55], ethylene glycol diglycidyl ether (EGDE) [56,57], glyoxal [51], epichlorohydrin (EPI) [28,31], benzoquinone [58], cyclodextrin (CD) [59–61], etc. The fact that the crosslinking agents cited before are neither safe nor environmentally friendly, has led to the use of water-soluble crosslinking agents such as sodium trimetaphosphate, sodium tripolyphosphate, or carboxylic acids [13].

Table 1
Removal of Hg(II) from aqueous solution by chitosan.

Chitosan origin	Maximum adsorption capacity (mg g ⁻¹)	Physical form	Type of study	Chitosan characterization	pH	Isotherm	Reference author
Lobster shell	815 430	Particles	Equilibrium studies Equilibrium and dynamic studies		4.0	L L	McKay et al. [107] Peniche Covas et al. [74]
Crab shell	51.6 (C ^o = 5.22 × 10 ⁻⁵ M)	Powder	Equilibrium and kinetic studies		5.0	L	Huang et al. [108]
Shrimp shells		Surface membranes	Kinetic studies	IR, 13C RMN	6.0		Lopes et al. [75]
Red lobster shells	361.1 (pH 2.5), 461.4 (pH 4.5)	Flakes	Equilibrium studies	FTIR	2.5; 4.5	L; F	Taboada et al. [76]
Commercial chitosan	520	Solid state (flakes)/dissolved state	Equilibrium and kinetic studies		4.0–6.0		Guibal et al. [109]
Commercial chitosan		Solid/dissolved state	Equilibrium and kinetic studies	FTIR, SEC	2.0–6.0		Kunkoro et al. [27]
Crab discards	754.3 (PS = 1.19 mm), 1095.5 (PS = 0.5 mm), 1127.4 (PS = 0.177 mm)	Particles	Dynamic studies		5.0–7.0		Gamage and Shahidi [77]
Commercial chitosan		Particles	Equilibrium studies		3.0; 4.5; 6.0	L; F; R-P	Shafaei et al. [78]
Shrimp shells	106.4	Particles	Equilibrium and kinetic studies		4.0–10.0	L	Benavente et al. [110]; Benavente [79]

L: Langmuir, F: Freundlich, R-P: Redlich Paterson isotherms.

The identification of chitosan and chitosan derivatives has been carried out by different non destructive techniques (Table 2): X-ray diffraction (XRD) [62], scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) [31,63], wide angle X-ray diffraction (WAXRD) [64], X-ray photoelectron spectroscopy (XPS) [65,66], X-ray fluorescence spectroscopy (XRF) [31,63], infrared spectroscopy (IR) [67,68], Fourier transform infrared spectroscopy (FTIR) [69,70], attenuated total reflectance micro-Fourier transform infrared (ATR-FTIR) [31,63], thermogravimetric analysis (TGA) [71], nuclear magnetic resonance (NMR) [70], one-pulse magic angle spinning and cross-polarization nuclear magnetic resonance spectroscopy (13C-CPMAS-NMR) [72,73], size exclusion chromatography (SEC) [27], etc.

2. Removal of Hg(II) from aqueous solutions by chitosan

As we have mentioned before, the extent of Hg(II) removal by chitosan depends on the source of chitosan, the degree of deacetylation, and experimental conditions (pH, particle size, ionic strength, etc.). Results on Hg(II) adsorption onto chitosan from different researchers are shown in Table 1.

The results of different researchers are summarized as follows. Equilibrium and kinetic studies on removal of Hg(II) from water solutions by chitosan from lobster shell was investigated by Peniche-Covas et al. [74]. The researchers reported that adsorption data followed Langmuir isotherm ($Q_m = 429.3 \text{ mg g}^{-1}$) and that intraparticle diffusion was the rate-limiting step.

Thin chitosan membranes prepared by stirring chitosan powder (93% degree of deacetylation) in acetic acid were used to study the kinetics of Hg(II) ions removal from aqueous solution at different temperatures [75]. A rise of temperature accelerated the mass transfer of Hg(II) to the membranes surfaces, resulting Avrami kinetic equation the best fit to experimental data.

Chitosan obtained from red lobster shells in the form of flakes (0.35–0.45 mm) was used in experimental studies on Hg(II) adsorption at pH 2.5 and 4.5, where Hg concentration ranged from 10 mg L^{-1} to 10^4 mg L^{-1} [76]. Langmuir model was the better fit for experimental data. The chitosan adsorption capacity for Hg(II) increased from 361.1 mg g^{-1} (pH 2.5) to 461.4 mg g^{-1} (pH 4.5). Hg(II) adsorption capacity by chitosan was similar to that of commercial resin Amberlite IRA-68.

We already mentioned that protonation of amino groups results in chitosan dissolution in acidic solutions. Under acidic conditions, it is possible to use chitosan without crosslinking treatment. In this case, when the polymer becomes saturated with metal ions, it is necessary to recover the metal-bound macromolecules by an ultrafiltration process. This is the base of the polymer-enhanced ultrafiltration process (PEUF). Guibal et al. [36] studied the mercury recovery on chitosan by sorption in solid-state chitosan and chitosan in dissolved state (PEUF). The maximum sorption capacity of chitosan flakes was 519.6 mg g^{-1} corresponding to 0.53 mol Hg per mol of free amino groups. The poor diffusion properties of chitosan flakes caused that particle size controlled the Hg(II) uptake. To maintain chitosan soluble, the researchers used HCl that affects Hg speciation, due to the formation of chloride species that can be adsorbed onto protonated amino groups in acidic media. Although the Hg(II) uptake by chitosan in a dissolved state was similar to that on solid state, the kinetics of the process were greatly improved. There was a much more efficient use of amino groups when chitosan was used in the liquid form due to a better availability of amino groups (inter and intra hydrogen bonds between the chains of the polymer break during the dissolving step) and to a better accessibility to internal sorption sites (lower diffusion control).

Kunkoro et al. [27] also used the PEUF technique for Hg(II) removal by chitosan. The researchers compared chitosan

and poly(ethylenimine) performance. Comparison of molar metal/amine group ratio at saturation of chitosan in its solid state and dissolved state (PEUF process) showed that dissolving the polymer improves the accessibility of sorption sites and enhances sorption capacity. They found that the maximum binding capacity at saturation obtained was $480 \text{ mmol Hg mol}^{-1}$ monomer unit. The presence of chloride ions strongly influenced the mercury retention, due to the possibility of protonated chitosan (in acidic solutions) attracting anionic chloride-complexes.

The effect of the degree of deacetylation in the removal of Hg(II) from wastewaters by chitosan obtained from crab discards was studied at pH 5.0, 6.0 and 7.0 by Gamage and Shahidi [77]. Different types of chitosan were obtained by selecting different times of deacetylation: type I: 20 h, 91.39% degree of deacetylation; type II: 10 h, 89.30% and type III: 4 h, 86.40%. It was observed that Hg(II) was highly chelated (89.8–97.5%) by the three types of chitosan and under the 3 pH on study.

Shafaei et al. [78] studied the effect of pH and chitosan particle size on the Hg(II) adsorption capacity. The researchers concluded that Langmuir isotherm was the best fit for experimental data. The higher adsorption capacity obtained was 1127 mg g^{-1} at pH 6.0 and chitosan particle size 0.177 mm.

Hg(II) equilibrium and kinetic adsorption experiments on chitosan at different Hg(II) ion concentrations and with different particle sizes of chitosan have been performed [79]. The chitosan was obtained from residual shrimp shells. The results showed that experimental data fitted Langmuir isotherm and that maximum adsorption capacity was 106.3 mg g^{-1} (pH 4.0). The kinetics of the mercury adsorption onto chitosan resulted best described by a pseudo-second-order equation. Desorption of adsorbed Hg(II) onto chitosan was achieved by using NaCl solutions, due to the formation of metal ion-stable complexes at high chloride concentrations: HgCl_4^{2-} , HgCl_3^- and HgCl_2 . The electrostatic repulsion between these mercury-species and the amino groups of chitosan was responsible of Hg(II) desorption.

Although chitosan has a very low specific area ($2\text{--}30 \text{ m}^2 \text{ g}^{-1}$) compared to commercial activated carbons ($800\text{--}1500 \text{ m}^2 \text{ g}^{-1}$), it shows outstanding sorption capacity for Hg(II) ions ranging from 430 to 1127 mg g^{-1} specially in pH close to neutral, due to the presence of large number of functional groups of high chemical reactivity in its chemical structure. Regeneration of the sorbent can be performed in acidic media. Some disadvantages are the fact that chitosan is soluble in acidic media and cannot be used as adsorbent under these conditions, except after physical or chemical modification. In addition, the amine groups of chitosan, although effective for metal ion adsorption, do not have good selectivity for different metal ion adsorption. Also it has to be taken into account that sorption capacity depends on the origin of the polysaccharide and the degree of N-acetylation, the latter difficult to control in terms of reproducibility. Industrial production of chitosan by alkaline chitin deacetylation is not an environmental friendly process, due to the high amounts of alkaline waste produced, however, the use of cultures of yeast and fungi that contain chitosan in their cell walls and septa could be an alternative friendly route.

3. Removal of Hg from aqueous solutions by chitosan derivatives

Results on Hg(II) adsorption onto chitosan derivatives from different researchers are shown in Table 2. It is important to note that the maximum adsorption capacities of the adsorbents presented in this paper depend on experimental conditions, such as temperatures, adsorbent dose, particle size, pH, ionic strength, presence of competitive ions, etc., and they should be taken into account only in a qualitative comparison manner. The original papers should be read for details on experimental conditions.

3.1. Substitution N/O groups

Although chitosan dissolves in aqueous medium at pH less than or equal to 6.5, acidic solutions may not be desirable in many of chitosan's applications (e.g. cosmetics, food, and biomedicines).

Water insolubility at neutral pH is due to intramolecular and intermolecular hydrogen bonding. Chitosan is a multi-nucleophilic polymer due to the presence of the NH_2 and OH functional groups. The initial sites where substitution occurs are the more nucleophilic amino groups. However, the experimental conditions and protection of the NH_2 groups allows O-substitution of the C6 HO groups. Substitution of the NH_2 groups reduces the intermolecular hydrogen bonding and creates space for water molecules to fill in and solvate the hydrophilic groups of the polymer backbone [80]. N-alkylated derivatives can be obtained by treatment of chitosan with aldehydes or ketones via formation of Schiff base intermediates aldimines (from reactions with aldehydes) or ketimines (from reactions with ketones) followed by reduction of the imine with sodium borohydride.

The adsorption of Hg(II) ions by N-(o-carboxybenzyl)chitosan, N-carboxymethylchitosan and chitosan dithiocarbamate was studied at neutral pH by Muzzarelli and Tanfani [81]. Also, chitosan mercaptanes derivatives: (N-(2-hydroxy-3-methyl aminopropyl) chitosan, N-(2-hydroxy-3-mercaptopropyl) chitosan and 6-O-(mercaptoacetate-N-mercaptoacetyl)chitosan), prepared by using mercaptoacetic acid and 1-Cl-2,3-epoxy propane were used for Hg(II) removal from wastewater [71]. The Hg(II) maximum adsorption capacity was: 435.3, 587.8 and 164.5 mg g^{-1} , respectively (pH 4.5). The lower adsorption capacity of 6-O-(mercaptoacetate-N-mercaptoacetyl)chitosan was probably due to steric hindrance. In spite of the fact that the Hg(II) adsorption capacity by the three derivatives was in the same order of magnitude than the ones reported by chitosan (Table 2), these derivatives presented higher thermal stability than chitosan, allowing wider applications for wastewater treatment.

3.2. Grafting

As it was mentioned before, grafting of chitosan allows the formation of functional derivatives by covalent binding of a molecule, the graft, onto the chitosan backbone, increasing functional sites involved in metal complexation. Azacrown ethers have specific selectivity for heavy metals, but they are too soluble to be recovered after used. So, crown ethers were grafted to chitosan in order to increase metal adsorption capacity and selectivity [82]. In this study, the NH_2 group in chitosan was protected by reaction with benzaldehyde. After reaction with epoxy activated aryl azacrown ether, the Schiff's base was removed to give chitosan OH-azacrown ether (CTS-OC). Chitosan NH_2 -azacrown ether (CTS-NC) was obtained by reaction of chitosan with aryl azacrown ether without protection of the NH_2 groups. Results demonstrated that the Hg(II) maximum adsorption capacity was 144.4 and 126.4 mg g^{-1} (pH 6.0) for CTS-OC and CTS-NC, respectively and that the selectivity of chitosan for Hg(II) in the presence of Cd^{2+} and Pb^{2+} was improved.

Adsorption of Hg(II) onto poly(ethyleneimine) grafted chitosan microspheres was studied by Zhou et al. [83]. Grafting of ethylenimine was carried out to increase the content of amino group. The adsorption rate was fast, probably due to small diameter of the chitosan derivative microspheres, less than $10 \text{ }\mu\text{m}$. The Hg(II) maximum adsorptive capacity was 441.3 mg g^{-1} and selective separation of Hg^{2+} and UO_2^{2+} was performed at pH <3. Adsorption of Hg(II) by ethylenediamine modified chitosan magnetic microspheres was also studied by Zhou et al. [84].

The Hg(II) adsorption capacity of a series of insoluble chitosan derivatives prepared by grafting ester and amino-terminated

Table 2
Hg(II) removal from aqueous solution by chitosan derivatives.

Chitosan derivative	Crosslinking agent	Q_m (mg g ⁻¹)	Physical form	pH	Isotherm	Derivative characterization	Reference author
1. Substitution N/O groups N-(2-hydroxy-3-methyl aminopropyl) chitosan N-(2-hydroxy-3-mercaptopropyl)chitosan 6-O-(mercaptoacetate-N-mercaptoacetyl) chitosan		435.3 (pH 4.5), 587.8 (pH 4.5), 164.5 (pH 4.5)	Particles	2.5; 4.5	L	SEM;FTIR, elemental analysis, TGA	Cardenas et al. [71]
2. Grafting Chitosan NH ₂ -azacrown ether (CTS-NC) chitosan OH-azacrown ether (CTS-OC) Poly(ethyleneimine) grafted chitosan Ethylenediamine grafted magnetic chitosan Ester and amino-terminated hyperbranched polyamidoamine polymers grafted on chitosan	GLA	144.4 (CTSOC), 126.4 (CTSNC) 441.3 455.4 421.3–641.92	Particles Microspheres Microspheres	3.5–6.0		FTIR, WAXRD FTIR, WAXRD	Yang et al. [82] Zhou et al. [83] Zhou et al. [84] Qu et al. [64]
3. Polymerization Calix[4]arene based chitosan polymer (C[4]BCP)		74.22 (C° = 0.02 mM, pH 1.5)		1.5–4.5		IR, FTIR	Tabacki and Yilmaz [69]
4. Crosslinking 6 HO-cross-linked chitosan Dihydroxy azacrown ether crosslinked chitosan (CCTS-AE)	EDGE Epoxy activated dihydroxyazacrown ether	22.1	Beads Particles	1.0–7.0 1.0–7.0		FTIR, WAXRD, 13C-NMR	Oshita et al. [85] Yang et al. [70]
Chitosan immobilized in polyvinyl alcohol	GLA	1895.7 (C° = 1000 mgL ⁻¹)	Beads	4.0			Son et al. [86]
Natural chitosan (CS) GLA-crosslinked chitosan (GLACCS) EPI crosslinked chitosan (EPICCS)	GLA; EPI	CS: 25.3, GLACCS: 75.5, EPICCS: 30.3	Membranes	5.0–7.0	L	SEM-EDX, ATR-FTIR, XRD, XRF	Vieira and Beppu. [31,63]
Natural chitosan (CS) GLA-crosslinked chitosan (GLACCS)	GLA	Membranes: 415 (CS); 888 (GLACCS), spheres: 375 (CS); 647.9 (GLACCS)	Membranes spheres and microspheres	6.0	L	SEM	Vieira and Beppu [87]
Natural chitosan (CS) GLA-crosslinked chitosan (GLACCS) EPI crosslinked chitosan (EPICCS)	GLA; EPI	581.7 (CS), 662.0 (GLACCS), 702.1 (EPICCS)	Membranes		L and extended L		Vieira and Beppu [88]
Crosslinked chitosan innobilized in alginate gel bead (AGCC 5:10)	GLA	666	Particles	5.0	L	SEM-EDX, porosimeter	Chang et al. [89]
HDI-crosslinked deacetylated chitin DBD-crosslinked deacetylated chitin TMA-crosslinked deacetylated chitin	Diisocyanatohexane (HDI) dibromodecane (DBD) trimellitic anhydride (TMA)	361.1–371.1		7	L and F	SEM, XRD, 13C-CPMAS-NMR, WAXRD	Trimukhe and Varma [72,73]
4.1 N/O substitution of crosslinking chitosan Poly aminated chitosan	EDGE	3170 mol m ⁻³	Beads		L	SEM	Kawamura et al. [22,40,41,90,91]
N-(2-pyridylmethyl) crosslinked chitosan (PMC) N-(2-thienylmethyl)crosslinked chitosan (TMC) N-(3-methylthio-propyl) crosslinked chitosan (MTPC)	EPI	421.3 (MTPC)				IR, elemental analysis	Baba et al. [28,92]
Cross linked chitosan azacrown ethers(CCAE I) cross linked chitosan azacrown ethers(CCAE II)	EPI	84.3 (CCAIE), 98.3 (CCAIEI)	Particles	3.5–7.0		WAXRD, FTIR	Yang et al. [93]

Table 2 (Continued)

Chitosan derivative	Crosslinking agent	Q_m (mg g ⁻¹)	Physical form	pH	Isotherm	Derivative characterization	Reference author
Diethiocarbamate crosslinked chitosan resin	EDGE	0.12 mmol mL ⁻¹	Beads	4.0			Ninomiya et al. [94]
Cross-linked aminated chitosan	GLA	453.4	Beads	2.0–9.0	L	IR, SEM-EDX	Jeon and Holl [29]
Cross-linked aminated chitosan	GLA		Spherical granular				Jeon [95]
Cross-linked aminated chitosan	GLA	476	Beads	7.0			Jeon and Ha Park [96]
Ethylenediamine crosslinked chitosan 3 amino-1,2,4 triazole-5 thiol crosslinked chitosan	GLA and EPI	461.4, 443.3		1.0–6.0	L		Atia [97]
Magnetic crosslinked chitosan	GLA + thiourea	613.8		5.0	L	IR	Donia et al. [68]
tris(2-Aminoethyl)amine chitosan resin	EDGE			>3.0		IR	Hakim et al. [67]
Crosslinked carboxymethyl chitosan		127.1 (pH 5)		2.0–7.0	L		Song et al. [98]
4.2 Graft polymerization of crosslinked chitosan							
Chitosan + CT = PCS resin; PCS + SN = PCSSN resin; chitosan + EPI + ON = PCOON resin	Chloromethyl thiiirane (CT), N,N-diethylaminomethyl oxirane (ON), N,N-diethylaminomethyl thiiirane (SN)	PCS: 523–923, PCSSN: 503.5, PCOON: 714.1		5.6			Ni and Xu [99]
Thiol (cysteine) grafted chitosan	GLA	1604.8 (pH 7)	Spherical beads	4.0–10.0	F	N ₂ gas BET, SEM	Merrifield [47] Merrifield et al. [38]
Polyacrylamide grafted on crosslinked chitosan (chitosan g-polyacrylamide)	EDGE	322.6	Beads	4	L	FTIR, XPS	Li et al. [65]; Li and Bai [66]
Thiourea modified magnetic chitosan (TMCS)	GLA	652.2	Microspheres	2.0–10.0	L	XRD, FTIR, TGA	Zhou et al. [62]
5. Composite membranes carrying a dye							
Procion brown MX 5BR immobilized poly(hydroxymethacrylate/chitosan)	2-Hydroxyethylmethacrylate (HEMA) + azobisisobutyronitrile (AIBN)	68.2	Membrane	2.0–6.0		FTIR, SEM	Genc et al. [100]
Reactive yellow 2 composite pHEMA/chitosan resin	2-Hydroxyethylmethacrylate (HEMA) + azobisisobutyronitrile (AIBN)	39.6 mmol m ⁻²	Membrane disks	2.0–7.0		FTIR, SEM	Bayramoglu et al. [101]
Procion green H-4G poly(hydroxymethacrylate/chitosan)	2-Hydroxyethylmethacrylate (HEMA) + azobisisobutyronitrile (AIBN)	48.1	Membrane	2.0–6.0		SEM, FTIR	Genc et al. [102]

XRD: X-ray diffraction; SEM-EDS: scanning electron microscopy coupled with energy dispersive X-ray spectroscopy; WAXRD: wide angle X-ray diffraction; XPS: X-ray photoelectron spectroscopy; XRF: X-ray fluorescence spectroscopy; IR: infrared spectroscopy; FTIR: Fourier transform infrared spectroscopy; ATR-FTIR: attenuated total reflectance micro-Fourier transform infrared; TGA: thermogravimetric analysis; NMR: nuclear magnetic resonance; 13C-CPMAS-NMR: one-pulse magic angle spinning and cross-polarization nuclear magnetic resonance spectroscopy; SEC: size exclusion chromatography.

dendrimer-like polyamidoamine (PAMAM) into chitosan was studied [64]. Hyperbranched polymers represented by “dendrimers” have received considerable attention because of their multifunctional properties. Results showed that the adsorption capacity for Hg(II) ions were higher for the amino-terminated products than those for the ester-terminated products. When the percentage of grafting was high, the adsorption capacity decreased due to the existence of strong steric hindrance and crosslinked structure. Hg(II) maximum adsorption capacity ranged from 762.3 mg g⁻¹ for chitosan to 641.9–421.3 mg g⁻¹ for hyperbranched polymers. The results showed that the products exhibited better adsorption capabilities for Au³⁺ and Hg²⁺ than for other ions.

The results reported (Table 2) indicate that grafting of chitosan improves chitosan Hg(II) selectivity in the presence of other metals in the solution although in some of the studies, the maximum adsorption capacity of chitosan seems to be higher than that of the derivatives.

3.3. Polymerization

The preparation and characterization of a calix[4]arene-based chitosan polymer C[4]BCP and its use for Hg(II) adsorption was reported [69]. Calix[*n*]arenes are cyclic oligomers composed of phenol units very well known as ionophores and for the fact they provide a unique three-dimensional structure. Immobilization of a calix[4]arene derivative, *p*-tert-butylcalix[4]arene bearing dinitrile and mono carboxylate groups onto chitosan was performed in the presence of a coupling reagent *N,N'*-diisopropylcarbodiimide (DIC). The presence of NHC=O group enhances the adsorption of polarizable transition metal ions, such as Hg(II). The Hg(II) adsorption capacity onto C[4]BCP was 74.2 mg g⁻¹ (C° = 0.02 mM) whereas onto chitosan it was 24.0 mg g⁻¹ under the same experimental conditions (Table 2).

3.4. Crosslinking

Partial crosslinking of chitosan by di or polyfunctional reagents is generally performed in order to prevent its dissolution in acidic media or to improve metal sorption properties (to increase sorption capacity and/or to enhance sorption selectivity). The adsorption capacity depends on the extent of crosslinking and decreases with increase of crosslinking [12]. Crosslinking with glutaraldehyde (GLA), epichlorohydrin (EPI) and EDGE are the most common techniques, although different mechanisms are involved as GLA and EDGE tend to crosslink chitosan bonding through the amino groups and EPI through the hydroxyl groups [26].

The results of different researchers are summarized as follows (Table 2). Crosslinked chitosan was obtained by crosslinking the 6-OH group of chitosan with EDGE after the amino groups were protected by formation of Schiff's base with benzaldehyde [85]. After the crosslinking step, deprotection of amino groups was carried out with HCl. The adsorption behavior of Hg(II) ions was studied, and the method applied to the removal of Hg existing as an impurity in commercially available concentrated HCl. 97% Hg in the commercial HCl was removed by chitosan resin. Hg adsorbed on the resin was easily desorbed with 1 M HCl and 0.05 M thiourea solutions.

A new type of crosslinking chitosan was prepared using dihydroxy azacrown ether as the crosslinking agent [70]. In this study, the NH₂ group in chitosan was protected by reaction with benzaldehyde. After reaction with epoxy activated dihydroxy azacrown ether, the Schiff's base was removed by treatment with dilute HCl ethanol solution to give chitosan O-azacrown ether crosslinked chitosan (CTS-AE). The adsorption capacity for Hg(II) ion increased with pH in the solution, mainly due to the presence of primary amine and secondary amine groups in CTS-AE which easily can accept hydrogen ions. The experimental results showed that this

chitosan derivative presents good adsorption capacities and high selectivity for Ag(I) in the presence of Hg(II) ions.

Chitosan beads immobilized in polyvinyl alcohol were crosslinked with GLA and used in Hg(II) adsorption experiments [86]. The maximum adsorption capacity reported was 1895.7 mg g⁻¹ in a single system, but in a mixed system (Cu(II), Hg(II) and Pb(II)), the adsorption capacity decreased to a third of the single value.

The effect of experimental conditions on the adsorption and desorption behavior of Hg(II) ions on natural chitosan and GLA and EPI crosslinked chitosan was studied by Vieira and Beppu [31,63]. The researchers reported that experimental data fitted Langmuir isotherm, and the maximum adsorption capacity increased from pH 5.0 to 6.0 and decreased at pH 7.0. This was explained by the fact that at low pH the chitosan amino groups are protonated, inducing an electrostatic repulsion with Hg(II) ions. The sorption capacities resulted: GLA-crosslinked chitosan > EPI crosslinked chitosan ~ natural chitosan. According to Hsien and Rorrer [52], crosslinking can enlarge the space between the chitosan chains improving the accessibility of amino groups for Hg(II) ions, producing a decrease in crystallinity. Also Monteiro and Airoidi [53,54] proposed that the imine bond in the GLA-crosslinked chitosan is also capable of adsorbing metallic ions. The results of natural and EPI crosslinked chitosan, indicated that adsorption of Hg(II) to chitosan does not occur through the hydroxyl groups, as the results did not change when the OH group was blocked by crosslinking.

Hg(II) adsorption/desorption cycles were carried out by Vieira and Beppu [87] on GLA-crosslinked chitosan membranes and spheres in order to determine the number of cycles for repeated use without considerable loss in adsorption capacity. The researchers also carried out static and dynamic studies using GLA-crosslinking chitosan membranes, spheres and microspheres to study the effect of adsorbent geometry in adsorption. The adsorption capacity values determined by the dynamic method was for membranes and spheres 65% and 77%, respectively of the values obtained by the static method, probably due to the low residence time. The researchers also studied the adsorption competition between Cu(II) and Hg(II) ions in binary and single metal experiments [88].

Chitosan powder was crosslinked with GLA and afterwards homogeneously immobilized in alginate gel bead (AGCC) by Chang et al. [89] for removing Hg(II) from aquatic systems. The Hg(II) maximum adsorption capacity on the AGCC (5:10) bead was 666.0 mg g⁻¹, over 20 times higher than that of plain alginate bead (32.0 mg g⁻¹). Decreasing the bead size of the AGCC resulted in rapid increase of the initial sorption rate for Hg(II) ions, but the uptake capacity resulted independent of bead size, implying that the sorption occurred in the whole mass of AGCC and not only on the external layer of AGCC bead.

An interesting study where chitin was crosslinked using diisocyanatohexane (HDI), trimellitic anhydride (TMA) and dibromodecane (DBD) followed by deacetylation in strong aqueous alkali was reported [72,73]. Only the OH groups were utilized in the crosslinking reaction, and the acetyl amino groups of chitin were hydrolyzed only after the crosslinking step, so the amino groups resulted available to Hg(II) adsorption and not partially used in crosslinking. The Hg(II) maximum adsorption capacities for all products (chitosan, deacetylated chitin, HDI-crosslinked deacetylated chitin, DBD-crosslinked deacetylated chitin, TMA-crosslinked deacetylated chitin and HDI-crosslinked chitosan) were very similar and ranged between 361.1 and 371.1 mg g⁻¹. The crosslinked derivatives resulted insoluble even in low pH media and could be used in the powder form, being unnecessary the additional step of preparing beads.

Crosslinked chitosan derivatives, generally insoluble in acidic and alkaline solutions, are relatively easy to prepare with inexpensive reagents, and in different shapes, beads, membranes, etc.

These derivatives are higher stable with temperature than chitosan. Also, the crosslinked beads present faster kinetics. In spite all these advantages, crosslinked chitosan derivatives have not been fully used at industrial scale, due to the fact that although crosslinking increases stability in acidic and alkaline media, it involves a loss in chain flexibility, and a decrease in the adsorption capacity, as amino functional groups involved in crosslinking are not available for complex formation with heavy metals. Also, as the crosslinking density increases, the polymer hydrophobic character increases and diffusion of metal ions into the polymer net becomes slower.

3.4.1. Chemically modified crosslinked chitosan: substitution of N/O groups

As was mentioned before, the cross-linking step may cause a significant decrease in metal uptake efficiency, especially in the case of chemical reactions involving amine groups. To preserve the adsorption capacity of chitosan beads new crosslinkers that prevent the amine groups to be used in the cross-linking reaction are desirable. In addition, the amine groups of chitosan, although effective for metal adsorption, do not have good selectivity for different metal ions [66]. So, efforts have been directed towards chitosan modification by cross-linkers with chelating properties to improve the adsorption capacity.

The results of different researchers are summarized in Table 2. Substitution of various functional groups by organic acids, amine bases and sulphur compounds onto the chitosan backbone improving Hg(II) adsorption capacity was the main goal of different researchers, among them, the use of polyaminated highly porous chitosan beads (PEI-CS) prepared from by EDGE crosslinking of chitosan beads followed by reaction with EPI and polyethyleneimine [22,40,41,90,91] and the use of N-(2-pyridylmethyl)chitosan (PMC), N-(2-thienylmethyl)chitosan (TMC) and N-[3-(methylthio)propyl]chitosan (MTPC) [28,92]. TMC and MTPC which contain an S atom presented higher selectivity to Hg(II) ions than PMC, attributable to de fact that Hg(II) is a soft acid that prefers to associate with soft ligand atoms on the basis of the HSAB concept. MTPC presented the higher Hg(II) adsorption capacity (421.3 mg g^{-1}), due to the higher coordination ability of the thioether group than the thienyl group and to the existence of a propyl chain spacer unit, which would allow for better flexibility of the main ligating atom, the S atom.

Azacrown ether chitosan derivatives (CCA-E-I; CCA-E-II) prepared by reaction between EPI crosslinked chitosan and azacrown ethers increased the Hg(II) selectivity of chitosan [93]. Also a chitosan based resin possessing the dithiocarbame moiety (DTC-chitosan resin) synthesized using EDGE cross linked chitosan as a base material and CS_2 [94] was tested satisfactorily for Hg(II) removal. The modification of OH groups on chitosan by chemical reactions using ethylenediamine and carbodiimide was also studied [29,95,96].

The uptake of Hg(II) ions by chitosan crosslinked with GLA (CR) subsequently treated with EPI (CR-CI) followed by reaction with ethylene diamine (CR-amine) or 3-amino-1,2,4-thiazole-5 thiol (CR-azole) was studied by Atia [97]. The concentration of active sites was in the sequence CR-azole > CR-amine > CR, nevertheless CR-amine showed higher uptake for Hg(II) ions (461.4 mg g^{-1}) compared to CR-azole (443.3 mg g^{-1}).

Hg(II) adsorption behavior of crosslinked carboxymethyl chitosan was reported by Song et al. [98]. The researchers studied the effect of various experimental factors and reported that the maximum adsorption capacity was 124.4 mg g^{-1} (pH 5.0).

Donia et al. [68] modified magnetic chitosan by use of a Schiff's base cross-linker (GLA + thiourea) and studied the removal of Hg(II) solutions by the obtained resin. The increase in the maximum adsorption capacity was attributed to the presence of the free pair of electrons on N and S atoms suitable for coordination with soft acid Hg(II) ion.

A novel chitosan-based chelating resin (CCTS-TAA) was synthesized for Hg(II) adsorption by Hakim et al. [67] from EDGE-crosslinked chitosan (CCTS) followed by chemical modification with tris(2-aminoethyl)amine moiety (TAA). The CCTS-TAA resin possesses tertiary and primary amine groups, presenting the tertiary amine higher affinity and selectivity for Hg(II).

In order to increase the adsorption capacity of chitosan beads, some functional groups have been introduced to crosslinked chitosan bone skeleton. According to the HSAB theory, Hg(II) is classified as a soft ion, capable to form strong bonds to groups containing N and S atoms (CN⁻, RS⁻, SH⁻, NH₂⁻, etc. The best results seem to be for aminated crosslinked chitosan (Table 2).

3.4.2. Graft polymerization of crosslinked chitosan

It is a well known fact that resins containing function groups of S and N, such as mercapto and amino groups, have high adsorption properties towards Hg(II) ions. So, chelating resins based on chitosan are of interest for wastewater treatment. Chitosan was reacted with chloromethyl thirane (CT) to synthesize a series of crosslinked chelating resins (PCS) containing amino and mercapto groups with different ratio chitosan/CT [99]. The Hg(II) adsorbing capacity of chitosan reported was 676.0 mg g^{-1} whereas Q_m for the series PCS resins ranged from 922.8 to 523.6 mg g^{-1} (pH 5.6).

The thiol group (-SH), well known to form stable complexes with soft heavy metals of high polarizability such as Hg, was grafted to crosslinked chitosan. The adsorption capacity of GLA-crosslinked chitosan beads for Hg(II) ions was enhanced by graft polymerization of cysteine, a thiol-containing compound [38,47]. Equilibrium studies determined that the adsorption capacity was 1604.8 mg g^{-1} at pH 7.0.

Removal of Hg(II) ions was achieved with EDGE-crosslinked chitosan beads grafted with polyacrylamide (chitosan g-polyacrylamide) via surface-initiated atom transfer radical polymerization (ATRP) [65,66]. The selectivity of the new resin for Hg(II) ions over Pb(II) ions can be attributed to the ability of Hg(II) ions to form covalent bonds with the amide by replacing a hydrogen atom from the amide group.

Magnetic adsorbent technology has received considerable attention in recent years, as magnetic adsorbents can be used to adsorb contaminants from aqueous effluents followed by separation from the medium by a simple magnetic process. Thiourea-modified chitosan magnetic microspheres (TMCS) were prepared by grafting of sulphur groups, using EPI as crosslinking agent, on magnetic chitosan microspheres crosslinked with GLA [62].

In a general way, chitosan beads are crosslinked to improve their physical characteristics such as porosity and resistance against solubility principally in solutions of pH <4. However, crosslinked chitosan lacks high specificity towards Hg(II) ions and also, as crosslinking consumes some of the reactive sites on the polymer, it also diminishes the adsorption capacity, unless the crosslinking agent provides with new functional sites. Grafting of different functional groups in the crosslinked chitosan seems to enhance the adsorption capacity and the selectivity and to decrease the time needed to reach equilibrium.

3.5. Composite membrane carrying a dye

The performance of adsorptive membranes is due to its microporous or macroporous structure, the presence of available reactive groups for metal ion binding and to physical and chemical stability under harsh conditions. Genc et al. [100] reported the use of Procion Brown MX 5BR immobilized poly(hydroxyethylmethacrylate/chitosan) composite membrane (pHEMA/chitosan) for removal of Hg(II) from aquatic systems. The interpenetrating network synthesis was achieved by mixing chitosan with 2-HEMA monomer and azobisisobutyronitrile (AIBN).

Procion Brown MX 5BR was covalently immobilized onto the composite membrane via the nucleophilic reaction between the chloride of its triazine ring and the amide and hydroxyl groups of the membrane. The Hg(II) maximum adsorption capacity reported was 68.2 mg g⁻¹ and desorption using 0.010 M HNO₃ solution was 95% after five adsorption/desorption cycles. Competitive adsorption of Cd(II), Pb(II) and Hg(II) ions proved that the membrane showed high selectivity for Hg(II) ions.

Also, Bayramoglu et al. [101] studied the removal of Hg(II) ions from wastewaters by a composite membrane from

poly(hydroxyethylmethacrylate) and chitosan (pHEMA/chitosan) carrying a dye ligand, Reactive yellow-2. Reactive Yellow-2 is an aromatic polysulphonated triazidine dye, with three acidic sulphonate groups and three basic secondary amino groups. The OH and NH₂ groups of the composite membrane react with the Cl of the triazine ring of the dye forming covalent bonds. The reported maximum Hg(II) adsorption capacity was 52.7 mmol m⁻² membrane-dye, whereas in the plain membrane it was 18.82 mmol m⁻².

Another dye, Procion Green H-4G immobilized pHEMA/chitosan membrane was used for Hg(II) removal from aqueous solutions

Table 3

Hg(II) removal from aqueous solution by low-cost materials.

	Maximum adsorption capacity (mg g ⁻¹)	Isotherm	pH	Reference author
Inorganic materials				
2-Mercaptobenzothiazole treated clay	2.71	L	1.0–7.0	Dias et al. [111]
2-Mercaptobenzimidazole-clay	102.49 (30 °C) 190.33 (60 °C)	L	2.0–9.0	Monahar et al. [112]
Natural zeolites (clinoptilolite)	57.5	L-F	8.5	Chojanaki et al. [113]
Char, pozzolana, yellow tuff, GAC	1.38	linear L(pozzolana)	6.5–7.3	Di Natale et al. [114]
Mesoporous aluminosilicate		D-R	5.5	Wu et al. [115]
Mesoporous silica-coated magnetic particles	14		2.0	Dong et al. [116]
Dithiocarbamate-anchored polymer/organosmectite composites	Hg(II):157.3, CH ₃ Hg(I): 214.6, C ₆ H ₅ Hg(I): 90.3		1.0–8.0	Say et al. [117]
Zeolites synthesized from fly ash			4.5	Somerset et al. [118]
Industrial by-products				
Coal	10		7–8.5	Karthikeyan and Chaudhuri [119]
Coal fly ash		F	3.5–4.5	Sen and De [120]
Fe(III)/Cr(III) waste industrial product	37.3	L and F	4.0–10.0	Namasivayam and Senthilkumar [121]
Activated C from waste materials				
From waste slurry generated in fertilizer plants	560		2.0	Srivastava et al. [122]
From coirpith	154	L and F	2.0–12.0	Namasivayam and Kadirvelu [123]
From fertilizer waste	726.2 (27 °C)	L and F	2.0–6.0	Mohan et al. [124]
From cloth	65		2.0–6.5	Babic et al. [125]
From biomass (apricot stones and furfural) and coals	Coals: 37–105, apricot stones: 153 furfural: 174	L	2–10.0	Ekinci et al. [126]
From bagasse pith	172.4–188.7 (30 °C)	L	4.0–9.0	Krishnan and Anirudhan [127]
From furfural	174	L and F	5.5	Yardim et al. [128]
From coconut shell	15.19	L and F	2.0–10.0	Goel et al. [129,130]
From sago west	55.6	L and F	2.0–10.0	Kadirvelu et al. [131]
From <i>Eichornia crassipes</i>	28.4	L and F	5.0	Kadirvelu et al. [132]
From organic sewage sludge		F	1.0–12.0	Zhang et al. [133]
From fruit shell of <i>Terminalia catappa</i>	94.43	L, F and RP	1.0–10.0	Inbaraj and Sulochana [134]
From coirpith			5.0	Namasivayam and Sangeetha [135]
C aerogel	34.96	L and F	4.5	Kadirvelu et al. [136]
Natural and modified waste material				
Bicarbonate treated peanut hull carbon granular activated carbon	109.89, 12.38	L and F	1.5–10.0	Namasivayam and Periasamy [137]
Polyethyleneimine modified cellulose	288	L	7	Navarro et al. [138]
Formaldehyde polymerized sawdust	38.8	L	3.5–8.5	Raji and Anirudhan [139]
Used tyre rubber	14.65	L	2.0–7.0	Meng et al. [140]
Photofilm industrial waste sludge	11.76	L and F		Selvaraj et al. [141]
Polyacrylamide grafted on cotton cellulose	712.1		6.0	Bicak et al. [142]
Polysulphide treated coconut husk	88.17	L and F	5.5–10.0	Sreedhar et al. [143]
Acrylamide graft polymerization onto coconut husk	124.7	L	6.0	Sreedhar and Anirudhan [144]
Cellulose form sugarcane bagasse modified with urea	280	L	5	Orlando et al. [145]
Polyacrylamide grafted on banana stalk	138 (30 °C), 210 (60 °C)	L	6.0–9.0	Shibi and Anirudhan [146]
Formaldehyde pretreated <i>Pinus pinaster</i> bark		F	6.0	Vazquez et al. [147]
Marine macroalga <i>Cystoseira baccata</i> biomass	178 (pH 4.5), 329 (pH 6)	L	1.0–9.0	Herrero et al. [148]
Cation exchange resin of carboxyl banana stem	90.88	L	6.0–9.0	Anirudhan et al. [149]
Polyacrylamide grafted coconut coir pith	254.5	L and F	6.0–8.0	Anirudhan et al. [150,151]
Vulcanized rubber chips		F	1.81–7.89–12.4	Danwanichakul et al. [152]
Chemically treated sawdust (<i>Acacia arabica</i>)	20.62	L and F	2–12.0	Meena et al. [153]

L: Langmuir, F: Freundlich, R-P: Redlich Paterson isotherms.

[102]. The adsorption capacity reported was 48.1 mg g^{-1} for Hg(II) adsorption for the dye composite membrane, whereas it was lower when using the composite membrane carrying no dye: 18.1 mg g^{-1} . The Hg adsorption capacity decreased in competitive adsorption experiments, showing that this membrane had no Hg selective affinity. The researchers also determined that the adsorption capacities of the membranes did not significantly changed during five repeated adsorption/desorption cycles.

Metal chelating membranes have advantages as adsorbents in comparison to microspheres or beads because they are not compressible and present low internal diffusion limitations, but their adsorption capacity for Hg(II) ions seems to be lower than that of other chitosan derivatives (Table 2).

4. Comparison between chitosan and other low-cost adsorbents performance

A research of the recent literature has already been conducted on Hg(II) sorption by a wide variety of low-cost adsorbents. To compete with the commercial ion exchange resin which has an uptake capacity of $0.83\text{--}1.94 \text{ mmol g}^{-1}$ dry resin for strong acidic ion exchanger and $1.23\text{--}3.91 \text{ mmol g}^{-1}$ for the weak acid one, biosorbents must have at least an uptake capacity of $2\text{--}3 \text{ mmol g}^{-1}$ dry mass [29]. Some of the reported low-cost adsorbents include: (1) inorganic materials as zeolites, clay minerals, puzzolanes, iron oxides; (2) industrial wastes generated as by-products as lignin, iron (III) hydroxide and red mud, low rank coal lignite, fly ash, coal, etc.; (3) agricultural wastes, natural or chemically modified, such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut, hazelnut and coconut shells, cotton seed hulls, waste tea leaves, maize corn cob, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, sunflower stalks, coffee beans, etc.; (4) activated carbon (AC) prepared from waste materials (agriculture and wood industry, industrial activities, municipal waste, etc.). AC is an efficient adsorbent to remove several pollutants from aqueous solutions, but its large-scale production is limited by high production cost [103]. AC prepared from waste material might effectively compete with the commercial AC. Nevertheless, it should be taken in consideration that chemically modified wastes can enhance the adsorption of heavy metal ions, but the cost of the chemicals used in the treatments may increase the cost of the low-cost adsorbents.

The use of low-cost adsorbents for heavy metal removal from solution was reviewed by Bailey et al. [10], and Babel and Kurniawan [11], the use of waste materials for activated carbon preparation by Dias et al. [103], the use of chemically modified plant wastes as adsorbents by Wan Ngah and Hanafiah [104], and the use of agricul-

tural waste material by Sud et al. [105]. Also, a review of adsorbents prepared from the modification of cellulose was done by O'Connell et al. [106].

Results on Hg(II) adsorption from aqueous solutions by different low-cost materials are reported in Table 3. Although as noted before, the maximum adsorption capacity is reported in this paper to give some idea of sorbent effectiveness, as it depends on experimental conditions, a comparison between results reported in Tables 1–3 shows that chitosan and chitosan derivatives present outstanding removal capacities for Hg(II) (Fig. 1).

5. Conclusions

In recent years, increasing costs and environmental considerations has led to the use of new low-cost adsorbents derived from renewable resources. Performance comparison of different low-cost adsorbents is difficult because of inconsistencies in data, principally due to different experimental conditions (pH, temperature, ionic strength, particle size, presence of competing ions, etc.). Cost information of low-cost adsorbents is seldom reported in the publications because it depends on local availability and on the technology applied. Many times, chemically modification of different wastes increases the adsorption capacity, but the technology cost must be taken in consideration in order to produce real “low-cost” adsorbents.

In this paper, a review of Hg(II) adsorption by chitosan and by chemical modified chitosan by direct functional substitution, crosslinking and crosslinking followed by grafting suitable polymeric chains to the chitosan backbone is presented. In a great number of papers reviewed the experimental data of the Hg(II) adsorption process have been fitted to Langmuir model or to the Freundlich one. Regeneration and reusing of the chitosan derivatives is reported when it is possible. Chitosan and chitosan derivatives present outstanding adsorption capacity: 1127 mg g^{-1} for chitosan at pH 6.0 and particle size 0.177 mm [78], 1895 mg g^{-1} for GLA-crosslinked chitosan immobilized in polyvinyl alcohol [86], 1604.7 mg g^{-1} for GLA-crosslinked chitosan grafted with cysteine [38].

The use of chitosan and chitosan derivatives for removing Hg(II) ions from contaminated solutions presents many attractive features such as the outstanding adsorption capacity, high selectivity for Hg(II) ions and the fact that chitosan is obtained from natural raw sources (crustacean shell waste), an environmentally friendly material of low cost, instead of derived from petroleum based materials.

Nevertheless, there are also disadvantages in the use of chitosan or chitosan derivatives. Some of them are the fact that chitosan in flakes or powder is a crystallized polymer, so adsorption takes place in the amorphous region of the crystals, limiting the adsorption capacity. Chitosan beads have reduced crystallinity but they are soluble in acidic media. In the other hand, crosslinked chitosan derivatives, generally insoluble in acidic and alkaline solutions, show a decrease in the adsorption capacity as amino functional groups involved in crosslinking are not available for complex formation with heavy metals. In addition, the amine groups of chitosan, although effective for metal ion adsorption, do not have good selectivity for different metal ion adsorption. Nevertheless, their adsorption capacity can be improved by grafting functional groups onto the polymer backbone. Graft copolymerization of chitosan introduces desired properties and also enlarges the field of potential application of chitosan depending on the type of side chain.

Despite the fact that crosslinked chitosan beads and graft copolymerized chitosan represent a good alternative to replace activated carbon or ion exchange resins, more studies are needed to transfer the process to industrial scale.

The versatility in possible chitosan derivatives let us predict that the Hg(II) sorption performance (equilibrium uptake and removal

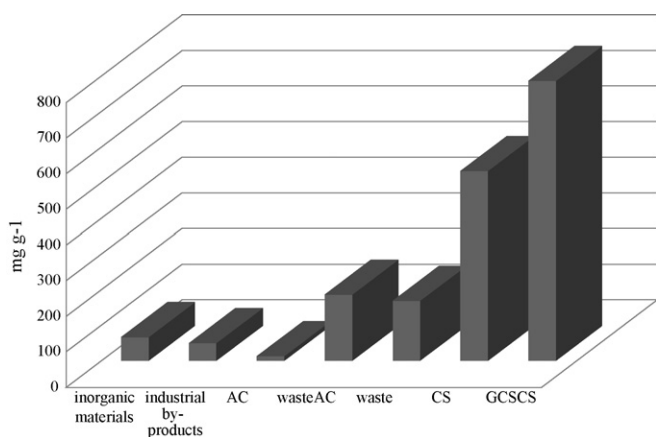


Fig. 1. Comparison of different low-cost adsorbents Hg(II) mean adsorption capacity (AC: activated carbon; CS: chitosan; GCSCS: graft polymerized crosslinked chitosan).

kinetics) and also the selectivity towards Hg(II) ions can be yet enhanced.

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