A Review on Chitosan for the Removal of Heavy Metals Ions

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Abstract

There has recently been an increasing interest in water treatment methods as a result of growing concerns over shortages of clean water. This paper aims to review the past and present researches on chitosan for the adsorption of heavy metals from the wastewater. Adsorption is considered to be the most efficient method for the removal of metal impurities from drinking water. Chitosan, a deacetylated derivative of chitin, has many commercial applications due to its biocompatibility, nontoxicity, and biodegradability. Moreover, amine groups are present on the backbone of chitosan. For this reason, chitosan has been used for the adsorption of heavy metals. To begin with, mechanism of adsorption of heavy metal ions on chitosan and disadvantages of heavy metal ions were reviewed. Further, a detailed review had been done on the adsorption capacities of crosslinked chitosan, chitosan nanofibers, chitosan nanoparticles, chitosan composites, modified/pure chitosan, and porous chitosan. Lastly, research gaps and future recommendations were given for further development and accurate results of adsorption.

Keywords: Chitosan; Heavy Metals; Adsorption; Crosslinked Chitosan

1 Introduction

1.1 The Chemical Construction of Chitosan

Chitosan is linear amino polysaccharide consisting of two basic units, glucose amine and N-acetyl glucosamine, acquired from the deacetylation of chitin in the alkaline environment [1]. Chitin is a natural polymer discovered 200 years ago. It is mainly extracted from cell walls of fungi as well as from the exoskeleton of crustaceans such as shrimp and crabs [2-6]. The structure of chitosan is composed of (1,4)-linked 2-amino-2-deoxy- β -D-glucan as shown in Fig. 1, its chemical name is poly [-(1, 4)-2-amino-2-deoxy-D-glucopyranose] [2, 7, 8]. The structures of chitosan contain amine (NH₂) groups, and as a result have good medical properties for instance biodegradability, biocompatibility and excellent antibacterial activity. It is the only cationic natural occurring

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polymer [9, 10]. Furthermore, chitosan is extensively used for the adsorption of heavy metal ions due to the presence of amine and hydroxyl groups [11–13].

Fig. 1: Chemical construction of chitosan

1.2 Adsorption at Solid/Liquid Interface

Solids and many solvents which do not dissolve in solution and has the tendency to form bonds with the ions present in solution are called ion exchangers; and the process of ion exchange that occurs at solid/liquid interface is known as ion exchange adsorption. Fig. 2 shows the schematic representation of adsorption solid/liquid interface. Various ion exchange minerals exist in nature such as: alumina silicates from zeolite group and clays of bentonite and montmorillonite.

Fig. 2: Schematic representation of adsorption at solid/liquid interface

There are three main types of ion exchanger's i.e. natural, semisynthetic and synthetic ion exchangers. Natural ion exchange materials were the first which found the applications in the purification of water. Bentonite clay and zeolites are common ion exchange materials. An example of zeolite structure is aluminate AlO_4 in which Al^{3+} ions are surrounded in tetrahedral by double negative charge of oxygen ions or OH^- groups with single negative charge. These excess negative charges are balanced with alkali metals or alkaline earth metal ions which are loosely bound with the crystal lattice. These metal ions can be displaced or substituted with the ions present in solution [14].

Semisynthetic ion exchangers are natural materials which have been subjected to chemical treatment. Sulfonated coal is regarded as typical semisynthetic ion exchange material, which is obtained by the sulfonation of natural coal by using concentrated sulphuric acid. It has been studied that cation exchangers with having high adsorption capacity can be obtained from certain types of coal [15].

Synthetic ion exchangers can be obtained by either inorganic or organic synthesis routes. An example of synthetic cation exchanger is made by inorganic synthesis is aluminosilicates type but of different chemical compositions depending upon the raw materials used for production. They have general composition:

Currently available ion exchangers are synthesized by organic route. There are synthetic resins which are insoluble in water, alcohols, ethers and some hydrocarbons. They have high exchange capacity and greater tensile strength and chemical resistance which make them suitable for many applications [15]. They can be cationic or anionic in nature; their composition can be represented as:

where R is the polymer frame, A^- is anionic group such as $-\text{COO}^-$ attached to the polymer by atomic bond, Me^+ is the cation, it can be a metal ion or H^+ ion bonded with the anion by an ionic bond and is capable to be changed. Similarly, B^+ is cationic group e.g. NH_2^+ and X^- is an anion like OH^- .

1.3 Complex Formation of Chitosan with Heavy Metal Ions

The ability of chitosan to adsorb metal ions through forming complexes was discovered when researchers expressed interest in it [16-19]. Studies show that the complexation ability of chitosan is influenced by its physical state, when it is in the form of powder, gel, fibre, particles or films [20, 21]. The degree of acetylation is however considered to be the major factor in the complexation process, proved by Micera [22] and Kurita [23].

Potentiometry is considered to be the fundamental method to describe the complex formation of chitosan with metals by studying acid-base reactions and metal-ligand interactions. The acid accepts a pair of the electron (metal) from the base (chitosan) and forms a covalent bond with the metallic ions. The only one free site available in chitosan monomeric unit, amine groups, initiates the covalent bonds with metallic ions. Equations (1), (2) and (3) described the interaction of chitosan with metals [21].

M. Rhazi et al [19] studied the adsorption process of copper at different pH values. It was discovered that when the pH of a solution is less than 5.30 there was no or very small complex

formed between copper Cu(II) ions and chitosan. When pH is greater than 5.30, amino groups made a covalent bond with copper ions and formed $[\text{Cu}(-\text{NH}_2)]^{2+}$ complex as shown in Fig. 3 and in the following equation (4) and (5):

Fig. 3: Structures of chitosan-copper complexes

Another type of complex was also investigated when pH goes above 5.80 where another amino group is incorporated $[\text{Cu}(-\text{NH}_2)_2]^{2+}$ as shown in Fig. 2 and in the equations (6) and (7).

This complex is stable up to pH 7.7; beyond this pH, copper hydroxides will precipitate and the procedure will become difficult to study.

1.4 Heavy Metal Ions Pollution in Water

Currently there are many industries discharging high quantities of heavy metals into the environment. The main sources of heavy metal ions are shown in Fig. 4. These metallic ions cause toxicity to both the ecosystem and human beings. As a result, the international community is now giving more attention to heavy metal pollution [24-27].

Fig. 4: Causes of heavy metal ions pollution in water

One of the major problems that has become a serious concern is water pollution due to heavy metals [28]. Very minute amount of heavy metals can cause serious water pollution due to their high toxicity and non-biodegradable nature [29–31]. Heavy metals also have the tendency to accumulate in living organisms, which is harmful for public health and may cause many disorders and diseases [32–36]. For example, lead $Pb(II)$ which is mostly found in textile dyeing, ceramics and glass industries, petroleum refining, battery manufacture and mining operations etc., [37, 38] can cause mental disorders and semi-permanent damage to the brain [39]. Cadmium $Cd(II)$ is another pollutant that is a product of metal plating, metallurgical alloying, mining and ceramics operations [40]. It causes a wide-range of syndromes such as renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [41]. Likewise, exposure of excess nickel $Ni(II)$ in the human body can cause lungs, cardiovascular and kidney diseases [42, 43]. Chromium $Cr(VI)$ is also a well-known carcinogen. In July 2008, the US national toxicology program showed clear evidence of carcinogenic activity of chromium [44]. It is extensively used in industries like chromate production, chromate pigment production and chrome plating [45, 46]. Studies have shown that lung cancer occurrences are increasing among workers of these industries [47–49]. Copper $Cu(II)$ is an important nutrient which is fused in many metalloenzymes responsible for haemoglobin formation and cross-linking of collagen, elastin and hair keratin, but in redox reactions copper has the ability to reduce from a $Cu(II)$ to $Cu(I)$ state which is toxic. This is due to the generation of super hydroxides and hydroxyl radicals during reduction [50–53]. Zinc $Zn(II)$ is also a vital metal for biological functions. But, when it is used in high concentrations it becomes toxic to animals, ecosystem and can cause nausea, anaemia and pancreas loss [54]. Its main sources are from battery production, galvanic industries mining effluents and acid amine drainage [55, 56]. Among metal pollutants mercury $Hg(II)$ is the most problematic. Nonferrous and ferrous metal production are common sources of $Hg(II)$ pollution [57]. $Hg(II)$ manifested critical health disasters in Japan and Iraq [58–61]. Excess of $Hg(II)$ ions is responsible for brain, gut lining and kidney failure [59].

2 Crosslinked Chitosan for the Removal of Heavy Metal Ions

In crosslinked chitosan, polymeric chains are interconnected with cross linkers, leading to the formation of a 3D network.

Chitosan was crosslinked with diethylenetriaminepentacetic acid when eliminating Cr(VI) ions from aqueous solution [62]. In another study, chitosan was crosslinked with trimesic acid for a similar purpose [63]. The adsorption coefficient was discovered to be higher with the latter crosslinking acid i.e. 192.3 mg/g and 129.53 mg/g when compared with the former at an optimized pH of 3 and 2. Furthermore, both were discovered to be beneficial for removing Pb(II) and Fe(II) ions from chrome plating effluent. Chitosan (CS)/Polyvinyl Alcohol (PVA) physically crosslinked nanoparticles were developed for the adsorption of manganese Mn(II) ions from an aqueous solution. Mn(II) is a major pollutant, which affects the colour, taste and odour of water. The adsorption capability of Mn(II) ions on CS/PVA nanoparticles was studied as a function of pH, adsorbent dose, contact time and different concentrations of solutions [64]. Adsorbent dose had a major effect on the removal of heavy metal ions; this can be attributed to the enhanced surface and more binding sites on CS/PVA nanoparticles. It was found that 83.5% metals ions were removed for 20 mg/L at 0.8g in 100 mL, which is similar to their earlier studies on the removal of Mn(II) ions from water [65].

In a different study, epichlorohydrin was chosen to crosslink with chitosan for the adsorption of Cu(II), Pb(II) and Zn(II) ions from an aqueous solution. The adsorption capacity for Cu(II) (35.40 mg/g) was found to be highest when compared to Pb(II) (13.05 mg/g) and Zn(II) (10.21 mg/g) [66]. However, when compared to pure chitosan, crosslinking has a negative effect on the adsorption of Pb(II) and Zn(II) ions, decreasing their removal efficiencies up to 6.39% and 1.07%. However in the case of Cu(II), it showed an increase in efficiency by more than twofold [67]. Similar studies on the adsorption of Cu(II), Pb(II) and Zn(II) by chitosan crosslinked with glutaraldehyde exhibited correlates with the results in [68]. Table 1 shows the maximum adsorption capacities of crosslinked chitosan.

3 Chitosan Composites for the Removal of Heavy Metal Ions

To enhance the removal and adsorption efficiency of hexavalent Cr(VI) ions, chitosan, graphene oxide and 1, 2-cyclohexylenedinitrilotetraacetic acid nanocomposite was synthesized for the first time. Graphene has more free groups available for adsorption i.e. hydroxyl, carboxyl and epoxy, which results in improved adsorption of heavy metals from aqueous solutions. Maximum adsorption of 166.98 mg/g for Cr(VI) ions was achieved in optimized conditions of pH, temperature and time [74]. In previously reported studies on the adsorption of Cr(VI) ions by chitosan composites, the highest adsorption capacity of 153.85 mg/g was reported [75]. In a further study, chitosan/organoclay composites were developed and the removal efficiency was also found to be less than an above-reported study that is 128.43 mg/g [76]. The adsorption capacity of chitosan can be varied by degree of deacetylation [77]. Habiba et al. studied the degree of effectiveness for the deacetylation of chitosan in chitosan/PVA/TiO₂ nanocomposites. They proved that a degree of deacetylation increased the adsorption efficiency of the composite. This is evident from the

Table 1: Maximum removal ability for heavy metal ions of crosslinked chitosan

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption ($q_{\max}$) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan-clay/Epichlorhydrin	Ni(II)	32.36	6.0	[69]
		Cd(II)	72.31		
2	Chitosan-PVA/Glutaraldehyde	Cd(II)	142.9	6.0	[70]
3	Chitosan/Silica	Cr(VI)	28.88, 23.40	5.0-6.0	[71]
4	Chitosan-halomonas/Glutaraldehyde	Pb(II)	24.15	5.0-7.0	[72]
		Cd(II)	23.88		
5	Chitosan/6, 6-piperazine-1, 4-diyl dimethylenebis (4-methyl-2-formyl) phenol	Cu(II)	76.88	6.5-8.5	[73]
		Ni(II)	38.15		
		Co(II)	27.11		
		Mn(II)	23.62		
		Fe(II)	23.45		
		Cd(II)	58.45		
		Pb(II)	84.94		
6	Chitosan/Epichlorohydrin	Cu(II)	35.46	6.0	[11]
		Zn(II)	10.21		
		Pb(II)	34.13		

presence of NH_2 groups in deacetylated chitosan which functions as essential sites for adsorption [78].

Comparative adsorption of Pb(II), Cu(II) and Cd(II) ions were investigated by chitosan/montmorillonite (Mt) composite [79]. Mt was used because of its good cation exchangeability [80]. Composite was reported to have the highest adsorption capacity for Pb(II). The sequence of the adsorption was $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$. This is due to the higher electronegativity of Pb(II) (3.29) as compared to Cu(II) (2.98) and Cd(II) (2.71) correspondingly. This is due to the high affinity between two atoms when the electronegativity difference of N or O is smaller [81-84]. In another work, chitosan/PVA magnetic composite was prepared by co-precipitation method [85] for the adsorption of Cu(II) ions. This composite can adsorb up to 143.0 mg/g of Cu(II) ions from wastewater [86].

A novel composite Chitosan/Hydroxyapatite membrane was prepared for removal of Pb(II), Co(II) and Ni(II) ions from aqueous solutions. Composite membrane demonstrated maximum adsorption ability for Pb(II) i.e. 296.7 mg/g as compared to Ni(II) (213.8 mg/g) and Co(II) (180.2 mg/g) [87]. In comparison to other studies, chitosan/clinoptilolite composite membrane claimed the highest adsorption of Co(II) (467.9 mg/g) [88] and chitosan/silica have enhanced the ability to adsorbed Ni(II) (254.3 mg/g) [89]. Further studies showed that chitosan/hydroxyapatite

Table 2: Maximum removal ability for heavy metal ions of chitosan composites

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption ($q_{\max}$) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/CDTA/GO	Cr(VI)	166.98	2.0-3.0	[74]
2	Chitosan/Clay	Cu(II)	181.5	7.0	[91]
3	Chitosan/Alumina	Cu(II)	86.2	4.0	[25, 92]
		Ni(II)	78.1		
		As(III)	56.50		
		As(V)	96.46		
4	Chitosan/Glucosamine	Cr(VI)	153.85	4.0	[75]
5	Chitosan/Graphene Oxide	Pb(II)	76.94	5.0	[93]
6	Magnetic Chitosan	Cr(VI)	17.29	1.0-3.5 for Cr(VI) 6.0-7.0	[94, 95]
		Pb(II)	27.95		
		Hg(II)	23.03		
		Cd(II)	27.83		
		Ni(II)	22.07		
		Cu(II)	216.6		
7	Chitosan/PVA	Cu(II)	143.0, 193.39	6.0	[86, 96]
8	Chitosan/Sulfhydryl/Grphene Oxide	Cd(II)	177.0	5.0	[97]
		Pb(II)	447.0		
		Cu(II)	425.0		
9	Chitosan/Anaerobic Granular Sludge	Pb(II)	97.97	6.0 3.0	[98]
		Cu(II)	83.65		
10	Chitosan/PVA/Silk Fibroin	Pb(II)	194.099	6.0	[99]
11	Chitosan/Fe-Hydroxyapatite	Pb(II)	1385.0	-	[100]
12	Chitosan/Magnetite	Ni(II)	63.33	4.0-6.0	[101]
		Pb(II)	52.55		
13	Chitosan/Perlite	Cu(II)	196.07	3.0-4.5	[102-105]
		Ni(II)	114.94		
		Cd(II)	178.6		
		Cr(VI)	153.8		
		Cu(II)	104.0		
14	Chitosan/Silica	Ni(II)	254.3	5.0	[89]
15	Chitosan/PVC	Cu(II)	87.9	4.0	[106]
		Ni(II)	120.5		
16	Chitosan/Sand	Cu(II)	10.87, 8.18	4.2	[107]
		Pb(II)	12.32		
17	Chitosan/Montmorillonite	Cr(VI)	41.67	4.0	[108]
18	Chitosan/Alginate	Cu(II)	67.66	6.0	[109]
19	Chitosan/Calcium Alginate	Ni(II)	222.2	5.0	[89]

composite was used for removal of Fe(II) ions from drinking water and adsorption capacity of 6.753 mg/g was reported [90].

In a different research, chitosan/clinoptilolite composite claimed to have good adsorption capacity against Uranium (UO_2^{2+}) and Thorium (Th^{4+}) ions from radioactive solutions. The maximum adsorption for Th^{4+} 328.32 mg/g and 408.62 mg/g for UO_2^{2+} ions were recorded [110]. Similar material was also used by incorporating zeolite particles for the removal of Cu(II), Co(II) and Ni(II) ions in further studies and the highest adsorption capacity 11.32 mmol/g, 7.94 mmol/g and 4.4209 mmol/g was reported [111, 88, 112]. Table 2 illustrates the maximum adsorption capacities of chitosan composite.

4 Chitosan Nanofibers for the Removal of Heavy Metal Ions

Polyethylene oxide (PEO)/CS nanofibers were tested for their capacity to adsorb Ni(II), Cu(II), Pb(II) and Cd(II) heavy metals from water. Under optimal conditions of pH, temperature and time, results showed the adsorption potential of nanofibers in increasing order, Ni(II) > Cu(II) > Cd(II) > Pb(II). This is due to smaller ionic radius of ions, as radius decreases charge density will increase and number of available sites for adsorption would be enhanced. Therefore, adsorption efficiencies were obtained 89%, 82%, 72% and 68% for Ni(II), Cu(II), Cd(II) and Pb(II) [113]. Similar nanofibers were also used for adsorption of Cu(II) ions from water used in paper making industry. They found to be highly efficient adsorbent for copper ions with 94.7% removal efficiency by using only 75 mg of nanofibers [114].

In previous studies slow adsorption rate of chitosan/PVA nanofibers was reported [115]. To improve rate of adsorption, zeolite nanoparticles were incorporated in nanofibers, these nanofibers proved to adsorb chromium, nickel and iron ions rapidly with maximum removal efficiencies of about 100% [116]. Ionic radius of these metals in decreasing order are Cr(VI) < Fe(III) < Ni(II) [117]. Adsorption was also reported in the similar sequence. Moreover, researchers also studied the effect of degree of deacetylation (DD) of chitosan/PVA nanofibers for adsorption of chromium and iron metal ions. They found that as DD is increased adsorption efficiency was improved for chromium due to increase in amino groups. On the contrary, adsorption efficiency was reduced for iron [118]. This was explained by low molecular weight of chitosan at higher DD due to which a polymer chain may be released from chitosan structure which creates steric hindrance with large Fe ions. Therefore, affecting the adsorption capacity [119].

Furthermore, pure chitosan nanofibers were also synthesized for adsorption of copper and lead ions. Adsorption capacity for copper and lead was 263.15 mg/g and 485.44 mg/g respectively [120]. For copper this value is 6 to 11 times higher than the capacities reported in different studies of chitosan [121-124].

5 Chitosan Nano Particles for the Removal of Heavy Metal Ions

Nanocomposites of chitosan/clay with silver (Ag) and gold (Au) nanoparticles were made to

achieve maximum adsorption of Cu(II) from aqueous solution. They used the surface properties of clay to give additional active sites for adsorption including cations exchange and large surface area. Researchers claimed that there is 100% efficiency of chitosan/clay/Ag nanocomposite for the removal of copper with maximum adsorption capacity of 181.5 mg/g [91]. This capacity is higher than the previously reported highest value for the adsorption of copper ions which was 153.9 mg/g when semi-IPN based hydrogel is used based on chitosan and gelatine [129]. Furthermore, chitosan and alginate nanocomposites were prepared by ion crosslinking method for the adsorption of chromium ions from wastewater [130]. Chitosan was also crosslinked with polyacrylamide to develop nanocomposite with copper; adsorption of lead ions from aquatic solutions in environmental conditions was investigated. The maximum adsorption capacity was found to be 38.93 mg/g [131]. A novel biodegradable and non-toxic nano sorbent based on chitosan-alginate nanoparticles was developed for the removal of mercury (Hg) ions from water. As chitosan is cationic and alginate is anionic in nature, the nano sorbent is efficient in adsorbing both negatively and positively charged heavy metal ions. Researchers claimed that it is the highest adsorption capability of this sorbent as compared to the values reported in the previous literature, where it was recorded as 217.39 mg/g at 30 °C [132]. Similarly, alginate coated chitosan nanoparticles were investigated for the removal of nickel ions from industrial effluents. It was found that 94.48% of nickel was adsorbed at a pH 3 [133]. In another work, quaternized chitosan microspheres (QCMS) were synthesized for removal of Cr(VI) ions from wastewater. It was discovered that 97.34% of chromium was detached under the optimal condition of pH 5 [134].

Further investigations were also made on magnetic chitosan/Fe₃O₄ nanoparticles synthesized by using gravity precipitation method. These particles were used as adsorbents for lead and cadmium ions from aqueous solutions and the maximum removal capacity was found to be 79.24 mg/g for lead and 36.42 mg/g for cadmium ions [145]. These nanoparticles proved to be most efficient for the adsorption of lead and cadmium than any other reported studies on Fe₃O₄ nanoparticles with different materials [146-148, 94, 149, 150]. Table 3 shows the maximum adsorption capacities of chitosan nano/micro particles.

6 Chemically Modified Chitosan for the Removal of Heavy Metal Ions

Badawi et.al. modified the chitosan with tannic acid for the adsorption of Pb and aluminium (Al) ions from water [151]. Tannic acid was previously used for the removal of metal ions because of its ability to form metal complexes [46]. This research reported tannic acid with chitosan for the first time. Results concluded that maximum adsorption was achieved at pH 6 by increasing metal ion concentration and temperature [151]. In another study [152] chitosan was modified with thiosemicarbazide (TSCS) through a condensation reaction for the removal of Cu(II) ions. TSCS has both sulphur and amino groups as compared to chitosan which has only an amino group. As a result, TSCS have more adsorption sites which leads to the increased removal of heavy metals. The adsorption rate however only increased up till 1.5 g/L of TSCS concentration, beyond this point, the adsorption rate remained constant due to the limitation of free sites. In another work [153] a group of researchers studied the kinetics and adsorption isotherms for the adsorption of Cu(II) ions on chitin as well as pure and modified chitosan. Chitosan was chemically modified with ethylenediamine tetra-acetic acid (CS-EDTA) to eliminate copper ions from wastewater and its adsorption was compared with pure chitosan and chitin. 110mg/g was found to be the highest

Table 3: Maximum removal ability for heavy metal ions of chitosan nanofibers

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption ($q_{\max}$) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/PEO	Ni(II)	175.1	5.5	[113] [114]
		Cd(II)	143.8		
		Pb(II)	135.4		
		Cu(II)	163.7, 106.38		
		Cr(VI)	136.0		
2	Chitosan/PVA	Fe(III)	136	-	[118]
		Cu(II)	485.44		
3	Chitosan	Pb(II)	263.15	2.0-3.0	[120] [125]
		Cr(VI)	68.3		
4	Chitosan/Graphene oxide	Cu(II)	423.8	3.0 & 6.0	[126]
		Pb(II)	461.3		
		Cr(VI)	310.4		
5	Chitosan/Hydroxyapatite	Pb(II)	296.7	-	[87]
		Ni(II)	213.8		
		Co(II)	180.2		
6	Chitosan/TiO ₂	Cu(II)	710.3, 579.1	6.0	[127]
		Pb(II)	526.5, 475.5		
7	Chitosan/polymethylmethacrylate	Cr(VI)	92.5	3.0	[128]

adsorption with CS-EDTA as compared to 58 and 67 mg/g for chitin and pure chitosan at pH 7 [154].

In a study, chitosan was also found to be a suitable biopolymer for the adsorption of reactive dyes from water bodies. This is due to the presence of amine and hydroxyl groups on chitosan; dyes have a strong tendency to be adsorbed at primary hydroxyl adsorption sites [155]. The temperature was found to be a major factor for the maximum adsorption of dye on chitosan; this is explained by the swelling behaviour of chitosan in previous studies. As temperature increases the internal structure of chitosan, it will swell enabling dye molecules to penetrate further [156].

In another research, the scientist made chitosan/CoFe₂O₄ magnetic particles modified with tetraethylenepentamine (TEPA) to have maximum adsorption and magnetic properties at the same time. These particles were used for the separate adsorption of copper and lead and also with solutions that have both ions. The maximum adsorption capacity in single solutions was found to be 168 and 228 mg/g for copper and lead, while in bi-component solutions, these values were decreased to 139 and 160 mg/g with a magnetization value of 63.83 emu/g [142]. This application was lacking in preceding studies of chitosan magnetic particles where it was not possible to maintain maximum adsorption and magnetic property [93, 101, 157, 158]. However, magnetic nanoparticles are chemically active and can be easily oxidised in the air which may result in the loss of magnetism. They also cause secondary pollution in the environment due to

Table 4: Maximum removal ability for heavy metal ions of chitosan nano/micro particles

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption ($q_{\max}$) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan-Fe ₃ O ₄	Cu(II)	21.5	5.5	[135]
		Co(II)	27.5		[136]
2	α -ketoglutaric acid- Chitosan	Cu(II)	96.2	6.0	[137]
3	Ethylenediamine-Chitosan	Pt(IV)	171.0	2.0	[138]
		Pb(II)	138.0		
4	Chitosan-Magnetite	Ni(II)	833.3	5.5	[139]
		Co(II)	588.2		
5	Chitosan	Pb(II)	398.0	5.5	[140]
6	Chitosan – Poly acrylic acid	Ni(II)	435.0	4.0	[141]
		Cu(II)	174.0		
7	Chitosan-Alginate	Hg(II)	217.39	5.0	[132]
		Ni(II)	20.09		[133]
8	Chitosan-Co Fe ₂ O ₄	Pb(II)	228.31	6.0	[142]
		Cu(II)	168.06		
9	Chitosan-MAA	Pb(II)	11.30	5.0	[143]
		Cd(II)	1.84		
		Ni(II)	0.87		
10	Chitosan - MnFe ₂ O ₄	Cu(II)	22.6	6.3	[144]
		Cr(II)	15.4		

their small dimensions [159, 160]. In order to eliminate these disadvantages, magnetic chitosan composite with macro particles was developed by adding porous activated carbon for the removal of copper ions and it showed successful results with a maximum capacity for adsorption at 216.6 /mg with 95% efficiency [95]. Elwakeel et al. modified magnetic chitosan with TEPA for the adsorption of uranium ions and the maximum adsorption capacity reached to 1.8 mmol/g [161].

In another study, chitosan was demonstrated as an efficient material for the removal of heavy metals from gold mining effluent. Equilibrium adsorption studies on mercury, copper, lead and zinc showed the maximum removal of these ions at higher pH values between 4 and 6 [169]. A. Ghee et al. comparatively studied chitosan dense and porous membranes for filtration by increasing polymer concentration and silica ratios. They found that the adsorption increased when polymer concentration is increased; this is due to the increase of amino groups. In a similar fashion, the ratio of silica increased when porosity and roughness is increased [170, 171], leading to higher surface area and more exposure to amino groups for the adsorption of copper [172]. These macroporous chitosan membranes were also used to compare adsorption of copper and nickel ion and it was found that copper ion adsorption was 19.87 mg/g which is higher than nickel (5.21 mg/g) [173].

Scientists proved that chitosan is a suitable bio sorbent for household purposes. In one study,

Table 5: Maximum removal ability for heavy metal ions of chemically modified chitosan

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption ($q_{\max}$) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/Xanthate	Pb(II)	76.9	5.0	[162]
		Cu(II)	34.5		
		Zn(II)	20.8		
2	Chitosan/Thiourea	Cu(II)	60.6	5.5	[163]
3	Chitosan/EGTA	Cd(II)	83.18	4.0	[164]
		Pb(II)	103.5		
4	Chitosan/Activated Carbon	Cd(II)	52.63	6.0	[165]
5	Chitosan/Glycine	Cu(II)	234.9	7.0-9.0	[166]
		Co(II)	281.28		
6	Chitosan/Polystyrene	Cu(II)	99.8	6.0	[167]
7	Chitosan/Diethylenetriamine	U(VI)	177.93	3.61	[168]

molybdate ions were successfully removed from common household contaminated groundwater. Maximum adsorption was found to be 265 mg/g, which is far below bio sorbent values reported in the earlier literature [174]. (Wu et al.) and (Bertoni et al.) achieved adsorption up to 1280 mg/g by using magnetic chitosan resin and green seaweed [175, 176]. Table 4 shows maximum adsorption capacities of modified chitosan.

7 Coated/Porous Chitosan for the Removal of Heavy Metal Ions

Indium (III) ions were adsorbed by using chitosan coated with bentonite beads. Research showed that using chitosan alone for the removal of heavy metals has disadvantages such as high cost and low chemical stability. So, several studies investigated to reduce above mentioned drawbacks by coating of chitosan with sand [177], calcium alginate beads [89], alumina [178], PVC beads [75] and bentonite beads. And in present study bentonite was found to be most efficient coating material for chitosan [179]. Bentonite coated chitosan displayed maximum removal percentage of indium from aqueous solution that is 99.6%. Similarly it was also used in different research for adsorption of Cr(VI) and azo dye AB10B. Adsorption capacity for chromium (66.6 mg/g) and for AB10B (847.5 mg/g) respectively was reported [180].

In other application of adsorption, chitosan was coated on commercially available cotton gauze by UV radiation to remove copper and chromium ions from water solutions. Main advantages of using cotton are: it helps to limit pressure drop during continuous filament due to its open structure and it is also low cost and easily available. Research showed the optimum values for adsorption of chromium and copper at pH 3 and 5 [181].

Porous foam of chitosan imprinted with Ni^{2+} was developed to improve selective adsorption of nickel from liquid solutions. This structure can provide good mechanical properties and high

adsorption rate. In this research adsorption capacity was found to be 69.93 mg/g [182]. Recently many similar studies of chitosan porous foams have been done. Particularly chitosan/polyvinyl alcohol foam was prepared for adsorption of copper ions, which also proves to be efficient adsorbent having capacity of 193.38 mg/g for copper [96].

Another porous chitosan/graphene oxide (PGOC) was developed by unidirectional freeze drying method [183]. Graphene also has good adsorption ability and high surface area [184, 185]. Reported material showed better adsorption capability for lead ions with 31% increase due to better interaction between carboxyl groups of graphene and lead ions [186].

Table 6: Maximum removal ability for heavy metal ions of coated/porous chitosan

Sr. No.	Type of Adsorbent	Adsorbate Ions	Maximum Adsorption ($q_{\max}$) mg/g	Optimum pH for Adsorption	Reference
1	Chitosan/Bentonite	In(III)	17.89	4.0	[179]
2	Chitosan/Cotton Gauze	Cu(II)	4.09	5.0 & 3.0	[181]
		Cr(VI)	1.47		
3	Chitosan/Resin	Fe(II)	0.075	-	[187]
		Cr(VI)	0.038		
		Pb(II)	0.185		
4	Chitosan/Diatomaceous Earth	Zn(II)	127.4	6.0	[188]
5	Chitosan/Calcium Silicate	Ni(II)	406.6	4.0-8.0	[189]
		Zn(II)	400.0		
		Pb(II)	796.0		
		Cu(II)	578.0		
		Cd(II)	425.0		

8 Research Gaps and Future Recommendation

- No studies were reported for adsorption of silver ions by using chitosan, which is a potential hazard in aqueous solutions.
- Simulation can be done of adsorption processes for accurate results and better understanding of adsorption processed.
- Chitosan coated on porous nanofibers may be used for improved adsorption of heavy metal ions due to their increased surface and area and porosity.
- Nano particles of chitosan possibly are incorporated in different polymeric structures like nano fibres, hydrogels, porous membranes, thin films for better adsorption of heavy metal ions from water.

9 Conclusion

In summary, chitosan is a natural low-cost polymer with amine groups on its backbone. It is proved to be the most efficient and effective for the removal of metal pollution by the adsorption method. According to the mechanism of adsorption of heavy metals on chitosan, the pH of a solution is the important factor to successfully adsorb the metal ions from wastewater. However, there are other factors which significantly affect the adsorption of metal ions i.e. contact time, adsorbent dosage, temperature, concentration etc are not covered in this review. Moreover, this literature comprehensively reported and compared the adsorption capacities of crosslinked chitosan, chitosan composites, chitosan nanofibers, chitosan nanoparticles, coated chitosan and porous chitosan. Finally, the world is facing a critical issue of heavy metal pollution in wastewater, which is dangerous for both the environment and humans. Water cleaning technologies can be better understand and improved by simulating the purification processes in the future.

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