Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(24):53-66
(http://www.derpharmachemica.com/archive.html)

Applications of Chitosan, Graft Copolymers of Chitosan and it's Derivatives for Metal Ion Sorption: A Review

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ABSTRACT

The industrial revolution leading to the unsustainable environmental development caused a big threat of the environmental pollution. The progressive increase of the industrial technology leads to increasing amount of water pollution in terms of release of lot heavy metal ions into the water bodies. The industrial effluents were loaded with the toxic metal ions like Pb, Hg, Cd, Cu, Ni, Fe etc. The heavy and toxic metal ions present in the water bodies are non-biodegradable and bio accumulative hence making the water bodies polluted. The increased level of these heavy metal ions in the water bodies leads to health hazards to the plants, animals and humans. This alarming situation leads to the large number of researchers to evolve some techniques of the removal of metal ions from water bodies. The classical methods like precipitation, ion exchange, electro-coagulation etc. were not much effective and expensive also. The use of the biopolymers proved satisfactory in this regard as these have tendency to sorb the metal ions effectively without any hazard to the environment as these are biodegradable and less expensive too. In the present review paper an effort is made in order to summarize the use of chitosan, graft copolymers of chitosan and its derivative in the sorption of different heavy metal ions.

Keywords: Graft copolymers, Chitosan, Metal ion sorption

INTRODUCTION

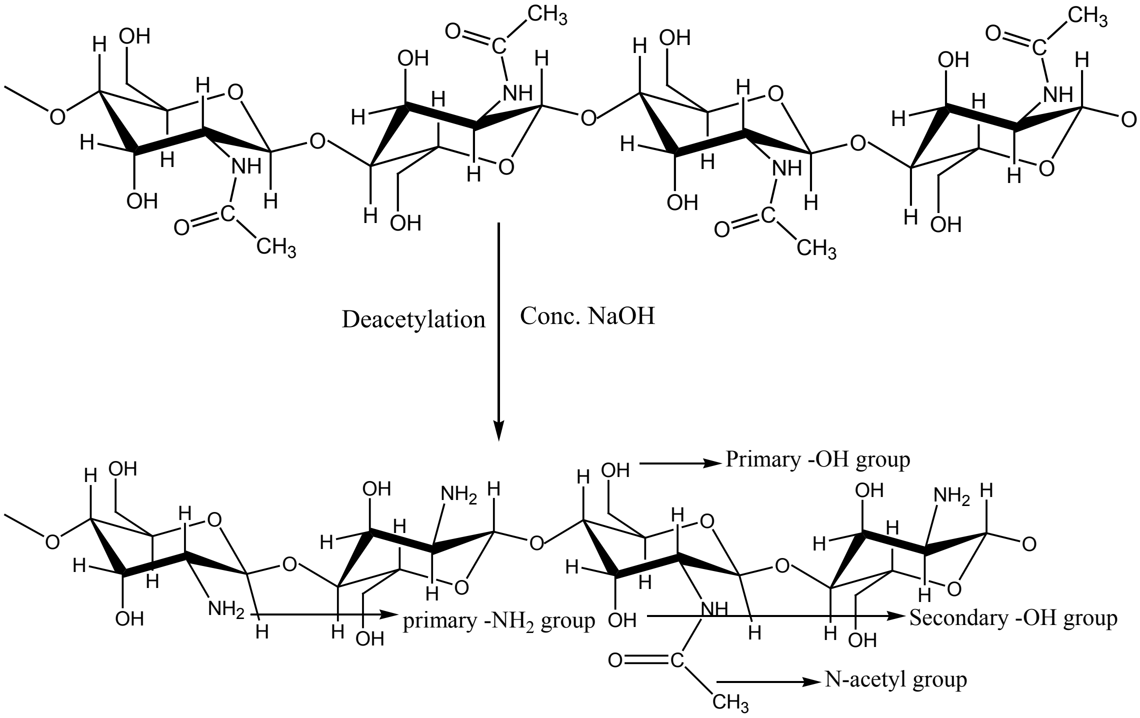
In today's scenario due to number of conservation issues of environment became an important economical and social concern [1]. One of the most implacable problems regarding pollution is the contamination of the water bodies by the heavy metal ions [2]. The development of the new agricultural techniques [3], industries like paper industry [4,5], battery industry [6,7], refineries [8], metallurgy [9], lather [10], textile [11], etc. and mining activities [12] discharges large amount of liquid waste containing heavy metal ions in to water bodies which causes hazard to the living organisms. The metal ions are non-biodegradable, lethal and bio accumulative in nature. The removal of the heavy metal ions is one of the foremost challenges to the researchers. Even the traces of the heavy metal ions present in the water leads to unwelcome effects to the flora and fauna [13]. Large numbers of methods were proposed for the removal of heavy metal ions from the water bodies [14]. The conventional methods like ion exchange [15], chemical precipitation [16], electro-coagulation [17], membrane separation [18] etc. were either expensive or not quite satisfactorily effective to the solution of problem. These methods also results into generation of metal sludge which proves to be quite complicated to eliminate. In comparison to these traditional methods the metal ion sorption seems to be improved substitute [19]. A large number of natural and synthetic sorbent were utilized for the absorption of different metal ions like cellulose [20], coconut husk [21], rice husk [22], wool [23], rice straw [24], tea leaves [25], cyclodextrin [26], poly acrylamide [27], activated carbon [28], fly ash [29] and clay [30]. But the use of biopolymers for the bio sorption is advantageous because the biopolymers are of renewable origin, cheaper, more effective and present alternative and cost effective resources.

Among large number of biopolymers available like cellulose, starch, dextrin, chitin etc. but chitosan is of special interest as it is generated from the waste material chitin [31]. Chitin being obtained from the waste material of seafood industry as waste shells of crustaceans consists of chitin 15-20 w/w which after deacetylation give chitosan a natural copolymer of glucosamine and

N-glucosamine [32]. Infect chitin is world's second most abundant polymer after cellulose [33]. But because of limited solubility of cellulose its applications are restricted hence chitosan become the best choice [34,35]. The literature survey reveals the utilization of chitosan and its derivatives in the sorption of large number of metal ions. It was evident from the literature survey that the biopolymer chitosan have very high adsorption capacity of large number of metal ions [36]. Chitosan having $–NH_2$ functional group in addition to the –OH group and is the only cationic biopolymer. Due to the high percentage of $–NH_2$ functional group helps the biopolymer into novel binding to the large number of metal ions such as mercury, copper, nickel [37]. Modifications of chitosan with the organic moieties results into improvement of its sorption abilities. An extensive research was done on modification of chitosan by graft copolymerization with different synthetic monomers [38]. The grafting improves the porosity, swelling properties and also inculcation of specific functional groups like –COOH, $−CONH_2$, −CN improves the chelation properties to the metal ions [39,40]. The crosslinking of the graft copolymers by the use of suitable crosslinker like MBA, glutaraldehyde, glyoxal, formaldehyde, pichlorohydrin etc. results into formation of the crosslinked graft copolymers having interwoven network like structure which can be utilized effectively for the metal sorption [41]. Crosslinking agents also enhance stability and porosity, mechanical properties of the chitosan itself or its copolymers. The literature survey revealed the active utilization of a lot of crosslinked chitosan graft copolymers in bio sorption of different metal ions [42].

Chitosan

Chitosan is the unique biopolymer obtained by the N-deacetylation of the chitin. Chitin is the waste product of the sea food industry; it is produced from exoskeleton of crustaceans like crabs, prawns, marine arthropods, seaweeds etc. Chitin is insoluble in water and in most of the inorganic solvents which limit its properties [43,44]. Chitosan differs from chitin by amine group $−NH_2$. In acidic medium, these groups give to chitosan an interesting cationic nature responsible for its flocculent activity. Chitosan has better solubility, less crystalline and is amenable to chemical modifications due to presence of functional groups as hydroxyl, acetamido and amine. Chitosan is more versatile than chitin because of the presence of $−NH_2$ group at C_2 position [34,45]. Chitosan is linear polyamine having acidic (−OH) and basic ($−NH_2$) function groups [46]. The derivatives of chitosan with desirable properties can be readily prepared by modifying the −OH (primary or secondary) and $−NH_2$ group [47].



Chemistry of chitosan

Chitosan is a linear polysaccharide consists of randomly distributed (β-(1→4)-linked D-glucosamine (N-deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan is produced by deacetylation of chitin. Chitin finds limitations in its applications because of its non-solubility and less interactive nature [48]. Chitosan differs from chitin by having extra $−NH_2$ group. The presence of $−NH_2$ group increases its solubility at lower pH in polar media and provides it characteristic cationic character [49]. The $−NH_2$ of chitosan has pKa value as 6.5 and it gives its characteristic acidic (cationic) character by protonation of $−NH_2$ group in acidic medium. This characteristic made chitosan water soluble and bio adhesive as a result of which it binds negatively charged membranes like mucosal membrane [50] and increases its unique properties like bio adhesiveness, flocculant, pollution removal etc.

Metal ion sorption

The unique properties of the chitosan like high biocompatibility, biodegradability, non toxicity and also having low cost and natural abundance motivated the researchers to explore this biopolymer in different industrial and environmental applications [51-54]. The literature survey reveals that a lot of work was done on the chitosan itself in the field of removal of heavy metal ions from the water bodies. In order to get the improved results, the functionality of the chitosan was modified with the desired functional groups like –COOH, $-CONH_2$, −CN etc. by graft copymerization technique.

Metal ion sorption by chitosan

Chitosan based materials can bind to the metal ions by forming chelates. As a result of this feature, these find potential applications in metal ion sorption. In 2004, Verma et al. investigated chitosan and its derivatives for the remval of metal ion through complexation. Chitosan can also form nano beads or composites which interact with the metal ion. The literature survey revealed that chitosan sorb a number of toxic metal ions like Hg(II), V(IV), Ag(I), Cd(II) etc. Chassary in 2004 studied the effective removal of metals by the chitosan and its derivatives. Guibal et al. studied the enhancement in the performance of metal ion sorption by the chitosan. Guilab gave a review on the application of the chitosan composites in the removal of the toxic metal ions. In 1995, Mitani studied the effect of the ionic strength on the adsoption capacity of chitosan beads. The adsorption of the metal ions from the water body can be done by the fabrication of nanoparticles, matrices, films etc. of chitosan. The sorption of metal ions studied w.r.t. time of contact, pH of the medium, concentration of metal ions and temperature. Dhanesh et al. studied the removal of Pb(II) from the waste water w.r.t. to time, concentration of metal ions and temperature and process was found to follow first order kinetics. Thilagan et al. studied pH dependent sorption of Cu(II) ions by blended chitosan/cellulose beads. The kinetics was studied by Langmuir adsorption isotherm and found to be pseudo order kinetics. Benavente studied chitosan for absorption of metal ions Cu(II), Hg(II), Pb(II) and Zn(II) from gold mine. The results showed that chitosan have absorption capacity as Hg(II)>Cu(II)>Pb(II)>Zn(II) (Table 1) [55-64].

Table 1: Literature survey of metal ion sorption by chitosan

S. No.	Sorbent	Metal ions sorbed	Ref.
1.	Magnetic chitosan nanocomposite	Pb(II) ions	[65]
2.	Chitosan	Cu(II) and reactive dyes	[66]
3.	Chitosan	Cu(II) ions	[67]
4.	Chitosan flakes, beads and crosslinked by glutaraldehyde	Cu(II), Mo(VI), and Cr(VI) ions	[68]
5.	Composites of chitosan	Cr(VI) ions	[69]
8.	Chitosan beads	Mo(I) and V(I) ions	[70]
9.	Crosslinked chitosan	Cu(II), Ni(II), and Zn(II) ions	[71]
10.	Crosslinked chitosan and non-crosslinked chitosan	Cu(II) and Cr(VI) ions	[72]
11.	Crosslinked and Cu(II) complexed chitosan	Cu(II) ions	[73]
12.	Chitosan, chitin and Rhizopus arrhizus	Cr(VI) and Cu(II) ions	[74]
13.	Chitosan and chitosan-copper complex	Cu(II) ions	[75]
14.	Chitosan particles	Cu(II) ions	[76]
15.	Chitosan	molybdate ions	[77]
16.	Chitosan	Cu(II) and Fe(III) ions	[78]
17	Chitosan flakes and other biosorbents	Cd(II), Cr(VI), Pb(II) and Hg(II) ions	[79]
18	Chitosan flakes	Zn(II), Cu(II), Cd(II), and Pb(II) ions	[80]
19	Chitosan coated Carbon	Cr(VI) and Cd(II)	[81]
20	Chitosan	Cu(II), Ni(II) and Cr(VI)	[82]
21	Chitosan-Magnetite microspheres	Co(II) and Ni(II) ions	[83]
22	Chitosan	Cr(VI) and Cu(II) ions	[84]
23	Chitosan and alginate	Cu(II), Cd(II), Pb(II), Ag(I) ions and acid dyes	[85]
24	Chitin and chitosan	Hg (II), Co(II), Ag(I), Mo(II), Cs (I), Zn(II), Fe(II), Au(III) and Cr (VI) ions	[86]
25	Chitosan	Cr(VI) ions	[87]
26	Chitosan flakes	Hg(II) ions	[88]
27	Chitosan flakes	V(IV) ions	[89]
28	Chitosan particles	Cd(II) ions	[90]
29	Chitosan and chitosan-copper complex	Cu(II) ions	[91]
30	Activated carbon modified with chitosan	Cr(VI) ions	[92]
31	Chitosan/magnetite composite beads	Pb(II) and Ni(II) ions	[93]
32	Chitosan membranes	Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions	[94]
33	Chitin and chitosan	Cr(VI) ions	[95]
34	Chitosan gel beads	Pt(II), Pd(II) ions	[96]
35	Chitosan/carbon nanotube composite beads	Hg(II) ion	[97]
36	Chitosan–poly (vinyl alcohol) /bentonite nanocomposites	Hg(II) ions	[98]
37	Chitosan membranes	Cu(II) and Hg(II) ions	[99]
38	Chitosan as nanofiller of graphite oxide	Hg(II) ions	[100]
39	Chitosan based ceramic ultrafiltration membrane	Hg(II) and As(III) ions	[101]

40	Chitosan-based granular adsorbents	Hg(II), Pb(II), Cu(II) ions	[102]
41	Magnetic chitosan microspheres	Cu(II), Cd(II) and Ni(II) ions	[103]
42	Chitosan-based granular adsorbent containing thiourea groups	Hg(II) and Pb(II) ions	[104]
43	Chitosan-coated nylon	Cu(II), Ni(II), Zn(II) and Co(II) ions	[105]
44	Silica gel/chitosan biocomposite	Zr(IV) ions	[106]
45	Chitosan composies	Cd(II) and Cu(II) ions	[107]
46	Silk fibroin/chitosan blend membranes	Cd(II) and Cu(II) ions	[108]
47	Chitosan supported onto agave fiber–postconsumer HDPE composites	Cr(VI) ions	[109]
48	Chitosan/poly (vinyl amine) composite beads	Cu(II) ions	[110]
49	Hemicellulose–chitosan biosorbent	Cu(II) and Pb(II) ions	[111]

Metal ion sorption by chitosan derivatives

Despite of the successful work done on chitosan in terms of the metal ion sorption but the modified chitosan seems to be next generation materials for such applications. The modification can be done by derivatization, graft copolymerization, crosslinking and synthesis of IPN's and semi-IPN's. Chitosan can be derivatized by methods like oligomerization, alkylation, acylation, quternization, hydroxyalkylation, carboxyalkylation, thiolation, sulfation, and phosphorylation. The derivatives of chitosan like N- succinyl chitosan, O-carboxyalkyl chitosan, N-carboxyalkyl chitosan, N-maleoyl chitosan, alkyl chitosan, metal-carboxyalkyl chitosan, glycol chitosan, thiolated chitosan, N-carboxybenzyl chitosan, N-carboxymethylidine chitosan, methacrylamide chitosan, quaternised chitosan, glycidyl chitosan, hexanoyl chitosan, N-[(2-hydroxy-3-trimethylammomium)propyl] chitosan (HTTC) etc. are finding more defined uses in industrial fields. Guibal studied the removel of Pt(II) and Pd(II) by the chitosan based derivatives, Becker reviewed sorption of metal ions like Ni(II), Zn(II) and Cd(II) by various derivatives of chitosan. The literature survey revealed that the derivatized chitosan proved to be an important an improved candidate for the sorption of the toxic metal ions from the water bodies. Hastuti and Siswanta studied removal of Pb(II) by the carboxymethyl Chitosan-Pectin composites and the results showed that the composites have enhanced capacity of the absorption of metal ion. Chitosan modified by ethylenediaminetetraaceticacid (EDTA) showed adsorption of Co(II), Ni(II), Cd(II), and Pb(II) ions from aqueous solution. Chitosan modified by thiourea was utilized used for the removal of Hg(II) (Table 2) [112-134].

Table 2: Literature survey of chitosan derivatives in metal ion sorption

Sr. No.	**Sorbent**	**Metal ions sorbed**	**Ref.**
1	N-carboxymethyl chitosan	Au (III) ions	[135]
2	N, O-carboxymethyl-chitosan	Cu (II) ions	[136]
3	Crosslinked carboxymethylchitosan resin	Pb (II) ions	[137]
4	Glycine modified crosslinked chitosan resin	Au (III), Pt (IV) and Pd (II)	[138]
5	Cross-linked carboxymethyl-chitosan resin	Zn (II) ions	[139]
6	Carboxymethyl chitosan nanoparticles	Pt (IV), Au (III) and Ag (I) ions	[140]
7	Porous chitosan–tripolyphosphate beads	Cu (II) ions	[141]
8	N-(2-carboxyethyl) chitosans	Flocculation/precipitation of Zn(II), Cu(II) and Ni(II) ions	[142]
9	N-(2-carboxyethyl) chitosans	Cu(II) ions	[143]
10	Chitosan derivatives containing methylthiocarbamoyl and phenylthiocarbamoyl groups	Selective adsorption of Cu (II) over Fe (III)	[144]
11	N-succinyl-chitosan and cross-linked N-succinyl-chitosan resin	Pb (II) ions	[145]
12	N-succinyl-chitosan and crosslinked N-succinyl-chitosan template resin	Cu (II) ions	[146]
13	Quaternized chitosan resin	Cr (VI) ions	[147]
14	Thiourea-modified chitosan resin	Ag (I) ions	[148]
15	Alkyl-substituted polyaniline/chitosan composites	Cr (VI) ions	[149]
16	O-crosslinked maleic acyl chitosan	Pb(II) and Cu(II) ions	[150]
17	N-Carboxymethyl Chitosan	Ca(II), Fe(II) ions	[151]
18	Azacrown ether chitosan (CTSC) & azacrown ether crosslinked chitosan (CCTSC)	Pd(II), Ag(II), Ni(II), Pd(II) and Cu(II) ions	[152]
19	Chitosan–zeolite composite	Cu(II) ion	[153]
20	Thiourea/Chitosan Composite Beads	Cu(II) ion	[154]
21	Mercaptoacetyl chitosan	Cu(II) ion	[155]
22	Novel magnetic thiourea-chitosan	Ag(I) ion	[156]
23	Xanthated chitosan	Cr(VI) ion	[157]
24	Magnetic nano-based particles of diethylenetriamine-functionalized chitosan	Uranium ion	[158]
25	Diethylenetriamine-functionalized chitosan magnetic nano-based particles	Nd (III), Dy (III) and Yb (III) ions	[159]

26	Chitosan functionalized by amino-terminated hyperbranched polyamidoamine	Hg(II) ion	[160]
27	N, O-carboxymethyl chitosan-polyether sulfone composite	Ni(II) ion	[161]
28	Poly (vinyl alcohol)/chitosan composites	Cu(II) ion	[162]
29	Polyaminated highly porous chitosan chelating resin	Hg(II) ion	[163]
30	Thiourea-modified magnetic chitosan microspheres	Hg (II), Cu (II), and Ni (II) ions	[164]
31	Polypyrrole-chitosan nonocomposite	Hg(II) ion	[165]
32	Chitosan–GLA beads and chitosan–alginate beads	Cu(II) ion	[166]
33	Polyaminated highly porous chitosan beads	Hg(II) ion	[167]
34	Chitosan-tripolyphosphate chelating resin	Cu(II) ion	[168]
35	Chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formylphenol	Cu(II), Cd(II), and Ni(II) ions	[169]
36	Chitosan derivatives from hydrochloric acid	Hg(II) ion	[170]
37	Chitosan functionalized by ester and amino terminated hyperbranched polyamidoamine polymers	Au(III), Pd(II), Pt(IV), Ag(I), Cu(II), Zn(II), Hg(II), Ni(II), and Cd(II) ions	[171]
38	Chitosan-based resins modified with tris (2-aminoethyl) amine moiety	Hg(II) ion	[172]
39	Chitosan mercaptanes	Cu(II) and Hg(II) ions	[173]

Metal ion sorption by chitosan based graft copolymers

Graft copolymerization is a suitable and convenient technique tomodify chitosan. It is a competent technique to amend the existing polymers by inculcating different side chains thus this technique helps to bring in desirable properties on the chitosan backbone and enlarges its spectrum of applications. The monomers with the desired functional groups can be inculcated onto chitosan in order to enhance its capability of removal of metal ions from water bodies. A lot of work had been done on the modification of chitosan by graft copolymerization by desired functional groups for the applications in metal ion sorption technologies. Wang et al. synthesized chitosan-*g*-poly (acrylic acid)/attapulgite hydrogel composite for the removal of Hg (II) ions from aqueous bodies. Merrifield et al. studied the enhancement in mercury uptakeby graft copolymerization of thiol onto chitosan. Pourjavadi et al. investigated nanocomposite hydrogels of chitosan-*g*-acrylic acid with high adsorption capacity for the removal of heavy metal ion. Kang et al. synthesized amidoximated Ch-*g*-PAN for the removal of heavy metals Zn(II), Cu(II), Pb(II) and Cd(II). The effect of pH on the adsorption of metal ions were studied and results showed that the adsorption constant increased with increase in pH for Cu(II) and Pb(II) but a little decreased for Zn(II) and Cd(II). Li et al. prepared chitosan-*g*-polyacrylamide beads by surface-initiated atom transfer radical polymerization (ATRP). The beads found tobe having appreciably faster adsorption kinetics and higher adsorption capacity for Hg(II) ions in comparison to the ungrafted chitosan (Table 3) [174-186].

Table 3: Literature survey of chitosan graft copolymers in metal ion sorption

Sr. No.	Sorbent	Initiator	Metal ions sorbed	Ref.
1	Polyaniline-*g*-chitosan beads	Ammonium persulfate (APS)	Cu (II) ions	[186]
2	Methacrylic acid-*g*-chitosan/ bentonite composite matrix	Potassium persulfate (KPS) and N,N-methylenebisacrylamide (MBA)	Th(IV) ions	[187]
3	Chitosan-*g*-N-vinyl formamide	Bromate/cyclohexanone redox pair initiator	Cu(II), Ni(II), Zn(II), Pb(II) and Hg(II) ions	[188]
4	Chitosan-*g*-poly(methylmethacrylate)	Microwave	Zn(II) ions	[189]
5	Chitosan-*g*-poly (vinyl acetate	Ceric ammonium nitrate (CAN)	Cu (II) ions	[39]
6	Ch-*g*-AAm	KPS	Cu(II) ions	[190]
7	Ch-*g*-2-amino-4,5-pentamethylene-thiophene-3-carboxylic acid-N-acrylol hydrazide	KPS and Mohr's salt ($FeSO_4$) redox pair initiator	Cu(II), Co(II) and Ni(II) ions.	[191]
8	Ch-*g*-AN	CAN	Cr(VI) and Co(II) ions	[85]
9	Ch-*g*- N-allyl maleamic acid	KPS	Cu(II) from H_2O	[192]
10	Ch-*g*- Thiourea	Ammonium thiocyanate	Au(III) , Pt(IV) and Pd(II) ions	[193]
11	Ch-*g*-DETA (Diethylene triamine) nanoparticles	Epichlorohydrin	Nd(III) , Dy(III),Yb(III) ions	[160]
12	Ch-*g*-AAm	KPS	Cu(II) ions	[192]
13	Chitosan-*g*-acrylonitrile	CAN	Cr(VI), Cu(II) and Ni(II) ions	[194]
14	Chitosan-*g*-magnetic bentonite	Plasma-induced method	Cs(I) ion	[195]
15	Chitosan-*g*-methacrylic acid	potassium peroxy monosulfate/cyclohexanone redox pair initiator	Cu(II), Ni(II), Zn((II), Pb(II) and Hg(II) ions	[196]
16	Chitosan-*g*-polyacrylonitrile	CAN	Pb(II) and Ni(II) ions	[197]
17	Poly(methacrylic acid-*g*-chitosan /bentonite	N,N′-MBA	Th(IV) ions	[198]
18	Poly(ethyleneimine)-*g*-chitosan microspheres	Suspension dispersion method	mercury and uranyl ions	[199]
19	Thiol-*g*-chitosan beads	Glutaraldehyde (GLA)	Hg(II) ions	[200]

20	Mesocyclic diamine-*g*-chitosan- crown ether	Epichlorohdrin and Benzaldehyde	Pb(II), Cd(II) and Cr(III) ions	[201]
21	Poly (methacrylic acid) -*g*-chitosan/bentonite	N,N′-MBA	U(VI) ions	[202]
22	Chitosan beads-*g*-acrylic acid	GLA, cobalt-60 gamma rays	Cd(II) and Pb(II) ions	[203]
23	multiwalled carbon nanotube-*g*- Chitosan	Plasma-induced technique	UO_2(II), Cu(II), and Pb(II) ions	[204]
24	Chitosan-*g*-poly (acrylic acid) hydrogel	Aqueous dispersion polymerization	Ni(II) ions	[205]
25	chitosan-*g*-styrene	Microwaves	Cr (VI) ions	[206]
26	Chitosan-*g*-poly (2-amino-4, 5-pentamethylene-thiophene-3-carboxylic acid N′-acryloyl-hydrazide) chelating resin	KPS and $FeSO_4$ redox pair initiator	Cu (II), Co (II) and Ni (II) ions	[193]
27	Chitosan-*g*-poly(acrylic acid)/ attapulgite / sodium humate composite hydrogels	APS and N, N'-MBA	Pb (II) ions	[207]
28	Poly (itaconic acid) -*g*-chitosan	GLA and epichlorohydrin	Pb (II) and Cd (II) ions	[208]

Metal ion sorption by the chitosan based crosslinked graft copolymers

As the chitosan act as hydrogel but it had certain limitations like solubility, porosity, efficiency etc. The crosslinking is an important tool of increasing pore size, functionality and performance of the chitosan biopolymer [209,210]. Chitosan itself, its derivatives or the graft copolymers can be crosslinked by using suitable crosslinker molecule. The crosslinking result into formation of irreversible network by chemical bonding like covalent bonding, inter- or intramolecular bridges, ionic bonding, photochemical crosslinking by UV rays, Gamma rays [211] etc. The properties of cross-linked hydrogels depend upon the density of the crosslinker molecule to the density of the polymeric units [212]. Cross-linked networks of chitosan can be synthesized by using the available functionalities of $–NH_2$ and –OH groups [213]. The literature survey expose that there are numeral cross linker mechanisms like covalent crosslinkers glutaraldehyde (GLA) [214], 1,4-butanediol diacrylate (BDDA) [215], genipine [216], formaldehyde [217], epoxy compounds [218], glycol di-methacrylate [219], dialdehyde, glyoxal [220], oxalic acid, diallyl phthalate (DP), ionic cross linkers [221] tripolyphosphate (TPP) anions [222], radiation cross linking by UV rays [223], Gamma rays [224,225] etc. used for the formation of cross linked graft copolymers [226]. The crosslinked chitosan (CRCH) synthesized by gamma radiations was utilized for the removal of Cr(VI) ion. In comparison to the non modified chitosan the crosslinked chitosan showed higher efficiency for adsorption of Cr(VI) at pH 3. The experimental results were best fitted in adsorptionmodels such as Langmuir, Freundlich and Dubinin-Radushkevich [227]. Gotoh et al. investigated crosslinked chitosan with alginic acid by gluteraldehyde most effectiveadsorbents for removal of Co(II), Cu(II), and Cd(II)from waste water. The anionicinteraction between amino groups of chitosan andcarboxyl groups of alginic acid makes thebeads strong and durable for the adsorption of Cu(II), Co(II) and Cd(II) ions under acidic conditions (Table 4) [228].

Table 4: Literature survey of crosslinked graft copolymers in metal ion sorption

Sr. No.	**Sorbent**	**Crosslinker**	**Metal ions sorbed**	**Ref.**
1.	Crosslinked chitosan / ZSM molecular sieve Composites	Glutaraldehyde (GLA)	Cu(II) ion	[228]
2.	Crosslinked chitosan-*g*-acrylonitrile copolymer	CAN & GLA	Cu(II) and Ni(II) ion	[229]
1.	Crosslinked Ch-*g*-AN	CAN initiator and GLAcrosslinker	Cr (VI) , Cu(II), Ni(II) ions	[199]
2	Cross Ch-*g*-xanthate	GLA	Cr(VI) ions	[158]
3	Cross Ch-*g*-thiourea Ethylene imine	GLA	Osmium and iridium metals	[230]
4	Cross-linked chitosan beads	GLA, epichlorohydrin (ECH) and ethylene glycol diglycidyl ether (EGDE)	Fe(II) and Fe(III) ions	[231]
5	Crosslinked chitosan	ECH	Cr(VI) and Se(VI) ions	[232]
6	Chitosan/PVA cross-linked hydrogel	EGDE	uranyl ion	[233]
7	Cross-linked chitosan beads	GLA, ECH and EGDA	Cu(II) ion	[234]
8	Cross-linked chitosan by barbital derivative	GLA	Hg(II), methyl Hg(II), Phenyl Hg(II) ions	[235]
9	Cross-linked magnetic chitosan-phenyl thiourea resin	Formaldehyde	Hg(II), Cd(II) and Zn(II) ions	[236]
10	Cross-linked chitosan films	GLA and ECH	Cu(II), Hg(II) and Cr(VI) ions	[237]
11	Chitosan- poly(vinyl alcohol) crosslinked hydrogels	GLA	Hg(II) ion	[238]
12	Genipin crosslinked chitosan/poly (ethylene glycol) films	Genipin	Pb(II) and Ni(II) ions	[239]
13	Cross-linked chitosan	GLA	Cr(VI) ion	[240]
14	Cross-linked chitosan membrane	GLA and ECH	Hg(II) ion	[241]
15	Porous chitosan beads	GLA	Cd(II) ions	[242]
16	Crosslinked magnetic chitosan resin modified with Schiff's base	GLA	Hg(II) ions	[243]

17	Chitosan-crosslinked calix[4]arene chelating polymer	N,N'-diisopropyl-carbodiimide	Co(II), Ni(II), Cd(II), Hg(II) and Pb(II) ions	[244]
18	Chitosan crosslinked by dihydroxy azacrown ether	Dihydroxy azacrown ether	Ag(I), Cd(II), Hg(II) and Co(II) ions	[245]
19	Crosslinked chitosans	Diisocyanatohexane, dibromodecane and trimelitic anhydride.	Hg(II), Cu(II), Cd(II) and Pb(II) ions	[246]
20	Crosslinked chitosan with epichlorohydrin	ECH	Cu(II), Zn(II) and Pb(II) ions	[247]
21	Crosslinked chitosan membrances	GLA and ECH	Hg(II) ions	[248]
22	Heparin coating epichlorohydrin crosslinked chitosan microspheres	ECH	Cu(II) ions	[249]
23	Crosslinked chitosan	NN′-[bis (2-hydroxy-3-formyl-5-methylbenzyl-dimethyl)]-ethylenediamine (H2fmbme)	Cu(II) ions	[250]
24	Amino protected crosslinked chitosan.	GLA and ECH	Cu(II) ions	[251]
25	l-lysine modified crosslinked chitosan resin	Chitopearl CS-03 purchaged	Pt(IV), Pd(II) and Au(III) ions	[252]
26	Heparin coating epichlorohydrin crosslinked chitosan microspheres	ECH	Cu(II) ion	[253]

Metal ion sorption by the interpenetrating networks (IPN's & s-IPN's)

The s-IPNs and IPNs are of greater importance due to the specificproperties [254,255] which can be utilized for various applications. In case of semi-IPNs only one component is present as linear (non-crosslinked) while the other component is crosslinked [256]. Chitosan based s-IPNs and IPNs can be synthesized in the form of beads, microsphere, beads or matrices [257,258]. These can be synthesized by the methods like precipitation, emulsionpolymerization, spray drying [259,260] etc. The grafting and crosslinking reactions between chitosan gelatinin anaqueous medium result into synthesis of granular semi-IPN hydrogel. These hydrogels were utilized for adsorption of Cu(II) ions by complexation and ion exchange interactions between the –COOH and –NH_2 functional groups [261]. The sub micro-porous blend films of polyethylene glycol cross-linked chitosan used for the removal of Fe ions from the aqueous solutions. The adsorption was studied w.r.t. pH, contact time and metal ion concentration [262]. Though, single-network or single component (s-IPNs) hydrogels have feeble mechanical strength and time-consuming response to swelling [263-267]. In order to enhance the mechanical properties and fast response to swelling IPNs or multi component networks have been synthesized [268-271]. IPNs consist of two or more than two juxtaposed networks, with number of interactions and entanglements between the networks [272-275]. As a result of the chemical crosslinking the inter-woven or inter-network entanglements in the IPNs are permanent and cannot be detached [276,277]. The synthesis of IPNs enhances the performance and properties of the hydrogels. In IPNs the individual properties of one and more polymers were combined or in some cases the networks with entirely new properties were designed [278,279]. Therefore the fabrications of IPNs being an attractive field for the researchers to synthesize smart hydrogels with high porosity, bio-adhesiveness, elasticity, swelling and stimuli-responsive behaviour etc. (Table 5) [278-280].

Table 5: Literature survey of s-IPN's and IPN'sof chitosan in metal ion sorption

Sr. No.	**Sorbent**	**Initiator/ Crosslinker**	**Metal ions sorbed**	**Ref.**
1.	Granular pH-sensitive chitosan-based semi-IPN hydrogel	N,N'-MBA	Pb (II) ions	[281]
2.	Chitosan-graft-polyacrylamide semi-IPN hydrogels	N,N'-MBA	Hg(II) ions	[282]
3.	Chitosan/poly (acrylic acid) blending hydrogel beads	GLA	Cu(II) ions	[283]
4.	Microporous chitosan/polyethylene glycol blend membrane	GLA	Iron and manganese ions	[284]
5	Procion Brown MX 5BR immobilized poly (hydroxyethylmethacrylate/chitosan)	Azobisisobutyronitrile (AIBN) initiator	Hg(II) ion	[285]
6.	Poly (HEMA/chitosan)membranes	UV radiations initiator	Hg(II), Cd(II) and Pb(II) ions	[286]
7.	Procion Green H-4G immobilized poly (hydroxyethylmethacrylate/chitosan)	AIBN	Cd(II), Pb(II) and Hg(II) ions	[287]
8.	Poly (vinyl alcohol)/chitosan IPN	Sodium alginate	Cu(II), Pb(II), Zn(II) and Cd(II) ions	[288]
9.	Poly (2-hydroxyethylmethacrylate)/chitosan	UV radiations and AIBN	Zn(II) and Fe(III) ions	[289]
10.	Chitosan IPN	GLA	Iron (III) ion	[290]
11.	Poly (maleic acid)-grafted crosslinked chitosan nanomaterials	GLA	Hg (II) ions	[291]
12.	Cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base	Glyoxal	Cu (II), Cd (II) and Ni (II) ions	[292]
13.	Cross-linked chitosan resins	ECH	Cr(VI) ions	[293]
14.	Chitosan-Based Lead Ion-Imprinted Interpenetrating Polymer Network	Ethylene glycol dimethacrylate	Pb(II) ions	[294]

CONCLUSION

The interest of use of chitosan in the environmental and industrial application is expanding due to its unique characteristics. Chitosan itself is a good hydrogel and bind to number of metal ions by complexation technique. With the development of technology the chitosan is modified in number of ways in order to introduce suitable functional groups for the enhanced performance. The present review deals with utilization of chitosan based materials for the removal of metal ions from water bodies. The chitosan can be modified in various ways like derivatization, graft copolymerization, crosslinking, IPNs and s-IPN formation. Graft copolymerization is considered tobe one of the highlycapabletechnique of modification leading to introduction of widevariety of functional groups onto chitosan resulting into formation of novel molecules for effective removal of the metal ions.

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