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ADSORPTION OF HEAVY METAL IONS: ROLE OF CHITOSAN AND CELLULOSE FOR WATER TREATMENT

Mudasir Ahmad, Shakeel Ahmed, Babu Lal Swami and Saiqa Ikram*

Department of Chemistry, Jamia Millia Islamia, New Delhi, 110025, India

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Correspondence to Author:
Saiqa Ikram

Department of chemistry, Jamia
Millia Islamia, New Delhi, 110025,
India

E-mail: sikram.chem@gmail.com

ABSTRACT: Rapid industrialization and modernization have introduced substantial amounts of toxic heavy metals into the aquatic and terrestrial environment which possess a serious threat to the flora and fauna. In recent years, considerable research work has been done and is currently underway on a number of natural biopolymers and their modifications to remove different kinds of heavy metal ions. Chitosan and cellulose, both naturally occurring polysaccharides are the most effective adsorbents for the removal of heavy metal ions from waste water. This review is aimed to provide relevant and recent information on the application of chitosan, cellulose and their respective derivatives for the removal of toxic heavy metal ions.

INTRODUCTION: Majority of industries and mainly the mining operations, tanneries and metal plating play a vital role in contaminating the environment with heavy metals [1]. Heavy metals particularly mercury (Hg), chromium (Cr), lead (Pb) and cadmium (Cd) have lethal effects on all forms of life even at low concentrations.

Various methods including chemical precipitation [2], nano filtration [3], solvent extraction [4], ion exchange [5], reverse osmosis [6] and adsorption [7] have been extensively studied in recent decade to decontaminate the polluted waters. Out of all these methods, adsorption is particularly attracting scientific focus mainly because of its high efficiency, low cost, easy handling and high availability of different adsorbents.

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Over the past few years, several research studies have been conducted globally on natural polymers and various methods have also been developed to enhance their metal binding [8] properties.

Adsorption process is known to depend upon various experimental conditions such as particle size, pH, metal concentration, ligand concentration and competing ions [9].Scientists have focused their momentum for the search of low cost and easy available biomaterials for the waste water treatment. Chitosan[10], alginate [11], cellulose [12] and lignin[13] are some of the well known natural polymers that have received considerable attention for water treatment. Characteristics of various types of biopolymers are shown in (**Table 1).** A vast literature is nowadays available on all of these biopolymers. In view of their excellent properties to be used as efficient materials for heavy metal adsorption this review will highlight some of the recent studies conducted on chitosan and cellulose for water treatment. In addition this review will focus on various derivatives of these polymers that have been developed to enhance their efficiency in removal of toxic and heavy metals.

Chitosan:

Chitosan is a versatile polyaminosachride produced by alkaline N-deacetylation of chitin involving deproteination and deacetylation. Owing to many attractive properties such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, and presence of very reactive amino(-NH_2) and hydroxyl(-OH) groups in its backbone, chitosan has been used as an effective material for the removal of heavy metals from waste waters[14]. Mostly the adsorption depends on the pH values and the chitosan is very sensitive to pH [15]. Chitosan has the property to increase its metal binding efficiency by undergoing chemical modification with the cross linking reagents including ethylene glycondiglycidyl ether, formaldehyde, glyoxal, epichlorohydrin, glutaraldehyde, and isocyanates[16].

The reagents used in cross linking not only stabilize the chitosan in acidic solution, making it insoluble in acidic medium but also enhance its mechanical properties [15]. **Table 2** shows adsorption capacities and experimental conditions of chitosan composites for removal of various heavy metals from waste water.

TABLE 1: DIFFERENT BIOPOLYMER, SOURCE AND THEIR CHARACTERISTICS [17].

Biopolymer	Source	Characteristics
Chitosan	crustaceans and fungi	biocompatible, biodegradable, antimicrobial activity, antistatic activity, nontoxic, chelating property, deodorizing property, film forming ability, chemical reactivity, polyelectrolyte nature, dyeing improvement ability, cost-effectiveness, thickening property, wound healing activity.
Alginate	Brown Algae	Biocompatibility, biodegradable, drug delivery, wound healing, tissue engineering , adsorbent for heavy metals
Cellulose	Green plants, Algae and oomycetes	Tasteless, odourless,hydrophilic ,biodegradable, insoluble in water and most organic solvents, adsorbent
Lignin	Vascular green plants	Antioxidant, Antifungal, Extraction of heavy metals in various methods.

TABLE 2: SHOWS ADSORPTION CAPACITIES AND EXPERIMENTAL CONDITIONS OF CHITOSAN COMPOSITES FOR REMOVAL OF VARIOUS HEAVY METALS FROM WASTE WATER.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Temp. (oC)	pH	Kinetic model	Isotherm	Reference
Polyelectrolyte complex pectin/chitosan	lead (II)	30.1	-	5	-	−	18
Chitosan	Lead(II)	-			Ist order Kinetics	−	19
Magnetic chitosan resin (EMCMCR)	Copper (II)	-	25	6	-	Langmuir adsorption	20
Chitosan blended with Cellulose	Copper (II)	-	-			Langmuir, Freundlich	21
Chitosan coated carbon	Cr (IV) Cd(II)	-	-	5.0, 5.5	Pseudo second-order	Langmuir adsorption	22
Chitosan	Cr (VI)	11.6	25	5	-	-	23
CS/PEG	Fe	-	-	-	-	Freundlich	24
Semi-IPN hydrogels/CS	Cu (II)	261.3	-	-	-	-	25
Bromine pretreated chitosan	Pb(II)	0.001755	-	-	-	Freundlich	26
Chitosan-magnetite microparticles	NI,CO	588.24,833.34 resp.	-	-	-	Langmuir, Freundlich	27
Chitosan produced from shrimp shell waste	Cu(II), Hg(II), Pb(II) and Zn(II)	79.94, 109.55, 58.71, 47.15	-	6	-	Langmuir, Freundlich, Redlich-Peterson and SIPS	28
Chitosan–silica hybrid	Co (II), Ni (II), Cd (II), Pb(II)	0.63mmol/g	-	-	-	Langmuir and Sips	29
Grafted chitosan of polyacrylonitrile	Cr (VI) and Cu(II	-	-	-	-	Langmuir	30

Chitosan derivatives have been used extensively investigated as adsorbent [31] among them are chitosan derivatives containing nitrogen phosphorous and sulphur as hetero atoms and other derivatives such as chitosan crown ethers and chitosan ethylenediaminetetraacetic acid(EDTA)/ diethylenetriaminepentaacetic acid (DTPA) complexes [32]. Recently chitosan composites have been developed for the adsorption of heavy metals from waste water. Different kinds of substances have been used to form composites with chitosan such as polyelectrolyte films formed by initially mixing chitosan with acetate to form carboxymethyl chitosan mixed with pectin to form CMC/pectin films showing an increase in adsorption capacity for the removal of Pb (II) ions from the treated waste water[18].

Adsorption of Lead (II) ion on chitosan has found to be dependent on contact time, concentration, temperature, and pH of the solution. The removal processes fits the first order kinetics [19]. Ethylene diamine modified cross linked magnetic chitosan resin (EMCMCR) was used for the adsorption of Cu (II) ion from waste water. The best results of adsorption were observed at pH of 6.0, temperature of 25^0C with the initial concentration of 200 ppm. The adsorption was best with Langmuir adsorption model [20]. Removal of Cu(II) ions from aqueous solution was took place by chitosan/cellulose blended beads cross linked by formaldehyde and was found to be highly pH dependent.

The experimental was best fitted data with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The energy of adsorption showed that the process is physical adsorption process [21]. Chitosan coated carbon type adsorbent was used for the removal of Cr(IV) and Cd(II) from aqueous solutions at pH of 5.0 and 5.5 respectively at optimum temperature. The experimental data is best fitted with Langmuir adsorption and follows pseudo-second-order kinetics [22].

Chitosan-zeolite(CZ) composite was prepared by using zeolite and chitosan for the adsorption of Cu(II) ions from the treated waste water [23]. Polyethylene glycol cross-linked chitosan films with sub-micrometer porous structure also used for Fe removal from aqueous solutions. The adsorption process was studied by several parameters such as contact time, pH and metal ion concentration [24]. Granular semi-IPN hydrogel was prepared in an aqueous media by grafting and crosslinking reactions between chitosan (CTS), gelatin (GE), acrylic acid (AA), and N, N-methylene-bis-acrylamide for adsorption of cu(II) ions. The hydrogel strength, reuse, recovery properties and adsorption for Cu(II) ion was tested systematically and it was observed that the complexation and ion-exchange interactions occurs between the functional groups (COO^- and NH_2)[25].

Treatment of chitosan with 30% bromine increases Pb(II) ions adsorption due increase the surface area and porosity by means of physicochemical interaction with cationic sites of its skeleton, owing to the anionic alteration at amino linkages of chitosan which facilitates Pb(II) ion removal by chemical interaction[26].

Chitosan-magnetite nanoparticles was used for the adsorption of nickel (Ni) and cobalt (Co) ions from aqueous solutions [27]. Chitosan derived from shrimp shell waste used for the removal of Cu(II), Hg(II), Pb(II) and Zn(II) from gold ore stalking solutions containing cyanide. Experimental results was testing by using the Langmuir, Freundlich, SIPS and Redlich–Peterson isotherm models and maximum adsorption capacity for Cu(II) (79.94 mg/g), Hg(II) (109.55 mg/g), Pb(II) (58.71 mg/g) and Zn(II) (47.15 mg/g) and is best fitted with Langmuir equation [28]. Ethylenediaminetetraacetic acid (EDTA) ligand gets combined together with chitosan-silica hybrid materials for synthesizing a noval type adsorbent for decontaminating the Co(II), Ni(II), Cd(II), and Pb(II) ions from aqueous solution [29].

Graft copolymerization of polyacrylonitrile on chitosan surface in presence of ceric ammonium nitrate was used for removal of Cr(VI) and Cu(II) ions from aqueous media [30]. Thiourea modified chitosan was synthesised in two steps, O-carboxymethylation first and secondly the polymeric Schiff base of thiourea/gluteraldehyde was used for the adsorption of Hg(II) [31]. Beads of thiourea-modified chitosan was used for the adsorption of Cu(II) was prepared by several media(citric acid, sodium hypophosphite, glutaraldegyde, and SiO_2) [32]. Graft copolymerization of chitosan with polyacrylonitrile in presence of ceric ammonium nitrate used for the removal of Pb(II) and Ni(II) ions from aqueous solutions [33]. In order to facilitate the adsorption efficiency, thechitosan was combined with sodium alginate and was used for the removal of heavy-metals ions of Cu(II), Cd(II), Pb(II) and Ag(II) ions from waste water [34].

The macromolecule flocculant-mercapto-acetyl chitosan was synthesized by reacting CTS and L-cysteine, as adsorbent was used to chelate the heavy metals for the removal of Cu(II) ions with 100% removal rate [35]. TheCu(II) and Ni(II) ions are removed from metal solution by using crosslinked chitosan synthesized by graft copolymerization of chitosan with acrylonitrile in presence of ceric ammonium nitrate as initiator.

The adsorption efficiency of adsorbent was depends on pH of the solution, adsorbent dosage and contact time [36]. Cr(VI) ion was removed through crosslinked chitosan(CRCH) which was synthesized by gamma irradiation in the presence of carbon tetrachloride. The adsorption efficiency and product formed CRCH was compared with simple chitosan at pH 3. CRCH showed higher adsorption capacity of Cr (VI) ion and its experimental results was best fitted with adsorption models such as Langmuir, Freundlich and Dubinin-Radushkevich. The most important role of CRCH, for treating the wastewater containing Cr(VI) ion, after adsorption Cr(VI) ion through column; the column can be easily regenerated and skillfully reused [37]. Alginic acid and chitosan, both naturally occurring polysaccharides are the most effective adsorbents for removal of Co(II), Cu(II), and Cd(II) from waste water.

The combined use of alginic acid and chitosan was expected to form a rigid matrix due to anionic interaction between amino groups of chitosan and carboxyl groups of alginic acid and the crosslinking between the two was successfully takes place through gluteraldehyde. The crosslinking makes the beads durable and facilitates the adsorption of Cu(II), Co(II) and Cd(II) ions under acidic conditions [38].

Cellulose:

Polysaccharides are among the most abundant among all the polymers present on earth [39] derived from various sources shown in **Fig.1**.Cellulose has been used in the form of wood and cotton for thousands of years as an energy source, building material and for clothing. Cellulose consists of β-D-glucopyranose repeat units which are covalently linked by acetal functionalities between the equatorial OH group on carbon atom (C4) and carbon atom (C1), hence the name β-1,4-glucan. As a result, cellulose possesses an extensive linear chain polymer with a large number of hydroxyl groups (three groups per anhydro glucose unit (AGU)) and a thermodynamically preferred conformation $4C_1$ (a bond between carbons 4 and 1). The length of the polymeric cellulose chain depends on the number of constituent AGU unit's, degree of polymerization (DP) and varies with the origin and treatment of the cellulose raw material[40].

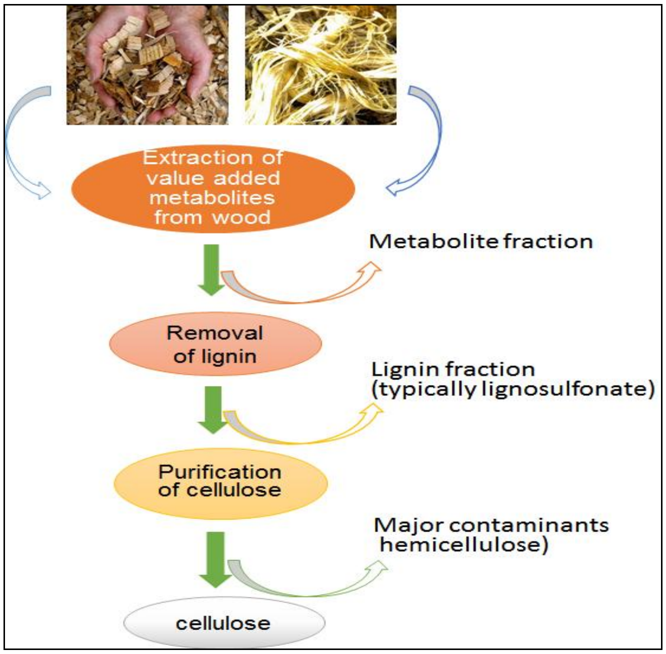

FIG.1: SHOWS THE EXTRACTION OF CELLULOSE FROM DIFFERENT WOOD SOURCES

This molecular structure gives cellulose a characteristic property of hydrophilicity, chirality and degradability. Chemical reactivity is largely a function of the high donor reactivity of the OH groups [41]. In particular, two main approaches have been tried in the conversion of cellulose into compounds capable of adsorbing heavy metal ions from aqueous solutions. The first method involves a direct modification of the cellulose backbone with the introduction of chelating or metal binding functionalities. Alternative approaches have been focused on grafting of selected monomers to the cellulose backbone either directly by introduction of metal binding capability or with subsequent functionalization of these grafted polymer chains with known chelating moieties [42].

Pure cellulose has very few applications compared to the diversity of applications of its modified form [43]. Chemical modifications increase its adsorption capacity for heavy metals in aqueous and non-aqueous media [44]. Moreover, chemical modifications can also be used to vary several other properties of cellulose, such as hydrophobicity or hydrophilicity, elasticity, adsorptivity, microbial resistance, heat and mechanical resistance [45]. Chemical modification of a polysaccharide surface follows the same principles as those established for other media, such as silica gel. However, the hydroxyl groups (-OH) on cellulose are less reactive and the start of a chemical modification takes place at the primary hydroxyl found on carbon 6 (C6), which may occurs through several different methods. However, modifications can also occur on the secondary hydroxyl groups (-OH) present on carbons 2 and 3.

The major modifications of cellulose occur through halogenation, oxidation, etherification and esterification [46]. Adsorption capacities and experimental conditions of cellulose/modified cellulose for removal of various heavy metals ions from wastewater are shown in **Table 3**.

TABLE 3: ADSORPTION CAPACITIES AND EXPERIMENTAL CONDITIONS OF CELLULOSE FOR REMOVAL OF VARIOUS HEAVY METALS FROM WASTE WATER

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Tem. (oC)	pH	Kinetic model	Isotherm	Reference
Cellulose grafted with acrylonitrile	Cr (VI)	-	-	5.0	pseudo second-order	Freundlich	47
CelEnEs	Pb(II)> Cd(II)> Ni(II)> Co(II)> Cu(II)> Zn(II)	-	-	-	-	Freundlich	48
Collagen/cellulose hydrogel beads	Cu (II)	1.06 mmol/g	-	6	-	Langmuir	49
M-CS/PVA/CCNFs	Pb (II)	171.0	-	-	Pseudo second-order	Langmuir	50
Mercerized cellulose	Cu(II),Cd(II), Pb(II)	30.4, 86.0, 205.9	-	-	-	Langmuir	51
Cellulose/Zr$_{O2}$	NI(II)	79.0	-	-	-	Langmuir	52
Bifunctional cotton fabric waste	Co(II), NO_3^-	38.5,11	-	5,4.5	Pseudosecond order	Freundlich, Langmuir	53
Cell-g-PGMA-PEI	Cu(II)	102	28	3.5-7.0	pseudosecond order	Langmuir, Freundlich	54
Welan gum-modified cellulose	Cd(II), P(II) and Cu(II)	83.6, 77.0, 67.4	-	5.0	pseudo-first-order	Langmuir	55
Cellulose acetate (CA)/silica composite	Cr (VI)	19.46	30	1.0	-	Langmuir	56
Oxidized cellulose-based materials	Hg (II)	258.75	30	4.4	pseudosecond order	Langmuir	57
Microfibrillated cellulose	Ni(II), Cu(II) and Cd(II)	2.734, 3.150 and 4.195 mmol/g	-	-	pseudo-second-order	-	52
Cellulose modified	Hg(II)	172.5	30	5.1.	pseudo-second-order	Freundlich	58
Magnetite cellulose–chitosan hydrogels	Cu(II), Pb(II) , (II)	44.7^{-5}, 28.1^{-3}, 94.1^{-7}	-	5.0	-	-	55
Carboxylated cellulose(NaSCNCs)	Pb (II)cd (II)	259.7,465.1		5.5 , 6.5	pseudo-second-order	Langmuir	59
Cellulose (AM-Fe-PGDC)	arsenic(V)	105.47	25	6.0	pseudo-second-order	Langmuir	60
Magnetic cellulose−chitosan composite	Cu(II)	65.8	25	5.0	pseudo-second-order	Langmuir	61

In particular, two main approaches have been tried in the conversion of cellulose into compounds capable of adsorbing heavy metal ions from aqueous solutions. One of these methods involves a direct modification of the cellulose backbone with chelation or metal binding functionalities producing a wide range of heavy metal adsorbents. An alternative approach has been focused on grafting of selected monomers to the cellulose backbone either directly by introducing metal binding capability or with subsequent functionalisation of the grafted polymer chains. With known chelating moieties such as graft copolymerization of acrylonitrile on to cellulosic material derived from sisal fiber in presence of ceric ammonium nitrate (as initiator) used for making adsorbent to remove Cr(VI) ions from aqueous media. By using this material as adsorbent, Cr(VI) ions removal was found to be optimum at pH 5 and the experimental data was best fitted with Freundlich isotherm and kinetic studies revealed that the process follows pseudo second-order kinetic [47]. For the removal of divalent metal sorption of Pb(II), Cd(II), Ni(II), Co(II), Cu(II), Zn(II) cellulose was modified with thionyl chloride to increase its reactivity.

This modified Cellulose was reacted with ethylenediamine (CelEn) and subsequently reacted with ethylene sulfide to obtain a solid substance, CelEnEs[48]. Collagen/cellulose based hydrogel beads (CCHBs) from 1-butyl, 3-methylimidazolium chloride are used for the adsorption of Cu(II) ion from aqueous solutions. The three-dimensional macroporous structure of modified cellulose containing amino groups is believed to be the main active binding site of Cu(II) ions [49]. Modification of cellulose with maleic anhydride was used for the synthesis of a novel type adsorbent (CM) for the removal of Hg(II) ions. The titration method was employed to find the degree of carboxyl group of CM and was found to be 2.7mmolg^{-1}.

The effect of different experimental parameters such as temperature contact time and pH was evaluated during removal process. The experimental data was best fitted with Freundlich isotherm model and kinetic studies revealed that it will follows pseudo second order kinetics with maximum adsorption capacity of Hg(II) was found to be 172.5 mg g^{-1} [50]. Mercurized cellulose modified by succinic anhydride was used for the preparation of new chelating material for Cu(II), Cd(II), andPb^{2+}ions [51]. Microfibrillated cellulose (MFC) type adsorbent was synthesized by the graft copolymerization of aminopropyltriethoxysilane (APS) for the removal of Ni(II), Cu(II) and Cd(II) ions from aqueous solution and the maximum adsorption capacities for Ni(II), Cu(II), and Cd(II) ions of the modified APS/MFC adsorbent was 2.734, 3.150 and 4.195 mmol/g, respectively [52]. For the removal of cobalt (Co(II) and nitrate (NO_3) ions, a new type of adsorbent was synthesized by radiation induced graft copolymerization of glycidylmethacrylate and methacrylic, the subsequent chemical modification with triethylamine, which produced bifunctional cotton fabric waste bearing $N^+ (CH_2CH_3)_3$ and COOH groups carrying the potential application of adsorption [53]. Benzoyl peroxide (BPO) as initiator for graft copolymerization of glycidyl methacrylate (GMA) onto cellulose and subsequent modification with polyethyleneimine (PEI) produces improved synthesis of a branched polyethyleneimine (PEI) modified cellulose-based adsorbent (Cell-g-PGMA-PEI) for adsorption of Cu(II) from aqueous medium. The efficiency of adsorbent capacity increases by decreasing the side reaction of epoxide ring opening during graft copolymerization of glycidyl methacrylate (GMA) onto cellulose which increases the epoxy groups, anchors to immobilize branched PEI moiety [54].

Adsorption of Cd(II), Pb(II) and Cu(II) ions with novel welan gum-modified cellulose adsorbent was prepared through emulsification, regeneration and modification with the maximum adsorption capacities of 83.6, 77.0 and 67.4 mg/g respectively. Moreover, the adsorption capacities for the three metal ions increased with the increase in temperature and the maximum adsorption occurs at pH 5 [55].

Cellulose acetate (CA) with tetraethoxysilane (TEOS) as a silica source in presence of coupling reagent 3-ureidopropyltriethoxysilane was used for the synthesis of novel NH_2-functionalized cellulose acetate (CA)/silica composite nanofibrous membranes with electrospinning technology which was employed for the removal of Cr(VI) ions from aqueous media [56]. A new sensor type adsorbent for rapid, selective, simultaneous detection and removal of Hg (II) ions was prepared from cellulose by etherified, oxidized, and modified to schiff base by reaction with L-lysine for synthesis of new oxidized cellulose-based materials. The experimental data follows pseudo second-order kinetics and Langmuir isotherm with high maximum adsorption capacity of 258.75 mg g^{-1} [57].

Polyvinyl alcohol (PVA) blended chitosan and carboxylated cellulose nanofibrils(CCNFs) was used for the preparation of magnetic hydrogel beads (m-CS/PVA/CCNFs), and used as adsorbents for removal of Pb(II) ions [58]. A cellulose type nanoadsorbent is used for the removal of Pb(II)and Cd(II) from aqueous solutions. This nano adsorbents was prepared by hydrolysis of cotton to obtain cellulose nanocrystals(CNCs) subsequently, the CNCs were then chemically modified with succinic anhydride in order to obtain SCNCs. The sodic nanoadsorbent(NaSCNCs) was further prepared by treatment of SCNCs with saturated $NaHCO_3$ aqueous solution [59].

In order to determine the adsorption potential of anion exchanger, Fe(III)-coordinated amino-functionalized poly glycidylmethacrylate-grafted TiO_2-densified cellulose (AM-Fe-PGDC) was used for As(V) ion removal from aqueous solutions proposed by Anirudhan et al. Its adsorption rate was influenced by initial contact time and metal ion concentration and its experimental data was found to be fitted with pseudo-second-order kinetic model [60]. The noval property of surface adsorption of cellulose nanofibers (CNF), chitin nanocrystals (ChNC) and cellulose nanocrystals (CNC) type adsorbents obtained from bio residues to remove Ag(II) ions from contaminated water.

Surface adsorption on the nanoparticles through electrostatic interactions is considered to be the best mechanism for the heavy metal ion adsorption from aqueous solutions, the negative charged CNC species and negatively charged functional groups being most suitable for chelation of positive to other native bionanomaterials [61]. Graphene oxide/carboxymethyl cellulose (GO/CMC) based column is used as adsorbent for removal of Ni(II) ions. GO/CMC monoliths changed the porous structure by incorporation of GO and increased their compressive strength [62]. A novel magnetic cellulose-chitosan composite microsphere was synthesized by a method combining the emulsification procedure and cellulose-chitosan regeneration from ionic liquid without surface modifications. The composite microspheres exhibited porous structure, large surface area, and affinity on metals, leading to the efficient uptake capacity ofCu(II) ions [63].

Zeolite/cellulose acetate blended (ZCAB) fibers, as adsorbent for Adsorption of Cu(II) ion was prepared by wet spinning method and tested in a packed bed up-flow column. The adsorption process is influenced by several parameters, such as the pH of solution, initial metal concentration, bed depth and flow rate [64]. Cellulose matrix modified by ZrO_2 for the synthesis of cellulose/ZrO_2nanohybrid was used for selectivity adsorption toward eight metal ions, including Cd(II), Co(II), Cr(II), Cu(II), Fe(II), Ni(II), Zn(II) and Zr(II). These nanohybrids show best towards the Ni(II) ion and absorption was found to be 79 mgg^{-1} [65].

Reaction between cellulose di-acetate (CA) and chitosan (CS) was used for the synthesis of several membranes having the affinity for chelation of Cu (II) ions from aqueous solutions. These membranes attracted the attention of researchers especially in the field of wastewater treatment for removing the heavy metals [66]. The coating of bamboo culmic cellulose on carbon culms for processing a rigid matrix structure with good mechanical strength, the coating provides a stable adsorbent that was stable under acidic conditions for the adsorption of Cr(II), Cd(II), and Pd(II) metal ions from aqueous media and adsorption efficiency values 93%, 76% and 82% respectively [67]. For the adsorption of heavy metals, a new route was used for the synthesis of magnetite cellulose-chitosan hydrogel microspheres in which ionic liquids are used as solvents.

These magnetic hybrid hydrogel having high adsorption capacities for various heavy metal ions such as Cu(II), Pb(II) and Fe(II) ions and the consistent equilibrium adsorption capacity was found to be 44.7±5mgg^{-1}, 28.1±3mgg^{-1} and 94.1±7mgg^{-1} respectively [68]. A novel type cellulose adsorbent bearing chemically grafted thiosemicarbazide was used for adsorption of Co(II), Hg(II) and Cd(II) ions [69]. Hydroxylamine was used for the Introduction of amidoxime group in cellulose-graft polyacrylonitrile (C-g-PAN). The prepared amidoximated grafted cellulose acts as adsorbent for adsorption of Co(II), Cu(II), Ni(II) ions [70]. Biodegradable adsorbent of chitosan (chitin)/cellulose composites which was prepared by using ionic liquids for adsorption of Cu(II), Zn(II), Cr(VI), Ni(II) and Pb(II) ions.

The adsorption capacities of various metal ions are 0.417mmol/g, 0.303mmol/g, 0.251mmol/g, 0.225mmol/g and 0.127mmol/g, respectively. X-ray photoelectron and infrared spectra determines the strong hydrogen bonding between chitosan and cellulose in these composites. The presence of hydroxyl(-OH) and amine(-NH2) groups is believed to be the metal binding sites on composite skeleton[71].

CONCLUSION: In general, chitosan and cellulose are economically feasible because they are easy to prepare and involve inexpensive chemical reagents. Both of these polymers could be used as alternative to replace the traditional, costly and environmentally toxic adsorbents currently used for adsorption of heavy metals. Adsorption efficiency of chitosan and cellulose is not good enough in pure form; therefore, modification of these biopolymers is necessary to increase the adsorption capacities and their applicability in different mediums. This field of research has a vast area for improvement in the hope that biopolymers can be applied commercially instead of laboratory scale.

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REFERENCES:

1. Quek SY, Wase DAJ, Forster CF: The use of sago waste for the sorption of lead and copper. Water SA 1998; 24(3):251-256.
2. Hu X, Li Y, Wang Y, et al: Adsorption kinetics, thermodynamics and isotherm of thiacalix[4]arene-loaded resin to heavy metal ions. Desalination 2010; 259(1-3):76-83.
3. Al Rashdi B M, Johnson DJ, Hilal N: Removal of heavy metal ions by nanofiltration. Desalination 2013; 315:2-17.
4. Cerna M. Monitoring E: Use of solvent extraction for the removal of heavy metals from liquid wastes. Environmental Monitoring and Assessment 2014; 34:1-6.
5. Vaaramaa K, Lehto J. Removal of metals and anions from drinking water by ion exchange: Desalination 2003;155(2):157-170.
6. Zhang H, Zhao X, Wei J, Li F: Sorption behavior of cesium from aqueous solution on magnetic hexacyanoferrate materials. Nuclear Engineering Desalination 2014; 275:322-328.
7. Coskun R, Soykan C, Sacak M: Removal of some heavy metal ions from aqueous solution by adsorption using poly(ethylene terephthalate)-g-itaconic acid/acrylamide fiber. Reactive Functional Polymers 2006;66(6):599-608.
8. Deans J, Dixon B: Uptake of Pb2+ and Cu2+ by novel biopolymers. Water Research. 1992; 26(4):469-472.
9. Kannan N, Sundaram M M: Kinetics and mechanism of removal of methylene blue by adsorption on various carbons comparative study. Dyes and Pigments 2001:5125–40
10. Ahmed S, Ahmad M, Ikram S: Chitosan: A Natural Antimicrobial Agent- A Review. Journal of Applicable Chemistry 2014; 3(2):493-503.
11. Ahmed S, Ikram S. Chitosan & its Derivatives: A Review in Recent Innovations. International Journal of Pharmaceutical Research 2015; 6(1):14-30.
12. Phan N H, Rio S, Faur C, Coq L L, Cloirec P L, Nguyen T H: Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications. carbon; 2006:44(12):2569–2577
13. Ehara K, Saka S, Kawamoto H: Characterization of the lignin-derived products from wood as treated in supercritical water. Journal of Wood Science 2002; 48:320-325.
14. Wu F C, Tseng R L, Juang R S: Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. Journal of Hazardous Material2001; 81(1-2):167-177.
15. Chiou M S, Ho P Y, and Li H Y: Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. Dye. Pigment. 2004; 60(1):69-84.
16. Crini G, Badot P M. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Progress in Polymer Science 2008; 33(4):399-447.
17. Islam S, Shahid M, Mohammad F: Green Chemistry Approaches to Develop Antimicrobial Textiles Based on Sustainable Biopolymers-A Review. Industrial Engineering Chememistry Research 2013;52(15):5245-5260
18. Hastuti B, Siswanta D: The Synthesis of Carboxymethyl Chitosan-Pectin Film as Adsorbent for Lead (II) Metal. International Journal of Chemical Engineering and Applications 2013; 4(6):349-353.
19. Dhanesh S, Mishra M, Mishra AK, Anjali S: Removal of Lead from Waste Water Using Low Cost Adsorbent. International Research Journal of Environment Sciences2013; 2(9):23-26.
20. Peter M, Gopalakrishnan S, Kannadasan T: Adsorption of Copper by Ethylenediamine-modified cross-linked magnetic chitosan resin (EMCMCR). American Journal of Engineering Research2013; (05):114-121.
21. Thilagan J, Gopalakrishnan S, Kannadasan T. cellulose and cross linked by formaldehyde,(b) chitosan

immobilised on red soil,(c) chitosan reinforced by banana stem. Journal ofengineering technology 2013; 3(1):35-60.

22. Soundarrajan M, Gomathi T, Sudha PN: Understanding the Adsorption Efficiency of Chitosan Coated Carbon on Heavy Metal Removal. International Journal of Scientific and Research Publication 2013; 3(1):1-10.
23. Wan Ngah W S, Teong L C, Toh R H, Hanafiah M A K M, Utilization of chitosan–zeolite composite in the removal of Cu(II) from aqueous solution: Adsorption, desorption and fixed bed column studies.Chemical Engineering Journal2012;209; 46–53.
24. Reiad NA, Abdelsalam OE, Abadir EF, Harraz FA. Preparation , Characterization and Application of Chitosan / Polyethylene Glycol Blend Film for Removal of Iron from Water. International journal of Sustainable Water and Environmental Systems2013; 5(1):43-49.
25. Wang W, Huang D, Kang Y, Wang A : Biointerfaces One-step in situ fabrication of a granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu 2 + ion. Colloids and Surfaces B 2013; 106:51-59.
26. Shanmugapriya A, Hemalatha M, Scholastica B, Arul A, Prasad T; Adsorption studies of lead (II) and nickel (II) ions on chitosan-G-polyacrylonitrile. Der Pharma Chemica 2013; 5(3):141-155.
27. Hritcu D, Dodi G, Popa MI. Heavy Metal Ions Adsorption on Chitosan-Magnetite Microspheres. International Review of Chemical Engineering 2012; 4(May):364-368.
28. Benavente M, Moreno L, Martinez J: Sorption of heavy metals from gold mining wastewater using chitosan. J. Taiwan Inst. Chem. Eng. 2011; 42(6):976-988.
29. Repo E, Warchoł JK, Bhatnagar A, Sillanpää M. Journal of Colloid and Interface Science Heavy metals adsorption by novel EDTA-modified chitosan – silica hybrid materials. J. Colloid Interface Sci. 2011; 358(1):261-267.
30. Shanmugapriya A, Ramya R, Ramasubramaniam S, Sudha PN, Nadu T. Studies on removal of Cr (VI) and Cu (II) ions using Chitosan. Archives of Applied Science Research 2011; 3(3):424-435.
31. Wang L, Xing R, Liu S, Cai S, Yu H, Feng J, Li R, Li P: Synthesis and evaluation of a thiourea-modified chitosan derivative applied for adsorption of Hg (II) from synthetic wastewater. International Journal of Biological Macromolecules 2010;46524–46528
32. ZuoX: Preparation and Evaluation of Novel Thiourea/Chitosan Composite Beads for Copper(II) Removal in Aqueous Solutions. Industrial Engineering Chemistry Research 2014; 53: 1249−1255
33. Li H, Huang: Microwave Preparation and Copper Ions Adsorption Properties of Crosslinked Chitosan / ZSM Molecular Sieve Composites.Journal of Applied Polymer Science 2013:86-93.
34. Qin Y, Cai L, Feng D, Shi B,Liu J,Zhang W,Shen y: Combined Use of Chitosan and Alginate in the Treatment of Wastewater. Journal of Applied Polymer Science2007; 104:3581–3587.
35. Zhang C, Zhang M, Chang Q: Preparation of mercaptoacetyl chitosan and its removal performance of copper ion and turbidity. Desalination Water Treatment 2013:1-4.
36. Ramya R, Sankar P: Adsorption of Cu (II) and Ni (II) ions from metal solution using crosslinked chitosan-g-acrylonitrile copolymer. International Journal of Environmental Sciences 2011; 1(6):1323-1338.
37. Ramnani SP, Sabharwal S. Adsorption behavior of Cr(VI) onto radiation crosslinked chitosan and its possible application for the treatment of wastewater containing Cr(VI). Reaction Functional Polymer 2006; 66(9):902-909.
38. Gotoh T, Matsushima K, Kikuchi K-I. Preparation of alginate–chitosan hybrid gel beads and adsorption of divalent metal ions. Chemosphere 2004; 55(1):135-140.
39. Fox S C, Li B, Xu D, Edgar K J: Regioselective Esterification and Etherification of Cellulose: A Review, Biomacromolecules 2011; 12: 1956–1972.
40. Zhou J, Chang C, Zhang R, Zhang L. Hydrogels prepared from unsubstituted cellulose in NaOH/urea aqueous solution. Macromole Bioscience 2007; 7(6):804-9.
41. Klemm D, Heublein B, Fink H P, Bohn A. Cellulose: fascinating biopolymer and sustainable raw material. Angewendate. Chemie. International Eddition 2005; 44(22):3358-93.
42. Aoki N, Fukushima K, Kurakata H, Sakamoto M, Furuhata, and K I: Reactive Functional Polymer 1999; 42: 223–233.
43. Jorge RA, Chqas AP: Ion-exchange equilibria between solid aluminium pectinates and Ca , Mn II , Cu II and Fe III ions in aqueous solution. Journal of Chemical Society 1988;84:1065-1073
44. Kamel S, Hassan EM, and El-Sakhawy M: Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper (II) ions.Journal of Applied Polymer Science2006; 100(1):329-334.
45. McDowall DJ, Gupta BS, Stannett VT: Grafting of vinyl monomers to cellulose by ceric ion initiation. Progress in Polymer Science 1984; 10(1):1-50.
46. O’Connell DW, Birkinshaw C, O’ Dwyer TF: Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresource Technology 2008; 99: 6709–6724.
47. Hajeeth T, Sudha PN, Vijayalakshmi K, Gomathi T: Sorption studies on Cr (VI) removal from aqueous solution using cellulose grafted with acrylonitrile onomer. International Journal of Biological Macromolecule. 2014; 66:295-301.
48. Silva Filho EC, Lima LCB, Silva FC, Sousa KS, Fonseca MG, Santana S a a. Immobilization of ethylene sulfide in aminated cellulose for removal of the divalent cations. Carbohydrate Polymer. 2013; 92(2):1203-10.
49. Wang J, Wei L, Ma Y, Li K, Li M, Yu Y, Wang L, QiuH: Collagen/cellulose hydrogel beads reconstituted from ionic liquid solution for Cu(II) adsorption. Carbohydrate Polymer. 2013; 98(1):736-43.
50. Zhou Y, Jin Q, Hu X, Zhang Q, Ma T: Heavy metal ions and organic dyes removal from water by cellulose modified with maleic anhydride. Journal of Material Science 2012; 47(12):5019-5029.
51. Gurgel LVA, Júnior OK, Gil RPDF, Gil LF: Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride. Bioresource Technological 2008; 99(8):3077-83.
52. Hokkanen S, Repo E, Suopajärvi T, Liimatainen H, Niinimaa J, Sillanpää M: Adsorption of Ni(II), Cu(II) and Cd(II) from aqueous solutions by amino modified nanostructured microfibrillated cellulose. Cellulose 2014; 21(3):1471-1487.
53. Sokker HH, Gad YH, Ismail SA. Synthesis of Bifunctional Cellulosic Adsorbent by Radiation Induced Graft Polymerization of Glycidyl Methacrylate- co -Methacrylic Acids. Journal of Applied Polymer Science2012. doi:10.1002/app.(online)
54. Tang Y, Ma Q, Luo Y, Zhai L, Che Y, Meng F: Improved synthesis of a branched poly(ethylene imine)-modified cellulose-based adsorbent for removal and recovery of

Cu(II) from aqueous solution. Journal of Applied Polymer Science2013; 129(4):1799-1805.

55. Liu J, Xie T H, Deng C, Du KF, Zhang N, Yu J J: Welan Gum-Modified Cellulose Bead as an Effective Adsorbent of Heavy Metal Ions (Pb 2+ , Cu 2+ , and Cd 2+) in Aqueous Solution. Seperation Science and Technology 2014; 49(7):1096-1103.
56. Taha A, Wu Y, Wang H, Li F: Preparation and application of functionalized cellulose acetate/silica composite nanofibrous membrane via electrospinning for Cr(VI) ion removal from aqueous solution. Journal of Environment Management 2012; 112:10-6.
57. Kumari S, Chauhan GS: New Cellulose − Lysine Schi off - Base-Based Sensor − Adsorbent for Mercury Ions.ACS Applied Material Interfaces 2014; 6 (8): 5908–5917.
58. Zhou Y, Fu S, Zhang L, Zhan H, Levit M V: Use of carboxylated cellulose nanofibrils-filled magnetic chitosan hydrogel beads as adsorbents for Pb(II). Carbohydrate Polymer 2014; 101:75-82.
59. Yu X, Tong S, Ge M, et al. Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. Journalof Environmental Science 2013; 25(5):933-943.
60. Anirudhan TS, Divya L, Parvathy J: Arsenic adsorption from contaminated water on Fe(III)-coordinated amino-functionalized poly(glycidylmethacrylate)-grafted TiO 2 -densified cellulose. Journal of Chemical Technology and Biotechnology 2013; 88(5):878-886.
61. Liu P, Sehaqui H, Tingaut P, Wichser A, Oksman K, Mathew AP. Cellulose and chitin nanomaterials for capturing silver ions (Ag+) from water via surface adsorption. Cellulose 2013; 21(1):449-461.
62. Zhang Y, Liu Y, Wang X, Suna Z, Ma J , WubT, Xing F , Gao J:Porous graphene oxide/carboxymethyl cellulose monoliths, with high metal ion adsorption. Carbohydrate Polymers 2014; 101:392-400.
63. Peng S, Meng H: Nanoporous Magnetic Cellulose–Chitosan Composite Microspheres: Preparation, Characterization, and Application for Cu (II) Adsorption. Industrial Engineering 2014; 53(6):2106-2113.
64. Ji F, Li C, Xu J, Liu P: Dynamic adsorption of Cu(II) from aqueous solution by zeolite/cellulose acetate blend fiber in fixed-bed. Colloids Surfaces A Physicochemical Engineering Aspects 2013; 434:88-94.
65. Khan SB, Alamry K, Marwani HM, Asiri AM, Rahman MM: Synthesis and environmental applications of cellulose/ZrO2 nanohybrid as a selective adsorbent for nickel ion. Composites Part B Engineering 2013; 50:253-258.
66. Naim MM, Abdel Razek HEM: Chelation and permeation of heavy metals using affinity membranes from cellulose acetate–chitosan blends. Desalination Water Treateatment 2013; 51(1-3):644-657.
67. O. Ekebafe L, O. Ekebafe M, Erhuaga GO, Oboigba FM: Effect of Reaction Conditions on the Uptake of Selected Heavy Metals from Aqueous Media using Composite from Renewable Materials. American Journalof Polymer Science 2012; 2(4):67-72. 68
68. Liu Z, Wang H, Liu C, Jiang Y, Yu G, Mu X,WangX: Magnetic cellulose-chitosan hydrogels prepared from ionic liquids as reusable adsorbent for removal of heavy metal ions. Chemical Communication 2012; 48(59):7350-2.
69. Temerdashev Z, Konshina DN, Logacheva EY, Konshin V V: Sorption properties of cellulose filters with covalently immobilized thiosemicarbazide. Journal of analytical chemistry2011; 66(10):930-936.
70. El-Khouly A, Takahashi Y: Study of heavy metal ion absorbance by amidoxime group introduced to cellulose-graft-polyacrylonitrile. Journal of applied science2011; 120:866-873.
71. Sun X, Peng B, Ji Y, Chen J, and Li D: Chitosan (chitin)/cellulose composite biosorbents prepared using ionic liquid for heavy metal ions adsorption. AIChE Journal 2009; 55(8):2062-2069.

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