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

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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 metals¹. 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 precipitation², nano filtration³, solvent extraction⁴, ion exchange⁵, reverse osmosis⁶ and adsorption⁷ 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.

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 binding⁸ properties.

Adsorption process is known to depend upon various experimental conditions such as particle size, pH, metal concentration, ligand concentration and competing ions⁹. Scientists have focused their momentum for the search of low cost and easy available biomaterials for the waste water treatment. Chitosan¹⁰, alginate¹¹, cellulose¹² and lignin¹³ 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.

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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(-NH₂) and hydroxyl(-OH) groups in its backbone, chitosan has been used as an effective material for the removal of heavy metals from waste waters¹⁴. Mostly the adsorption depends on the pH values and the chitosan is very sensitive to pH¹⁵. 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 isocyanates¹⁶.

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 properties¹⁵. **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 CHARACTERISTICS¹⁷.

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 adsorbent³¹ 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) complexes³². 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 water¹⁸.

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 kinetics¹⁹. 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^oC with the initial concentration of 200 ppm. The adsorption was best with Langmuir adsorption model²⁰. 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 process²¹. 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 kinetics²².

Chitosan-zeolite(CZ) composite was prepared by using zeolite and chitosan for the adsorption of Cu(II) ions from the treated waste water²³. 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 concentration²⁴. 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 NH₂)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 interaction²⁶.

Chitosan-magnetite nanoparticles was used for the adsorption of nickel (Ni) and cobalt (Co) ions from aqueous solutions²⁷. Chitosan derived from shrimp shell waste used for the removal of Cu(II), Hg(II), Pb(II) and Zn(II) from gold ore staking 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 equation²⁸. Ethylenediaminetetraacetic acid (EDTA) ligand gets combined together with chitosan-silica hybrid materials for synthesizing a novel type adsorbent for decontaminating the Co(II), Ni(II), Cd(II), and Pb(II) ions from aqueous solution²⁹.

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 media³⁰. 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,

glutaraldehyde, and SiO₂)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 solutions³³. In order to facilitate the adsorption efficiency, the chitosan 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 water³⁴.

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 rate³⁵. The Cu(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 time³⁶. 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 reused³⁷. 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 glutaraldehyde. The crosslinking makes the beads durable and facilitates the adsorption of Cu(II), Co(II) and Cd(II) ions under acidic conditions³⁸.

Cellulose:

Polysaccharides are among the most abundant among all the polymers present on earth³⁹ 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 material⁴⁰.

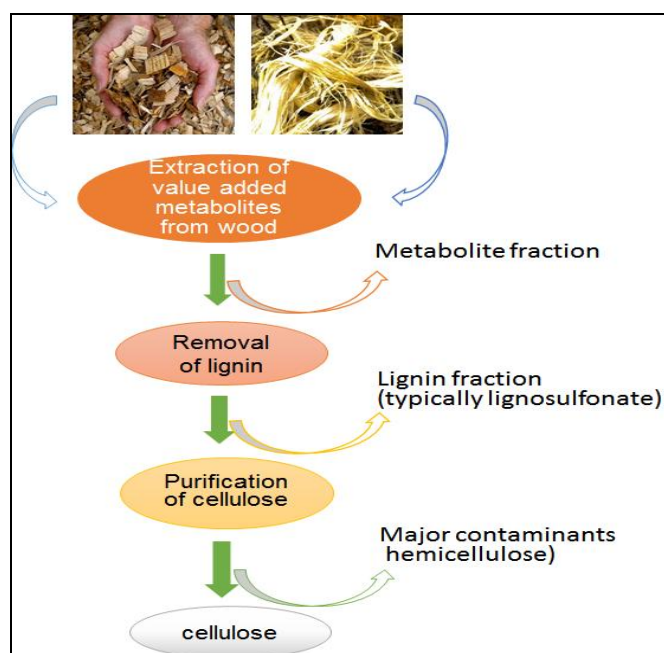


FIG.1: SHOWS THE EXTRACTION OF CELLULOSE FROM DIFFERENT WOOD SOURCES

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 groups⁴¹. 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 moieties⁴².

Pure cellulose has very few applications compared to the diversity of applications of its modified form⁴³. Chemical modifications increase its adsorption capacity for heavy metals in aqueous and non-aqueous media⁴⁴. 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 resistance⁴⁵.

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 esterification⁴⁶. 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/ZrO ₂	NI(II)	79.0	-	-	-	Langmuir	52
Bifunctional cotton fabric waste	Co(II), NO ₃ ⁻	38.5,11	-	5,4.5	Pseudo second order	Freundlich, Langmuir	53
Cell-g-PGMA-PEI	Cu(II)	102	28	3.5-7.0	pseudo second 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	pseudo second 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 kinetic⁴⁷. 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) ions⁴⁹. 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), and Pb²⁺ ions⁵¹. 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, respectively⁵². For the removal of cobalt (Co(II) and nitrate (NO₃) 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⁺ (CH₂CH₃)₃ and COOH groups carrying the potential application of adsorption⁵³. 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 moiety⁵⁴.

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 5⁵⁵.

Cellulose acetate (CA) with tetraethoxysilane (TEOS) as a silica source in presence of coupling reagent 3-ureidopropyltriethoxysilane was used for the synthesis of novel NH₂-functionalized cellulose acetate (CA)/silica composite nanofibrous membranes with electrospinning technology which

was employed for the removal of Cr(VI) ions from aqueous media⁵⁶. 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⁻¹⁵⁷.

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) ions⁵⁸. A cellulose type nano adsorbent is used for the removal of Pb(II) and Cd(II) from aqueous solutions. This nano adsorbent 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 nano adsorbent (NaSCNCs) was further prepared by treatment of SCNCs with saturated NaHCO₃ aqueous solution⁵⁹.

In order to determine the adsorption potential of anion exchanger, Fe(III)-coordinated amino-functionalized poly glycidylmethacrylate-grafted TiO₂-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 model⁶⁰. The novel 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 bio nanomaterials⁶¹. 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 strength⁶². 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 of Cu(II) ions⁶³.

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 rate⁶⁴. Cellulose matrix modified by ZrO₂ for the synthesis of cellulose/ZrO₂ nanohybrid 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 adsorption was found to be 79 mgg⁻¹⁶⁵.

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 metals⁶⁶. 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% respectively⁶⁷. 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 $44.7 \pm 5 \text{ mgg}^{-1}$, $28.1 \pm 3 \text{ mgg}^{-1}$ and $94.1 \pm 7 \text{ mgg}^{-1}$ respectively⁶⁸. A novel type cellulose adsorbent bearing chemically grafted thiosemicarbazide was used for adsorption of Co(II), Hg(II) and Cd(II) ions⁶⁹. 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) ions⁷⁰. 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 skeleton⁷¹.

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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