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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 severe threat to flora and fauna. In recent years, considerable research work has been done and is currently underway on some 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 wastewater. 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], nanofiltration [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. The adsorption process is known to depend upon various experimental conditions such as particle size, pH, metal concentration, ligand concentration and competing for ions [9].

Scientists have focused their momentum for the search of low cost and easy available biomaterials for the wastewater 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. Given 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. Also, 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 wastewater.

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, an adsorbent for heavy metals
Cellulose	Green plants, Algae, and oomycetes	Tasteless, odorless, 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 WASTEWATER

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

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 wastewater. 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 fit the first order kinetics [19]. Ethylenediamine modified cross-linked magnetic chitosan resin (EMCMCR) was used for the adsorption of Cu (II) ion from wastewater. The best results of adsorption were observed at pH of 6.0, the temperature of 25 ºC with the initial concentration of 200 ppm. The adsorption was best with Langmuir adsorption model [20]. Removal of Cu(II) ions from aqueous solution 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 a 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 wastewater [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]. The 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 occur 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 using 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 were 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 were 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 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 solution [29].

Graft copolymerization of polyacrylonitrile on chitosan surface in the presence of ceric ammonium nitrate was used for removal of Cr(VI) and Cu(II) ions from aqueous media [30]. Thiourea modified chitosan was synthesized in two steps, O-carboxymethylation first and secondly the polymeric Schiff base of thiourea/glutaraldehyde was used for the adsorption of Hg(II) [31]. Beads of thiourea-modified chitosan were used for the adsorption of Cu(II) was prepared by several media(citric acid, sodium hypophosphite, glutaraldehyde, and SiO_2) [32].

Graft copolymerization of chitosan with polyacrylonitrile in the presence of ceric ammonium nitrate used for the removal of Pb(II) and Ni(II) ions from aqueous solutions [33]. 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 wastewater [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 a 100% removal rate [35]. 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 the presence of ceric ammonium nitrate as an initiator.

The adsorption efficiency of adsorbent was depended on the 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 were compared with simple chitosan at pH 3. CRCH showed higher adsorption capacity of Cr (VI) ion, and its experimental results were 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 the 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 successfully took place through glutaraldehyde. 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 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 a long linear chain polymer with a large number of hydroxyl groups (three groups per anhydrous 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].

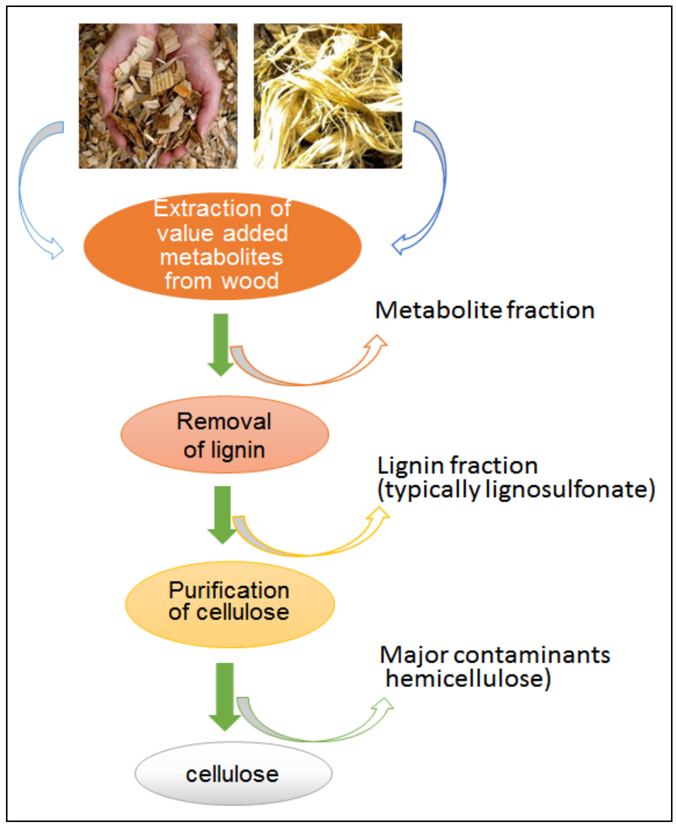

FIG. 1: SHOWS THE EXTRACTION OF CELLULOSE FROM DIFFERENT WOOD SOURCES

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 the 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, absorptivity, 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 occur through several different methods. However, modifications can also occur on the secondary hydroxyl groups (-OH) present on carbons 2 and 3.

The significant 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 WASTEWATER

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Tem. (oC)	pH	Kinetic model	Isotherm
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	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	-
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	-	-
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 functionalization of the grafted polymer chains. With known chelating moieties such as graft copolymerization of acrylonitrile on to cellulosic material derived from sisal fiber in the presence of ceric ammonium nitrate (as initiator) used for making adsorbent to remove Cr(VI) ions from aqueous media. By using this material as an adsorbent, Cr(VI) ions removal was found to be optimum at pH 5, and the experimental data were 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 is 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 the carboxyl group of CM and was found to be 2.7 $mmolg^{-1}$.

The effect of different experimental parameters such as temperature contact time and pH was evaluated during the removal process. The experimental data were best fitted with the Freundlich isotherm model, and kinetic studies revealed that it would follow pseudo-second-order kinetics with a 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 Pb^{2+}ions [51]. Microfibrillated cellulose (MFC) type adsorbent was synthesized by the graft copolymerization of aminopropyl-triethoxysilane (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 glycidyl methacrylate 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 an initiator for graft copolymerization of glycidyl methacrylate (GMA) onto cellulose and subsequent modification with polyethyleneimine (PEI) produces an improved synthesis of a branched polyethyleneimine (PEI) modified cellulose-based adsorbent (Cell-g-PGMA-PEI) for adsorption of Cu(II) from the 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 the 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 the 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 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 to obtain SCNCs. The sodic nano-adsorbent (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 glycidyl methacrylate-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 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 bionanomaterials [61]. Graphene oxide/carboxymethyl cellulose (GO/CMC) based column is used as an adsorbent for the 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 the 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) ions [63].

Zeolite/cellulose acetate blended (ZCAB) fibers, as an adsorbent for Adsorption of Cu(II) ion, was prepared by the 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 the 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].

The 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 micro-spheres 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 ± 5 mgg^{-1}, 28.1 ± 3 $mgg^{-1,}$ and 94.1 ± 7 mgg^{-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 an adsorbent for adsorption of Co(II), Cu(II), Ni(II) ions [70]. The biodegradable adsorbent of chitosan (chitin)/cellulose composites which were 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 0.417 mmol/g, 0.303 mmol/g, 0.251 mmol/g, 0.225 mmol/g and 0.127 mmol/g, respectively. X-ray photoelectron and infrared spectra determine the strong hydrogen bonding between chitosan and cellulose in these composites. The presence of hydroxyl (-OH) and amine(-NH_2) 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 an 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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