

Hybrid bioadsorbents for heavy metal decontamination from wastewater: A review

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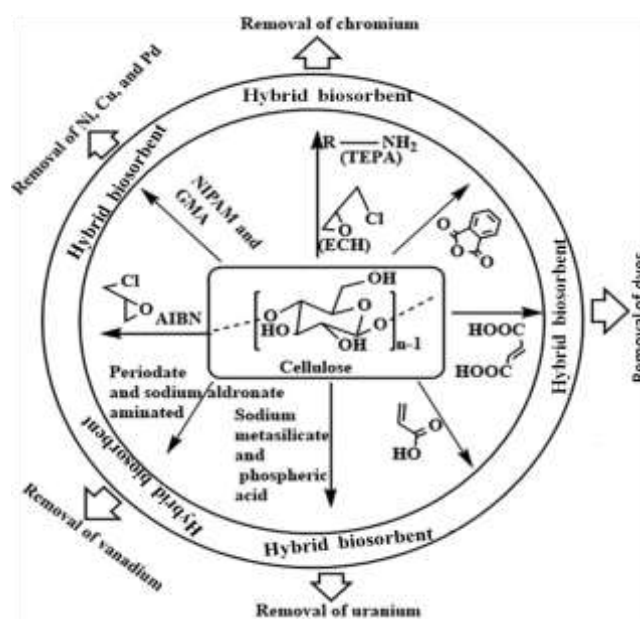
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Abstract

Wastewater containing heavy metals (HMs) beyond permissible limit has to be decontaminated by an appropriate treatment method. Numerous conventional methods have been applied for heavy metal decontamination including chemical precipitation, ion exchange, electrolysis and membrane applications, etc. Most conventional methods are less efficient for the decontamination of metals due to the resistance and persistence of HMs in wastewater. Even so, the conventional methods have their limitations; adsorption using low-cost hybrid bioadsorbents has been explored as an environmentally friendly method for the removal of metal ions from wastewater. This review has been summarized the sources and effects of different heavy metals in the water/wastewater. The possible treatment methods also highlighted their advantages and limitations. Factors affecting the biosorption process such as bioadsorbent dosage, solution pH, contact time, initial concentration, temperature, and ionic potentials attracting to metal ions have been evaluated by the published researches. Moreover, the possible mechanisms of metal biosorption were discussed in light of previous studies. According to this review, hybrid bioadsorbents are outstanding materials due to their exciting physicochemical properties and other characteristics including eco-friendly nature, low cost, nontoxic, high adsorption capacity, and reusability. This review could be considered as a precious pathway for exploring more low-cost, environmentally friendly hybrid adsorbents for metal decontamination from wastewater, eventually, the review will contribute to environmental remediation and purification applications of biomaterials.

Graphical Abstract



Keywords: Hybrid adsorbents; Bio-remediation; Heavy metal; Decontamination; Wastewater.

1. Introduction

Rapid trends of industrialization and urbanization are leading to contaminating the water with organic pollutants, heavy metals (HMs), and other inorganic contaminants [1]. Substantial number of previous studies reported that global water has been severely contaminated by HMs, that are present in a higher amount than the permissible limit [2, 3]. The excessive amount of heavy metals in water is due to uncontrolled anthropogenic activities such as; uncontrolled mine drainage, untreated municipal and industrial effluents as well as extensive agricultural inputs [2]. Moreover, natural weathering of parent rocks similarly contributes to water contamination by HMs.

Heavy metals are tending to accumulate in living organisms and these are non-biodegradable. The previous studies also reveal that the toxicity of metals into the environment bearing severe impacts on public health and subsequent stimulus the malfunction of the ecosystem [4-6], as seen in Table 1. The treatment of wastewater is a great concern of scientists; thus, they have been using different technologies based on physical, chemical, physio-chemical, and biological methods. Among other methods, the physicochemical treatments are the most used methods due to their diverse advantages including simple, cost-effective, rapid, and easy to operation [7-9].

Table 1. Sources, applications and toxicities of some selected heavy metals.

Metal	Natural sources	Applications	Toxicities/Health effects	References
Copper	Vegetation decaying, dust from Wind-blown, sea spray and forest fire	Transmission wires, copper alloys and coins, Electrical wiring, stoves, portable CD players	Nose, mouth and eyes irritation, Stomach ache and headaches	[4,6,10,11]
Chromium	Volcanoes eruptions, weathering from rocks and minerals, plants and animals decaying	Stainless steel production, Electroplating, leather tanning, wood preservation, and textile manufacturing	Liver and kidney damage, Nasal and sinus cancers, nasal and skin irritation, eye irritation and ulceration	[4]
Manganese	Volcanic eruption, sea spray, forest fire and vegetation decaying	Oxidizing agent, decolorize glass, depolarizer in dry cells	Growth of retardation due to toxicity, fever, sexual impotence, eye blindness and muscles fatigue	[6]
Lead	Sea and salt lake aerosols, forest fires and volcanic eruptions	Car batteries, pigments, lead crystal glass, radiation protection, architecture	Carcinogenic, anemia, abdominal, muscle and joint pains, kidney problems, and high blood pressure	[12]
Mercury	Volcanoes, geologic deposits of mercury and volatilization from the ocean	Batteries, fluorescent lights, felt production, thermometers and barometers	Headache, abdominal pain and diarrhea, paralysis, and gum inflammation, loosening of teeth, loss of appetite	[13]
Arsenic	Earth's crust, groundwater, geothermal processes	Rat poisons and preserve wood	Kidney and liver disorders, skin cancer and gangrene	[5]

Different physicochemical treatments methods have been used for decontamination of HMs in wastewater that includes chemical precipitation, coagulation, solvent extraction, ion exchange, cementation, membrane operation, and adsorption [9,14,4,5]. Most conventional methods are less efficient due to the resistance and persistence of HMs in wastewater [14,4,5]. Nonetheless, these methods have their own limitations such as discharging of toxic slurry, challenges of sludge management, and precarious working environments [4]. Therefore, it is demanding to find environment-friendly and cost-effective water remediation methods. Adsorption is one of the best methods having high competency, simple, and cost-effective for HMs decontamination from wastewater.

Nemours adsorbent materials like; alumina (Al_2O_3) [7], activated carbon [15], graphene oxide [4], titanium dioxide (TiO_2) [16], kaolin clay [17], and silica [4, 6], etc. have been reported as adsorbents for sequestration of metal ions from wastewater. Amongst the materials, researchers are encouraging attention to be paid the development of low-price and efficient adsorbents that are naturally available and environmentally friendly materials especially those derived from biological sources. Moreover, researchers are using different hybrid adsorbents due to their unique characteristics such as; available reactive sites, a good number of active groups, extended surface area, and regeneration potentials [4, 6-8]. Although hybrid adsorbents are the most promising, commercial use is still faltered due to their irregularities, lack of selectivity, toxic effect, and uncertainty of separation from treated water [18]. To overcome these issues and improve the adsorption capacity as well as facile separation, scientists are trying to fabricate hybrid materials by surface functionalization and coating with various metal oxides [6,8], polymers [4], inorganic materials [4], carbon [15], and biomolecules [19]. Biomolecules as the biological sources of adsorbent or biosorbent including starch, chitosan, silk fibroin, sericin, alginate and xylans and other agricultural byproducts such as peel, rice husk, seed shell of sunflower, eggshell have received top priority for hybridization of adsorbents with other commercial pristine materials for HMs decontamination from wastewater due to their outstanding characteristics including low cost, chemically stable, non-toxic, environmentally friendly, hydrophilic nature and biodegradable behaviors [20-23].

The primary focus of this review was heavy metal decontamination from wastewater using hybrid

bioadsorbents. The hybrid bioadsorbents are considered promising, eco-friendly, and economically convenient for the field of purification, separation, and environmental remediation. The novelty of this review is the investigation of adsorption behaviors and exploring their mechanisms.

2. Wastewater treatment technologies

Assortment of suitable remediation methods of HMs contamination is a big challenge. Different technologies ranging from biological to complex engineering methods were proposed for HMs decontamination from wastewater. Among other methods, the physicochemical treatments are the most used methods due to their diverse advantages such as ease of operation, cost-effectiveness and speedy method as well as the flexibility to change the temperature during the process. The Physicochemical treatment refers to the process which includes the physical interaction involved in the chemical reaction of atoms and molecules as well as interferes in the changes or formation in the structure of atoms and molecules. The Physicochemical treatment for decontamination of HMs from water includes various techniques; among them, the most used methods are ion exchange, membrane operation, chemical precipitation, and adsorption. Generally, plants for physicochemical treatment are adaptable to modifying their requirements and can accommodate various seasonal flows and multifarious discharge. Moreover, the physicochemical treatment requires low installation cost, and the treatment system necessitates a narrow space. The methods offer several merits and demerits compared to each other's those are related to economic, management and capacity of remediation. The major merits and demerits of various treatment methods have been summarized in Table 2. Among these methods, adsorption has been employed for many years and is considered one of the most promising methods for the removal of HMs from wastewater [4,6,9,14].

2.1. Adsorption

Adsorption is a physiochemical separation and transfer of molecules and atoms from one phase to another, which is characterized as a surface phenomenon [24]. The process of adsorption can take physical, chemical or active forms. If adsorption occurs due to weak or Van der Waals forces between the molecules, it is termed as physical adsorption or physisorption. On the other hand, if adsorption occurs due to interactions between molecules of adsorbates

and adsorbents by chemical bonding, it is termed chemisorption. Mechanism of the adsorption process is referring to molecules and atoms of adsorbates being isolated in a fluid phase that is being transferred on the surface of the adsorbent (solid phase) such as commercial materials, biomaterials, composites/hybrid and nanomaterials. Actually, from molecular aspects, adsorption occurs due to electrostatic attractions, as result of the adsorbate being removed from the liquid phase to the surface of the adsorbent. Adsorbents can be made from different material sources such as organic, inorganic, agricultural residues, and other biological sources [23, 25].

2.2. Hybrid adsorbents

A number of natural and agricultural adsorbent has been reported including natural zeolites, clays and soil constituents, chitosan, red mud, and fly ashes [20,23,25]. These are reported as poor adsorbent properties, heterogeneous surface structure, uneven

pore size distribution and insufficient range of metal selectivity, but they are abundant, low cost; moreover, they can be improved by chemical modification. On the other hand, researchers have been using numerous commercial adsorbent materials such as; alumina, activated carbon, silica, titanium dioxide TiO₂, halloysite nanotube (HNT), and graphene oxide, etc. [4,7,8,15,16]. The main disadvantages of these traditional adsorbents are their low adsorption efficiencies, comparatively fragile interactions with metal ions, and complications of capturing and regeneration of some of them from wastewater [4]. To overcome these drawbacks, researchers are emphasizing to hybridization of pristine materials in order to gain improved physical and chemical characteristics such as enlarged surface area, available functional groups, and reactive sites as well as potentials of regeneration [26]. Recent trends of adsorption process are using modified hybrid materials for the removal of metal ions that are reported including [4,6-8]. The studies find that hybrid adsorbents showed good adsorption capacities,

Table 2. Some merits and demerits of various treatment methods of metal ions removal from wastewater.

Methods of treatment	Merits	Demerits	References
Ion exchange	Speedy and no sludge	High operating costs, suitable metal capturing resins are limited	[27]
Chemical precipitation	Easy to operation and low cost required	Huge sludge production, Extra cost for sludge management	[28]
Membrane filtration	Selectivity of metal separation is high, Low space and low pressure required,	Operation cost is high because of membrane fouling	[29]
Coagulation-flocculation	Quickly suspended solids are settled out, sludge settling is easy	Huge sludge production, extra cost for sludge management	[30]
Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumption	[31]
Adsorption	Operating conditions are easy, Low-cost, pH range is wide	Non-selective in adsorption of metals	[4]
Adsorption with modification	High surface area, accessible surface sites, short intra-particle diffusion distance	Selectivity is very low, production of waste materials	[6]
Photocatalysis	Simultaneously removed of metals as well as organic pollutants, by-products are less harmful	Time-consuming process, applications are limited	[32]

chemical and thermal stability, and a wide range of metal selectivity [4]. Nevertheless, the main difficulty for modification of hybrid adsorbents is to pick novel types of materials. Recently, researchers have been emphasizing modifying the hybrid adsorbents with bioadsorbent abundant, because they are naturally low cost, nontoxic, and environmentally friendly with good adsorption efficiencies [33].

3. Sources and properties of bioadsorbents

The bio-wastes or residue are considered environmentally friendly, renewable, and cost-effective adsorbents. They are mainly coming from agricultural and food wastes that include orange peel, rice husk, seed shell of sunflower, eggshell, walnut shell, sawdust, carrot pulp, pomegranate peel, soybean, and cottonseed hulls, and olive stone. [20-23]. The previous studies have been found that the adsorption capacity of pristine bio-materials is not promising and these are explored as poor surface properties compared with hybridized materials. Therefore, bio-based materials are essential for the improvement of surface properties for potential uses far from the customary applications of separation and purification field [33]. Researchers have been hybridized the bio-based adsorbents emerged with various materials including silica, graphene, carbon-based, polymeric and inorganic (metal oxides) materials for the removal of metal ions from wastewater [33]. Among other modifications, the polymerizations of bioadsorbents have gained great attention to improve the metal adsorption capacity of the hybrid bio-adsorbents. Last few decades, biopolymeric adsorbents have been used as promising preferences in comparison to conventional materials due to their excellent features including adaptable surface properties, suitable pore size, easy regeneration, and ideal mechanical rigidity [34]. Generally, polymeric bioadsorbents can be classified into synthetic functionalized and carbohydrate polymers. Chitosan, starch, cellulose, and other carbohydrate molecules are composed of extended chains of monosaccharides and subsequently, these are bound with glycosidic linkages. These types of carbohydrate biopolymers are extensively used for metal ions removal and found as efficient adsorbents due to their available functional groups such as amine, hydroxyl, and carboxyl [35]. Among other carbohydrate-based bioadsorbents, the modification of cellulose with organic fragments having functional groups has definitely taken place in hybrid material and cellulose backbone treated by their responding

hydroxyl groups (chemical activator). The embedded organic moiety triggers extraordinary metal adsorption from wastewater. On the other hand, synthetic biopolymer adsorbents having carboxyl and amino groups can have enhanced adsorbent properties due to their interaction between functional groups and targeted metal ions as well as being bound to the polymeric matrices. Different synthetic biopolymers have been reported as applied for metal ions adsorption that include poly (amidoamine co- acrylic acid), poly (N-vinyl caprolactam-co-maleic acid), poly (styrene-co-maleic acid), poly (anthranilic acid/4-nitroaniline/formaldehyde), and poly (acrylonitrile-co-styrene), [36-38]. The biomaterials including starch, cellulose, polysaccharides, alginates, pectin emerged with animal protein including silk, wooden, gelatin, collagen, chitosan/chitin, gum as well as plant-based proteins and lipids provide the opportunity of rendering exciting advantages of metal ions adsorption [39-43]. The hybrid bioadsorbents offer exciting advantages for metal adsorption with their renewable surface features, biocompatibility, non-toxicity, non-polluting traits, mechanical integrity and economically low-cost materials [38,39].

4. Factors affecting the biosorption of heavy metals from wastewater

A substantial number of previous studies have been found that the heavy metal adsorption onto hybrid biosorbent is highly dependent on operating factors that include solution pH, metal ions concentration, reaction time, biosorbent dose, temperature and biosorbent surface area, etc. [4,6,7].

4.1. Effect of solution pH

The stability and solubility of metal ions immensely affected by solution pH; in addition, functional groups available in hybrid bio-adsorbents have extremely fluctuated with different pH values in the bio-sorbent process. Numerous function groups including carboxyl, hydroxyl, carbonyl, sulfonate, amine, thioether, imine, phosphonate, phosphodiester, and imidazole have been conveyed by different biosorbents subsequently these reactive functional groups highly dedicated to the changes of pH values. Some studies found that the metal solution pH range among 3.0-10 is predominantly shown as negative charges on the surface of biosorbent. The functional group of hybrid biosorbent carries positive charges at lower values of 3.0-10 pH range due to the effect of protonation [44-46].

4.2. Effect of temperature

Temperature of the biosorption process is another factor that influences the efficacy of metal biosorption. The overall efficiency of metal ions' biosorption is not affected at a reaction temperature of 20-35°C. But in some cases, with further increments in temperature, the efficiency of metal sorption will increase, while in the maximum cases biosorption will not potentially be conducted because at high temperatures, the reactive sites of materials might be devastated. Most of metal ions' biosorption were energetically exothermic, hence, biosorption of metal ions is mostly suitable at lower temperatures [47,48].

4.3. Effect of surface area of the bioadsorbent

Mainly, adsorption process is one kind of surface phenomenon and surface interaction between adsorbent and pollutant, the reactive sites of biosorbent are mostly dependent on the surface area of the biomaterial enabling metal ions to form a mass over the surface of the solid phase (biosorbent). Because the enlarged surface area of the material contains more reactive sites than the relatively narrow

surface of the material, the efficacy of metal biosorption varies with the influence of surface area. Surface area can be calculated using Brunauer-Emmett-Teller (BET) model. BET is one of the popular models for calculating surface area of biosorbent when it is occurring as physical biosorption or without any chemical reaction between pollutant and biosorbent molecules [49, 50].

4.4. Effect of concentration and biosorbent dose

Because the reactive sites are fixed for per unit of biosorbent, therefore, the removal efficiency of heavy metal ions onto biosorbent is usually higher in low concentration due to availability of surface-active sites; however, after saturation, the percentage of removal efficiency decreases [4,6]. The mass of biosorbent and pollutant concentration showed parallel influences on the removal efficiency.

Alfarra et al. [51] recently reviewed the metal adsorption behavior using hybrid bio-adsorbents and summarized the salient factors affecting biosorption as illustrated in Table 3.

Table 3. Factors affecting the biosorption of heavy metals from wastewater [51, 52].

Factors affecting metal adsorption onto bio - adsorption	Effects
Dose of biosorbent	Per unit of biosorbent dose has fixed reactive sites, the metal removal efficacy reduces when upsurges of metal ions beyond availability sites in the dose of biosorbent.
pH medium	Usually, removal efficacy is higher on positively charged metal ions than the negatively charged metal ions
Particle size of biosorbent	Generally, batch mode of adsorption can be achieving higher removal efficiency by the small size of biosorbent because more reactive sites enable to participated same surface area.
Metal ions concentration	Increment of metal concentration in per unit of biosorbent dose subsequently removal efficacy reduces due to unavailable reactive sites on the surface biosorbent.
Agitation speed	Removal efficacy increases with agitation speed, but maybe the physical structure of the biosorbent could destroy.
Temperature	Adsorbent kinetic energy can help in more metal biosorption but the physical structure could devastate at high temperatures.
Ionic strength	The removal efficacy decreases when other ions are available in solution because of competition for the same vacant sites of biosorbent.
Coexistence of other pollutants	Coexisting pollutants lead to a low rate of metal removal efficacy due to co-binding competition on the same surface site of biosorbent.

5. Hybrid bioadsorbents for heavy metal decontamination

Increasing trend of urbanization and industrialization is leading to water contamination by heavy metals [4,5]. Therefore, researchers are looking for special concerns to treat and decontaminate wastewater. Because of their unique properties such as being eco-friendly, low-cost, naturally abundant, available functional groups, active sites, and regeneration potential, hybrid bioadsorbents are being considered as alternative suitable materials for metal biosorption [53]. Some recently reported hybrid biosorbents have been highlighted and tabulated in Table 4. Among other bio-based hybrid materials, biopolymers including alginates, lignin and chitosan have been widely used and found as exclusives materials for water purification and heavy metal decontamination. On other hand, the cellulose-based functional materials offer excellent adsorption capacity for the applications of metal decontamination [54]. Chitosan-based polymeric bioadsorbent has been found as versatile surface properties with excellent biosorption capacity of metal ions especially Cr(VI) removal due to electrostatic interaction between the protonation of amine-containing chitosan and the negatively charged chromate ions, the possible scheme as seen in Fig. 1 [54].

Among others, alginate-based bio-sorbents have been found as alternative biomaterials with an abundant presence of surface functional groups (e.g., carboxyl and hydroxyl) that could be capturing the positive charged (cationic) metal ions through electrostatic interaction between the crosslinking cations and potentials contaminants [55]. In last few decades, alginate-based biopolymer composites merged with other engineered and natural materials including alginate gels and other polymers, are comprehensively considered for the sequestration of heavy metal ions from wastewater [56-59]. To enhance the capacity performance and constancy of alginate for different utilizations, numerous biopolymers have been combined into alginate hydrogel (microspheres) [55]. Adane et al. [60] hybridized activated carbon with teff husk (THC) and applied it for the removal of Cr(VI) from wastewater. A 95.6% Cr(VI) elimination was achieved under optimum operating conditions in acidic media at solution pH 1.9, 20.2 g/L THAC was used for 87.8 mg/L chromate ions. Biosorption data of chromate ions onto THAC followed the Langmuir isotherm model and pseudo-second-order kinetic models. Li et al., [61] prepared starch-based hybrid biosorbent

(CMS-SS) to evaluate its biosorption behaviour toward Cu(II) ions from wastewater. Fabricated bio-composite was applied for bivalent copper ions, the biosorption was found fitted to Langmuir isotherm model with maximum monolayer efficiency of 653.31 mg/g. Adsorption efficiency onto the modified material was much higher than the efficiency of the pure material due to low electrostatic attraction among pollutants and the material's surface. The modified biosorbent showed better adsorption capacity because of the improved surface/ structural properties and available functional groups of material. Dawodu et al. [62] fabricated the heinsia crinite seed coat (HCSC) and evaluate the biosorption of Cr(VI) from contaminated environment. Factors affecting the biosorption process were investigated to optimize the operating conditions. The experiment was disclosed that the HCSC is found as promising biosorbent for Cr(VI) decontamination with removal capacity of 231.7 mg/g from wastewater under optimum reaction conditions at solution pH 2.0 using 0.3 g biosorbent within 30 min. of reaction time. Energetically this biosorption was suggested as physical, spontaneous and endothermic in nature. Experimental results were well fitted with the pseudo-second order kinetic and Freundlich isotherm models.

Plohl et al., [63] synthesized the carboxymethyl chitosan (CMC) based hybrid biopolymer MNPs@S@CMC, subsequently evaluated for sequestration of bivalent copper ions from wastewater. The Cu(II) adsorption onto MNPs@S@CMC was well-fitted to the Langmuir isotherm model with a maximum capacity of 350 mg/g which was better adsorption than pristine materials. Sodium alginate (SA) based hybrid biosorbent was modified and applied for the sequestration of U(VI) ions from contaminated effluent. Monolayer biosorption capacity of uranium ion was 210 mg/g under optimum conditions. Adsorption mechanism of this adsorption was directed prominently through ion-exchange and coordination reaction among metal ions and surface functional groups of biomaterials. Belachew and Hinsene, [65] synthesized the cetyl trimethyl ammonium bromide (CTAB) with kaolin for Cr(VI) biosorption from wastewater. Biosorption was conducted using 0.1 g of CTAB-kaolin for 10.0 mg/L chromate ions solution at optimum condition. A 99 % of removal capacity was achieved within 180 by using kaolin-CTAB biosorbent. The experimental results fitted to the well-known Langmuir and pseudo-first-order kinetic models as directing monolayer and chemisorption process for Cr(VI) biosorption onto CTAB-kaolin.

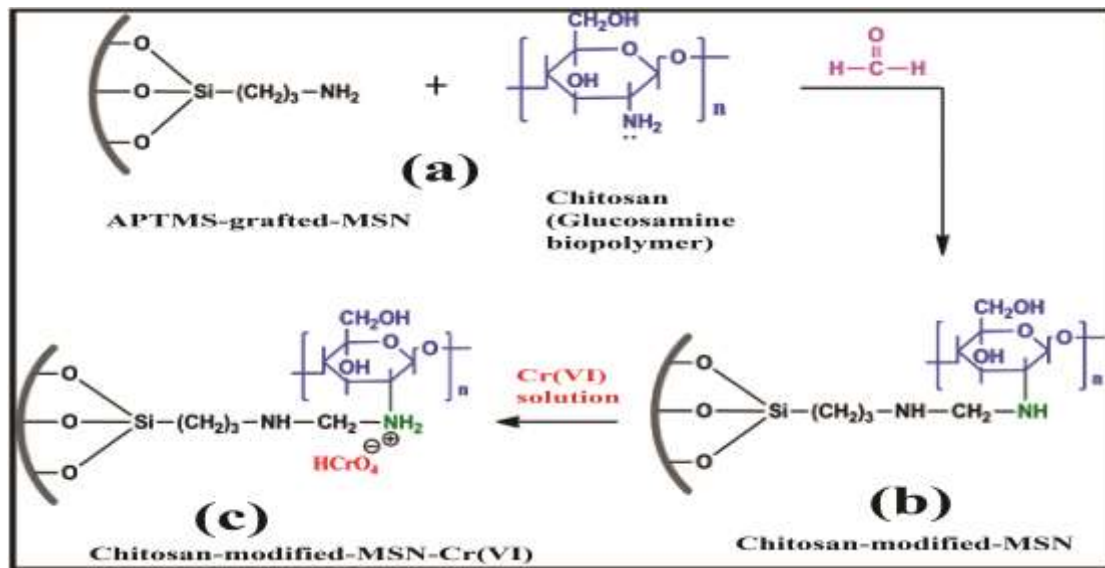


Fig. 1 Proposed mechanism of Cr(VI) adsorption onto chitosan-based biopolymer [54].

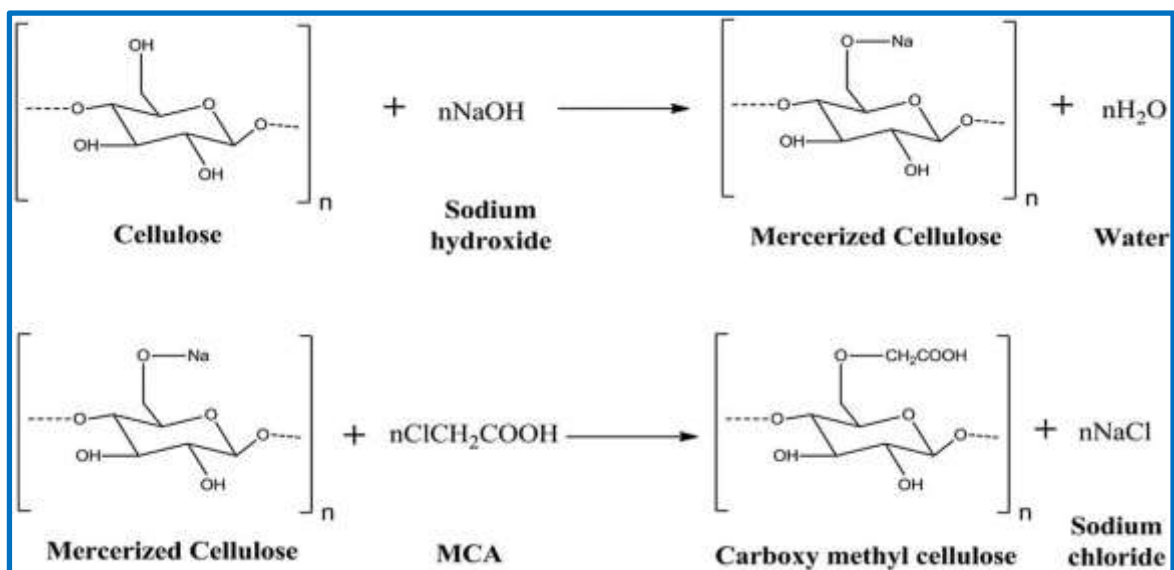


Fig. 2 Schematic synthesis mechanism of carboxymethyl cellulose (CMC) from cellulose [67].

Klapiszewski et al., [66] fabricated a lignin-based biosorbent hybridised with silica, which significantly improved biosorption of Pb(II) ions from wastewater when used. The adsorption data fitted the Langmuir model with a maximum monolayer capacity of 89.02 mg/g for Pb(II) removal and this novel hybrid biomaterial was showed reasonable regeneration capacity. Bio-polymeric gel beads with CMC were synthesized (Fig. 2) and applied by Kumar et al. [67] for the adsorptive removal of Cr(VI) from contaminated effluent.

The effect of different factors including the mass of biosorbent, solution pH, reaction time were evaluated

to optimize the biosorption of Cr(VI) onto modified material. A maximum of 98.6 % chromate ions was removed within 15 min. of biosorption at solution pH 4.0 and 25.0 °C. Orange peel waste with silica nanospheres ($\text{SiO}_2@\text{OPW}$) was modified by Saini et al., [68] and applied for capturing Pb(II) from wastewater. An excellent biosorption rate was achieved at optimum conditions as 200 mg/g by hybrid biosorbent, while pure OPW showed 166.7 mg/g biosorption capacity for the extraction of studied metal ions. Better efficiency was gained using hybridized material, which may be attributed to good electrostatic attraction among metal ions and abundant

functional groups of material. The modified bio-composite was found to be a good recyclable material for at least five regenerations of adsorption-desorption cycles. In another study, Sathy and Sahoo [69]

developed a novel chitosan-g PMMA/silica BNC as an extraordinary, low cost and eco-friendly biopolymer and applied for highly toxic Cr(VI) adsorption from contaminated solution.

Table 4. Metal ions adsorption capacity of different hybrid bioadsorbent from wastewater.

Sl. No	Name of the composite	Metals/Adsorpt ion capacity	Adsorption conditions						References
			Mass (g)	pH	Temp. (°C)	Time (min.)	Conc. (mg/L)	Vol. (mL)	
1	Teff husk activated carbon (THAC)	Cr(VI) 95.59%	0.022	1.92	25	124	87.6	20	[60]
2	Silica-sand/anionized-starch composite (CMS-SS)	Cu(II) 383.08 mg/g	0.03	5.0	25	60	1000	30	[61]
3	Heinsia crinita seed coat (HCSC)	Cr(VI) 231.7 mg/g	0.3	2.0	25	30	-	-	[62]
4	Carboxy-methyl chitosan onto silica-coated maghemite nanoparticles (MNPs@S@C MC)	Cu(II) 350 mg/g	0.01	6.0	25	60	50	10	[63]
5	Amino-functionalized mesoporous silica into sodium alginate (aMSP/SA)	U(VI) 210 mg/g	0.01	4.0	40	240	600	10	[64]
6	Cetyltrimethylammonium bromide-kaolin(CTAB-kaolin)	Cr(VI) 99%	0.1	-	25	180	10	-	[65]
7	Silica/lignin (SiO ₂ /lignin)	Pb(II) 89.02 mg/g	0.05	5.0		60	100	100	[66]
8	Bio-polymeric gel beads with CMCh https://www.google.com/clk?sa=l&ai=DChcSEwjTtY6C3qDwAhXZiNUKHRsPDoEYABAAGgJ3cw&ae=2&sig=AOD64_2yVPqUq2_RY1KbhvoD	Cr(VI) (94.6% - 98.4%)	0.2	4.0	25	15	-	-	[67]

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9	Orange peel waste with silica (SiO ₂ @OPW)	Pb(II) 200 mg/g	0.02	6.0	27	60	50	50	[68]
10	(Chitosan-gPMMA)/silica BNC	Cr(VI) 92.5 mg/g	0.01	4.0	25	60	500	20	[69]

At pH 4.0, 98% of Cr(VI) ions were removed using a modified bio-composite, and the material is regarded as a promising adsorbent for wastewater purification with regeneration capacity.

The chitosan-based eco-friendly hybrid biopolymer materials were found to be biodegradable and non-toxic for metal adsorption. Among bio-materials, alginates have been explored as good candidates for modification and polymerization of bio-composite for separation sciences, especially wastewater purification techniques, including the adsorption process. According to previous researches, hybrid biosorbents have been considered as promising candidates for the separation and sequestration of impurities including heavy metals from contaminated solution/wastewater. The chitosan and alginate-based bio-composites were found as excellent hybrid materials with improved properties including physical, chemical and mechanical strength in contrast to pure bio fragments. Biomaterials having biocompatibility have modified encapsulated materials that frequently lend synergetic functionalities of their novel derivatives when coupled with newly improved properties. Therefore, these types of encapsulated materials and hybrid adsorbents could be cheaper and simply decontaminated as well

as easily regenerated after treatment, which led to significant contributions in the field of environmental remediation and wastewater treatment.

6. Biosorption mechanism of heavy metal ions

An inclusive understanding of heavy metal biosorption mechanisms of hybrid biosorbents is important for future hybridization of biomaterials to enhance their performance in purification applications. Generally, the biosorption of heavy metals occurs through numerous interactions that are inclusively dependent on the functional groups available in the hybrid biosorbents, surface properties of biosorbents, chemical nature of heavy metals, and adsorption conditions including solution pH, temperature, and metal concentration, etc. [67].

The most common heavy metal biosorption mechanism is electrostatic interactions, but other chemical bonding, such as chelation, complexation, coordination, ion-exchange, and other secondary types of weak bonds such as hydrogen bonding and Van der Waals forces, have been reported in previous research as seen in Fig. 2[70].

industrialization and numerous sources of heavy

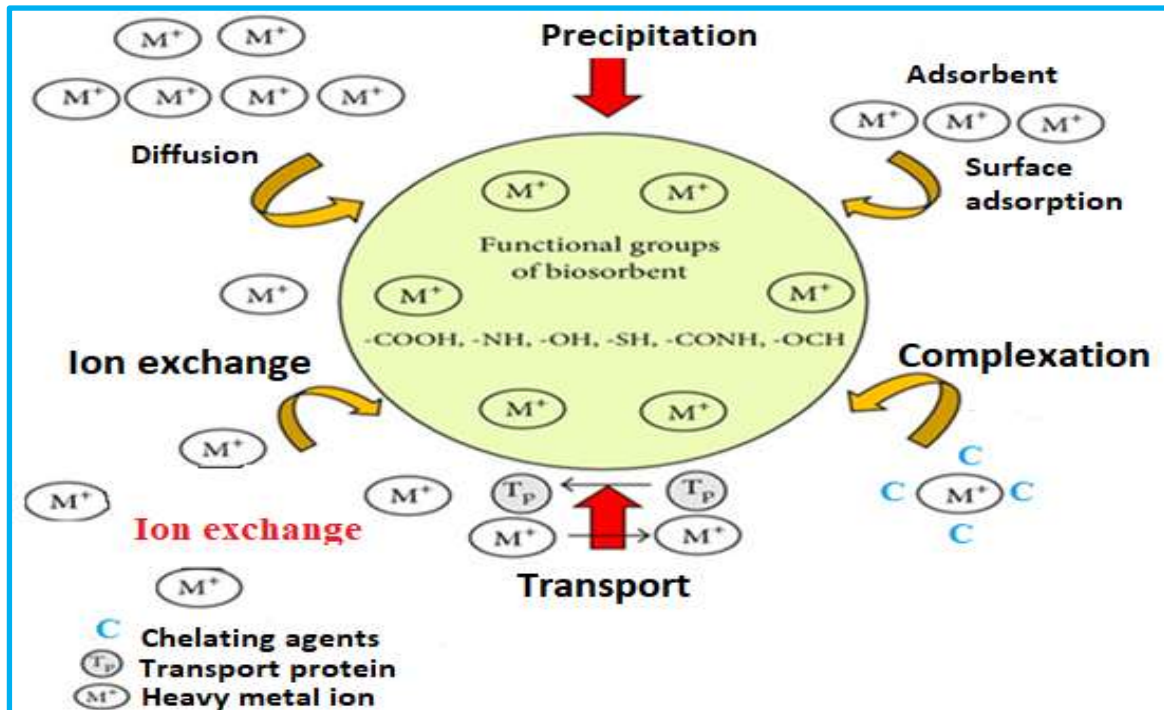


Fig. 3 Biosorption mechanisms of metal ions [70].

Kumar et al. [67] recently reviewed metals biosorption mechanisms and found that the heavy metal ions were effectively responded on cellulosic biosorbent by chelation, complexation, and other weak bonding including electrostatic forces and Van der Waals bonding [67]. Metal ions may have the properties to form complexes with functional groups of hybrid cellulosic biosorbent. This complexation interaction between metal ions and biosorbent decreases the metal's concentration in the contaminated solution. The chelation occurred by acting on hybrid cellulosic composites as ligands and subsequently donating the electrons. Consequently, the chelated form could reduce the metal ion concentration in the wastewater.

7. Future prospect and challenges of bioadsorbents materials

Metal decontamination from wastewater is immense challenge due to rapid trends of

metals continuously released in the aquatic system [71]. The biosorption method using hybrid biomaterials is the most reliable method for the removal of metal ions due to economically convenient, eco-friendly and nontoxic nature of biomaterials. In this review, some recent studies have been reviewed on metal adsorption using hybrid biomaterials. The biological fragments were reported as outstanding alternatives for the fabrication of robust hybrid adsorbents due to their availability and potentiality. The following prospects of biosorbent are considered by scientific communities:

- The biological fragments that are naturally available could be fabricated with highly efficient commercial adsorbent and minimizing cost without compromising adsorption efficiencies and environmental side effects, hence, hybrid biosorbent could be environmentally friendly nontoxic, and commercially convenient apart from high costing adsorbents;
- The biosorption process using hybrid biomaterial could be a rapid and efficient compared with other high-costing complex methods including chemical precipitation, membrane filtration, and ion exchange, etc;
- Biomaterials that are naturally available and have a wide range of selectivity are being commercialized for purification and environmental applications;

- At a lower concentration of metal ions, the hybrid biosorption can proceed due to the higher attraction between metal ions and biomaterials. Therefore, the biosorption of heavy metals would be promising.

Therefore, biosorbents have good future prospects for purification of contamination and subsequently prevention of emerging pollutants, including heavy metal ions as well as organic and inorganic contaminants.

8. Conclusions

Hybridization of biomaterials is considered one of the best alternative adsorbents for the application of purification and environmental engineering. The Scientific community is now concerned about using sustainable materials with cost-effective and environmentally friendly ways. Day by day using bio-based materials are taking new horizons due to their biodegradable and biocompatible nature which is suitable for sustainable environmental engineering. Moreover, researchers and academicians are more focused on environmental conservation by modifying sustainable biomaterials to reduce the threats of global warming. Bio-materials as excellent sources of pristine materials come from numerous renewable resources and could be used as capability reinforcement in composites for commercial and industrial applications. Limitations which include biocompatibility and hydrophilic nature may be resolved via appearing various surface adjustments and chemical treatment techniques. In this regard, the properties of biomaterials can be tailored to enhance their mechanical, thermal, and physiological overall performance in versatile applications.

This review discussed the use of hybrid biosorbents as efficient materials for heavy metals decontamination. The materials have excellent removal capacities ranging from 90–100%, which is higher than pristine materials. The majority of the biosorption processes examined proceeded very quickly, within 30–180 minutes of reaction time. Heavy metal biosorption is influenced by process variables such as solution pH, temperature, biosorbent dose, ionic strength, and contact time. Furthermore, according to the studies reviewed, the majority of biosorptions represented the Langmuir isotherm model and pseudo-second-order kinetic models. The energetically biosorption of the studied metals was realistic, spontaneous, and endothermic at 25–35 °C. Further research into optimizing and commercializing

biosorbents for environmental remediation, including wastewater treatment, is recommended.

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