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Review

Review of chitosan composite as a heavy metal adsorbent: Material preparation and properties

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ABSTRACT

A large amount of wastewater is typically discharged into water bodies and has extremely harmful effects to aquatic environments. The removal of heavy metals from water bodies is necessary for the safe consumption of water and human activities. The demand for seafood has considerably increased, and millions of tons of crustacean waste are discarded every year. These waste products are rich in a natural biopolymer known as chitin. The deacetylated form of chitin, chitosan, has attracted attention as an adsorbent. It is a biocompatible and biodegradable polymer that can be modified and converted to various derivatives. This review paper focuses on relevant literature on strategies for chemically modifying the biopolymer and its use in the removal of heavy metals from water and wastewater. The different aspects of chitosan-based derivatives and their preparation and application are elucidated. A list of chitosan-based composites, along with their adsorptivity and experimental conditions, are compiled.

1. Introduction

Water is a necessity required to sustain life. However, it is under serious threat because of the huge magnitude of pollution caused by industrial, agricultural, and domestic activities. Water bodies contaminated by heavy metals are grave problems because of their toxic nature and bioaccumulation (Jordan, Ghulam, & Hartling, 2014; Tscheikner--Gratl et al., 2019). Metal contamination may be due to domestic or industrial waste products, agricultural or municipal discharge, geologic weathering, and direct atmospheric precipitation (Dawson & Macklin, 1998; Salomons & Forstner, 1984). These pollutants are often toxic. Long-term exposure to these pollutants can have acute and chronic effects on humans and animals. Heavy metals, dyes, phenols, detergents, insecticides, and pesticides are some common pollutants (Akpor, 2014; Wasana, Perera, Gunawardena, Fernando, & Bandara, 2017). Owing to the ability of metals to remain in the environment for a long amount of time, they play a significant role in ecotoxicology. Bioaccumulation and biomagnification are common phenomena for heavy metals n the food chain (Yin, Wang, Lv, & Chen, 2019). They are non-biodegradable in nature (Ebrahimpour & Mushrifah, 2010; Strom, 2008; Weber et al., 2013). Heavy metals at high concentrations exert significant environmental and ill effects on human health (Jaishankar, Tseten, Anbalagan, Mathew, & Beeregowda, 2014; Wongsasuluk, Chotpantarat, Siriwong, & Robson, 2014).

Li, Li, Lee, Liu, and Miao (2015) reported that in some urban areas in China, such as Kunming, Zhuzhou, Chenzhou, Shaoguan, and Chongqing, have heavy metal levels above the permissible WHO limits because of urbanization and industrialization. Qu et al. (2018) observed alarming levels of As, Cr, Pb, Cd, Hg, Cu, and Zn in the Wen-Rui Tang River, which are discharged by nearby leather tanning and electroplating industries. Approximately 43 industrial groups in India have been recognized by the Central Pollution Control Board (CPCB) and the India's environmental regulatory authority as sources of pollution (CPCB 2009). The CPCB declared West Bengal, Orissa, Jharkhand, and Durgapur as heavily polluted areas.

A study on rivers in India showed that wastewater discharged into the upper river reaches accumulate to the lower reaches and heavily pollutes the areas (Kumar, Sharma, Minakshi, Bhardwaj, & Thukral, 2018, 2020). Port Jackson, Botany, Kembla, Newcastle, Yamba, and Eden in Australia (Jahan & Strezov, 2017), Phewa and Gosainkunda

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Lakes in Nepal (Rupakheti et al., 2017), and Khanpur Lake in Pakistan (Iqbal & Shah, 2013) show similar trends in heavy metal pollution. An extensive study showed that Fe, Mn, Mn, Co, As, and Ni levels in China exceeded the maximum permissible limits (MPLs) of WHO (2017) and USEPA (2009) (Kumar et al., 2019). In India, Fe, As, and Cr level are beyond the MPL for drinking water, and Mn, Ni, Cd, and As levels were greater than the acceptable limits of USEPA. The Hg levels in Greece were high relative to the WHO and USEPA guidelines. Ni and Cr levels in South Africa and Iran were higher than the acceptable WHO levels. In Turkey, Ni levels exceeded the recommended values for drinking water. In the US, Ni, Cd, and Cr levels were much higher than the recommended values. The levels of Mn, Co, Cu, Ni, Cd, Cr, and As in Pakistan were higher than the permitted WHO and USEPA limits. Bangladesh and Nigeria have Co, Ni, Cr, and As levels exceeding acceptable levels. In Germany, Ni and Mn levels were much higher than the permitted USEPA (2009) levels (Kumar et al., 2019). However, a general perception regarding heavy metals in water bodies is yet to be established to a significant level and is restricted to literature.

The removal of heavy metals from water bodies is essential for safe water consumption and human activities. Therefore, access to clean and safe water is essential, and wastewater must be treated. On this basis, several methods, ranging from coagulation to adsorption and electrochemical methods, have been studied (Jena & Raj, 2008; Kottaichamy, Begum, Chattanahalli et al., 2020; Kottaichamy, Begum, Nazrulla et al., 2020; Nellaiappan, Pillai, & Kumar, 2018). Wastewater treatment depends on the nature of pollutants. Adsorption processes that can be used for organic and inorganic pollutants have been widely studied (Ishihara, Nguyen, Mori, Nakamura, & Hattori, 2015)

2. Chitin sources

Over the past few decades, the rise of Asian affluence has led to an increase in the demand for seafood and a surge in the worldwide seafood processing industry (Yadav et al., 2019), causing an exponential increase in the production of marine products from crabs, prawns, shrimps, and krills (Hamed, Özogul, & Regenstein, 2016). Fig. 1 illustrates the sources of chitin. Approximately 6–8 million tons of seafood waste is generated every year. The heads, tails, and shells of shrimps are unwanted by-products of processing industries (Mao et al., 2017). The surge in shrimp waste has directed considerable attention to chitin extraction (Tarafdar & Biswas, 2013). Living organisms produce 10^{12}–10^{14} tons of chitin in the ocean annually (Dhillon, Kaur, Brar, & Verma, 2013). Arthropods in freshwater and marine environments generate approximately 2.8×10^{10} and 1.3×10^{12} kg chitin in a year, respectively (Cauchie, 2002). These amounts are sufficient for the extraction of commercially competent polymers.

Chitin extracted from marine waste materials is usually deacetylated to chitosan. Chitin and chitosan have substantial economic values because of their versatile biological properties. However, chitin is crystalline and insoluble in nature and thus has a limited commercial application. Chitin is converted to various derivatives, such as chitosan and chitooligosaccharides (Choi, Ahn, Lee, Byun, & Park, 2002), and glucosamine modifies its biological properties. These derivatives can be used in food, medical, agriculture, textile, and cosmetic industries (Harish Prashanth & Tharanathan, 2007). Therefore, this review paper focuses on the periodic developments in the field of extraction of chitosan, its functionalization and modifications and the impact on the performance for heavy metal extraction. The paper would also discuss about the mechanisms for the heavy metal extraction, its merits and demerits, isothermal models and the kinetics relating to the same. This paper also gives a brief idea on the trends in using chitin and chitosan for heavy metal analysis.

3. Chitin and chitosan

Chitin is an abundant natural polysaccharide and primarily isolated from crustacean biomass. It is a linear cationic heteropolymer containing *N*-acetyl-D-glucosamine units, some of which are linked to D-glucosamine units by β-(1–4) glycosidic bonds. It exists as a matrix of proteins, minerals (calcium carbonate and phosphate), and lipids (unsaturated fatty acids; (Hou et al., 2016). Chitin is generally obtained from marine resources because of its commercial uses and is economical and abundant source (Gagné & Simpson, 1993; Zhao et al., 2019). Chitin is obtained from marine animals, such as prawns, squids, shrimps, mussels, and crabs (Ni'mah, Harmami, Ulfin, Suprapto, & Welny Saleh, 2019; Nwe, Furuike, & Tamura, 2014; Zhao et al., 2019). The shells of these crustaceans are composed of three fundamental components, namely, (1) chitin, (2) minerals, and (3) proteins. Chitin is a semi-crystalline polymer composed of nanofibrous units linked to proteins, forming chitin–protein complexes (Duan, Huang, Lu, & Zhang, 2018). It is found in various crystalline forms, namely, α, β, and γ, and has varying degrees of deacetylation (Aam et al., 2010). It acts as a skeleton. Meanwhile, minerals (mainly inorganic carbonate salts) provide strength to the shells. α Chitin mainly constitute shrimp shells, crab carapaces, yeast and fungal cell wall, insect cuticles, and lobster shells (Joao, Silva, & Borges, 2015; Kaur & Dhillon, 2014). The antiparallel orientation of polysaccharide chains in α chitin ensures maximum bonds. Hence, this form of chitin is the most stable form, possessing approximately 80 % crystallinity index of chitin fibers. β Chitin is found in aphrodite chaetae, squid pens, lorica produced by protozoa and seaweeds. Polysaccharide chains are arranged in parallel, and chitin fibrils have approximately 70 % crystallinity index. This type of arrangement increases the spaces between neighboring polysaccharide chains, thereby increasing the reactivity and solubility of β chitin (Joao et al., 2015). A blend of α- and β- chitin forms γ chitin, that is, parallel and antiparallel polysaccharide chains are formed. Fig. 2 illustrates the structures of chitin and chitosan.

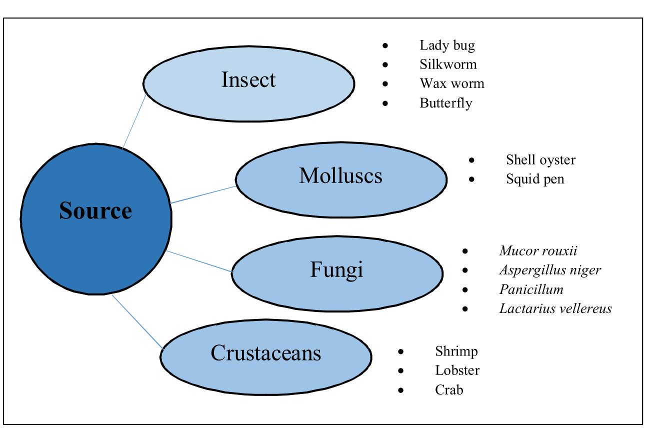

Fig. 1. Chitin sources.

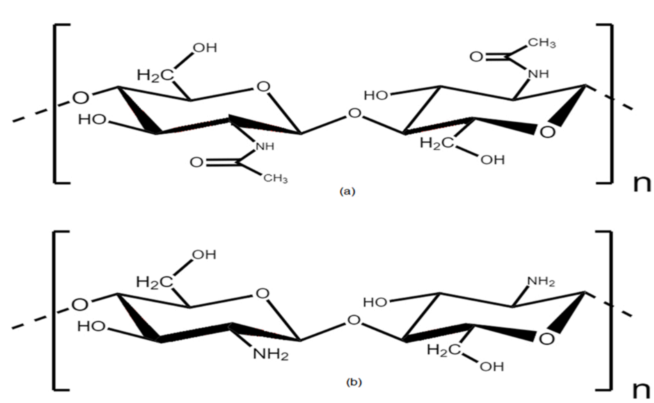

Fig. 2. Structures of (a) chitin and (b) chitosan.

Table 1
Percentage compositions of chitin and protein in various marine resources.

Type	Chitin (%)	Protein (%)	References
Prawn shell	36.43	32.77	Samar, Khalaf, and El-razik (2013)
Squid gland	31.2	36.52	Abdulkarim, Isa, Abdulsalam, Muhammad, and Ameh (2013)
Crab shell	16.73	16.68	Abdou, Nagy, & Elsabee, 2008)
Mussel	23.25	9.9	Abdulkarim et al. (2013)
Insect cuticle	36.6	39.8	Gonil and Sajomsang (2012)

Chitin is commercially produced through pulping (Barber, Griggs, Rogers, Gurau, & Shamshina, 2018) or ionic liquid extraction (Shamshina, Barber, Gurau, Griggs, & Rogers, 2016; Shamshina, 2019). Chitin extraction affects the preparation process of a material and its properties (Younes et al., 2016). The conventional method for chitin extraction reduces the molecular weight of chitin, nonuniform chain scissors, and the degree of acetylation (DA) (Khor, 2001). This method includes the demineralization of raw materials with concentrated HCl, deprotonation with NaOH, and decolorization with organic solvents or oxidants at high temperatures (60–100 °C) for 12–48 h. Chitin extraction through ionic liquid extraction allows the effective control of final products, that is, a high degree of acetylation is achieve, and polymer degradation does not occur. Minerals and proteins from raw materials must be removed for chitin extraction. Raw materials constitute approximately 20 %–30 % chitin, of which 20 %–40 % are proteins, 30 %–60 % are minerals, and 0 %–14 % are lipids (Crini & Badot, 2008; Hobel, 2004; Kurita, 2006). Table 1 illustrates the percentages of chitin and proteins in various marine resources.

The deacetylated form of chitin is chitosan. The deacetylation of chitin occurs in the presence of concentrated alkali solutions at high temperatures. Chitosan comprises the pyranose cycles of β-(1,4)-2-amino-2-deoxy-β-D-glucose N- glucosamine with glycosidic linkages (Muzzarelli et al., 1986). The deacetylation process results in randomly distributed acetylated or deacetylated units along chitosan chains. The ratio between glucosamine and N-acetglucosamine determines the DA in chitosan. The influence of DA on the chemical (solubility, tensile strength, surface area, flexibility, porosity, conductivity, and viscosity) and biological properties (adsorptivity, antioxidant, biodegradability, biocompatibility, and bioavailability) relies on method conditions (Benhabiles et al., 2012; Park & Kim, 2010). Fig. 3 shows the processes involved in extraction of chitin and chitosan.

Chitosan is characterized by its biocompatibility, biodegradability, and nontoxicity (Aranaz et al., 2012; Younes et al., 2016). Its exceptional biological properties (antimicrobial, antibacterial, and coagulant, bioadhesive, and wound healing capacity) (Abou-Zeid et al., 2011; Ibrahim, Reda, & Kligner, 2020; Ibrahim, Saad, & Aly, 2016; Nawalakhe et al., 2012; Seyam, Hudson, Ibrahim, Waly, & Abou-Zeid, 2012) render it an excellent candidate for cosmetic, medical, and pharmaceutical applications and the preservation of agricultural commodities (El-Alfy, El-Bisi, Taha, & Ibrahim, 2020; Ibrahim, Dakrory, Klingner, & El-Masry, 2015; Ibrahim, El-Bisi, Taha, & El-Alfy, 2015; Ibrahim & El-Zairy, 2016; Ibrahim, Mostafa, & Kandile, 2020; Ibrahim, Farid, Samir, & Mosaad, 2018). It has uses in the food industry, wastewater treatment, and many other industrial applications (Díaz-Rojas et al., 2006; Muzzarelli & Muzzarelli, 2005).

4. Chitin and chitosan derivatives for the removal of heavy metals

Chitosan exhibits low solubility in neutral pH because of its inter- and intramolecular hydrogen bonds, its low antioxidant properties due to the lack of H atom donors, limited reactivity due to its high hydrophilicity, rigidity, and brittleness. These properties have been studied and can be improved through modification through chemical, mechanical, or enzymatic methods.

4.1. Chemical modification

The process for chemically modifying the functions of chitosan include the introduction of functional groups, such as alkyl, carboxymethyl, and phenolic compounds. This process enhances the properties of chitosan without affecting its inherent properties, such as cationic characteristic, solubility, and adsorptive properties. Previously studied methods for modifications include alkylation, acylation, sulfation, quaternization, carboxyalkylation, phosphorylation, and hydroxyalkylation. In 1988, Shimahara and Takiguchi isolated chitin for commercial purposes, and their method is still used in the commercial extraction of chitin. Kumari, Kumar Annamareddy, Abanti, and Kumar Rath (2017) concluded that shrimp has the best DA and DM values among known chitin sources. Younes et al. (2016) used response surface methodology (RSM) to optimize adsorption capacity. Srinivasan, Kanayairam, and Ravichandran (2018) extracted chitin from shrimp shells for medical applications. Another type of chemical method used for chitin extraction is the use of deep eutectic solvents (DES). Hong, Yuan, Yang, Zhu, and Lian (2018) found that the purity of extracted chitin is based on the type acid used. Chloride-maloic acid has the highest purity among DES. Residual $CaCO_3$ can be converted to levulinic acid, which can be used as a calcium supplement. Different types of DES show different abilities during the depolymerization and demenaralization of chitin. The purity of chitin can be confirmed through 13C NMR with high yield (Saravana et al., 2018), and pure chitin can be used as standard chitin film. Using NaClO (Kaya, Baran, & Karaarslan, 2015) for 10 min. before deprotonation and demineralization significantly reduces the time of chitin extraction. The resulting product has the same physiochemical properties as commercially obtained chitin. This method is rapid and saves time and energy. Chitin obtained through the fermentation of shrimp waste with *Lactobacillus brevis* (Aranday-García, Saimoto, Shirai, & Ifuku, 2019) results in chitin with a high molecular weight, reduced crystallinity, and high Young's modulus, which are beneficial for polymer reinforcement. Chitin extraction using *Lactobacillus plantarum* isolated from meat products (Neves et al., 2017) show 40 % greater performance than commercial chitin. Table 2 illustrates the chemical and enzymatic extraction methods for chitin.

4.2. Enzymatic modification

Chitosan can be modified either through enzymatic or chemical approaches. Chemical modification traditionally involves the use of highly reactive reagents and specific laboratory conditions. Chemical

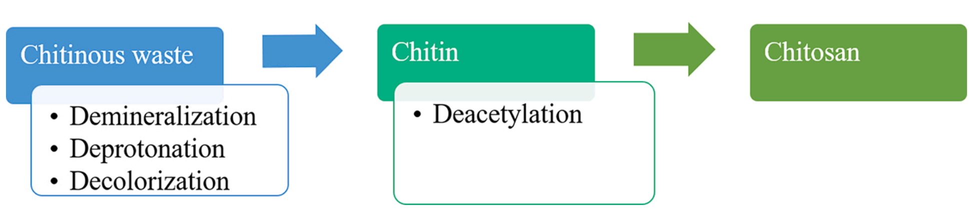

Fig. 3. Process of chitosan extraction.

Table 2
Extraction of chitin and various composites.

Sl. no.	Experimental condition	Classification	Benefits	Author
Chemical:				
1	Conventional method, conc. HCl and conc. NaOH	Chemical	High DA and DM	Kumari et al. (2017), Shimahara and Takiguchi (1988), Srinivasan et al. (2018), Younes et al. (2016)
2	Deep Eutectic solvent	Various solvents, chemical	CaCo3 in Shells was converted to levulinic acid calcium salt	Hong et al. (2018), Saravana et al. (2018)
3	NaClO pretreatment	Chemical	Reduced time for chitin extraction	Kaya et al. (2015)
5	Microbes like *Lactobacillus*	Microbial	High Young's modulus	Aranday-García et al. (2019), Neves et al. (2017)
Enzymatic:				
10	Protease	Chemical + enzyme	Enzymetic deprotenization	Hajji et al. (2014), Younes et al. (2012)
11	Alcalase	Enzyme	80 % deprotenization and complete deminaralization in 8 h	Abdelmalek et al. (2017)
12	Lipase and protease	Lipase	New approach for the synthesis of multi-enzyme biocatalysts	Özacar et al. (2018)

approaches usually require many chemical cross-link reagents, which may have toxic side effects. Hence, enzymatic methods are preferred and widely studied. Enzymes act as catalysts and are highly specific. The specificity of enzymes offers control over the modification process and reduces the risk of toxicity. The commonly used enzymes are lipases and proteases. Synthesized chitin in the presence of enzymes such as lipases and protease are effective biocatalysts. Chitin obtained by using *Loligo vulgaris*, Alacase®, and an enzyme/protein mixture results in a high level of deprotonization (Abdelmalek, Sila, Haddar, Bougatef, & Ayadi, 2017). Immobilized proteases and lipases from sunflower seeds (Özacar, Mehde, Mehdi, & Özacar, 2018) can be used in producing cheap multi-enzyme biocatalyst. Various types of crude microbial proteases can be used in extracting chitin from shrimp shells (Hajji et al., 2014). Structural difference between α-chitin and β-chitin was studied using 13C NMR. Younes et al. (2012) used RSM to describe the relationship between the factors and shrimp shell deproteinization response with the crude enzyme of *Bacillus mojavensis* A21.

4.3. Synthesis of chitosan

Radiation can be used to degrade biological polymers. It improves the recyclability of chitosan, hence reducing pollution (Hien et al., 2000; Nagasawa, Mitomo, Yoshii, & Kume, 2000). In 2002, Choi et al. (2002) studied the effect of the irradiation of chitosan in acetic acid solution with various dose rates and yield. The results suggest the formation of chitosan oligomers. In the same year, Jia and Shen (2002) studied the preparation process of chitosan with low molecular weight. The preparation method included 85 % phosphoric acid and irradiation at different temperatures and time intervals. The product showed a reduced viscosity and has an averaged molecular weight ranging from 7.1×10^4 to 21.4×10^4. The treatment period was 35 days. Other physical methods include the use of ultrasound, microwave, and thermal treatment. These methods are effective in preparing chitosan composites. Soaking in a NaOH solution at high temperatures for few hours results in a high yield of chitosan that is soluble in an acidic medium (Hajji et al., 2014; Kaya et al., 2015; Sedaghat, Yousefzadi, Toiserkani, & Najafipour, 2017). Microwave irradiation in the presence of NaOH (El Knidri, El Khalfaouy, Laajeb, Addaou, & Lahsini, 2016) for short duration at 350 W is a fast and efficient method. Alternate irradiation in the presence of NaOH (Birolli, Delezuk, de, & Campana-Filho, 2016) and ultrasound assisted deacetylation of chitin (Fiamingo et al., 2016) produce a high yield of acid-soluble chitosan. Exposure to UV irradiation at different time intervals improved the flame-retardant properties of chitosan (Kundu, Wang, Hou, & Hu, 2018; Ragab et al., 2018). Deacetylation of chitosan in NaOH solution under 600 W microwave irradiation increases antimicrobial activity (Santos et al., 2019). (Li et al., 2019)) modified chitosan films with glow discharge plasma (GDP) to produce films with high thermal stability, tensile strength, and water vapour permanent (WVP). (Alves et al., 2018) produced nanochitosan with diameter of less than 30 nm and molar mass between 3 and 21 kDa through milling, autoclaving at 121 °C, and thermal shock drying. (Nasrin et al., 2017) obtained polylactic acid (PLA) laminated chitosan with high mechanical and thermal properties. Table 3 illustrates various methods for synthesis of chitosan.

Table 3
Methods used in chitosan synthesis.

Sl. No.	Experimental condition	Classification	Benefits	Author
1	12.5 NaOH (140 °C for 4 h), soaking in 18 M NaOH (24 h), heating (90 °C for 7 h)	Chemical	Soluble in acidic medium	Hajji et al. (2014), Kaya et al. (2015), Sedaghat et al. (2017)
2	50 % NaOH, 8 min irradiation at 350 W	Microwave radiation	Fast, easy, efficient	El Knidri et al. (2016)
3	40 % NaOH, alternate irradiation (45 min), Ultrasound-assisted deacetylation chitin in 40 % NaOH (50 min, 60 °C) irradiation	Ultrasound irradiation	High yield of acid-soluble chitosan	Birolli et al. (2016), Fiamingo et al. (2016)
4	Exposure UV/ ozone at different time intervals	UV irradiation on phosphorylated chitosan	Improve flame-retardant properties	Kundu et al. (2018), Ragab et al. (2018)
5	Deacetylation in NaOH solution under microwave irradiation at 600 W	Chemical and microwave	High anti-microbial activity	Santos et al. (2019)
6	GDP of 0–800 W for 1min	Glow discharge plasma	High thermal stability, tensile strength, WVP	(Li et al., 2019)
7	Solubilized mixture of HAc and NaOAc, autoclave 121 °C at 1 atm for 5 min, thermal shock drying	Milling	Nanochitosan diameter <30 nm, M_v < 21 kDa	(Alves et al., 2018)
8	PLA-laminated chitosan by hot pressing	Hot press method	Mechanical and thermal properties	(Nasrin et al., 2017)

5. Modification of chitosan

Isolated chitin is converted into chitosan by various enzymatic and chemical methods (Philibert, Lee, & Fabien, 2017). Various kinds of alkalis or acids are used in chitin deacetylation. Glycosidic bonds are susceptible to acids; hence, alkalis are considered appropriate options (Hajji et al., 2014). Chitin deacetylation can be achieved heterogeneously or homogeneously. Deacetylated chitin in a range of 85 %–99 % and can be used as an insoluble filtrate. It is processed using hot and concentrated NaOH solution. At 25 °C, chitin is dispersed in concentrated NaOH solution for 3 h and then suspended in crushed ice. The end product is soluble chitosan with a DA of approximately 48 %–55 % (Yadav et al., 2019).

Chitosan composites have various uses. They are widely used to remove pollutants from water, wastewater, and drug delivery systems. He, Bardelli, Gehin, Silvester, and Charlet (2016) modified chitosan geothite capsules with iron(oxyhydr) oxide for arsenic removal. These chitosan geothite bionanocomposites can purify arsenic-containing water by forming inner sphere complexes. The Freundlich isotherm model excellently fits to the adsorption kinetics of As(III) and As(V) at pH values of 5 and 9. Sulfactant-modified chitosan beads for lead and cadmium removal was developed by Pal and Pal (2017, 2019). Thiol-modified chitin nanofibers for arsenic adsorption has an adsorptivity of 149.9 mg/g (Yang et al., 2015). The arsenic adsorption isotherm is best described by the Langmuir model and exhibits a correlation coefficient (R^2) of 0.997. Zeolite NaP1 and NaP1CS chitosan composites for Cu(II) removal show high adsorptivity (Bandura, Franus, Madej, Kolodynska, & Hubicki, 2020). The Langmuir isotherm model is the best model for Cu(II) ion adsorption, which is endothermic and follows the pseudo-second order model near intraparticle diffusion model. Chitosan/clay/magnetite composites for Cu(II) and As(V) adsorption show multimetal adsorptivity (Cho et al., 2012). The Freundlich isotherm model provides the best fit to Cu(II), whereas the Langmuir and Freundlich models provide a good fit to As(V). The adsorption processes follow pseudo-second order kinetics. Chitosan/clinoptilotile/magnetite nanocomposites show high Pb(II) adsorption capacities (Javanbakht, Ghoreishi, Habibi, & Javanbakht, 2016). The adsorption isotherm was best fitted by the Langmuir isotherm with a maximum theoretical adsorption of 136.99 mg/g at pH 6 and 333 K. Chitosan clay biocomposite beads for Cr(VI) and Pb(II) removal show high adsorptivity (Biswas, Rashid, Debnath, & Haque, 2020). Chitosan-manganese dioxide bionanocomposites are used in the removal of Pb (II) (Anwar, 2018b). These CS-(Mn)2 composites can be recycled five times while showing no considerable change in adsorptivity. Porous poly(L-lactic acid)/chitosan nanofibers for Cu(II) adsorption was developed by Zia et al. (2020). Chitosan is coated with a direct immersion coating method provides a high surface framework that effectively adsorbs Cu(II) ions. Again, the Langmuir isotherm best describes the adsorption kinetics. Zeolite imidazolate framework-modified bacterial cellulose/chitosan is used in Cu(II) and Cr(VI) removal (Li et al., 2020). The mechanism suggests coordination, ion exchange, and electrostatic interaction. The ions can be physically adsorbed on aerogels and combined through coordination reaction. These aerogels have prospective application in water treatment. (Wang et al., 2020) developed thermo-sensitive ion--imprinted polymers based on multiwalled carbon nanotubes (MWCNT). Their adsorptivity can be controlled by temperature. Sulfactant-modified chitosan beads are used in Cd(II) adsorption (Pal & Pal, 2017, 2019). Contained distilled water is best described by the Langmuir model, whereas real wastewater is best described by the Freundlich model. The formation of bilayers on the surfaces of chitosan beads result in the removal of Cd(II) ions. Magnetic Fe_3O_4-chitosan@bentonite composites are used in the removal of Cr(VI) and show high adsorptivity (Feng, Ma, Zhang, Zhang, & Xiao, 2019). The electrostatic interaction of Cr(VI) with protonated amine groups and Cr(VI) accepting electrons from hydroxyl groups and other electron donors reduces Cr(VI) to Cr(III). The Langmuir isotherm best describes the isotherm kinetics. Cd(II) and Cr (VI) is removed using carboxymethyl/chitosan composites (Borsagli & Borsagli, 2019), which show excellent regeneration and recyclability. The polyelectrolyte characteristics of the functional groups of the composites are influenced by polymer chains, and the Langmuir isotherm provides the best isotherm kinetics. Magnetic Loofah biochar-modified chitosan reduces Cr(VI) and Cu(II) (Xiao et al., 2019). The Freundlich model best describes the isotherm kinetics of the composite. Even after three cycles, the adsorption capacity remains relatively high, and ion exchange and surface complexation are the primary mechanisms. Acrylonitrile-modified chitosan (carbon disulfide) is used for Pb(II) and Cu(II) adsorption (Ali et al., 2020). Chitosan anchored with thiocarbamate groups improves sorption capacity with its Lewis basic centers. The Langmuir model is the best fitted model for its isotherm kinetics. Most of the isotherm models follow pseudo second order kinetics, indicating monolayer coverage and a rate-limiting chemisorption step . Upadhyay, Sreedhar, Singh, Patel, and Anitha (2021) explained fixed bed column studies. Basically, in a column system, effluent streams are directed into a column stuffed with adsorbents. As stream flows through the column, metal ions are adsorbed into packed adsorbents. Table 4 summarizes the experimental conditions, metal adsorptivity, and isotherm model for each type of modification.

Chitosan modified by various chemical and mechanical processes improves the stability and durability of a material. Modified chitosan has been studied for its ability to remove heavy metals from wastewater. Adsorption using chitosan composites is a promising alternative to processes using conventional adsorbents in removing heavy metal ions. The use of cross-linking agents, such as glutaraldehyde, formaldehyde, ethylene glycol diglycidyl ether, isocyanates, and various alteration methods, can enhance the physical, chemical, and biological properties of chitosan. The adsorption process of chitosan composites differs from that of the various forms of chitosan.

6. Trend analysis

According to Pubmed, since 1953, the number of articles published on chitosan is 31,258. There has been an exponential increase in the number of articles published since 2001. This might be due to an increasing shift towards use of environmentally friendly raw materials. In the past 20 years alone, about 30,172 research articles were published. This means that at least 4 papers were published every day for the past 20 years. In 2020, more than 4000 papers were published on chitosan and its various application. A similar trend is seen in the publication of articles on chitin and its application. Over 4400 research articles have been published since 2019. This means that over 60,000 papers have been published on chitin and chitosan, its synthesis, modification, application, and various other thermodynamic studies (Pubmed). There are more than 76,000 articles in scopus alone related to chitosan and over 7000 papers on heavy metal and chitosan. Out of which over 1100 papers were published in 2020 alone.

Chitin and chitosan used as an adsorbent is fairly new and an upcoming area of research with huge potential. In the last decade there has been an increase in the number of articles published. Over 2100 articles were published in the past decade. Since 2019, over 500 articles were published on chitosan as a heavy metal adsorbent (Pubmed). There is an increasing trend in the number of published articles on this research (Fig. 4). This shows how studies in chitin and chitosan are still in the initial stage. There is room for developments and inventions. There is

Table 4
Modification of chitosan for heavy metal removal.

No.	Modification	Condition	Metal	Adsorptivity	Isotherm	Merits	Demerits	Kinetics	Author
1	Thiol-modified chitin nanofibers	C_o = 10–100 mg/L; m = 0.5 wt %; pH = 4–11; T = 25 °C	As(III)	149 mg/g	Langmuir	Large surface-to-volume ratio	pH dependent (pH 7)	PSO	Yang et al. (2015)
2	Ion-imprinted polymers-MWCNT	C_o = 20–100 mg/L, pH = 2, T = 25 °C	Pb(II)	83.20	Langmuir			PSO	(Wang et al., 2020)
3	Iron(oxyhydr)oxide modified chitosan geothite capsule	pH = 5–9, T = 25 °C	As (III), (V)	12.8 μmol/m^2	Freundlich	Green synthesis	NPs <1 nm not easily removed	PSO	He et al. (2016)
4	Zeolite NaP1 and NaP1CS	pH = 6, C_o = 25, 50, 75, 100 mg/L, m = 0.1 g	Cu(II)	1.25 mg/g	Langmuir	Adsorption increased with increased conc.	Acidic medium (0.5 M HCl)	PSO	Bandura et al. (2020)
5	Chitosan/clay/magnetite	pH = 3–9, C_o = 16– 356 mg/L	Cu(II); As(V)	17.4 mg/g; 5.9 mg/g	Langmuir, Freundlich	Thermodynamic, spontaneous		PSO	Cho et al. (2012)
6	Chitosan/clinoptilotile/ magmetite nanocomposite	pH = 6, T = 59.85, °C, C_o = 10, 30, 50, 70, 90 mg/L	Pb(II)	136.99 mg/g	Langmuir	Simple magnetic serperation	Long time to reach eqm.	PSO	Javanbakht et al. (2016)
7	Chitosan clay biocomposite beads	pH = 9, 9.2, T = 60 °C; C_o =25 mg/L	Cr (VI); Pb(II)	73 mg/g; 2.38 mg/g	Langmuir, Freundlich, Dubinin-Radushkevich	Multi metal, dye removal		PSO	Biswas et al. (2020)
8	Chitosan-manganese disoxide bionanocomposite	pH = 7, T =80 °C, C_o = 100 mg/g	Pb (II)	0.02	–	Reuseable	Moderate antimicrobial efficacy	PSO	Anwar (2018a)
9	Porous poly(L-lactic acid)/ chitosan nanofibres	pH = 7, T =25 °C, C_o = 50–200 mg/L	Cu(II)	111.66 mg/g	Langmuir	High surface framework	Controlled conditions	PSO	Zia et al. (2020)
10	Zeolite Imidazolate Framework (ZIF) modified bacterial cellulose/ chitosan	pH = 6, T =25 °C	Cu(II); Cr(VI)	200.6 mg/g ; 152.1 mg/g	Langmuir	Env. friendly	Complex system	PSO	Li et al. (2020)
11	Sulfactant modified chitosan beads	pH = 7, C_o = 10-100 mg/L, T =23 °C	Cd(II)	125.0 mg/g	Langmuir, Freundlich, Sips	High adsorptivity	Difficult disposal	PSO	Pal and Pal (2017, 2019)
12	Magnetic Fe_3O_4-chitosan@bentonite composite	pH = 2, T =25 °C	Cr(VI)	62.1 mg/g	Langmuir	Good magnetism, high stability	pH dependent	PSO	Feng et al. (2019)
13	Carboxylmethyl/chitosan	Ph = 8.5, T =25 °C	Cd(II); Cr (VI)	147.2 mg/g; 95 mg/g	Langmuir	Both cation and anion complexation	Dependent on –NH_2 pKa	PSO	Borsagli and Borsagli (2019)
14	Magnetic loofah biochar modified chitosan	pH = 3, 7; T =25 °C	Cr (VI); Cu(II)	30.14 mg/g; 54.68 mg/g	Freundlich	40 % high asorption	Long time to reach eqm.	PSO	Xiao et al. (2019)
15	Acrylonitrile modified chitosan (carbon disulphide)	T =25 °C	Pb(II); Cu(II)	2.5 mg/g	Langmuir, Temkin, Freundlich	High adsorption		PSO	Ali et al. (2020)

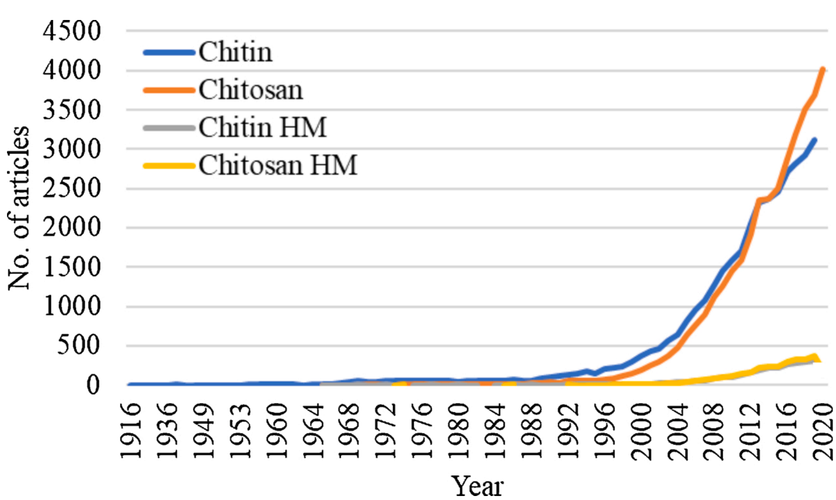

Fig. 4. Trends in chitin and chitosan used for heavy metal analysis (Pubmed).

tremendous potential in studies of chitin and chitosan in various fields of studies.

7. Conclusion and future aspects

Chitosan-based adsorbents have been a point of interest for many researchers. Chitosan can be modified using different chemical, physical, and biological pathways. Chitosan can be used as an adsorbent for heavy metals, such as As, Cu, Cd, and Pb. The presence of two reactive functional groups (NH_2 and OH) makes chitosan easier to modify and functionalize. Each modification method improves the physical and mechanical properties of chitosan as adsorbent. Crosslinked chitosan exhibits stability, reusability, high efficiency, and selectivity in addition to its unique sorption mechanisms. Hence, chitosan is a good alternative to commercial adsorbents.

Adsorption is usually spontaneous and endothermic in nature, that is, enthalpy and entropy yield negative Gibbs free energy. Most heavy metal adsorption mechanisms follow the Langmuir isotherm model and pseudo-second order kinetics, suggesting surface-level chemisorption. This phenomenon limits the potential of chitosan as an adsorbent. Hence, further research is required on the kinetic mechanism and adsorption model of chitosan. The optimization of adsorption through modeling systems, such as RSM, should be conducted to explore adsorption mechanisms. Thus, researchers should focus on other kinetic models for data fitting.

The trends of development using chitin and chitosan for heavy metal analysis have exponentially increased due to their low cost, good adsorptive capacity, thermal stability, biodegradability, reusability, nontoxicity, and renewable capacity. However, the ability chitosan as an adsorbent requires further research, and chitosan composites that can adsorb multiple heavy metals should be explored. Testing and treatment of real wastewater should be highly encouraged. At present, the use of chitosan-based adsorbents is still limited to laboratory research. Large-scale industrial applications of chitosan are yet to be implemented. Research on the application of adsorption for water remediation is necessary. Moreover, studies on extraction of heavy metals, such as Au and Pt, should focus on desorption for its recovery. Development of multi-metal sensors could be a breakthrough in research. Research is open for a substantial amount of input, especially with the discovery of substances, such as graphene and carbon nanotubes.

Commercialization of chitosan composites as excellent sensors should be explored. Given the enormous benefits of chitosan, it has great potential as a water purifying substance. Thus, chitosan is expected to be extensively manufactured in the future. Accordingly, green synthesis pathways for manufacturing and batch production of chitosan must be explored.

Declaration of Competing Interest

The authors report no declarations of interest.

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