

# Nano-composites based on Chitin for the Removal of Heavy Metals from Wastewater: A Mini Review

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**Abstract:** Water pollution, mostly due to industrial discharge, is considered to be one of the significant challenges globally. There are various industries like leather tanning, electroplating, textile and dyeing units which heavily contribute to the pollution of aquatic system by heavy metals. These heavy metals being non-biodegradable and toxic assemble in the living beings, leading to severe health issues and damage to the environment. Among various water treatment mechanisms, adsorption is considered as one of the most effective ways to treat waste water, offering advantages such as simple design, non-toxicity, cost effectiveness, and better efficiency in discarding pollutants in spite of very low concentrations. In the past, natural polymer based composites for adsorption process has gained significant popularity. In this context, chitin-based nanocomposites have shown great potential on account of their renewable, biocompatible, and eco-friendly traits, making them ideal candidate for the elimination of heavy metals. Chitin, owing to its built-in antibacterial properties, functional versatility and biodegradability, is utilized to fabricate composites and nanocomposites that effectively bind the metal ions and remove it from wastewater. The unique structure of chitin, with numerous functional groups, provides effective chelation sites that facilitate excellent binding of metal ions. This review highlights the extraction, properties and modification of chitin. Further it deals with the development of chitin based composites as effective adsorbents in heavy metal ions eradication out of the contaminated water.

**Keywords:** Chitin; nanocomposites; Toxic effects; Heavy metals; Wastewater treatment

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## 1. Introduction

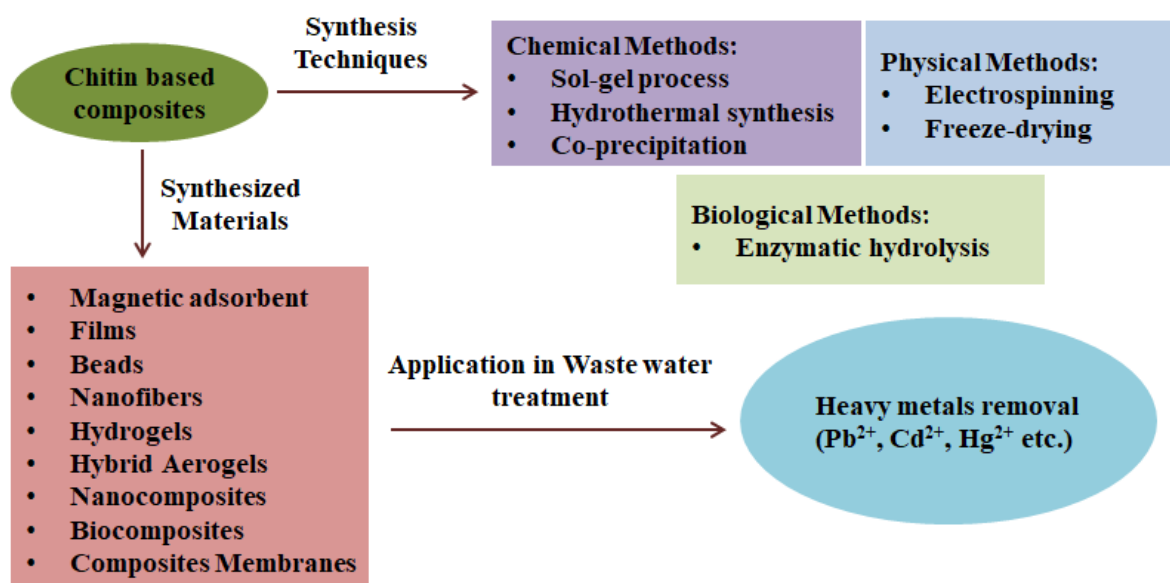
Water pollution is among the prime issues threatening the living community all over the world. The benefit to acquiring clean and safe water for human use and consumption is decreasing progressively owing to the increasing demand and contamination caused by various natural or human activities [1]. Harmful and toxic heavy metal pollution of water is a critical environmental plight jeopardizing life everywhere. Several industries such as leather tanning, electroplating, textile and dyeing units discharge untreated water resulting in heavy metal pollution [2], [3]. Cadmium (Cd), Mercury (Hg), Nickel (Ni), Copper (Cu), Lead (Pb) etc. are some of the toxic heavy metals discharged from chemical plants or industries, which should be removed effectively. These heavy metals do not degrade naturally and with time accumulates in living organisms. Although, intake of different heavy metals in a trace amount is crucial for humans, but excessive exposure or intake of them can cause serious health issues. Additionally, there are reports of various abnormalities that may occur including nausea, vomiting, diarrhoea, asthma, pneumonia, skin diseases, kidney or liver dysfunction, and types of cancers [4]-[6].

The toxicities and the health demerits of heavy metals as per World Health Organization (WHO) are presented in Table 1 [7]-[9].

The removal of heavy metals out of the aquatic bodies is an urgent need of the hour because, unlike organic pollutants, they cannot be completely removed; they can only be transformed or controlled [10]. There are diverse reported strategy to eliminate heavy metal polluters from wastewater and improve the water quality, like ion exchange, chemical and physical precipitation, reverse osmosis, solvent extraction, cyanide treatment, membrane filtration, electrochemical precipitation, and adsorption processes [11] [12]. Although reverse osmosis is regarded to be a potent approach in removing heavy metal ions, its application is restricted by narrow pH range and high operational cost [13]. Similarly, most of the technologies for removing heavy metals have limited applications, owing to their complex methodologies and high expanses. As a result it is essential to look into innovative approaches that use readily available and cost-effective materials for waste water treatment. In this context, adsorption has been one of the most useful and advantageous method for handling contaminated water. The adsorption process exhibits extraordinary characteristics, including simple design, use of low cost and non-toxic materials, and possess high adsorption capacity in discarding pollutants despite lower amount [14] [15]. Recently, natural polymer based adsorbents are mostly studied materials as a substitute to typical waste water handling methods for the removal of toxic contaminants [16]. Some examples include chitin/chitosan based adsorbents, cellulose based adsorbents, lignin and pectin based materials etc. Verma et al., synthesized chitosan polymer based adsorbent using  $\beta$ - cyclodextrin and ethylenediaminetetraacetic acid for the withdrawal of Hg(II), Cd(II), Ni(II) and Cu(II) ions with excellent adsorption capacities [17]. Hamed et al., utilizes cellulose-amine based adsorbent for the elimination of Cu(II) and Pb(II). The findings exposed enhanced performance of the adsorbent in withdrawing heavy metals in the sewage sample following pseudo 2<sup>nd</sup> order kinetics [18]. In a different study Ge et al., constructed lignin microspheres derived adsorbent for Pb(II) ion adsorption. It was established that owing to high amine groups, the adsorption magnitude increased and it could be used up to 5 cycles [19]. The sorption of heavy metals is influenced by multiple factors like pH of the solution, time of contact, concentration, dosage of adsorbent, and temperature [20]. Similarly, Zhang et al., synthesized pectin derived hydrogel composite utilizing grapefruit peel for the riddance of Cu(II) ions from aqueous solution. The composite showed good adsorption performance, with better mechanical properties [21].

In the past few years, chitin-derived nano-composites have revealed extraordinary prospects in waste water treatment because of their biodegradable, biocompatible, low-cost and eco-friendly features [22] [23]. Also, they consist of various reactive functional groups that may be modified further to form various chemically or biologically functionalized derivatives of chitin for particular functions [24]. Chitin, the second most plentiful natural polymer, is generally detected in the exoskeletons of shellfish or insects, as well as in the mushroom cell walls. It is also found in various organisms, including mollusks, crustaceans, insects, fungi and algae [25] [26]. Chitin exhibits numerous valuable features like antibacterial effects, non-toxicity, tunable functionalities and biodegradability, which is why it is exploited for the advancement of composites and nanocomposites in effectual removal of heavy metal ions from the waste water [27] [28]. The structure of chitin contains amino and hydroxyl groups that interact with various metal ions and serve as chelating sites for excellent metal binding [29].

Also, numerous researchers in the recent past are attracted towards the development of sustainable and eco-friendly nanocomposites based adsorbents with versatile properties like easy processability, enhanced productivity, excellent adsorption performance and better surface to volume ratio. The nano-scale dimension contributes to a vast surface area, suitable for adsorption of toxic pollutants, making the material attractive enough for environmental remediation. Nanocomposites are multi-component materials consisting of a continuous phase and a dispersed phase, with at least one dimension in the nano-meter range [30]-[32]. They possess excellent mechanical and thermal properties with strong capacity for adsorbing heavy metal ions. With natural polymer based matrixes these nanocomposites serves as a sustainable alternative to synthetic adsorbents in waste water treatment with outstanding selectivity, chemical stability and high sorption capacity. This review summarized the utilization of chitin-derived nanocomposites as excellent adsorbents for the eradication of heavy metal ions in waste water. It mainly highlights the preparation methods, properties, and advantages of chitin nanocomposites, addressing their efficiency in adsorption of toxic metals. Additionally, the review highlights various factors influencing the performance of adsorbents, like surface area, functional groups, pH and adsorption kinetics. The potential applications and future prospects for improving the productiveness of these materials in water management have been explored as well. Figure 1 demonstrates the schematic diagram of the overall present review including different synthesis techniques of the materials and applications.



**Figure 1.** Schematic Diagram of Chitin Nanocomposite Synthesis and Applications

## 2. Methodology

The study basically summarizes the recent advancement in heavy metal removal from waste water through chitin based nanocomposites. A thorough review of the research published over the last 10 years in the domain of chitin derived nanocomposites was conducted. The selection of papers were done by focussing on the studies related to modification of chitin, development of chitin based nanocomposites and their aptness in wastewater treatment for heavy metal riddance particularly. Also comparison of chitin based composites for the

elimination of heavy metal ions with different other adsorbents were discussed but special focus was given to chitin and modification made in chitin. The review includes sections such as a) chitin sources and its structural properties b) study on extraction and modification of chitin c) waste water treatment applying chitin adsorbents and examining it as a potential adsorbent d) analytic techniques used in the characterization of the developed chitin based nanocomposites e) heavy metal pollution and getting rid of it applying chitin based materials. The literature survey was conducted utilizing standard academic databases like Google Scholar, ResearchGate and other scientific repositories. To scrutinize relevant journals keywords including ‘chitin’, ‘chitosan’, ‘heavy metal ions’, ‘contaminated’, ‘toxic effects’, ‘removal’, ‘wastewater treatment’, ‘functionalization’, ‘modification’, ‘polymer’, ‘nanocomposites’, ‘adsorption’ ‘remediation’ were used. This review intend to put forward insights regarding the progression made in the field of chitin based nanocomposites and its utilisation in removal of heavy metals out of the wastewater by covering a decade of advances.

**Table 1.** Harmful effects of various heavy metals in health of humans

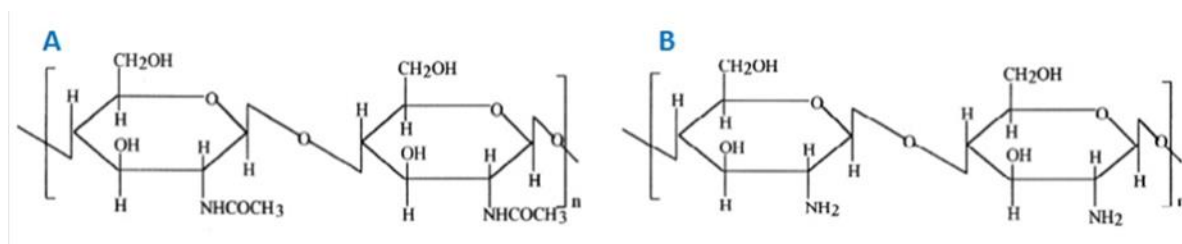
<b>Heavy Metals</b>	<b>Contamination source</b>	<b>Standard limits for drinking water as per WHO (mg/L)</b>	<b>Toxic effects</b>
<b>Lead: Pb (II)</b>	Industrial discharge, lead based gasoline, mining activities	0.01	Kidney and liver dysfunction, disrupt reproductive health, neurological issues in children etc.
<b>Arsenic: As (III) As (V)</b>	Industrial and agricultural waste, groundwater	0.01	Skin lesions, cancer risk, neurological effects etc.
<b>Mercury: Hg (II)</b>	Industrial discharge, agricultural runoff, electronic materials	0.006	Neurological damage, kidney dysfunction, cardiovascular issues etc.
<b>Chromium: Cr (IV) Cr (III)</b>	Mining activities, textile industries, nuclear power plant	0.05	Lung cancer, skin rashes, ulcer etc.
<b>Cadmium: Cd (II)</b>	Metal plating, Ni-Cd batteries, fertilizers	0.003	Kidney and lung damage, Itai-Itai disease, reproductive toxicity, bone deformities etc.
<b>Copper: Cu (II)</b>	Industrial effluents, plumbing corrosion	2.0	Gastrointestinal distress, anemia, jaundice etc.
<b>Cobalt: Co (II)</b>	Mining and metallurgical process, battery, metal plating, electronic waste	0.01	Skin allergy, respiratory issues, kidney toxicity, diarrhea etc.
<b>Nickel: Ni (I)</b>	Mining, electroplating, batteries, electronics	0.07	Respiratory issues, dermatitis, kidney damage etc.

### 3. Chitin

#### 3.1. Sources & Structural Properties

Chitin is a natural biopolymer that is found amply in nature following cellulose. It basically exists in the exoskeletons of crustaceans (crabs, shrimp, lobsters), insects, aquatic invertebrates, arthropods and in the fungal or yeast cell walls [33] [34]. Chitin is linear polysaccharide consisting of N-acetylglucosamine units connected through  $\beta$ -(1,4) glycosidic bonds [35] and appears as three main polymorphic forms -  $\alpha$ ,  $\beta$ , and  $\gamma$ , each one with different microfibrils arrangement [36]. The chains in  $\alpha$ -form of chitin are aligned in anti-parallel structure and are the most stable due to strong and rigid hydrogen bonding [37]. The  $\alpha$ -form is the most abundant, usually obtained from crustaceans (e.g., crab, shrimp) and other hard-exterior invertebrates. It also occurs in yeast and fungal cell walls. The chains in  $\beta$ -form are positioned in parallel alignment and are less stable. The  $\beta$ -form of chitin is mostly spotted in mollusks like squid pens [38], also in the pipes prepared by pogonophoran and vestimetiferan worms. The  $\gamma$ -form consists of two parallel and one anti-parallel chitin strain, available in cocoons of insects [39]. The  $\beta$ -structure can be converted to  $\alpha$ -structure but the reverse is by no means feasible. It has been investigated that chitin separation mostly depends on factors like polymer arrangement, crystallinity, purity, source and composition [40]. A key specification, which regulates the solubility and functionality of the molecule, is the degree of acetylation (DA). For example, when the DA exceeds 50%, chitin becomes insoluble [41].

Chitosan is an important derivative of chitin, which is procured by separating sufficient amount of acetyl groups ( $\text{CH}_3\text{-CO}$ ), in order to increase the solubility in different acidic medium [42]. Generally, chitosan is a fiber-like homopolymer with  $\beta$ -(1 $\rightarrow$ 4)-linked N-acetyl-D-glucosamine [43]. The structure of chitin and chitosan are presented in Figure 2. The primary difference between them is the acetyl moiety of the polymer and the latter being more chemically reactive. Chitosan has free amino groups with lower degree of acetylation. There are numerous advantages of chitosan including non-toxicity, biocompatibility, biodegradability, and antimicrobial effects, making them promising materials for a wide array of applications, including environmental remediation [44] [45].

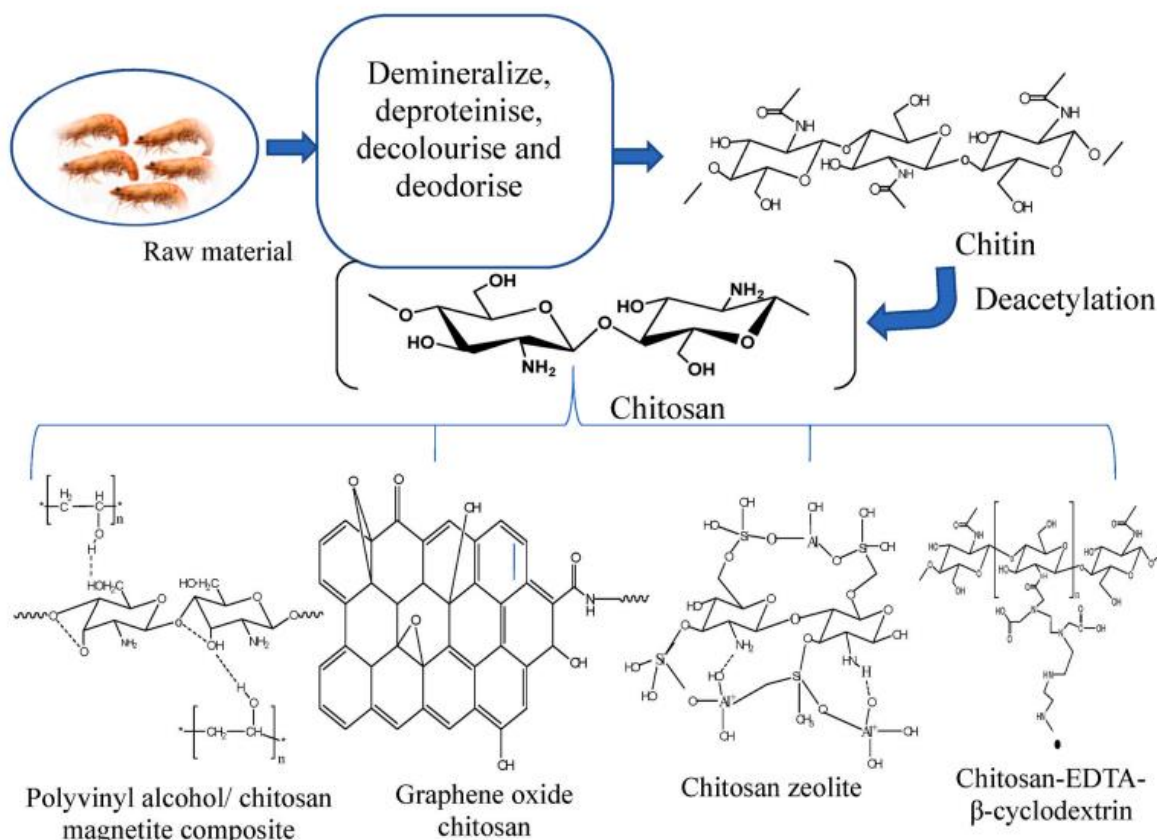


**Figure 2.** Structure of A) chitin and B) chitosan. Reprinted under Creative Common Attribution (CC BY) License. Copyright Elsevier. [46]

#### 3.2. Modification of Chitin

Chitin, a polysaccharide widely obtained from sea-based food resources, mainly crustacean and cephalopod shells, insect cuticles and fungal cell walls. Figure 3 shows various techniques for the modification of chitin and chitosan derivatives. Extraction of chitin from the raw materials can be done by biological as well as chemical methodologies. The chemical technique is commonly used due to its efficiency and high yield. This primarily involves demineralization, deproteinization and deacetylation. In addition, decolorization can be

achieved utilizing multiple organic as well as inorganic solvents. For example, glacial acetone and sodium hypochlorite are used to remove pigments [47]. The demineralization process is done to eliminate calcium carbonate and calcium chloride; the predominant inorganic constituent in crustacean exoskeletons. This is mostly achieved using inorganic acids or strong organic acids. HCl is commonly utilized on account of its superior competence in mineral dismissal. The subsequent step in chitin segregation is deproteinization, which involves removing proteins from the raw materials using an alkaline solution. Various chemical reagents were explored for this purpose, comprising KOH, Na<sub>2</sub>CO<sub>3</sub>, NaOH, Ca(OH)<sub>2</sub> etc. However, NaOH remains the most widely used reagent due to its effectiveness [48]. The order and intensity of these processes are tailored based on the composition of raw material being processed. The chemical process for extracting chitin generates substantial quantities of hazardous alkaline and acidic waste, posing significant environmental risks. As an alternative, biological methods have emerged as a sustainable approach to chitin and chitosan modification. Recently, there are several reports that suggest that enzymatic techniques can effectively replace traditional chemical deproteinization methods. In a study, chitin was separated from the shells of *Portunus segnis* and *Penaeus kerathurus* through crude digestive alkaline proteases out of the viscera of *P. segnis*, as an alternative to chemical remedy for the deproteinization step of chitin extraction [49].



**Figure 3.** Tailoring of chitin to chitosan by deacetylation and some derivatives. Reprinted under Creative Common Attribution (CC BY) License. Copyright Elsevier. [58]

Surface modification is a highly effective approach to enhance the application of  $\alpha$ -chitin. In this regard, Ablouh et al., utilizes an acidic medium and ultrasonication, to alter the surface properties of  $\alpha$ -chitin and increase its adsorption performance. The modification showed a substantial increment in the surface area of  $\alpha$ -chitin, while the crystallinity index reduced appreciably. The modified  $\alpha$ -chitin displayed a magnificent experimental adsorption capacity, highlighting its potential for wastewater treatment [50]. In another work,  $\beta$ -chitin was successfully extracted from the waste *Uroteuthis duvauceli* squid pens. The extraction process utilized the association of decolorization, demineralization, and deproteinization methods. The extracted  $\beta$ -chitin was later chemically modified by a one-pot etherification reaction with acrylamide in an environmentally friendly aqueous solvent system containing NaOH and urea. The resulting acrylamide-modified  $\beta$ -chitin derivatives exhibited notable water solubility and reduced decomposition temperatures. These changes were attributed to the breakdown of the crystalline structure of  $\beta$ -chitin while modification [51]. A study developed carboxymethyl chitin microspheres (CMCHm) utilizing an organic solvent-free heating method. To synthesise the microspheres, carboxymethyl chitin (CMCH) and polyethylene glycol (PEG) were separately dissolved in NaOH. These solutions were combined under ice bath conditions and stirred for few minutes. The resulting aqueous two-phase system was then heated in an oil bath at 60°C for 20 minutes to produce CMCH microsphere dispersions. These dispersions were thoroughly rinsed with deionized water to discard impurities. Eventually, the CMCH microspheres were frozen using liquid nitrogen and freeze dried to acquire the ultimate product. To improve the functional properties of the microspheres calcium ions were loaded into the microspheres to produce CMCHm-Ca<sup>2+</sup>, while dopamine was *in-situ* polymerized onto the microspheres, resulting in CMCHm-PDA [52]. In another study, chitin powder was dispersed in deionized water and stirred continuously for a day to facilitate nano-fibrillation. The resulting suspension was processed in a grinder for several min, followed by homogenization. To have a porous structure, the chitin nanofiber suspension underwent freeze-drying, resulting in a chitin nanofiber sponge. The surface of the sponge was modified using tannic acid (TA) and Ca<sup>2+</sup> ion through a layer-by-layer deposition technique. For this, solution of TA and CaCl<sub>2</sub> were prepared in a tris(hydroxymethyl)aminomethane solution. Upon immersing the chitin sponge in the TA solution for 10 min, it immediately turned purple indicating the formation of a TA coating. To discard the residual impurities, the modified sponge was rinsed thoroughly with deionized water [53]. In a study Zhang et al., dissolved chitosan in glacial acetic acid under constant stirring condition and then mixed it slowly at room temperature with graphene oxide suspension. The blend was stirred continuously and treated with ultrasound for one hour for better dissolution of the mixture. Again, it was stirred at room temperature for another 16 h. Finally, the graphene oxide/chitosan composite was isolated through filtration and centrifugation. It was further washed properly and dried at 60 °C under vacuum [54]. In a different report polyvinyl alcohol (PVA)/chitosan (CS) magnetite was prepared by mixing PVA and CS solution and then Fe<sub>3</sub>O<sub>4</sub> was added. The mixture was stirred constantly for ten minutes for better dispersion of the nanoparticles. Later, in the mixture few drops of glacial acetic acid were added followed by crosslinking with glutaraldehyde vapour for almost 24 hours to get the desired product [55]. In another study, chitosan solution was added to powdered zeolite and stirred at 45°C for almost two hour maintaining pH = 6. For preparation of the beads, the gel mixture was poured in a NaOH precipitation bath using a syringe. Hence, the cross-linked gel coagulates to uniform and stable beads. The beads were then rinsed properly

with distilled water, dried and stored for further use [56]. EDTA modified  $\beta$ -cyclodextrin ( $\beta$ -CD)/chitosan was constructed by dissolving  $\beta$ -CD and chitosan in hydrochloric acid. The mixture was stirred constantly to form a uniform solution at 85 °C for half an hour followed by addition of cross-linker glutaraldehyde. After heating the mixture for another 1.5 h, NaOH was added to the system at pH 8-9 and continued heating for half hour. Finally, the product was cooled, washed and dried for further use [57].

#### 4. Development of Chitin based Nanocomposites

The development of chitin-based nanocomposites has gained significant interest for environmental remediation ascribed to their renewable, biodegradable and biocompatible properties. The existence of *N*-acetamido groups in chitin helps in the formation of strong inter- and intra-molecular hydrogen bonds that contribute to the stability and structure of the material [59]. Chitin's low density, high surface area, hydrophilicity, chemical reactivity, and biodegradability makes it an ideal candidate as a nano-size reinforcing fillers in polymer nanocomposites. These materials are compelling in adsorbing heavy metal ions out of the contaminated water, offering an environmentally safe and efficient solution for wastewater treatment. Some common methods used for fabricating chitin based nanocomposites include melt mixing, solution casting, electrospinning, *in situ* polymerization, sol gel technique, freeze drying method, blending with other biopolymers or fillers, chemical crosslinking etc.

In a study Zhong et al., used an acidified ethanol/water medium to disperse chitin nanofibrils (ChNFs) in a solution of chitin propionate (CP), forming ChNF-CP nanocomposites. CP was synthesized *via* modifying chitin through propionylation to enhance the solubility. The ChNFs enhanced the tensile strength and modulus of the nanocomposites by 66% and 97%, respectively, with a 15% ChNF content. Additionally, there was an increment in maximum degradation temperature by 40°C, with a notable rise in storage modulus above the glass transition temperature [60]. Similarly, nanocomposites films based on chitin nanofibrils (CNF) and carrageenan was prepared through solution-casting method. A specified ratio of CNF was mixed with distilled water and stirred for an hour. Glycerol plasticizer was added onto the mixture and stirred vigorously for few minutes, followed by gradual addition of carrageenan and mixed thoroughly at 95°C for 30 minutes. The resulting solution was cast onto a levelled, Teflon-coated glass plate, dried and kept for further analysis [61]. A study highlighted the construction of composite nanofibers *via* electrospinning chitosan with chitin nanofibrils as the filler. Various amounts of chitosan powder were dispersed in water and stirred at 200 rpm for 40 minutes to allow partial swelling. Glacial acetic acid was then added while stirring to create a 70% solution followed by an additional 40 minutes of stirring at 500 rpm. The solution was then left to stand at 4°C for three days before spinning. Separately, the chitin nanofibrils were dispersed in water using an ultrasonic disperser at 40 kHz with a power of 1.3 kW, undergoing ultrasonic treatment for 40 minutes. Nanoparticle dispersions were prepared in concentrations from 1.0 to 30 wt% relative to the chitosan. [62].  $\beta$ -chitin/gelatin/nanohydroxyapatite (GE-nHAp) composite scaffold was prepared by Teimouri and co-worker through freeze-drying method. For the preparation of GE-nHAp composite scaffolds, gelatin (GE) hydrogel was mixed with  $\beta$ -chitin hydrogel and stirred at room temperature for 12 hours. Then, nanohydroxyapatite (nHAp) was added while stirring to ensure uniform dispersion for 24 hours. The mixture was ultrasonicated for 2 h to reduce particle size,



and then crosslinking agent (glutaraldehyde) was added, making the composites water-insoluble. The ultimate solution was poured into culture plates, pre-frozen (at  $-20\text{ }^{\circ}\text{C}$ ) upto 12 hours, and freeze-dried at  $-80\text{ }^{\circ}\text{C}$  till 48 h. In an effort to remove any remaining cross-linker, the scaffolds were rinsed with deionized water and freeze-dried again [63].

In a study by Rubentheren et al., nanosized chitin whisker and tannic acid cross-linked chitosan composite was prepared *via* casting-vaporation method. The solution of chitosan was synthesized by dissolution of chitosan powder with acetic acid under magnetic stirring at  $35\text{ }^{\circ}\text{C}$  for 3 hr. Next, the chitin whiskers were added steadily to the above solution forming a mixed suspension. Following this, different amounts of tannic acid was loaded into the suspension and stirred magnetically at  $35\text{ }^{\circ}\text{C}$  until fully homogeneous. It was established that with the addition of chitin whiskers the mechanical and physicochemical effects of the nanocomposite rises [64]. Cellulose/chitin films were designed by Duan et al., by dispensing the individual hot solutions in a petri dish using a syringe and then cooled at room temperature. Finally, the films underwent Soxhlet extraction with 100 mL of ethanol for 24 hours to assure total elimination of the ionic liquid. The prepared material showed outstanding mechanical properties [65]. Squid  $\beta$ -chitin was exfoliated in an aqueous solution of acrylic acid (AA) to prepare chitin-polyacrylic acid (PAA) composite film through *in situ* polymerization. The diameter of the chitin microfibrils were reported to be 4–6 nm, having aspect ratio greater than 250. The exfoliation process involved stirring chitin in aqueous AA for 4 to 5 hours, producing a viscous dispersion. An aqueous solution of 25% AA and hydrogen peroxide was then mixed in the above solution. The concentration of AA in the mixture was optimized to achieve final PAA composites with 1, 2, or 3 (w/w %) chitin after polymerization. The mixture was degassed to remove oxygen, and then polymerized at room temperature over 24 hours. The composite films were formed by casting the dispersion onto a polyethylene surface and drying under ambient conditions, followed by vacuum drying at  $140\text{ }^{\circ}\text{C}$  for 4 hours [66]. In an additional study by Salairaj et al.,  $\alpha$ -chitin/silver nanocomposite (CNP/AgNP) was synthesized successfully with improved antimicrobial activity. Firstly, the shrimp shells were collected and pre-treated with alkali and acid to remove various impurities and then it was further acid hydrolysed, homogenized, lyophilized and ultrasonicated to obtain pure  $\alpha$ -chitin nanoparticles (CNP). CNP was mixed with AgNP suspension and stirred well for 30 minutes. The mixture was centrifuged for 10 min and then the nanocomposite pellet was washed properly and dried above room temperature [67]. Similarly, chitin nanowhiskers (ChNW) were extracted and utilized in the preparation of hybrid ChNW/ZnO-Ag NPs. The nanowhiskey was needle shaped with length and width of 150-260 nm and 8-40 nm respectively, along with  $\sim 90\%$  crystallinity index. The thermal properties of the nanowhiskers increased with addition of ZnO Ag NPs. Also, the final material had excellent UV-resistance properties and antimicrobial activity upon incorporation of the chitin whisker/ZnO-Ag nanoparticles. [68]. In a study Wang et al., prepared chitin/grapheme oxide based composite film for wastewater treatment, where  $\text{Cu}_2\text{O}$  based photo-catalyst was *in situ* synthesized within the chitin matrix. Lately,  $\text{Cu}_2\text{O}$  has been studied hugely as a p-type semiconductor owing to its ease of preparation, small band gap, non-toxicity, easy availability and excellent stability under light. For the preparation of the composite, graphite powder was dispersed in cold and concentrated  $\text{H}_2\text{SO}_4$  consisting  $\text{NaNO}_3$ , followed by slow addition of  $\text{KMnO}_4$  with continuous stirring at  $20\text{ }^{\circ}\text{C}$ . After that the mixture was heated to  $35\text{ }^{\circ}\text{C}$  with constant stirring for atleast one hour, and then deionized water was added slowly, raising the temperature above  $90\text{ }^{\circ}\text{C}$  for 12h. Finally, yellow coloured suspension was obtained

and the solid product was isolated by centrifugation and then the powdered product was vacuum dried at room temperature. This green and simple method of synthesis improved the catalytic efficiency of the adsorbent and prevents agglomeration of nanoparticles [69].

## 5. Characterization of Chitin based Nanocomposites

It is critical to comprehend the structure, properties and suitability of the prepared material for a number of utilizations. Some usual strategy employed for the characterization of chitin based nano-composites includes Fourier Transform Infrared Spectroscopy (FTIR). It is operated to determine functional groups in the nanocomposites, providing insights on structural changes. It also helps to confirm interactions between chitin and other materials or nanoparticles in the composite. FTIR spectroscopy was employed to inspect the chemical components and interaction of gelatin-chitin nanoparticle based nanocomposites designed by Sahraee et al. A significant peak observed at 3200-3500  $\text{cm}^{-1}$  corresponds to O-H stretching and N-H stretching vibration due to hydrogen bonding among the chains of gelatin. Another peak around 2958  $\text{cm}^{-1}$  was found in each films with varying chitin concentrations (0, 3, 5 and 10%) for amide-B, indicating  $\text{NH}_3^+$  and CH asymmetric interactions. Chitin nanoparticles were reported to react with gelatin by hydrogen bonds between the groups of N-H and O-H. The peak intensity around 3300  $\text{cm}^{-1}$  was reported to be increasing with rise in amount of N-chitin. Prominent peaks at 1628  $\text{cm}^{-1}$  for amide-I related to C=O stretching vibration, and 1575  $\text{cm}^{-1}$  for amide-II were reported due to N-H bending and C-N stretching vibration. Additionally, sharp peaks at 1618  $\text{cm}^{-1}$  and 1652  $\text{cm}^{-1}$  for  $\alpha$ -chitin was due to C=O stretching in the amide I band. The peak intensity about 1550  $\text{cm}^{-1}$  associated with N-H bonds of N-acetyl group of chitin increased with higher N-chitin concentration. The synergy between N-chitin and gelatin matrix was due to shifting of 3481  $\text{cm}^{-1}$  band to elevated wave numbers, indicating more pronounced N-H and O-H stretching vibrations [70]. X-ray diffraction (XRD) is operated to analyse the crystallinity of nanocomposites. The method helps to govern the degree of crystallinity, changes in the crystal structure, and the dispersion of nanomaterials within the matrix. Aouadi et al., investigated the structural characteristics of chitin/zinc nanocomposites by XRD. It was found that the primary peaks of chitin i.e., 9.2°, 19.18°, and 27.3° were found in the composite demonstrating  $\alpha$ -configured crystal structure. Additionally, new peaks were identified 37.2°, 39.9°, 44.3°, and 54.9° attributed to Zn. This study showed that zinc was incorporated into the chitin structure, owing to the hydrolysis of zinc acetate at higher temperature. The XRD data of the ZnO nanoparticles showed well-defined, relatively broad and intense peaks, indicating a nanocrystalline structure. The detected peaks aligned with the hexagonal wurtzite structure of ZnO [71]. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are employed to study the surface morphology and internal structure of the nanocomposites, respectively. They provide detailed images of the composites nanoscale features, particle size, dispersion, and interfacial interactions. In a study by Heiba et al., mesoporous chitin-blended  $\text{MoO}_3$ -Montmorillonite (MMT) nanocomposites were synthesized. SEM micrographs of the untreated Chitin- $\text{MoO}_3$ -MMT nanocomposite showed a sharp, dense nanorod-like structure with 60-77.7 nm lengths. Following the adsorption of Cu(II) and Pb(II) ions, significant alterations were observed like the nanorod structures disappeared, and the surface roughness increased. This change was attributed to metal binding, which will likely cover the exterior and bring about a relaxation in the composite

appearance. Additionally, the interchangeable cations in MMT may be restored by Pb(II) and Cu(II), further altering the appearance of the composite [72]. Cheikh et al. lead a research on the honeycomb alliance of chitin nanocrystals (ChNCs) in nanocomposite films. TEM analysis showed that the ChNCs appeared as polydisperse, rod-like structures with 150-1500 nm lengths, having number-average length of  $628 \pm 264$  nm, and 10-60 nm widths. The particles consisted of a few laterally associated elementary crystallites, which remained intact throughout the preparation process [73]. Thermogravimetric Analysis (TGA) studies the thermal stability of chitin-based nanocomposites. By measuring weight loss with increasing temperature, TGA reveals the decomposition temperatures and thermal stability enhancement due to the nanofiller addition. Maalihan et al., reported the impact of photocurable chitin nanowhiskers (pCNW) on the thermal properties of the methacrylate (MA) nanocomposites. Both neat MA and pCNW/MA composites showed a two-step decomposition pattern, indicating that the addition of pCNW did not alter the degradation mechanism of MA. But, the addition of 1wt% pCNW raised the initial decomposition temperature from 294 to 322 °C, demonstrating a slight enhancement in thermal resistance. Additionally, the mass residue at ~600 °C increased from 1.16% to 5.67%, likely due to the aromatic and pyranose ring structures in the MA resin and pCNW, which promote char formation. DTG analysis confirmed two main degradation stages, side-chain loss at ~370–378 °C and backbone depolymerization at ~456–470 °C. The pCNW-filled nanocomposites exhibited higher  $T_{max}$  values than neat MA, suggesting improved thermal stability in the composites [74]. It is also essential to assess the mechanical properties of the composites and nanocomposites like tensile strength, elasticity, and toughness. It helps to understand the flexibility and rigidity of the material with addition of nanomaterials. The mechanical properties of thermoplastic starch (TPS) and chitin nanofiber (ChNF)/TPS nanocomposites were evaluated *via* stress-strain curve by Tanpichai et al. It was reported that, neat TPS films had a tensile strength of 2.37 MPa, Young's modulus of 45.3 MPa, and elongation at break of 35.6%. With the addition of ChNFs the properties of the nanocomposites increased. Nanocomposites having 1 phr ChNFs showed a tensile strength of 4.56 MPa and Young's modulus of 110.3 MPa, showing increase of 92% and 143%, respectively. This enhancement was due to the homogeneous ChNFs dispersion in starch. The highest improvement was found with 7 phr ChNFs, having tensile strength and Young's modulus of 9.50 MPa and 318.7 MPa, respectively. However, at 9 phr ChNFs it was found that properties declined slightly due to ChNF aggregation, limiting stress transfer [75].

## **6. Application of Chitin based Nanocomposites as Heavy Metal Adsorbent**

The usage of chitin based adsorbents for the elimination of heavy metals from contaminated water is increasing significantly due to their high availability, excellent adsorption performance, biodegradability, and non-toxicity. Also, the advancement in nano-based technology has enabled the development of chitin-based composites with enhanced chemical, mechanical and other functional properties, which finally increases the overall adsorption performance of the material. In this section, the consequences associated with heavy metal pollutants and innumerable applications of chitin-based nanocomposites for their removal have been discussed.

### *6.1. Heavy Metal Pollution*

Out of the 90 natural elements known, 53 are categorized as heavy metals with an atomic number of  $\geq 23$  and density exceeding  $5 \text{ gm cm}^{-3}$  [76] [77]. These metals are integral to various biological systems and processes, as they have two wide categories according to their biological relevance: essential and non-essential. Essential heavy metals such as copper, iron, manganese, cobalt, zinc etc. are known for maintaining various biological processes in organisms and also serve as important cofactors for enzymes [78]. On the other hand, non-essential heavy metals namely cadmium, chromium, mercury and lead are devoid of known physiological and biological properties and are predominantly toxic. Although trace amounts of heavy metals are non-toxic, concentration exceeding certain level makes it highly harmful for living organisms. Further, increased levels of heavy metals cause bioaccumulation inside the human body due to absence of proper elimination mechanism which results magnification of toxic effects [79]. Their toxicity extends across biological systems, disrupting cellular processes through mechanisms such as oxidative stress, lipid membrane damage, and protein denaturation. These effects are attributed to the presence of partially filled d orbitals, which facilitate interactions with cellular macromolecules, leading to the formation of non-specific, harmful complexes in the cells. The sources of heavy metal contamination in the environment are multifaceted, comprising both natural and anthropogenic activities. Natural geological processes such as volcanic eruptions and various ventures by human are accountable for discharge of heavy metals in the surrounding [80]. Industries such as thermal power plant, oil refineries, chemical manufacturing, and mining are notable beneficiaries to the discharge of heavy metals, releasing high levels of these pollutants into ecosystems. Improper disposal practices, agricultural runoff containing metal-laden fertilizers and pesticides, and urban wastewater further increases the problem.

The accumulated heavy metals cannot be destroyed; however they can be converted into non-toxic forms. Heavy metals have the capacity to interact with biological macromolecules, causing oxidative stress and inducing chronic toxicity in living organisms. The presence of partially filled d orbitals, which can result in complex, non-specific molecules within the cells, is primarily responsible for the harmful effects of heavy metals [81]. Long-term exposure to high concentrations of heavy metals is associated with a number of chronic diseases in humans, including skin diseases, various forms of cancers, central nervous system abnormalities, immunological suppression, bone damage, respiratory issues, and renal failure [82]. Given the pervasive nature and detrimental impact of heavy metal contamination, it is necessary to implement beneficial methodologies for their removal. These strategies must be economical, eco-friendly, and sustainable to ensure the minimization of environmental and biological damage. The development and adoption of such solutions are crucial to protect the ecosystems and well-being of humans from the toxic outcome of heavy metal pollutants.

### *6.2. Removal of Heavy Metals using Chitin Nanocomposites*

In recent times, environmental pollution is widely regarded as a global challenge, specially the heavy metal pollution in wastewater. Owing to intensification of industrial development and extreme chemical usage worldwide, toxic heavy metals are introduced into aquatic environment, which is a matter of concern. Hence, it is crucial to deal with the heavy metal-contaminated water prior to discharging it into the surrounding. Chitin consists of

various functional groups like amino (-NH<sub>2</sub>) and hydroxyl (-OH), which provides multiple binding sites for heavy metal ions, increasing their affinity and adsorption efficiency. Also, they can be tailored chemically or enzymatically to numerous derivatives for precise functions. To improve the mechanical properties and chemical stability various synthetic or natural polymers can be blended with chitin or chitin based derivatives. In the recent past, nano-sized particles like graphene oxide, silica, metal oxides or magnetic nanoparticles, have been extensively utilized to upgrade the adsorption ability of the chitin based materials. These nanocomposites exhibit increased surface area, chemical stability, and selectivity for specific heavy metals like copper, cadmium, lead, and mercury. The expansion of chitin and chitosan-based nanocomposites for water purification is a domain of on-going study with appreciable relevance, yet the adsorption-desorption study needs special attention. The separation of the used materials from the treated water is another obstacle which is an equally crucial task for method designing. Recently, magnetic nanotechnology has been explored extensively owing to its nanosized properties and magnetic effects. This technology offers improved kinetics for the adsorption of metal ions from untreated water owing to its higher surface to volume ratio, smaller size, and the lack of internal diffusion resistance. Magnetic features help in effortless recovery of the adsorbents *via* external magnetic field, thereby enhancing the chances of reuse [83]. Overall, chitin-based nanocomposites are promising candidate for the wastewater treatment, delivering a sustainable and effective solution for managing heavy metal pollution. Table 2 highlights the performance comparison of adsorption abilities of chitin based materials with various adsorbents along with their advantages and disadvantages.

In a study, chitin was chemically modified by reaction with 8-hydroxyquinoline and magnetite to obtain magnetic adsorbent chitin 8-quinolyl ether (C8QE), for cadmium ions removal from polluted water. The optimal removal efficiency of C8QE was 119.9 mg/g within 10 minutes at pH 7 and 298 K temperature. Kinetic and thermodynamic study showed that Cd(II) removal followed a pseudo second order kinetics and involve electrostatic, exothermic, and spontaneous chemical process. Additionally, the prepared material could be reused up to four times with higher removal efficiency [84]. Similarly, a study highlighted the development of eco-friendly chitin modified iron-enriched hydroxyapatite nanocomposite (HAP-Fe<sup>0</sup>-Ct) for the remediation of Cr(VI)-contaminated groundwater. The nanocomposite demonstrated adsorption activity of 13.9 ± 0.46 mg/g and 100% removal of Cr (VI) within 3 h. It was reported that no Cr (VI) leaching occurred during acid washing at pH 3.5, indicating effective chemisorption of chromium onto the nanocomposite [85]. In another study, chitin was physically mixed with magnetite nanoparticles and multiwalled carbon nanotubes to develop a magnetic nanocomposite with improved adsorption ability for Cr(VI) ion. The study revealed that the removal efficiency rise with higher CMM dosages and lower solution temperatures. The kinetic and thermodynamic study indicated that the nanocomposites follow pseudo-second-order kinetics with spontaneous and exothermic characteristics [86]. Another study focussed on the development of iron nanoparticles (FeNP), utilizing aqueous leaf extract of *Corchorus olitorius* and chitin nanoparticles (CNP), derived from *Penaeus semisulcatus* shells to fabricate iron/chitin nanocomposite. The use of plant extracts has emerged as a potential strategy in the synthesis of metal nanoparticles. This technique of green biosynthesis includes benefits such as cost-effectiveness, non-toxicity, safety and eco-friendly approach. The composites efficiency to remove heavy metals improved with increase in the concentration of adsorbent. The removal rates were found to be 98.90% for Cr<sup>3+</sup>, 94.20% for Cd<sup>2+</sup> and 90.30%

for  $\text{Ni}^{2+}$  within 30 min. It is worth mentioning that chitin had good selectivity and sorption performance for heavy metals on account of hydroxyl and amino groups into the polymer matrix. The reactive functional groups interact with the heavy metal ions *via* complexation reactions or ion exchange that facilitate excellent binding of metal ions. Additionally, loading of FeNP in CNP allows better dispersion, prevents agglomeration and provides numerous surface active sites to interact with the heavy metals and enhance their adsorption ability and selectivity [87].

Nowadays, hydrogel based bio-adsorbents has gained enough attention because of the presence of hydrophilic network structure that are competent in absorbing substantial amounts of water into their three-dimensional networks. They have the ability to lower the concentration of metal ion in waste water offering more surface active sites. Also various studies successfully reported the practise of clay derived adsorbents in eliminating heavy metals from untreated water, as they possess excellent selectivity, better specific surface area, outstanding cation exchange capacity, and surface hydrophilicity. In a study, hydrogel film based on chitin-halloysite nanoclay (CTH) was prepared for adsorption of heavy metal ions applying halloysite nanoclay (HCN) of varied weight percentage (0, 0.1, 0.5, 1, and 4). It was found that the prepared material showed greater removal efficiency of 8.2, 4.2, 2.1 mg/g for Pb(II), Cu(II), and Cd(II) respectively [88]. In another study Heiba et al., showed that chitin based  $\text{MoO}_3$ -montmorillonite nanocomposite was used for Pb(II) and Cu(II) immobilization. The adsorption capacity were 19.03 and 15.92 mg/g for Cu(II) and Pb(II) respectively. It was found that the adsorption followed Langmuir isotherm and pseudo 2<sup>nd</sup> order kinetics, indicating monolayer chemisorption. The thermodynamic analysis revealed that the adsorption was endothermic and spontaneous, with 25.94 and 29.37 kJ/mol activation energies for Cu(II) and Pb(II) respectively [89]. Chitin nanofiber-polydopamine (CNDA) composites were fabricated through modification of chitin nanofibers with dopamine. The material demonstrated excellent adsorption abilities for  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  ions [90].

Chitosan, derived from the deacetylation of chitin, is a linear polysaccharide comprised of glucosamine and *N*-acetyl glucosamine units associated *via*  $\beta(1-4)$  glycosidic bonds. Unlike chitin, which is largely indissoluble in organic solvents and water caused by its rigid structure and high intermolecular hydrogen bonds, chitosan dissolves readily in dilute acidic solutions. This solubility significantly increases its practical applications. Chitosan exhibits exceptional adsorption properties for metal ions, attributed to the abundant hydroxyl and amino functional groups. These groups enable chitosan to set up complexes with metal ions through mechanisms like chelation, hydrogen bonding and electrostatic attraction. Compared to chitin, chitosan demonstrates a superior adsorption capacity, primarily due to its higher concentration of amino groups. Additionally, chitosan-based composites and nanocomposites have been widely investigated for wastewater treatment by removal of toxic metal ions.

Recently, magnetic nanomaterial based adsorbents are getting enough recognition in removal of heavy metals out of the untreated water ascribed to various advantages like cost-effectiveness, better recovery of the adsorbent, excellent removal performance and recyclability. Chitin magnetic nano-materials with their improved adsorption efficiency, easy separation, very little secondary pollution, selectivity, and sustainability are explored by various researchers in the remediation of wastewater by separating pollutants. In this respect, Horst et al., prepared nano-composites based on chitosan and magnetite for elimination of Cu(II), Zn(II), Cd(II) and Cr(II). The maximum adsorption capacity of the magnetic adsorbents

was found to be 188, 159, 72, 46 mg/g for Cu(II), Cd(II), Zn and Cr(II) respectively. It was also reported that the adsorbent was efficient for almost 5 to 8 cycles. The study highlighted that coordination bond among the nanocomposites functional groups and metals were responsible for the adsorption mechanism. In addition to that, electrostatic attraction and ion exchange also performed a crucial part in the linkage of heavy metals [91]. Similarly Singh et al., synthesised beads composed of chitosan/polyvinyl alcohol (CS/PVA), poly(ethyleneimine), and  $\text{Fe}_3\text{O}_4$  to separate Cr(VI) from aqueous solutions. The prepared material undergoes physisorption exhibiting magnetic properties. The material showed adsorption capacity of 199.8 mg/g for Cr(VI) ion. The adsorption process obeyed Langmuir isotherm model and pseudo-first-order kinetics [92]. Thakur et al., fabricated magnetic ternary nano-composite (NC) to decrease the concentration of Pd, Cd, Cu and Ni ions in polluted water. The removal of Pb(II) ions by the NC obeyed pseudo 2<sup>nd</sup> order kinetics, and the adsorption process followed Langmuir isotherm model. To simulate real wastewater atmosphere, a combination of Pb(II), Cd(II), Ni(II), and Cu(II) ions was exposed to the NC that achieved a remarkable purification efficiency of over 99% [93]. Peralta et al., developed a magnetic chitosan composite to effectively separate toxic heavy metals such as Cu(II), Pb(II), and Ni(II) from water. The adsorption process achieved equilibrium within 120 minutes, with adsorption capability of 108.90, 216.80, 220.90 mg/g for Ni(II), Cu(II), and Pb(II) respectively. The study showed that amino and hydroxyl groups present in chitosan played a pivotal part in assisting the adsorption of these heavy metals, demonstrating the potential of the prepared magnetic composite as a productive material for water remediation [94].

A study investigated the application of graphene-based two-dimensional materials for treatment of heavy metal contaminated wastewater. Shahzad et al., fabricated ethylenediaminetetraacetic acid (EDTA)-functionalized magnetic chitosan (CS) graphene oxide (GO) nanocomposites (EDTA-MCS/GO) with reduction precipitation technique. These nanocomposites were employed for the separation of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{As}^{3+}$ , from aqueous solutions. On account of their vast surface area, hydrophilic properties, and varied functional groups, the nanocomposite exhibited exceptional adsorption capabilities of 206.52, 207.26, 42.75 mg/g for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{As}^{3+}$  respectively. Furthermore, the nanocomposites demonstrated strong reusability, maintaining high adsorption capacity [95]. Similarly, Anush et al., designed a novel adsorbent applying graphene oxide functionalized chitosan magnetite in the removal of Cu(II) and Cr(VI) ions from waste water. High adsorption capacities were found for the prepared nanocomposites with 111.11, 142.85 mg/g for Cu(II) and Cr(VI) respectively. Also, results showed that the material was recoverable and could be reused again [96].

A bionanocomposite was developed by combining chitosan, nanoclay, and biochar to discard toxic metal ions in untreated water. The composite exhibited increase in adsorption capacities of 121.50, 336.00, 134.60 mg/g for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  respectively. It was established that Freundlich isotherm model accurately described the adsorption behaviour of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , whereas Temkin model described the adsorption of  $\text{Pb}^{2+}$ . FTIR analysis suggested that the immobilization of these heavy metals takes place mainly through interactions with the  $-\text{NH}_2$  groups in the composite. The study demonstrated that modification of biochar with chitosan/clay nanocomposites significantly enhanced its ability to immobilize heavy metals [97]. Similarly, a study highlights the synthesis of composite adsorbent by combination of chitosan (Cs) with crosslinked polymethacrylic acid (PMA) and halloysite nanotube (HNT),

for eliminating Pb(II) and Cd(II) from water. At a feed amount of 100 mg/L for each metal ion, an adsorbent quantity of 0.25 g/L at pH 6, the composite having 4 wt% Cs and 3 wt% HNT demonstrated high adsorption efficiency. The adsorption capability of Pb(II) and Cd(II) in single-metal systems was 357.4 mg/g and 341.6 mg/g, respectively. However, for both metal ions as a binary mixture, these values decreased to 313.7 mg/g for Pb(II) and 303.6 mg/g for Cd(II) [98]. Gokila et al., designed chitosan-alginate nanocomposites for the separation of Cr(VI) ions from contaminated water. The adsorption equilibrium data showed a strong fit with the Freundlich isotherm, demonstrating the materials capability for multilayer adsorption. Furthermore, the chitosan-alginate nanocomposites exhibited an impressive sorption capacity, highlighting their efficiency as adsorbents. The kinetic study demonstrated that the elimination of Cr(VI) undergoes pseudo 2<sup>nd</sup> order reaction, highlighting chemisorption process [99].

**Table 2.** Performance of Chitin and Other Adsorbents in Wastewater Remediation

Heavy Metals	Types of adsorbent	Adsorption efficiency (mg/g)	Advantage	Disadvantage	Ref.
Pb <sup>2+</sup>	Chitin/lignin based material	91.74	Improved sorption capability	Moderate desorption efficiency	[100]
	Magnetic chitosan based composites	216.80	Separated easily from the aqueous medium utilizing external magnetic field, reusable till 6 cycles.	Application is restricted below pH=4	[101]
	Graphene oxide based material	75.41	Renewable, eco-friendly, and cost effective	Limited reusability	[102]
	Zeolite type adsorbent	25.88	Cost effective adsorbent	Insufficient adsorption capacity	[103]
	Magnetic carboxylated cellulose nanocrystal composite	63.78	Convenient and cost effective method of heavy metal removal	Insufficient adsorption capacity	[104]
	Magnetic montmorillonite	38.15	Widely available, large surface area	Effective at pH ~6	[105]
Ni <sup>2+</sup>	Chitin/lignin based material	70.41	Good adsorption performance	Applicable for highly acidic conditions	[100]
	Magnetic Chitosan	386.09	High adsorption capacity	After 6 cycles adsorption percentage decreases	[106]
	Magnetite graphene oxide nanocomposite	12.24	Adsorbent could be regained <i>via</i> external magnet	Applicable up to 3 cycles with low adsorption efficiency	[107]
	Zeolite adsorbents	47.00	Removal of Ni(II) is up to 94%	Very low adsorption efficiency	[108]
	Carboxymethyl cellulose adsorbent	43.68	Green and cost effective adsorbent	Low adsorption capacity	[109]
	Montmorillonite based adsorbent	8.33	Better surface area, naturally abundant	Very low adsorption capacity	[110]



Heavy Metals	Types of adsorbent	Adsorption efficiency (mg/g)	Advantage	Disadvantage	Ref.
Cu <sup>2+</sup>	Chitin based materials	110.00	Bio-degradable with high adsorption performance	Applicable for neutral pH	[111]
	Magnetic chitosan based composites	216.80	Sustainable adsorbent with high adsorption capacity	Application is restricted below pH=4	[101]
	Magnetic graphene oxide nanohybrids	51.29	Cost effective and eco-friendly method of preparation	Low adsorption capacity	[112]
	Zeolite adsorbent	15.26	Economical and abundant	Low adsorption capacity	[113]
	Carboxymethyl cellulose/clay composites	54.60	Increased mechanical and thermal properties	Low adsorption capacity	[114]
	Montmorillonite clay based adsorbent	32.36	Long pH range, No chemical treatment	Low adsorption performance	[115]

## 6. Conclusion and Future Prospects

Waste water discharged from various industries or chemical plants require immediate attention in order to decrease environmental pollution and health risks. The industrial effluents basically contain heavy metal ions, which causes serious health issues and disruption in ecological processes. Amid varied waste water treatment methods, adsorption is regarded as the most advantageous technique in competently separating heavy metal ions from wastewater. It possesses various advantages compared to other conventional techniques like availability, cost-effectiveness, high sorption capacity, selectivity and environment friendliness. Chitin-based composites/nanocomposites owing to its unique adsorption characters and functional versatility hold significant potential in the contamination of heavy metals ions from the aquatic surrounding. Chitin a naturally abundant polymer can be easily functionalized chemically or biologically into various derivatives for specific functions. Some example includes graphene oxide based chitosan, cellulose based chitin composites, chitosan magnetic adsorbents etc. The composites derived from chitin/chitosan had high mechanical and thermal properties, maximum adsorption capacity, excellent chemical stability, better reusability and high surface area. Although chitin based composites/nanocomposites have shown promising results, further research in this particular area is crucial to improve the physiochemical characters, adsorption performance, selectivity, pH range and reusability to increase its commercial application. Also, effective strategies should be adopted for the simultaneous determination of various metal ions from wastewater as there may be the possibility of having more than one metal ion in the water body. Although various chitin based materials retained their efficiencies in heavy metal removal, focus should be given to the long term stability of the adsorbents. Also, emphasis should be given in the characterization of the material so that more detailed understanding of the composite structure and adsorption mechanism can be obtained. Usually, experiments are done using aqueous solution; however, waste water containing toxic contaminants should be explored to ensure better removal

performance by the adsorbent. The utilization of chitin based materials as adsorbents have a great potential for the advancement in natural polymer based composites or nanocomposites in the context of waste water treatment. Hence, more comparative and systematic study may be required in the future to ensure large scale commercial application.

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The authors declare no conflict of interests.

### Declaration on AI Usage

The authors declare that “Artificial Intelligence (AI) tools were used in the preparation of this manuscript as follows: ChatGPT, developed by OpenAI, was utilized for grammar and language editing with all outputs reviewed and edited by the authors. The authors remain responsible for the content's integrity and originality.”

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