Review Article

Chitosan Biopolymer and Its Nanocomposites: Emerging Material as Adsorbent in Wastewater Treatment

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Water pollution is a global issue because of potentially lethal toxins. Polymeric nanomaterials are making their way into water treatment processes and are being utilized to efficiently remove a variety of pollutants. Polymeric nanomaterials are a popular option for a solution because they have a high adsorption capacity and a high surface charge. Nanocomposites have recently come to the attention of those working in the field of water treatment in order to more effectively remove contaminants. Polymeric composites are based on biopolymers and are being developed. These all quickly reached the industrial standards because of their low impact on the natural world. Chitosan is one of the biopolymers that are used extensively. Moreover, it is one of the most highly preferred biopolymers. It is simple to scale up and is readily available. The incorporation of nanomaterials into the biopolymer enables better control over the shape, size, and morphology of the particle, as well as an increase in the efficiency with which contaminants are removed. This is an excellent review that examines recent developments in the formation of chitosan-based polymeric nanocomposites and their performance in removing various contaminants including heavy metals, dyes, pesticides, pharmaceutical waste, and radionuclides from water.

1. Introduction

The increased globalization and industrialization have led to many different contaminants polluting our water sources. As the demand for pure drinking water increases day by day, the depletion of water resources leaves mankind with no other option other than the use-reuse cycle. But this gets a bit complicated as the water is polluted by many different kinds of pollutants [1, 2]. The main pollutants in water not only damage the health of people but also affect the organisms present in the water bodies [3]. Pollutants affect the plants too in the water; the presence of pollutants, or specifically dyes, hinders the penetration of sunlight, which results in less photosynthetic activity [4]. There have been many research studies carried on discussing the harmful effects of pollutants in water. Water gets polluted due to a variety of contaminants such as detergents, fertilizers, pesticides, dyes, pharmaceuticals, and heavy metals [5]. Apart from these organic pollutants such as hydrocarbons, phenols, oils, and greases are also part of the contaminants. The role of hospitals and industries in polluting the water sources are worth mentioning, leading to microbial contamination. There are
studies to date revealing the presence of microplastics in marine water [6]. And the removal of these harmful pollutants is the need of the hour. This is achieved by many different water treatment methods.

Earlier, many different processes such as ion-exchange, ultrafiltration, reverse osmosis, oxidation, flocculation, and adsorption are used. The use of membranes for the removal of pathological contaminants is also carried out. But the adsorption technique is the widely used process to remove organic, anionic, or cationic pollutants [7]. With increasing pollutants, the already present methods for water treatment have become inefficient, resulting in the need for new treatment methods. Nanotechnology with nanomaterials of innumerable characteristics can be used for the treatment of groundwater, surface water, wastewater, and other water sources contaminated by toxic pollutants [8]. The size of nanoparticles plays a crucial role in the adsorption and desorption of nanomaterials [9]. With the advent of nanotechnology, nanofiltration, nanofiber filters, and carbon nanotubes are used for remediation allowing the detoxification of contaminants [10]. Cellulosic nanomaterials are utilized as efficient nanosorbents due to its renewability, low cost, sustainability, and biodegradability [11]. The metal and metal oxide nanomaterials have also found their way into wastewater treatment and have been used for some time. Metal nanoparticles of silver, gold, and metal oxide nanoparticles of titanium dioxide, zinc oxide, and aluminum oxide are also used in disinfection and decontamination processes. The other nanoparticles used are magnetic nanoparticles, having high surface area, high reactivity, and strong adsorption capacities [12]. Magnetic nanoparticles are mostly employed for the removal of heavy metals. Nanoparticles are also used as nanoadsorbents and as components of core-shell structures [13]. Nano zero-valent iron particles are used for the remediation of groundwater which is mostly contaminated with perchlorates and hydrocarbon fluids. The advancement of nanotechnology into wastewater treatment is also visualized in the form of nanofiltration membranes [14], created from thin polymer films. Nanofiltrations are characterized by the charge-based repulsion mechanism and are applied mostly to reduce hardness, odor, color, and heavy metal ions from groundwater. Another advent of nanotechnology is the use of nanocomposite membranes, which are based on the membrane structure and location of nanomaterials. These nanocomposites are classified into conventional nanocomposites thin-film nanocomposites [10], and surface-located nanocomposites. Research is underway to enhance the use of nanotechnological products in removing micro- and nanoplastic from the drinking water [15].

Polymers gained much importance in wastewater treatment owing to its properties and versatility. Today, polymer-based nanocomposites are applied for the removal of toxic substances. Both natural and synthetic polymers are playing a key role in wastewater treatment, but natural polymers garnered much of the attention as they are cheap and more effective [10]. Natural polymers/biopolymers have specific structure, physiochemical properties, chemical stability, and high reactivity. The presence of functional groups helps in the synthesis of new bioadsorbents which shows higher affinity towards hydrocarbons and metals. Among the biopolymers, polysaccharides are put into much use due to their ecofriendly nature, biodegradability, non-toxicity, and so on. They are also capable of binding to different molecules through physical and chemical interactions [16]. This adsorption capacity makes them an ideal candidate for water treatment. Chitin and chitosan are the most studied and experimented polysaccharides for the removal of pollutants, especially water-soluble pollutants, metal ions, and organic pollutants [17]. Chitin and chitosan are also cost-effective, and hence, there is much focus on the use of these polymers.

2. Chitin

Chitin and chitosan are the second most abundant polysaccharide with distinctive chemical, physical, and biological properties. Chitin, a poly (β-(1–4)-N-acetyl-D-glucosamine), was first identified during 1884 [18]. Chitin is white, hard, and inelastic in nature. It is found as crystalline microfibrils that form certain crustaceans’ structural components and on yeast and fungi [19]. It is also found in other lower-living organisms such as house cricket (Brachytrupes portentosus) [20]. Even though chitin occurs in other living forms, it is widely extracted from crustaceans’ shell. Newer extraction processes from other living organisms are much researched due to the growing demand. Chitin, the homopolymer, occurs in 3 forms, namely, chitin-α (antiparallel chains), chitin-β (parallel chains with intrasheet H-bonding), and chitin-γ (both parallel and antiparallel chains) [21]. The third form γ-chitin is rather seen as a combination of both α and β forms. α-Chitin is mostly found in the exoskeleton of crustaceans, yeast cells, and arthropod cuticles and is the most abundant polymorph, while β-chitin is extracted from squid pens. β-Chitin can be easily converted to its α-form [22]. Chitin is insoluble in inorganic and organic solvents due to the strong inter- and intramolecular hydrogen bonding network. As chitin is insoluble, chitosan, the deacetylated product of chitin, has garnered attention and is used in most industries.

3. Chitosan

Chitosan is one of the most important derivatives of chitin and is obtained through deacetylation. Chitin is abundant in nature, but chitosan is only present in trace amounts and is derived from chitin [23]. Chitosan is a linear polymer of D-glucosamine and N-acetyl-D-glucosamine. Chitosan contains many functional groups such as amino and hydroxyl groups, the reason for its flexibility and being a choice of different applications. Morphologically, chitosan is found in many different forms like crystalline, semicrystalline, and unorganized. Its molecular weight is between 300 and 1000 kDa [24], which depends on the source of chitin.

3.1. Structure. Chitin and chitosan are similar to cellulose but differ in their properties. The molecular formula is depicted as (C₆H₁₁NO₄)ₙ [25]. Deacetylation of α-chitin
results in removing acetyl groups from chitin, thereby leading to the formation of amino groups, the end product being chitosan. Chitosan is a co-polymer of β-(1→4)-2-acetamido-D-glucose and β-(1→4)-2-amino-D-glucose N-acetyl glucosamine and glucosamine, the two usual sugars, whose proportion depends on alkaline treatment. It contains one primary amine and two hydroxyl groups for each monomer [26]. Chitosan is chemically active due to repeated primary and secondary hydroxyl groups, and an amine group on the deacetylated unit. D-glucosamine contains a free amino group, and they take up a positive charge. This attributes to the properties like antimicrobial property and solubility [26]. In solid state, chitosan is a semicrystalline polymer which is white or slightly yellow in appearance. In solid state, chitosan molecules are crystallites of high order containing two major crystalline polymorphs. Chitosan is crystalline, which makes it accessible to reagents [27]. Chitosan has two forms, namely, the hydrated form named “tendon chitosan” and the anhydrated form named “annealed chitosan.” These chitosan forms contain two antiparallel chitosan molecules accommodating a two-fold helix conformation, which is stabilized by the hydrogen bonds. Water molecules present in between the crystal cells stabilize the structure by multiple hydrogen bonds. The tendon form of chitosan can be transformed into an annealed form by heating, which is reversible [3]. Chitosan exhibits four crystalline polymorphs. The structural properties of chitosan are similar to that of chitin. As it is polycationic, it allows the formation of various complexes. Chitosan is nonthermoplastic; it degrades before melting [28]. Chitosan is insoluble in water and most organic solvents, but soluble in aqueous acid solutions such as citric, formic, acetic, and lactic acids and also in solvents like 10-camphor sulfonic acid, p-toluene sulfonic acid, and dimethyl sulfoxide. Chitosan is mainly characterized by the degree of deacetylation and molecular weight [29]. These affect the biological and physicochemical properties of chitosan. Chitosan is differentiated from chitin by its degree of N-acetylation and the presence of amino groups. When the acetylation degree is less than 50%, the polymer is chitosan [28].

4. Properties of Chitosan

Certain specific properties of chitin and chitosan make it a versatile substance for application in different fields. As chitosan is a deacetylable product, most researchers consider the product as chitosan when the degree of deacetylation is greater than 70% [28]. There is a need for a precise method to evaluate the physicochemical properties of chitosan. Most properties of chitosan are affected by the molecular weight and the degree of deacetylation. Chitosan is susceptible to chemical modifications [30]. The high charge density is pH 6.5. As chitosan has varied applications, the properties have a vital role to play on the same.

4.1. Physicochemical Properties

4.1.1. Structure. Chitosan molecules are mostly organized in highly ordered crystallites in amorphous regions. As mentioned above, two kinds of crystalline polymorphs exist: the tendon chitosan and the annealed chitosan [19]. There are reports of up to four crystalline polymorphs of chitosan with organic and inorganic acids. In these polymorphs, the anhydrous Type I salts, in the chitosan backbone chain, retain the twofold helix of the unmodified chitosan molecule. This is the Type I form, and when conformational changes occur by salt formations of types II, IIa, and III, the chains get arranged in antiparallel helicoids of the differentiated fold [30].

4.1.2. Molecular Weight. The molecular weight determines most functional properties of chitosan. Molecular weight and degree of acetylation form the most significant characteristic of chitin and chitosan. Both these make an impact on the functional properties on chitosan either in solid state or solution. Molecular weight mostly affects the hydrated colloidal forms and the viscoelastic properties of solutions [19]. Research shows that high-molecular-weight chitosan exhibits better elongation and stability than others; membrane crystallinity and molecular interactions are higher than low-molecular-weight chitosan. The molecular weight of chitosan is determined using viscometry, light scattering method, HPLC, and so on. As chitosan’s molecular weight influences the properties, chitosan may be available in the molecular weight range of 3-4 orders. The molecular weight of chitosan can be reduced by chemical, physical, or enzymatic hydrolysis [19].

4.1.3. Degree of Acetylation. The degree of acetylation determines most properties of chitosan. The most notable change is that chitosan becomes polycationic in acidic media as the amino groups are ionizable. The degree of acetylation determines most functional properties such as the extent of swelling, solubility, biocompatibility, biodegradation, and bioactivity. As the degree of acetylation is a very important criterion, it is important to determine it to analyze chitosan quality [19]. The degree of Acetylation is mostly characterized by UV spectroscopy, potentiometry, and 1H-NMR infrared spectroscopy [19].

4.1.4. Functional Properties. The above-mentioned chemical properties of chitosan contribute to distinctive properties. The N-acetyl glucosamine groups of chitosan for form hydrophobic interactions and hydrogen bonds which in turn stabilizes the molecule with supplementing rigidity and reinforcing the structure. Some functional properties of chitosan are given as follows.

4.1.5. Solubility. Chitosan is soluble in aqueous media; it is considered a weak base. This is because the amino groups distributed in the chitosan molecule are protonated, getting a charge density as high as one cationic charge per
glucosamine unit. Diluted inorganic acids except sulfuric acid are suitable solvents for chitosan [19]. Chitosan is insoluble in nonpolar organic solvents. Chitosan thermally degrades before attaining the glass transition phase, and hence, the preparation of gels, sponges, films, fibers, and so on is carried out through chitosan solutions [19].

4.1.6. Adsorption Capacity. The process involving ionic, hydrogen, hydrophobic bonding, or Van der Waals force is known as adsorption. The functional groups of chitosan generate interactions with various molecules. Adsorption capacity depends on its physicochemical characteristics and the characteristic of the adsorbate. Chitosan is known for its adsorption capacity towards metal ions and is hence used in various waste management systems [31].

4.1.7. Viscosity. Viscosity determines the extent of penetration, and the molecular weight plays a significant role in determining the viscosity. Viscosity increases with the degree of acetylation. It decreases with storage time and temperature and also in the presence of an electrolyte. When the particle size is lesser, the viscosity is lower [32].

4.2. Biological Properties. The biological properties exhibited by chitosan are mostly due to the physicochemical properties. They are nontoxic, biodegradable, and biocompatible and have high humidity adsorption. Chitosan is biodegradable naturally by enzymes such as chitinases and chitobiases which are found in prokaryotes and higher animals. Chitosan is considered biocompatible as it does not hamper the living systems which come in close contact to it. The toxicity LD50 is about 16 g/kg similar to salt and sugar toxicity [28]. The biocompatibility of chitosan attributes to the presence of N-acetyl glucosamine which is structurally similar to glycosaminoglycans. The bioactivity of chitosan is another aspect of interest. Chitosan exhibits varied biological activities including antibacterial, antiviral, and antifungal, which are of biomedical interest [33].

5. Extraction of Chitin and Chitosan

5.1. Extraction of Chitin. Chitin and chitosan are extracted mainly by two methods: chemical and biological methods. The factors and conditions that control chitin’s characteristics are purity, degree of deacetylation, polydispersity index, and molecular weight [28]. The major sources for the production of chitin and chitosan are the crustaceans mainly crab and shrimp. Also, they are found in the cell wall of certain fungi and insects. The chemical extraction method is highly applied for commercial purpose even though it affects the properties of chitin and is hazardous to the environment. The chemical extraction method is given in Figure 1.

The chemical extraction method involves the following steps: deproteinization, demineralization, and discoloration. Deproteinization involves the depolymerization of the biopolymer using chemicals to break the chemical bond between the protein and the chitin [34]. Many types of chemicals such as NaOH, KOH, and Na₂CO₃, and are used as deproteinizing agents, and the reaction condition may vary for each of them. NaOH is most commonly used, resulting in partial deacetylation of chitin and lowers the molecular weight by the biopolymer’s hydrolysis. The next step is the demineralization, where minerals mainly calcium carbonate is removed by the treatment of strong acids. The acids commonly used are H₂SO₄, HNO₃, HCl, HCOOH, and CH₃COOH [35]. This process release of carbon dioxide occurs by the decomposition of calcium carbonate into calcium salts by treating with hydrochloric acid [36]. Following this is the discoloration process, which is the additional step in the extraction process. This is done to remove the pigments such as β-carotene and astaxanthin from the extraction source to get the colorless product. Organic or inorganic solvents such as sodium hypochlorite, hydrogen peroxide, and acetone are used for this purpose.

Figure 1: Schematic representation of chemical extraction of chitin.
Due to certain drawbacks in the chemical extraction process, the biological method thrives more attention in selecting the utilization of enzymes and microorganisms to extract chitin [37]. This method is ecofriendly and does not alter the structure of chitin. In this method, deproteination is employed by using proteolytic microorganism (Figure 2). The most widely employed methods for chitin extraction are enzymatic deproteinization and fermentation using microbes [38]. Enzymatic deproteinization involves removing protein during the extraction of chitin using the proteolytic enzyme such as proteases. The primary sources of proteolytic enzymes are plants, animals, and microbes. In this process, various proteases are pepsin, alkalize, trypsin, papain, pancreatein, and so on [39].

Fermentation using microorganism is another process involved in this method of extraction. Here, the specific microbe can be selected and used for this process, and involves two types of approaches: lactic acid fermentation and nonlactic acid fermentation. In lactic acid fermentation, Lactobacillus sp. strain is used where lactic acid is acquired by modifying the glucose with a subsequent decrease in pH that prohibits the growth of spoilage microorganisms. Lactic acid thus reacts with calcium carbonate and forms calcium lactate precipitate, recovered and washed with water. Many factors such as the carbon source and its concentration, temperature, amount of the inoculum, and water are involved. Various features may influence the fermentation process, thereby increasing deproteination and demineralization efficiencies [33].

6. Conversion of Chitin to Chitosan
Chitosan is the polymers’ family obtained by the deacetylation of chitin using acid solution treatment and alkaline hydrolysis. Here to chitin can be converted to chitosan by either chemical or enzymatic [41]. In the chemical deacetylation process, chitin is deacetylated with the help of alkali or acids. Since glycosidic bonds are susceptible to acids, alkali deacetylation is more commonly used [42]. The deacetylation process is accomplished either by homogeneous or heterogeneous methods. In the heterogeneous method, chitin is added with hot concentrated NaOH for a few hours, and thereby the insoluble chitosan is obtained, which is deacetylated up to 85%–99%. In the homogeneous method, chitin is dispersed in concentrated NaOH at about 25°C for about 3 hours to prepare alkali chitin and then suspended in crushed ice at 0°C. Here, soluble chitosan, which is deacetylated up to 48–55% is obtained. The alteration in chitosan preparation may result in changes in viscosity, acetyl group distribution along the chain, molecular weight, etc. [43]. In the enzymatic deacetylation process, chitin is deacetylated with the help of the enzyme chitin deacetylase. This enzyme hydrolyses the N-acetamido bonds in chitin to form chitosan. Nevertheless, this enzyme was less effective in the naturally occurring chitin, which is crystalline and insoluble. To overcome this, crystalline chitin undergoes certain pretreatments such as grinding, heating, and sonication. The carbon and hydrogen structures are given in Figure 3(a) and the mechanism of chitin is given in Figure 3(b).

6.1. Chitosan Modification. Chitosan is a unique cationic polysaccharide which can be easily functionalized to different derivatives by chemical, radiation, and enzymatic methods (Figure 4). Of these various modification techniques, chemical modification technique is more widely employed. Even though chitosan has many functional properties and other biological activities, its application is limited due to its low solubility owing to its rigid crystalline structure. This problem can be overcome by modifying chitosan by chemical or other enzymatic methods to produce new derivatives. The molecular weights, degree of deacetylation, and crystallinity are the main features in chitosan, where the modification could be done to form a difference in their physiochemical properties [29].

The chemical modification could enhance the physical and chemical properties because of the hydroxyl and amino groups in chitosan. The most commonly used chemical alteration of chitosan is N-substitution, where the functional group of chitosan that reacts is the amino group. Also, O-substitution is often employed. The chemical reactions involved in this modification are quaternization, acylation, alkylation, phosphorylation, hydroxylation, graft copolymerization, and so on [45]. A chemical modification also retains the essential properties of chitosan and increases the chitosan derivatives’ application.

The most commonly used chemical modifications of chitosan are as follows: (i) N-substitutions without protective agents, where the amino group is transformed to quaternary ammonium salts through the chemical reaction with quaternary phosphonium or quaternary ammonium compounds, resulting in the formation of derivatives with enhanced water solubility and biological properties due to the positive charge which is permanent on the polymer. N, N, N'-Trimethyl chitosan chloride (TMC) is one of the most crucial quaternary chitosan derivatives [46]. The additional method applied is N-alkylation and N-arylation accomplished by the Schiff base intermediates between the amino group of chitosan and the aldehyde and ketone accompanied by Schiff’s reduction base intermediates. N-phosphorylation is also another crucial reaction for improving the chemical and biological property of chitosan. (ii) N-substitution using protective agents, where the -OH groups are protected by the chemoselective methods to synthesize homogeneous N-quaternized chitosan derivatives [46]. (iii) O-substitution using protective agents, here, chemical modification intrudes with the amino group of chitosan which would influence the bioactive properties. In such a manner, N-phthaloylation with phthalic anhydride enables chemical modification because of the phthaloyl group becomes deprotected efficiently to rejuvenate the free amino groups, enhancing the solubility of chitosan [47]. (iv) N, O substitutions, where the process involved is carboxylation, which is performed in two ways i.e., C6-hydroxyl oxidation and C2-amino substitution to make the insoluble chitosan to...
soluble ones. (v) Cross-linking reaction of chitosan, where the cross-linking agents generate ionic bonds or physical cross-linking resulting in a strong three-dimensional structure. Low-molecular-weight chitosan is subjected to cross-linking to obtain appropriate structural, thermal, and mechanical properties [48].

Chitosan is chemically modified by attaching photosensitizers, sugars, dendrimers, crown ethers, and cyclodextrins onto the polymer backbone. Photosensitizers are utilized when the light of a certain wavelength which is not readily available is required for a reaction. Even though synthetic polymers are mostly employed, in the year 1980, Tanaka et al. have reported the first synthesized photosensitive polymer derived from chitosan and from then, several studies were reported about its production [49]. The photoactive biopolymer can be employed as a biomineralization tool exploiting their photoexcitation mechanism in dental/bone repair. Dendrimers are members of polymers which are symmetrical macromolecules and are highly branched with multifunctional properties. The polymers could be dendronized through two approaches; they are attached to the to-process and macromonomer process. Dendronized chitosan was found to be very effective as a nonviral gene delivery vector [50].

Modifications of chitosan using
Cyclodextrins are done to combine the chitosan characters and properties of cyclodextrins altering their physical and chemical properties. Moreover, the modification of chitosan achieved by radiation includes radiation-induced polymerization, radiation cross-linking, and changes in the polymers’ morphology. Various other modifications are:

**Figure 3:** (a) Conversion of chitin to chitosan (molecular structural representation) [44]. (b) Pictorial representation of mechanism of chitin to chitosan conversion.
enzymatic modification, plasma-induced modification, etc. [28].

Chitosan and the modified derivatives are utilized in various fields. Due to the lack of toxicity, biodegradability, biocompatibility, and low allergenicity, chitosan derivatives are applied for various purposes. Due to these biological properties, they are utilized in drug delivery, and this nanoparticulate drug delivery is well suited for the treatment of various types of cancer [51]. Chitosan and its derivatives can also be utilized as an essential element in tissue engineering due to their ease of chemical modification, porous structure, and gel formation [4]. It is also employed in cosmetics for oral health care, hair care, and skin. They may also exhibit antimicrobial, antioxidant, and anti-inflammatory activities [52].

7. Chitosan Nanocomposites

Nanocomposites are multiphasic materials, where at least one phase has a dimension in the range of 10–100 nm. In short, nanocomposites are building blocks with dimensions in the nanometer range with unprecedented flexibility and improvement in their physical properties. Nanocomposites’ properties have substantial improvements due to the dissimilarities of the structure and chemistry [53]. Nanocomposites show increased thermal stability, mechanical properties, permeability, electrical conductivity, enhanced optical clarity, surface appearance, and increased chemical resistance. Nanocomposites are produced by blending fullerenes, inorganic nanoclusters, metal oxides, semiconductors, or clays with biological molecules, organic polymers, organometallic compounds, and sol-gel-derived polymers [54]. Nanocomposites are classified into polymer-based nanocomposites and nonpolymer-based nanocomposites. Polymer nanocomposites are further divided as ceramic, organic/inorganic, organic/inorganic-hybrid, and layered silicate. Nonpolymer-based nanocomposites are further classified as metal nanocomposite, ceramic nanocomposite, and ceramic-ceramic nanocomposite [34].

Recent improvements have led to the emergence of chitosan-based nanocomposites, wherein both the polymer and nanoparticle contribute to specific properties. The presence of nanoparticle in the chitosan polymeric matrix improves its intrinsic properties such as mechanical, chemical, and physical stability. It also endows chitosan with extraordinary physicochemical properties and high surface area. Chitosan nanocomposites are mostly created between chitosan and carbon, clay, polymer, metal/metal oxide materials through chemical or physical interactions [32]. The nanocomposite classification is given in Figure 5.

Chitosan nanocomposites are synthesized through both wet and dry methods. Most metal-chitosan nanocomposites are synthesized using related reducing salts. The physical method of polymer modification is the easiest process, where two or more polymers are blended to form a new material showcasing different physical properties [32]. Different physical methods such UV, radiolysis, and sonochemistry are employed for physical methods. Under chemical methods, electrochemical irradiation, chemical reduction, thermal decomposition, and green chemistry are the approaches undertaken to create chitosan nanocomposites [30]. Biosynthesis of chitosan nanocomposites is also much appreciated and used method due to the cons of physical and chemical methods. Nanocomposite preparation and their application are given in Figures 6 and 7.

8. Chitosan Nanocomposites for Wastewater Treatment

Chitosan by itself was used in water purification processes for many years. Chitosan effectively removes heavy metals, oil spills, and fine particulate matter from wastewater [19]. Also, chitosan and its derivatives have higher adsorbing and chelating effects and can adsorb or capture heavy metals. Chitosan also effectively absorbs radioactive elements. And, chitosan is a natural polymer floculant which helps in flocculating the active ingredients for reuse [11]. This led to chitosan being used along with nanoparticles to form nanocomposites for wastewater treatment. Chitosan-based materials are of much focus as the functional nanoparticles in them are used in both environmental and other applications. Chitosan nanocomposites are used in wastewater treatment from the removal of different pollutants which cause harmful effects to the environment and the population. Some aspects of chitosan nanocomposite and the different pollutants they remove are discussed here, along with the recent advancements in the particular area.

8.1. Heavy Metals. Heavy metals also known as trace elements or metallic elements, are elements that have an atomic density of 6 g/cm³ or greater. The most toxic heavy metals that pose serious risk to the environment present in the wastewater are lead, arsenic, cadmium, chromium, copper, nickel, zinc, silver, and so on [55]. Along with causing environmental and health issues, it also creates an upsurge in the treatment costs of wastewater. Many different adsorbents are used for effective removal of heavy metals, but with the recent trends in nanotechnology, and the modifications of natural polymers, chitosan nanocomposites are used effectively to remove heavy metals. This is because chitosan is nontoxic and alkali- and corrosion-resistant. The presence of active groups of chitosan effectively adsorbs the heavy metals, and when coupled with nanoparticles, chitosan composites can be recycled.
Nano particle synthesis

Polymer based

Organic/inorganic polymer

Organic/inorganic-hybrid

Ceramic/polymer

Layered silicate

Non-polymer based

Metal nanocomposite

ceramic nanocomposite

ceramic-ceramic nanocomposite

Top down approach (size reduction)

Physical method

Mechanical method

Mechanical/Ball milling

Chemical method

Vapour method

Thermal/Laser ablation sputtering

Bottom up method (clustering smaller particles)

Chemical method

Chemical etching

Chemical/Electrochemical Precipitation

Vapour deposition

Atomic/molecular condensation

Sol-gel process

Spray-pyrolysis

Laser-pyrolysis

Aerosol-pyrolysis

Biological method

Green synthesis

Plants and their extracts

Microorganisms-Bacteria and fungus

Figure 5: Pictorial representation of nanocomposite classification.

Figure 6: Pictorial representation of various methods of chitosan nanocomposites preparation.
Lead, which is widely used in the electroplating and metallurgy industries, and also other industries contaminates the water and remains in the environment indefinitely. Hence, there is a need to recover lead from contaminated water. Lead remains in the environment. While combining polyacrylic acid along with chitosan, the acidity resistance increases and with the incorporation of a magnetic nanoparticle, a magnetic nanocomposite is formed. This magnetic nanocomposite formed showed higher adsorption activity with a maximum adsorption capacity of 204.89 mg/g. The reaction followed a pseudo-second-order kinetics and fitted the Langmuir isotherm model [11]. Removal of lead, cadmium, and mercury ions from continuous flowing wastewater was a challenge, and this was made possible with taking inspiration from nacre. A multilayered hydroxyapatite/chitosan composite had high mechanical strength and could withstand high pressure while effectively adsorbing the heavy metal ions. Efficient removal of lead ions was noticed in this study [11].

Hexavalent chromium is mutagenic. Chromium also causes diarrhea, kidney dysfunction, and stomach cramps. It also affects the aquatic life. Effective adsorption of chromium was noticed while using chitosan-MnO₂ nanocomposite with a maximum adsorption capacity of 61.56 mg/g. Chromium adsorption includes both monolayer and multilayer adsorptions. Effective adsorption of chromium is due to the electrostatic attraction between the positive charge on the surface of the nanocomposite and the anions of chromium [57]. Effective removal of chromium was also observed while using two different functionalized nanocomposites with an adsorption capacity of 61.35 mg/g and 58.14 mg/g [58]. Removal of chromium was also facilitated using triethylene tetramine-modified hollow Fe₃O₄/SiO₂/chitosan magnetic nanocomposites which were created the facile way. The adsorption capacity exhibited was notable and was higher than most adsorbents [58]. Removal of different heavy metal ions such as Pb (II), Cd (II), and Hg (II) were carried out with chitosan-boehmite desiccant nanocomposite which was synthesized using one pot sol-gel route. This particular nanocomposite is reusable and has excellent adsorption capacities [58]. Arsenic causes many health hazards and constant inhalation of Arsenic leads to skin cancer. Effective adsorption of Arsenic from aquatic environment was observed while using a goethite/graphene oxide/chitosan nanocomposite with a maximum adsorption capacity of 289.42 mg/g, as given in Table 1.
<table>
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<tr>
<th>Nanocomposite</th>
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<th>Isotherm model</th>
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<td>Modified chitosan cinnamaldehyde nanocomposite</td>
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<td>Sm (III)</td>
<td>650 μg/mol</td>
<td>Langmuir-freundlich</td>
<td>Pseudo-first-order</td>
<td>30 min</td>
<td>[62]</td>
</tr>
<tr>
<td>Triethylenetetramine-modified hollow Fe₃O₄/SiO₂/chitosan</td>
<td>Cr (VI)</td>
<td>254.6 mg</td>
<td>Langmuir</td>
<td>Pseudo-second-order</td>
<td>15 min</td>
<td>[63]</td>
</tr>
<tr>
<td>magnetic nanocomposites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chitosan-boehmite desiccant composite</td>
<td>Pb (II), Gd (II),</td>
<td>—</td>
<td>Langmuir</td>
<td>Pseudo-second-order</td>
<td>—</td>
<td>[64]</td>
</tr>
<tr>
<td>Hg (II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chitosan modified molybdenum disulfide composites</td>
<td>Eu (III)</td>
<td>0.86 mmol/g</td>
<td>Langmuir</td>
<td>—</td>
<td>240 min</td>
<td>[65]</td>
</tr>
<tr>
<td>Magnetite modified chitosan cinnamaldehyde</td>
<td>Cr (VI)</td>
<td>58.14 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>80 min</td>
<td>[66]</td>
</tr>
<tr>
<td>nanocomposite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nacre-inspired hydroxyapatite/chitosan layered composites</td>
<td>Pb (II), Gd (II),</td>
<td>—</td>
<td>Elovich</td>
<td>Pseudo-first and</td>
<td>6 days</td>
<td>[22]</td>
</tr>
<tr>
<td>Hg (II)</td>
<td></td>
<td></td>
<td></td>
<td>second-order</td>
<td></td>
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</tr>
<tr>
<td>Goethite/graphene oxide/chitosan nanocomposite</td>
<td>As (III)</td>
<td>289.42 mg/g</td>
<td>Freundlich and sips</td>
<td>Pseudo-second-order</td>
<td>3000 min</td>
<td>[51]</td>
</tr>
<tr>
<td>models</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTiO₂-chitosan@NZrO₂-chitosan nanocomposite</td>
<td>Gd (III)</td>
<td>450 μg/mol</td>
<td>Langmuir-Freundlich</td>
<td>Pseudo-first-order</td>
<td>20 min</td>
<td>[62]</td>
</tr>
<tr>
<td>Chitosan modified molybdenum disulfide composites</td>
<td>Cr (IV)</td>
<td>3.04 mmol/g</td>
<td>Langmuir</td>
<td>—</td>
<td>180 min</td>
<td>[65]</td>
</tr>
<tr>
<td>Melamine grafted chitosan-montmorillonite nanocomposite</td>
<td>Fe³⁺</td>
<td>125.79 mg/g</td>
<td>Freundlich</td>
<td>Pseudo-second-order</td>
<td>120 min</td>
<td>[66]</td>
</tr>
<tr>
<td>Chitosan modified molybdenum disulfide composites</td>
<td>U (VI)</td>
<td>0.71 mmol/g</td>
<td>Langmuir</td>
<td>—</td>
<td>120 min</td>
<td>[65]</td>
</tr>
</tbody>
</table>
This was due to the presence of O–NHCO–, C=O, O–H, and Fe–O groups, but the major contributor was the complexion between as (III) ions and hydroxyl iron oxide [67]. Removal of trivalent gadolinium and samarium ions was done effectively by green synthesized novel NTiO2-Ch@NZrO2-chitosan nanocomposite. This nanocomposite has good sorption properties [62]. Ferric ion adsorption with the help of melamine grafted nanocomposite synthesized through graft polymerization showed effective adsorption capacities. Water contaminated with uranium causes deformity of bones and chronic kidney disease. Effective removal of U (VI), Eu (III), and Cr (VI) were carried out using chitosan modified molybdenum disulfide prepared through disulfide method. The removal of the metal ions is mainly due to the electrostatic attraction between the hydroxyl and the amidogen group [65].

8.2. Dye Removal. Dyes are used in many industries such as printing, textile, and painting which are the root causes for contaminating the water [68]. Most of the dyes that enter the water environment are toxic and may affect the photosynthetic activity by reducing the sunlight penetration that negatively affects the aquatic life and human life. So, it is essential to remove these dyes and protect the environment. For this, several physical, chemical, and biological methods are employed. Of these methods, adsorption is considered to be the most common physicochemical method used for this purpose. Various adsorbents are used for the dye removal; among them, chitosan is used due to the presence of its functional group and an abundant biopolymer in nature. It also undergoes several modifications and combines with other nanoparticles to form nanocomposite to overcome its various limitations.

Remazol brilliant blue R dye (RBBR) is a harmful dye from the textile industry which affects the aquatic life, and therefore, it is necessary to remove it from the contaminated water. For this, a desired and recoverable bioadsorbent was developed that is a new magnetic Schiff’s base-chitosan-benzil/zinc oxide/Fe3O4 nanocomposite. In addition to various adsorption parameters, parametric optimization by Box–Behnken design was done to optimize the synthesis condition. Here, the maximum adsorption capacity was found to be 620.5 mg/g, and the kinetic and isotherm models were the pseudo-second-order kinetic model and Freundlich model [65]. Acid blue 25 is an anionic dye that could be removed from the contaminated water with chitosan polymeric nanocomposite (CS-PVA@CuO). Here, the adsorption kinetics fits into the pseudo-second-order model and the maximum adsorption capacity are 171.4 mg/g. Also, the adsorption isotherm fits the Langmuir model [69].

Direct red 81 is a toxic sulphonated azo dye present in the contaminated water removed with the help of the adsorbent chitosan/zero-valent nanocomposite (CS-nZVI). The adsorption isotherm fits into the Freundlich model, and the kinetics are the pseudo-first-order [70]. Congo red is another dye that is present in the water that is very toxic to human, on entering the human body. This dye gets metabolized to benzidine, a carcinogen to humans and should be removed from the water. The adsorbent ZnO/chitosan nanocomposite was created by the in-situ precipitation method. When coming in contact with the dye, the adsorbent gets adsorbed in a single monolayer, and its maximum adsorption capacity was found to be 227.3 mg/g. It was also found that the Congo red adsorption was better exhibited by the Langmuir model [71]. Reactive red 120(RR120) dye is another dye found in the aqueous environment and could be removed with the help of a bio adsorbent hybrid cross-linked chitosan-epichlorohydrin/TiO2 nanocomposite (CTS-ECH/TNC) which is an inorganic-organic hybrid nanocomposite. The adsorption data are finely demonstrated by pseudo-second-order kinetic and the Langmuir isotherm model. The maximum adsorption capacity of CTS-ECH/TNC for the dye RR120 was found to be 210 mg/g [72]. Malachite green is a cationic dye which is eluted from the contaminated water with the help of the adsorbent chitosan–zinc oxide composite. The isotherm model fits into Langmuir model and shows an adsorption capacity of 11 mg/g. The adsorption kinetics was found to be a pseudo-second-order model [73]. Methyl orange is one of the most stable azo dye presents in the wastewater. The removal of this dye is done with the help of chitosan-silica nanocomposite. The process of adsorption best fits with the Langmuir model with the maximum adsorption capacity of 7 mg/g [74]. Methylene blue is a cationic dye which on the accumulation in wastewater causes many adverse effects to both human and the water environment. Chitosan/silica/ZnO nanocomposite is an adsorbent used to remove this dye from the contaminated water. Here, the adsorption isotherm fit with the Langmuir model and the followed adsorption kinetics are the pseudo-second-order model. The maximum adsorption capacity is 293.3 mg/g [75]. Rose Bengal is an anionic dye which is present in the industrial wastewater. This dye is removed with the help of molecularly imprinted polymer (MIP) and chitosan-TiO2 nanocomposite (CTNC). Here, the maximum adsorption capacity of the dye was found to be 79.369 mg/g. Also, the equilibrium data best fit to the Langmuir model and follows pseudo-second-order kinetics [76]. Direct blue 71 (DB71) and reactive blue 19 (RB19) are the two dyes that are adsorbed from the aqueous environment with the help of magnetic nanocomposite of chitosan/SiO2/CNTs (MNCSC). It was analyzed that the isotherm model is well fitted with the Langmuir model, and the kinetics are the pseudo-second-order model. The adsorption capacity of MNCSC for DB71 is 61.35 mg/g and for RB19 is 97.08 mg/g (Table 2) [78].

9. Other Contaminants

9.1. Pesticides. Pesticides used for plant and crop protection have resulted in yielding healthy and fruitful crops while polluting the environment [56]. The presence of pesticides poses adverse effects that vary with the concentration, contact time, and amount. These contaminants cause severe health hazards for humans too such as cancer, malformation, infertility, and DNA mutation [79]. Pesticides include insecticides, fungicides, biocides, and rodenticides [7]. The
Table 2: Different chitosan nanocomposites for removal of harmful dyes.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Dye</th>
<th>Adsorption capacity</th>
<th>Isotherm model</th>
<th>Kinetics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan-benzil/zinc oxide/Fe₃O₄ nanocomposite</td>
<td>Remazol brilliant blue R (RBBR)</td>
<td>620.5 mg/g</td>
<td>Freundlich model</td>
<td>Pseudo-second-order</td>
<td>[77]</td>
</tr>
<tr>
<td>Chitosan polymeric nanocomposite (CS-PVA@CuO)</td>
<td>Acid blue 25</td>
<td>171.4 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>[69]</td>
</tr>
<tr>
<td>Chitosan/zero-valent nanocomposite (CS-nZVI)</td>
<td>Direct red 81</td>
<td>61.35 mg/g</td>
<td>Freundlich model</td>
<td>Pseudo-first-order</td>
<td>[70]</td>
</tr>
<tr>
<td>Zinc oxide/chitosan nanocomposite</td>
<td>Congo red</td>
<td>227.3 mg/g</td>
<td>Langmuir model</td>
<td>—</td>
<td>[71]</td>
</tr>
<tr>
<td>Chitosan-epichlorohydrin/TiO₂ nanocomposite (CTS-ECH/TNC)</td>
<td>Reactive red 120</td>
<td>210 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>[72]</td>
</tr>
<tr>
<td>Chitosan-ZnO composite</td>
<td>Malachite green</td>
<td>11 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>[73]</td>
</tr>
<tr>
<td>Chitosan-silica nanocomposite</td>
<td>Methyl orange</td>
<td>7 mg/g</td>
<td>Langmuir model</td>
<td>—</td>
<td>[74]</td>
</tr>
<tr>
<td>Chitosan/Silica/ZnO nanocomposite</td>
<td>Methylene blue</td>
<td>293.3 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>[75]</td>
</tr>
<tr>
<td>Molecularly imprinted polymer (MIP) chitosan-TiO₂ nanocomposite (CTNC)</td>
<td>Rose bengal</td>
<td>79.365 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>[76]</td>
</tr>
<tr>
<td>Magnetic nanocomposite of chitosan/SiO₂/CNTs (MNCSC)</td>
<td>Direct blue 71 (DB71) reactive blue 19 (RB19)</td>
<td>97.08 mg/g</td>
<td>Langmuir model</td>
<td>Pseudo-second-order</td>
<td>[78]</td>
</tr>
</tbody>
</table>
presence of residues and metabolites of the pesticides impacts the water environment adversely. Many different processes show different approaches for the removal of these contaminants. Recently, there is much focus on the use of biopesticides for plant growth, but most botanicals are hydrophobic in nature, and using large amounts of organic pollutants to dissolve them again pollutes the environment. Adsorption is the most widely used process for pesticide removal. The use of chitosan nanocomposite is one such effective process for pesticide removal owing to chitosan’s high adsorption capacity due to the open groups.

Adsorption is the most widely used process for pesticide removal. The use of chitosan nanocomposite is one such effective process for pesticide removal owing to chitosan’s high adsorption capacity due to the open groups present [80].

Rotenone, a colorless, odorless, and isoﬂavone is a broad-spectrum insecticide. This insecticide is also toxic to fish and humans. The toxicity of rotenone is more signiﬁcant depending on the particle’s size, if the particle is smaller in size higher is the toxicity. Chitosan-graphene oxide nanocomposites exhibited better adsorption through the interactions between the hydrogen bonds of CS-GO nanocomposites and rotenone [7]. Organophosphate pesticides are used worldwide. They are toxic and work by damaging the enzyme system, which controls the nerve signals of the body. Adsorption of organophosphate pesticides with MIL-88(Fe) anchored TiO$_2$-chitosan (2D/2D) hybrid nanocomposite was achieved, where the reaction was oxidation reaction involved [81]. Methyl parathion, an organophosphate insecticide, can target organ damage on repeated exposure and is much toxic to aquatic life. Effective adsorption of methyl parathion pesticide was carried out using the two-hybrid polymers of bentonite intercalated with chitosan [82]. Organic herbicides are mostly non-selective; they kill fish and plants that come into contact while in a water body. An ionic liquid-modiﬁed chitosan/metal-organic framework composite was used to adsorb organic herbicides effectively. The adsorption process was found to be facilitated with the help of hydrogen bonding and electrostatic interaction [83]. Tricyclazole, a fungicide is used to protect rice but causes increased organ weight and decreased body weight. Chitosan-based magnetic molecularly imprinted polymer selectively recognizes and adsorbs tricyclazole from the water sample. This polymer was highly selective and speciﬁc [84, 85].

9.2. Pharmaceutical Wastes. Water contamination with many pharmaceutical wastes is becoming one of the signiﬁcant environmental issues caused due to their ecotoxicity accompanied by several health issues. The most commonly present pharmaceuticals in the wastewater are antibiotics, steroids, antidepressants, tranquillizers, analgesics, stimulants, and so on. Among the various removal methods, adsorption is found to be more effective for the removal of these compounds. Recently, chitosan-based nanocomposite is used as an ecofriendly biopolymer that shows effective adsorption of these pharmaceutical materials.

Oﬂoxacin is an antibiotic present in the wastewater mainly from the hospital wastes and may cause toxicity and affect the biological environment. Therefore, it is essential to remove this oﬂoxacin with the adsorbent horseradish peroxide immobilized chitosan graphene oxide nanocomposite (HRP-CsGO). Here, the adsorption kinetics and isotherm model ﬁts the pseudo-second-order and Langmuir model with the maximum adsorption capacity of 378 mg/g [86]. Metronidazole is another antibiotic present in the water which is effectively adsorbed with the help of Fe$_3$O$_4$-chitosan nanoadsorbent. Here, the adsorption maximum was 97.06 mg/g with Freundlich isotherm and pseudo-second-order kinetics [87]. Tetracycline is a commonly used antibiotic and is frequently found in the aquatic environment. This could be removed using a magnetic nanocomposite that is fabricated using chitosan, thiobarbituric acid, malondialdehyde, and Fe$_3$O$_4$ nanoparticles (CTM@Fe$_3$O$_4$). The nanocomposite shows an adsorption maximum of about 215.31 mg/g and the follows kinetic and isotherm are pseudo-second-order kinetic and Langmuir isotherm models [51].

Estradiol, one of the steroid hormones present in the wastewater, could be removed with the help of the chitosan/Al$_2$O$_3$-HA (hydroxyapatite) composite beads. The adsorbent shows a maximum adsorption capacity of about 39.78 mg/g which ﬁts into Langmuir and pseudo-second-order kinetics [1]. Diclofenac sodium is a nonsteroidal anti-inﬂammatory drug which could be adsorbed from the contaminated water with the AmCS@Fe$_3$O$_4$ composite (amine-functionalized chitosan (amino chitosan; AmCS) and Fe$_3$O$_4$). The corresponding isotherm is Langmuir, and the kinetics is the pseudo-second-order model with the maximum adsorption of 469.48 mg/g [29].

9.2.1. Fluoride. Fluoride ions are essential for the normal functioning of the human body, but exposure to the same beyond the recommended levels results in various health disorders. Excess fluoride can cause structural damage and to ligaments. Removal of fluoride was carried out with different physical and chemical methods earlier [88]. Recently, naturally occurring materials like clay and zeolites combined with biopolymers are used for removing the same. Glaucnite clay-functionalized chitosan nanocomposites prepared through simple blending and cross linking method showed effective adsorption of fluoride ions through physisorption process [89]. Chitosan-based magnetic nanocomposites containing Fe$_3$O$_4$@TiO$_2$ nanoparticles also exhibited effective adsorption of fluoride ions from water through the electrostatic and hydrogen bonding interactions [90]. The removal of groundwater fluoride with the help of chitosan-modiﬁed ZnO/ZnFe$_2$O$_4$ nanocomposites showed excellent adsorption properties. The process was spontaneous and endothermic. The morphology and the structural properties of the nanocomposites play a major role in adsorption [91].

9.2.2. Radionuclides. Radionuclides are radioactive atoms and are released from nuclear power plants. The most commonly found radionuclides in water are uranium, radon, and radium. Exposure to this ionizing radiation causes many different forms of cancer such as stomach, lung, and bone. Chitosan nanocomposites for adsorbing different
<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Contaminant</th>
<th>Kinetics</th>
<th>Isotherm model</th>
<th>Adsorption capacity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan-graphene oxide nanocomposites</td>
<td>Rotenone (pesticide)</td>
<td>Pseudo-first-order</td>
<td>Langmuir</td>
<td>92.59 mg/g</td>
<td>[93]</td>
</tr>
<tr>
<td>MIL-88(Fe) anchored TiO$_2$-chitosan(2D/2D) hybrid nanocomposite</td>
<td>Organophosphate (pesticide)</td>
<td>Pseudo-first-order</td>
<td>Langmuir–Hinshelwood</td>
<td>—</td>
<td>[81]</td>
</tr>
<tr>
<td>Chitosan and 2-hydroxyethyl methacrylate/methyl methacrylate-bentonite-based nanocomposite</td>
<td>Methyl parathion (pesticide)</td>
<td>Pseudo-first-order</td>
<td>Freundlich</td>
<td>868.5 mg/g</td>
<td>[82]</td>
</tr>
<tr>
<td>Chitosan/metal-organic framework composite</td>
<td>Organic pesticides (pesticide)</td>
<td>Pseudo-second-order</td>
<td>Temkin</td>
<td>—</td>
<td>[83]</td>
</tr>
<tr>
<td>Chitosan-based magnetic molecularly imprinted polymer</td>
<td>Tricyclazole (pesticide)</td>
<td>Pseudo-second-order</td>
<td>Freundlich</td>
<td>4579.9 μg/g</td>
<td>[84]</td>
</tr>
<tr>
<td>Horseradish peroxidase immobilized onto CsGON (HRP-CsGON)</td>
<td>Oloxacin (antibiotic)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>378 mg/g</td>
<td>[86]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-chitosan nanoadsorbent</td>
<td>Metronidazole (antibiotic)</td>
<td>Pseudo-second-order</td>
<td>Freundlich model</td>
<td>97.06 mg/g</td>
<td>[87]</td>
</tr>
<tr>
<td>CTM@Fe$_3$O$_4$ nanocomposite</td>
<td>Tetracycline (antibiotic)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>215.31 mg/g</td>
<td>[51]</td>
</tr>
<tr>
<td>chitosan/Al$_2$O$_3$-HA composite beads</td>
<td>Estradiol (steroid)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>39.78 mg/g</td>
<td>[1]</td>
</tr>
<tr>
<td>AmCS@Fe$_3$O$_4$composite</td>
<td>Diclofenac sodium (nonsteroidal anti-inflammatory drug)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>469.48 mg/g</td>
<td>[29]</td>
</tr>
<tr>
<td>Silica-chitosan nanocomposite</td>
<td>$^{152+154}$Eu (radionuclide)</td>
<td>Pseudo-second-order</td>
<td>Langmuir - Freundlich models</td>
<td>160 mg/g</td>
<td>[92]</td>
</tr>
<tr>
<td>Chitosan-acrylic acid-1-vinyl-2-vinylpyrrolidone/multiwalled carbon nanotubes composite</td>
<td>$^{152+154}$Eu (radionuclide)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>321.77 mg/g</td>
<td>[94]</td>
</tr>
<tr>
<td>Chitosan-acrylic acid-1-vinyl-2-vinylpyrrolidone/multiwalled carbon nanotubes composite</td>
<td>$^{60}$Co (radionuclide)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>369.91 mg/g</td>
<td>[94]</td>
</tr>
<tr>
<td>Chitosan-acrylic acid-1-vinyl-2-vinylpyrrolidone/multiwalled carbon nanotubes composite</td>
<td>$^{154}$Cs (radionuclide)</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>456.46 mg/g</td>
<td>[94]</td>
</tr>
<tr>
<td>Glauconite clay-functionalized chitosan nanocomposites</td>
<td>Fluoride ions</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>9.03 mg/g</td>
<td>[89]</td>
</tr>
<tr>
<td>Chitosan-based magnetic nanocomposite containing Fe$_3$O$_4$-TiO$_2$</td>
<td>Fluoride ions</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>15.385 mg/g</td>
<td>[90]</td>
</tr>
<tr>
<td>Chitosan-modified ZnO/ZnFe$_2$O$_4$ nanocomposites</td>
<td>Fluoride</td>
<td>Pseudo-first-order</td>
<td>Langmuir model</td>
<td>10.54–3.03 mg/g</td>
<td>[91]</td>
</tr>
<tr>
<td>Superparamagnetic chitosan nanocomposite</td>
<td>Oil spill</td>
<td>Pseudo-second-order</td>
<td>Langmuir model</td>
<td>157.79 mg/g</td>
<td>[95]</td>
</tr>
</tbody>
</table>
radionuclides are used as treatment method these days. A nanocomposite of chitosan-silica is used for the removal of $^{152+154}$Eu radionuclide from water. $^{154}$Eu and $^{152}$Eu is produced as a fission product and has half-life from 5 to 13 years. This is a main concern for health of living organisms and in humans particularly affects liver and bone cancer. The use of silica-chitosan nanocomposite is low-cost and ecofriendly. The nanocomposites were effectively adsorbed and the process is endothermic chemisorption [92]. The use of multiwalled carbon nanotube nanocomposites for removal of radionuclides like $^{152+154}$Eu, $^{60}$Co, $^{134}$Cs is reported where the nanocomposite shows removal capacity (Table 3) [94].

9.2.3. Microbes. Waterborne diseases are a major concern in many countries and to address this problem, there is an urgent need to devise effective water purification process. As UV radiation is not always suitable, filtration is the next sought-after process. The use of nanoparticles in a polymer matrix is a breakthrough in water treatment process. Chitosan-TiO$_2$ nanocomposite for effective removal of E.coli from water was reported [96,97]. The bacterial removal was due to the cell membrane damage caused by attaching to the composite. Oxidative stress and ROS are also important aspects that helped removal of E.coli [98].

9.2.4. Turbidity. Turbidity of wastewater is one concern during the purification of water. Flocculation is one method which is applied widely to remove the turbidity of water. Flocculants enhances removal of turbidity by flocking the suspended materials together and helps them settle down. Inorganic flocculants were used earlier, and recently, natural polymers are used as flocculants. Nanocomposites are used recently as flocculants. montmorillonite/chitosan/ammonium acrylate composites developed through gamma irradiation showed excellent flocculation activity in river water [58].

9.2.5. Oil Spills. Oil pollution is a universal disaster caused by the spilling of oil during transportation of the petroleum products or from oil and gas industrial discharges. This may cause dreadful effect to the aquatic environment which may leads to ecotoxicity and also loss of life [99]. The polyhydrocarbons present in the oil may cause direct or indirect effect to the aquatic life-forms which includes stunned growth, suffocation, anoxia, and hormonal imbalance. This may also cause trouble in the food chain and web of the marine biota. To overcome this pollution, many technologies such as dispersants, skimmers, and adsorbents are used. Nanotechnology offers the latest method to rectify this problem [100]. For this, a superparamagnetic nanocomposite of Fe$_3$O$_4$/chitosan was created using the co-precipitation method. This nanocomposite was utilized for the adsorption of oil from the polluted aquatic environment which follows the kinetics of pseudo-second-order and fits into the Langmuir isotherm model. The maximum adsorption capacity of the nanocomposite in removing the oil spills is found to be 157.739 mg/g [101].

10. Future Perspective

The use of chitosan nanocomposites proves a boon for the removal of different contaminants from water, but all these research studies are in the initial stage. Large-scale implementation still needs to take shape. Different other aspects of using chitosan nanocomposites like membrane filters and as sensors for sensing different contaminants can be looked into. Even though the composites are regarded ecofriendly, not much research had been undergone to evaluate the toxicity of the nanocomposites introduced into the environment. Effective methods for the same need to be devised.

11. Conclusion

Water is an essential component; consequently, improvements in technology are required so that pure drinking water can be supplied to meet the growing demand for it. The utilization of polymeric nanocomposites in water treatment ensures not only the retention of particulate matter but also the removal of contaminants from the water. The presence of nanoparticles guarantees a high surface area, which in turn guarantees a higher level of efficiency in the process. However, the most significant limitation that can occur with polymeric nanomaterials is the implementation of these processes on a large scale, which makes them only rarely adaptable for the treatment process. Recently, the use of biogenic nanomaterials has shown excellent adsorption properties, and these materials are biorenewable in their natural state. When utilizing polymeric nanomaterials for the treatment of water, certain aspects such as toxicity concerns, cost-effectiveness, and the nanomaterials’ potential contribution to secondary pollution need to be taken into consideration. The use of polymeric nanocomposites for the treatment of wastewater is a novel approach; consequently, a great number of additional studies need to be carried out in order to compare the performance of these different approaches and to develop improved strategies for locating low-cost, high-selectivity, and recyclable fabricated nanomaterials and nanocatalysts.

Data Availability

The data used to support the findings of this study are not included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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