

# Chitin and chitosan as adsorbents

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## 3.1 Introduction

Recently, different wastewater purification methods that include precipitation, filtration, solvent extraction, ion exchange, and adsorption have been examined. Adsorption is predominantly attracting scientific attention because of its high efficiency, low cost, and availability of different adsorbents (Mudasir et al., 2015).

Wastewater purification using chitin or chitosan is a significant application due to the ability of chitin/chitosan and their composites to eliminate pollutants from wastewater in heavy metal adsorption (Wang et al., 2010; Mouzdahir et al., 2010; Tran et al., 2010) for the removal of the dye from industrial wastewater (i.e., textile wastewaters) (Wan et al., 2010), as well as for the removal of other organic pollutants.

Antibacterial materials are being established to stop harmful bacteria and viruses from spreading. These materials can successfully control the development and reproduction of lethal bacteria and also control toxic pollutants. They contain an antimicrobial agent that prevents the ability of microorganisms to develop in the material. One of the most investigated properties of chitin and chitosan is their antimicrobial effect employed in the purification of wastewater applications (Devlieghere et al., 2004).

This chapter highlights the application of chitin/chitosan and their derivatives as adsorbents and flocculants in wastewater treatments.

## 3.2 Chitin and chitosan

Chitin is a polymer of  $\beta$ -(1 $\rightarrow$ 4) connected to *N*-acetyl glucosamine subunits as shown in (Fig. 3–1A). It is mainly used as raw material to produce other derivatives like chitosan, chitooligosaccharides, and glucosamine (Bhaskar et al., 2007), although chitin remains industrially unemployed due to its insolubility in aqueous and organic solvents (Chandumpai et al., 2004). Chitosan—the deacetylated derivative of chitin—is a polymer of  $\beta$ -(1 $\rightarrow$ 4) connected to glucosamine residues as shown in (Fig. 3–1B). It has some solubility in acidic solutions and has many applications in different fields like wastewater treatment, drug delivery, agriculture, and food (Cira et al., 2002; Imoto and Yagishita, 1971; Jo et al., 2008).

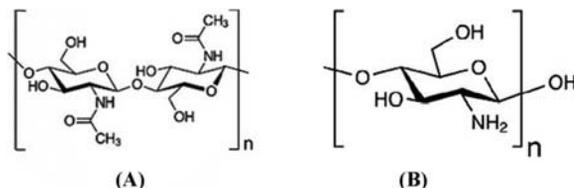


FIGURE 3-1 Chemical structure of (A) chitin and (B) chitosan.

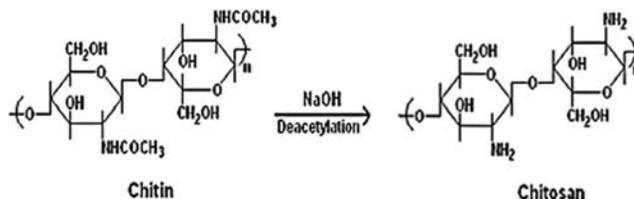


FIGURE 3-2 Deacetylation of chitin to give chitosan.

The conversion of chitin into chitosan is mostly done using strong alkali for the deacetylation of chitin as shown in (Fig. 3-2) (Zhang et al., 2012). Recently, chitin and chitosan were employed in environmental protection, especially wastewater treatment due to their good biocompatibility and adsorption efficiency. Chitosan had been used as adsorptive material for heavy metal ions, aromatic compounds, dyes, and microbes, which cause serious environmental problems owing to their severe toxicity.

The utility of low-cost polymers like chitin and chitosan to remove water pollutants is of great interest, as chitin and chitosan do not cause any pollution due to their biodegradation and nontoxicity (Ling et al., 2011).

Chitosan is more efficient than chitin in removing heavy metal ions, polychlorinated biphenyls (PCBs), and anionic dyes. However, chitin is more efficient than chitosan in removing polycyclic aromatic hydrocarbons from petrochemical wastewater.

Generally, chitosan of lower crystallinity and higher degree of deacetylation (*DD*) gives a better adsorption efficiency in wastewater treatment. The *DD* shows the portion of free amino groups that will be available to chelate with metals ions. Infrared spectroscopy and nuclear magnetic resonance (NMR) analysis are the most used methods to estimate the deacetylation degree. Infrared spectra of chitosan are usually obtained with a frequency range of 4000–400  $\text{cm}^{-1}$  and the *DD* is given by the following equation (Domszy and Roberts, 1985):

$$DD = 100 - \left[ \frac{A_{1654}}{A_{3450}} \times 100 / 1.33 \right].$$

Chitin and chitosan have a wide range of applications depending on their physical, chemical, and biological natures. The principal fields are drinking water and wastewater treatment.

### 3.3 Surface functionalization of chitosan

The chemical change is useful in increasing the water solubility of chitosan, thus broadening its uses. The existence of amino and hydroxyl groups is an interesting functionality to improve its properties. The chemical change can be some reactions like cross-linking, carboxymethylation, etherification, graft copolymerization, and esterification (Rafique et al., 2016).

#### 3.3.1 Cross-linking

Hydrogels are either natural or synthetic polymers; their chains are cross-linked via covalent or noncovalent bonds, giving three-dimensional networks (Fig. 3–3). Hydrogels can largely swell and retain large amounts of solvents while keeping their original shape (Shibayama and Tanaka, 1993). Chitosan hydrogels are made to be sensitive to any external effect like pH or temperature. In acidic medium, amino groups are protonated having electrostatic repulsion increasing the polymer swelling (Gil and Hudson, 2004). Chitosan can form hydrogels via both hydroxyl groups at C-3 and C-6 and the amino group at C-2. Amino groups react with cross-linking agents due to their nucleophilic character. Chitosan chains are cross-linked with glyoxal, dialdehydes, and glutaraldehyde (Muñoz et al., 2015).

Cross-linking of chitosan with glutaraldehyde and sulfosuccinic acid has been done to form membranes used in fuel cells (Dashtimoghadam et al., 2010). Genipin, a compound extracted from the fruit of gardenia jasminoides and American genipa has also been used as a cross-linker agent (Muzzarelli, 2009). Bodnar et al. reported the formation of chitosan nano-hydrogels, using dicarboxylic and tricarboxylic acids as cross-linking agents (Bodnar et al., 2005). Succinic, glutaric, and adipic acid were used recently as cross-linkers to form chitosan hydrogels (Valderruten et al., 2014).

#### 3.3.2 Graft copolymerization

There are numerous techniques used to modify the surface characteristics of chitosan to introduce new properties. However, graft copolymerization of synthetic polymers onto chitosan is of the most importance (Fig. 3–4). Chitosan and carboxymethyl chitosan have been grafted with methacrylic acid by using ammonium persulfate (APS) as an initiator to give derivatives much water-soluble (Xie et al., 2002; Sun et al., 2004). The copolymerization of aniline onto chitosan in the presence of APS has produced films and fibers with protonic conductivity (Yang et al., 1989). The different initiators such as potassium persulfate (PPS),

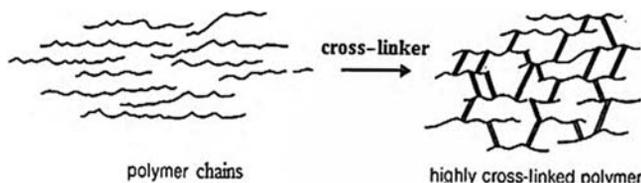


FIGURE 3–3 Cross-linking of polymeric chains.

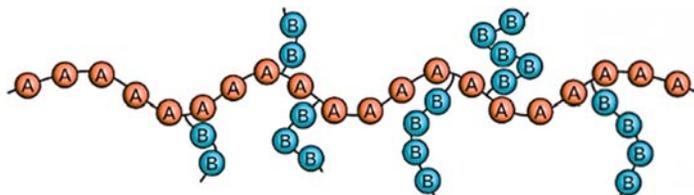


FIGURE 3–4 Structure of graft copolymer (A is backbone polymer and B is grafted branch).

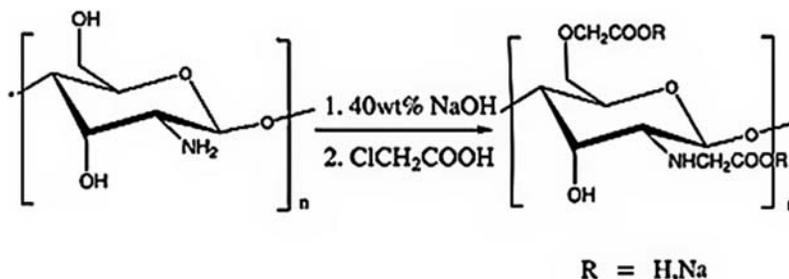


FIGURE 3–5 O- and N-carboxymethylation of chitosan.

ceric ammonium nitrate (CAN), 2,2-azobisisobutyronitrile (AIBN), and ferrous ammonium sulfate (FAS) were used for the initiation of the grafting copolymerization (Olteanu, 2007). Poly (ethylene glycol) (PEG) is a suitable polymer for graft formation due to its solubility in both water and organic solvents, low toxicity, good biocompatibility, and biodegradability. PEG graft with chitosan had been synthesized using hydroxyl groups of chitosan. The new material was soluble in water and aqueous solutions of a wide pH range (Gorochovceva and Makuška, 2004).

### 3.3.3 Carboxymethylation

Chitosan derivatives synthesis had been performed to increase chitosan water solubility. The most widely used modification is carboxymethylation. The procedure consists of suspending chitosan in isopropanol/NaOH aqueous solution with stirring at room temperature. Next, a monochloroacetic acid/isopropanol mixture is added to the mixture (De Abreu and Campana-Filho, 2005). During the reaction, O- and N-carboxymethylation may occur simultaneously (Fig. 3–5), but under controlled reaction conditions (like temperature and stoichiometry), it is possible to yield only one derivative (Rinaudo, 2006).

### 3.3.4 Etherification

Hydroxypropyl chitosan was synthesized from chitosan and propylene epoxide in alkaline medium (see Fig. 3–6). This modification allows to carry out graft copolymerization; for example, maleic acid was grafted onto hydroxypropyl chitosan to enhance its antimicrobial properties against *Staphylococcus aureus* and *Escherichia coli* (Xie et al., 2002).

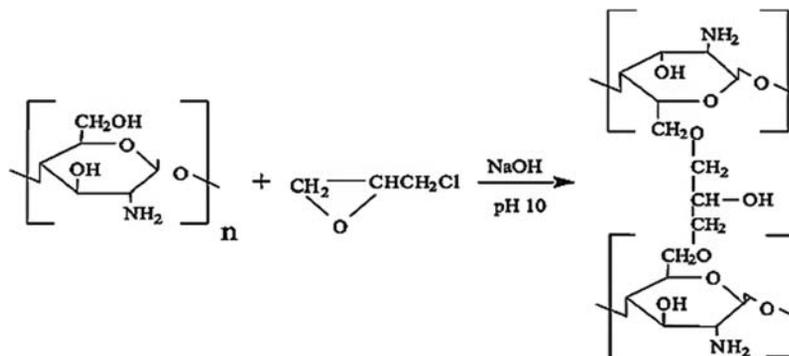


FIGURE 3-6 Etherification of chitosan.

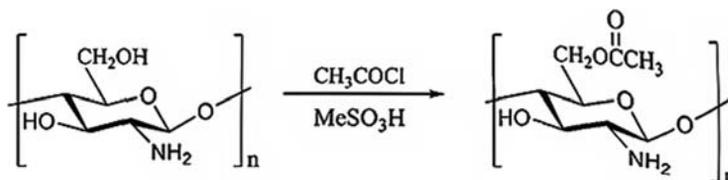


FIGURE 3-7 Esterification of chitosan.

### 3.3.5 Esterification

In addition, the esterification of chitosan is widely reported as a chemical modification in the literature. Synthesis of *N,O*-acyl chitosan using acetyl chloride/ $\text{MeSO}_3\text{H}$  as a solvent (see Fig. 3-7). Under these conditions, *O*-acetylated chitosan is the major product compared to the *N*-acetylated chitosan (Badawy et al., 2004). It has been shown that the acetylation of chitosan improves its antifungal activity (Badawy et al., 2005).

### 3.3.6 Phosphorylation

These derivatives are important due to their remarkable biological and chemical properties. They exhibit bactericidal properties. Synthesis of phosphorylated chitosan can be done by heating chitosan with orthophosphoric acid in *N,N*-dimethyl formamide (DMF) to be done on hydroxyl groups in carbons 3 and 6. Another way to prepare phosphorylated chitosan is via the reaction of chitosan with phosphorous pentoxide in methane sulfonic acid (Jayakumar et al., 2008) (Fig. 3-8).

## 3.4 Treatment of wastewater

### 3.4.1 Metal capture from wastewater

Environmental remedy is an important goal for all researchers worldwide. Thus they are developing new technologies for wastewater treatment that do not cause any environmental

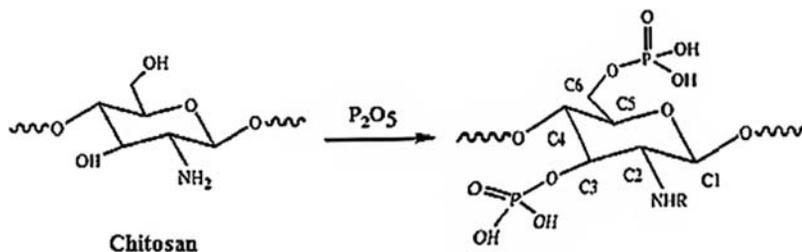


FIGURE 3–8 Phosphorylation of chitosan.

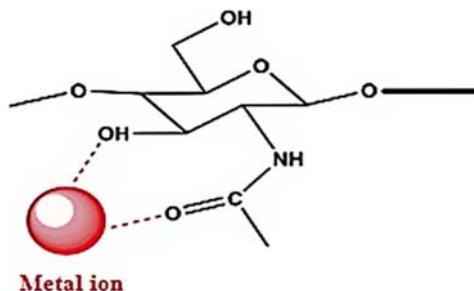


FIGURE 3–9 Chelation between chitin and metal ion M.

problems. [Karthikeyan et al. \(2005\)](#) examined  $\text{Fe}^{3+}$  removal by chitin. The particle size of 0.21 mm showed higher removal efficiency than sizes of 0.50 and 0.71 mm due to the higher surface area. An inhibition of adsorption was observed in presence of chloride together with  $\text{Fe}^{3+}$ . As the chloride ion concentration increased, the removal percentage of  $\text{Fe}^{3+}$  decreased. As the greater the chloride ion concentration, the greater are chances of formation of soluble chlorocomplexes with  $\text{Fe}^{3+}$ .

Chitin of pink shrimp was reported to capture  $\text{Pb}^{2+}$  from aqueous solutions ([Forutan et al., 2016](#)). Maximum adsorption was estimated to be 99.7% at pH 9, time 200 min, 5 g/L of biosorption dosage and the initial lead concentration 20 mg/L, the temperature of 30°C. Adsorption of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  by chemically modified chitin with polypyrrole was tested ([Karthik and Meenakshi, 2015](#)). The maximum metal uptake was found at pH 6 and equilibrium was attained in 60 min. Xiong tested chitin use for  $\text{Cd}^{2+}$  adsorption ([Xiong, 2010](#)). The maximum removal was obtained at pH 5.41. The increase in temperature from 288K to 318K was found to increase the adsorption efficiency from 87.1 to 102 mg/g. FTIR spectra before and after  $\text{Cd}^{2+}$  adsorption showed that the acetyl amino and hydroxyl groups were contributing to metal removal, as shown in (Fig. 3–9).

[Jaafarzadeh et al. \(2013\)](#) prepared chitin from extracted shrimp shells to examine its capability to adsorb  $\text{Zn}^{2+}$  in pH (3–7), initial  $\text{Zn}^{2+}$  concentration (50–500 mg/L), and the adsorbent dose (0.5–10 g in 250 mL) on metal uptake. The adsorbed metal amount in mg/g was found to rise by raising pH and the initial concentration while the opposite observation was noticed with the increase in the adsorbent dose. Chitin extraction from the exoskeleton of

the crab was produced and used as an adsorbent for  $Zn^{2+}$  (Jaafarzadeh et al., 2014). The highest uptake happened at pH 7 (studied pH range 3–7), and at solid: liquid ratio of 1:500 g/mL (studied dosage range 1:500–20:500 g/mL).

Chitin extracted from shrimp shells was also examined for  $As^{5+}$  adsorption (Jaafarzadeh et al., 2015). The best adsorption was attained at pH 4 and the removal was fast in the first 30 min, during which 40%–50% of the arsenate was removed. Unmodified chitin nanofibers and thiol-modified chitin nanofibers were prepared and examined to remove  $As^{3+}$  (Yang et al., 2015). The improved chitin had a better uptake efficiency, that is, 138 mg/g at pH 7.0 instead of 58 mg/g at pH 5, which was given by raw chitin nanofibers.

The adsorption of  $Cr^{6+}$  by Bargi fish scale and from chitin obtained from Bargi fish (*Heterotis niloticus*) was tested (Otuonye et al., 2014). The highest adsorption was found at pH 6–8 and chitin gave better results than fish scale. Saravanan et al. (2013) used chitin/bentonite for  $Cr^{6+}$  adsorption. Optimum uptake was obtained at pH 4 (pH studied in the range of 1–8). The adsorption was increased when the adsorbent amount was increased from 0.2 to 1 g, while a reduction of the Cr adsorbed happened in case of adsorbent dosages higher than 1 g. A high increase in uptake percentage was detected around 30 min and reached a maximum at 45 min. The Freundlich isotherm model was a better fit. Karthik et al. used polypyrrole-functionalized chitin to adsorb  $Cr^{6+}$  (Karthik and Meenakshi, 2014). The data revealed that with the rise in pH from 2 to 10, a decrease in the uptake percentage from 92.34% to 15.07% had occurred.

Nair and Madhavan (1984) used chitosan as an adsorbent for mercury removal from water and achieved a reasonable recovery. Peniche-covas et al. (1987) stated the adsorption kinetics of mercuric ions using chitosan. The data showed that the adsorption efficiency of Hg was affected mainly by time, the particle size, initial concentration of Hg ions, and chitosan quantity. Chitosan flakes of size 0.4–4 mm were used as an adsorbent for Cr (III) removal from wastewater and the data showed that the adsorption efficiency increased with a decrease in the size of the flakes.

Adsorption of phenol by both chitin and chitosan was most efficient in the pH range of 2.0–5.0. The adsorption results obeyed pseudo-first-order kinetics for chitosan and second-order kinetics for chitin. Complete adsorption of 30 mg/L phenol from contaminated wastewater showed possible usage of  $1 \times 10^{-2}$  g/mL of an adsorbent.

The parameters from industrial wastewater as measured by pH, conductivity, chemical oxygen demand (COD), total oil and greases (TOG), and dissolved solids (DS) were drastically reduced after treatment with chitin and chitosan (Aparecida et al., 2009). Thus chitin and chitosan were considered attractive low-cost natural adsorbents for the removal of phenol and other pollutants from industrial wastewaters (Aparecida et al., 2009).

*Adsorption* is the result of the unique interaction between an adsorbent and the adsorbate. These interactions depend mainly on the chemical structure of chitosan/chitin. The functional groups which create such interactions are, for example in chitosan: hydroxyl and amine groups as seen in (Fig. 3–10). Amine groups are subjected to be ionized, as a function of pH ( $pK_a$  in the range 6.0–6.7). That allows chitosan to be polycationic and to interact with anionic derivatives (such as some dyes) via electrostatic forces. In addition, when amine groups are nonionized, they have a free electron pair on the nitrogen atom, to attract

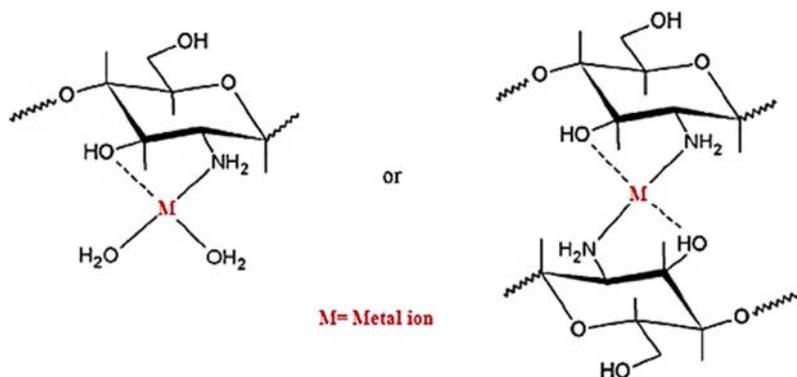


FIGURE 3-10 Chelation between chitosan and metal ion M.

electrons deficient chemicals, such as cations (Kurita et al., 1979). In an acidic medium ( $\text{pH} < 6$ ), protonation of amine groups is preferable for metal anions attraction. At very low  $\text{pH}$  ( $< 2-3$ ) the sorption of metal anions can be reduced due to the competition of counter anions for attaching to protonated amine groups. Thus the binding of metal anions (and anionic dyes) is maximum in the  $\text{pH}$  range: 2–3 and 5 (Desbrières and Guibal, 2018).

The sorption characters of chitosan depend on some parameters related to the medium ( $\text{pH}$ , presence of competitor ions, metal speciation, metal concentration) or the polymer (particle size, sorbent concentration). However, the effects of these parameters on metal adsorption are all involved with some criteria/mechanisms: (1) crystallinity and swelling behavior, (2) diffusion properties, and (3) metal speciation. The crystallinity of polymers influences their hydration and swelling performance. This parameter, in turn, affects the availability of sorption sites. This availability can be controlled both at equilibrium and in terms of kinetic behavior (Desbrières and Guibal, 2018).

Arvand and Pakseresht produced 3,4-dimethoxybenzaldehyde chitosan derivative (Chi/DMB) for Cd (II) elimination and evaluation from wastewater (Arvand and Pakseresht, 2013). An increase in metal uptake was noticed as  $\text{pH}$  increased from 1.0 to 9.0. Using the Langmuir isotherm model,  $Q_m$  was found to be 217.4 mg/g. Elimination of U (VI) from wastewater using chitosan-modified multiwalled carbon nanotubes (MWCNT-CS) was stated by Chen et al. (2013). The maximum ion removal was done at  $\text{pH} = 7$ . Using the Langmuir model,  $Q_m$  was found to be 71 mg/g. Chen and Wang prepared a xanthate-modified magnetic cross-linked chitosan (XMCS) derivative for the removal of Co (II) (Chen and Wang, 2012). The cross-linked magnetic chitosan was treated with NaOH solution and  $\text{CS}_2$  and stirred at room temperature (24 h) then washed with deionized water and was dried at  $70^\circ\text{C}$ . Using both Langmuir and Freundlich isotherms,  $Q_m$  was calculated to be 18.5 mg/g. Elwakeel et al. (2014) synthesized a resin based on magnetic modified chitosan for removal of  $\text{UO}_2$  (II). Chitosan was cross-linked using glutaraldehyde in the presence of magnetite then chemically reacted with tetraethylene pentamine (TEPA).  $Q_m$  was calculated to be 1.8 mmol/g using Freundlich, Langmuir, and Dubinin-Radushkevich models at  $\text{pH} 4$  ( $25^\circ\text{C}$ ).

Some physical and chemical modifications of chitosan have been carried out to improve its affinity and selectivity toward different sorbates (Inoue et al., 1996). Carboxymethyl chitosan has been synthesized by the reaction of chitosan with monochloroacetic acid in a suitable solvent (Tang and Hon, 2011). Carboxylic acids have also been grafted onto chitosan by Schiff's base condensation reactions (Muzzarelli, 1988). Another way for insertion both carbonyl and carboxylate moieties into chitosan was done via its reaction with acid anhydride (Shigemasa et al., 1999), grafting of crown ether onto chitosan using Schiff's base reaction (Peng et al., 1998; Tan et al., 1999).

The chelating adsorbent was synthesized from cross-linked chitosan microspheres with glutaraldehyde by spray drying using 8-hydroxyquinoline-5-sulfonic acid as a chelating agent (CTS-SX-CL) (Vitali et al., 2008). Adsorbent microspheres were characterized by Raman spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray microanalysis (EDX). Adsorption was found to be maximum for both  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  at pH 8.0. Twu et al. (2003) tested the sorption properties of chitosan/cellulose blend beads against  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ni}^{2+}$  ions. The studies proved that chitosan/cellulose blends have applications for metal ions adsorption.

Adsorption of  $\text{Cr}^{3+}$  ions from aqueous solutions using natural and cross-linked chitosan membranes was done using batch adsorption experiments (Baroni et al., 2008). pH (6.0 and 2.0),  $\text{Cr}^{3+}$  ions concentration and cross-linking agents effects on the adsorption properties of chitosan were examined. Sabarudin et al. (2007) prepared chelating resin based on chitosan. 2-amino-5-hydroxybenzoic acid (AHBA) was chemically attached to amino groups of cross-linked chitosan (CCTS) through the bridge of chloromethyl oxirane (CCTS-AHBA resin). Several metals, as  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and rare earth elements, could be adsorbed onto the obtained resin.

### 3.4.2 Dyes uptake from wastewater

Dismissing dyestuffs into water causes a major threat to the environment. Dyes are a serious class of pollutants, and can even be recognized by the human eye. Among different methods, adsorption occupies a noticeable role in dye removal. Adsorption is the cost-effective and potential method to remove dyes from effluents as shown in (Fig. 3–11).

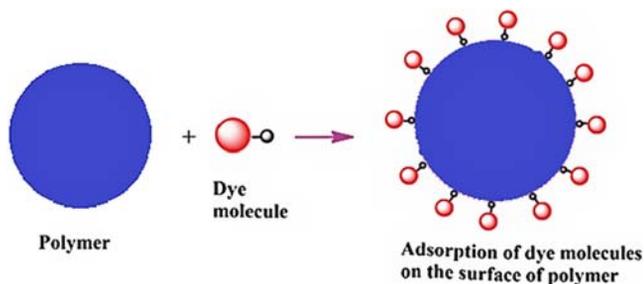


FIGURE 3–11 Dye adsorption on the surface of polymers.

Broad studies on the adsorption of the dyes on chitin by McKay (1987) and McKay et al. (1985) had shown that chitin can uptake extensive quantities of dyes out of aqueous solutions. However, chitosan with more amino groups was stated to be more active for chelating dyes than chitin (Park et al., 1995b). For example, Shimizu et al. (1995) investigated the adsorption behavior of *chrome violet* (C.I. Mordant Violet 5, a monoazo dye) to chitin and partially deacetylated chitin (DD = 65%) and found that the uptake ability of partially deacetylated chitin was so much greater than that of chitin as the content of amino groups in partially deacetylated chitin increased.

$\alpha$ -Chitin nanoparticles CNP—extracted from the shells of *Penaeus monodon*—were found to be encouraging material for the decontamination of water from dyestuff pollution. They have 49 nm average particle size with 96.8% DA and 83.73% crystallinity that bind dyes in a very small time of contact in normal conditions and does not need any harsh conditions for the adsorption process (Dhananasekaran et al., 2016).

The uptake of *eosin Y* from aqueous solution via modified nanoparticles chitosan was reported (Du et al., 2008). The nanoparticles were described by atomic force microscopy and zeta potential analysis. A batch method was engaged to study the uptake reaction. The data displayed that the uptake of *eosin Y* on chitosan nanoparticles was influenced by interaction time, dye concentration, pH, and temperature. The adsorption reaction follows the Langmuir isotherm model and the adsorption capacity was 3.3 g/g. The maximum pH value for dye removal was found to be 2–6. The dye was desorbed from the chitosan nanoparticles by raising the pH of the solution.

Investigation on *Congo red* (an anionic azo dye) adsorption by chitosan beads had been reported (Chatterjee et al., 2007). Adsorption was found to be temperature-dependent with maximum activity at 30°C. Congo red dye binds to the chitosan via both ionic interaction and physical forces (Fig. 3–12). Adsorption for Congo red–chitosan beads system was explained best by the Langmuir isotherm model and the reaction obeys pseudo-second-order rate equation.

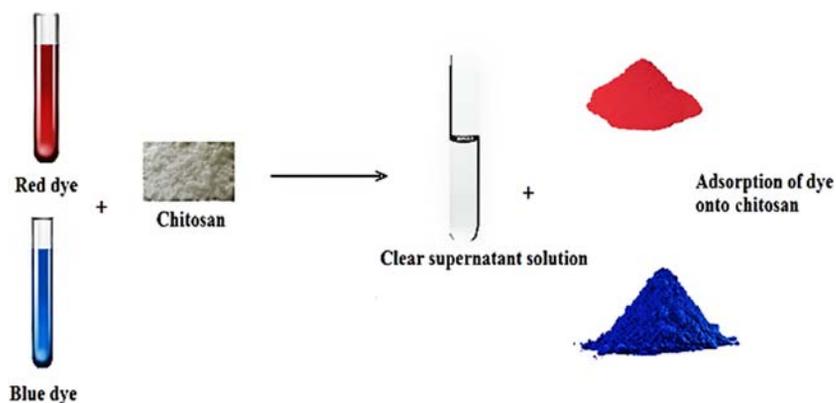


FIGURE 3–12 Dye adsorption by using chitin and chitosan.

Chiou and Li (2002) verified the reactive dye (*reactive red 189*) uptake from aqueous solutions by cross-linked chitosan beads in a batch system. Langmuir and Freundlich adsorption models were employed to report the adsorption isotherm. Pseudo-first- and -second-order kinetic models were applied to describe the kinetic behavior. Adsorption of *Remazol black 13* (reactive dye) onto chitosan in aqueous solutions was reported (Annadurai et al., 2008). The equilibrium adsorption of reactive dye on chitosan was described by Langmuir and Freundlich models. The maximum adsorption capacity ( $Q_m$ ) was 91.47–130.0 mg/g. The kinetic behavior of reactive dye adsorption followed pseudo-first and -second-order rate expression, explaining that intraparticle diffusion plays an important role in the adsorption step. Modified chitosan beads were employed for cationic dye *malachite green* (MG) removal out of aqueous solutions (Bekçi et al., 2008). The adsorption behavior was shown using the linear form of Langmuir and Freundlich models. Ninety percent of MG was removed at the maximum pH value of 8. The adsorption reaction obeyed pseudo-second-order.

A new chitosan adsorbent was successfully manufactured, which engaged to eliminate *orange II dye* (an azo dye) from textile wastewater. The textile wastewater can be treated using a relatively low quantity of the adsorbent. The use of chitosan can be measured as a favorable method for eliminating azo dye from wastewater effectively (Hajivandi et al., 2016). Carboxymethyl chitosan-graft-poly (2-methacryloyloxyethyl) trimethyl ammonium chloride was used for cationic and anionic dyes removal, namely *acid green 25* (AG25) and *basic bright yellow* (7GL) from water. The second-order reaction model was well explaining AG25 removal process whereas the cubic one is more appropriate for that of 7GL (Wu et al., 2015).

Dye removal from textile wastewater has been a big challenge over the last years as dyes discharged from the industries have high resistance (Ali et al., 2009). Direct and indirect toxic effects on health as they can cause different disorders such as tumor, cancer, allergies, skin irritation, heart defects, and mutations (Alver and Metin, 2012; Hariharasuthan et al., 2013). To overcome these health disorders, the coagulation/flocculation methodology has been either used alone or in combination with biological treatment since it enhances promoting the removal of the dye from textile industry effluents (Anjaneyulu et al., 2005). Researchers started to focus their interest in studying these adsorbents as an economic and feasible alternative treatment for dye wastewater.

### 3.4.3 Microbes uptake from wastewater

Waterborne viruses are still major sponsors for the universal problem of diarrheal diseases leading to death. Water treatment studies have reported coagulation as the most significant step in the removal of toxins from drinking water (Cleasby, 1989; Bellamy et al., 1993). The evolution of more active and environmentally safe coagulants can increase the reduction of the pollutants in treatment processes. The most existing biological coagulant is chitosan, which can be active in contaminants removal from drinking water (Kumar, 2000).

When chitosan is dissolved, the amino groups on the glucosamine units will be protonated, increasing solubility and increasing the positive charge (cationic property) on chitosan chains. The positive charge is an important character for a coagulant, as a coagulant with

higher positive charge density in water has a higher removal ability of negatively charged bacteria, viruses, and protozoans (Rinaudo, 2006). Chitosan molecules bind to bacterial cell surfaces. In the interacting sites, the cell membrane became locally detached from the cell wall, giving rise to “vacuole-like” structures below the wall. The detachment yields ions and water efflux decrease the internal bacteria pressure (Raafat et al., 2008) (Fig. 3–13). Although chitin had been considered as an interesting biomacromolecule with antimicrobial properties, applications are limited due to water insolubility. Thus the interest was directed to the synthesis of more water-soluble derivatives.

Jia et al. (2001) stated that *N*-propyl-*N,N*-dimethyl chitosan activity against *E. coli* is 20 times higher than that of chitosan, proving that the derivatives with cationic charge have higher activity. The antimicrobial activity would rise as the content of the alkyl moiety increases, as shown by Rabea et al. (2003), who stated that the antibacterial activity had improved with increasing the chain length of the alkyl substituent due to the influence of the hydrophobic portions of the derivatives.

In addition, to the quaternary salts of chitosan, other water-soluble derivatives such as hydroxypropyl and carboxymethyl chitosans were synthesized. Hydroxypropyl chitosan derivative with a high degree of substitution is water-insoluble, but after grafting with maleic acid they become more soluble in neutral pH with higher antibacterial activity than that of chitosan itself (Xie et al., 2002). In both neutral and alkaline media, the cationic nature of chitosan can no longer elucidate its antibacterial activity (Xie et al., 2002). In this case, the strong chelation capacity of amino groups in the chitosan chain might be a possible mechanism. Sun et al. (2006) studied carboxymethyl chitosan since it had both negative and positive groups. It was found that antimicrobial activities of carboxymethyl chitosan are affected either by the degree of substitution of the quaternary group or by the MW.

Ceramic water filters (CWFs) are water purification technology that is effective in improving the microbial quality of water and reducing diarrheal disease (Sobsey et al., 2008; Brown et al., 2008). CWFs are made of clay, water and combustible material like sawdust, rice husk, or other forms of agricultural waste particles. The supplementary components in the

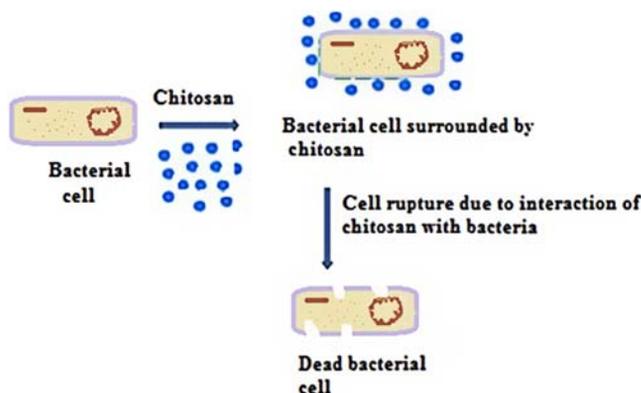


FIGURE 3–13 Killing bacterial cell mechanism by chitosan.

manufacture of CWFs are silver nanoparticles due to their antimicrobial character in the water decontamination process.

Ceramic porous structure joined the antimicrobial activity of silver nanoparticles giving rise to two purification methods: physical removal of microbial pollutants and chemical disinfection of microbes as they come in contact with silver (Lydia et al., 2016). Chemically modified water-soluble chitosan derivatives as coagulants were combined with CWFs to remove bacteria and viruses by chitosan coagulation followed by ceramic filtration. Effectiveness was evaluated to model water contaminated with turbidity, bacteria and viruses, respectively. The goal was to enhance the overall removal of viruses, bacteria, and turbidity removal from water by using the proposed dual treatment barriers of coagulation followed by ceramic filtration.

### 3.5 Chitosan-based nanocomposites as adsorbents

Current researches have enabled the advance in chitosan-based bio- and/or nano-hybrid materials for potential applications in antimicrobial packaging, corrosion protection, and toxic metal ions removal (Bilal et al., 2019). For this target, chitosan has been blended with several other polymers for example, poly(methyl-methacrylate), polycarbonate, polyaniline, polysulfide, and polystyrene (Winie and Shahril, 2015). Composites/blends of chitosan display enhanced material properties, for example, morphology, surface area, electrical conductivity, mechanical strength, and bioactive properties, that enable their usage in various fields such as membrane technology, biosensors, antimicrobial and biomedical materials, packaging, and textile sectors (Kausar, 2019).

Huang et al. (2011) synthesized chitosan-graft-ethylene diamine and evaluated its dye adsorption potential from aqueous solution. Results showed high sorption efficiency toward (anionic dye) eosin Y because of higher zeta potential due to a higher number of amino groups. Liu et al. (2018) prepared grafted carboxylate-rich chitosan flocculants, which had excellent desorption potential of MG (cationic dye) and nickel ions. Linda et al. (2016) prepared nanocomposite based on metal oxide nanoparticles incorporated into the chitosan matrix. The application of nanocomposite against the photocatalytic degradation of RhB dye from the aqueous environment was tested. Chitosan enhanced the RhB dye adsorption efficiency. The chelating ability of chitosan with metal ions contributes to the active photocatalytic degradation of RhB dye. Saad et al. (2020) synthesized ZnO/Ce-ZnO based nanoflowers made with chitosan via microwave-irradiation technique. The nanocomposite was employed for photocatalytic degradation of MG under visible light. The new nanocomposites, that is, ZnO-chitosan and Ce-ZnO-chitosan, exhibited improved photocatalytic degradation of MG by 54% and 87%, respectively. In addition, the new nanocomposites showed high stability and recyclability after several repeated cycles.

New adsorbents were performed by reacting (ethylene diamine tetraacetic acid) EDTA ligands with chitosan-silica hybrid materials. The adsorption potential of hybrid materials was examined toward Co (II), Ni (II), Cd (II), and Pb (II) as target metals as they showed the best adsorption efficiency (Eveliina et al., 2011). Chitosan Schiff bases (CSBs) are known as

sorbents for various applications. Lopez-de-Alba et al. (1987) have synthesized two different CSBs from the reaction of chitosan with salicylaldehyde /glutaraldehyde and tested them in adsorption of uranium (VI) ions. These CSBs could separate uranium (VI) and vanadium (V) ions from each other. Before this report, bare chitosan had been used for the adsorption of metal ions and comparatively, these CSBs display better adsorption behavior than bare chitosan (Muzzarelli et al., 1970). Thus more attention was given to CSB materials than to chitosan for the adsorption of metal ions or dyes.

Treatment of wastewater contaminated with toxic dyes using chitosan–starch-based polymer nanocomposites by coagulation-flocculation was investigated, indicating that the starch/chitosan nanocomposite provides better dye removal results as compared to the utility of chitosan alone due to electrostatic and hydrophobic interactions (Sami et al., 2017).

### 3.6 Conclusions

Industrial wastewater treatment was done by the utilization of natural polysaccharides such as chitin and chitosan-based materials via adsorption. Due to the variety of excellent features of chitin and chitosan, more attention had been attracted to them. They have the ability of chelating heavy metal ions in wastewater and they have the ability to adsorb different dyes in industrial wastewater. They are antibacterial and antifungal as well as antiviral properties, so they can remove microbes out from wastewater.

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# Nanocellulose: A sustainable and renewable material for water and wastewater treatment

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## 4.1 Introduction

Water is considered an essential and fundamental element for all forms of life existing on our planet (Babu et al., 2015). With the rise of the population, industrialization has also increased causing contamination of natural/fresh water with toxic substances, which has become one of the biggest challenges in the world and has raised serious concerns (Zeng et al., 2019; Zhuang et al., 2019). Various types of contaminants such as heavy metals, pharmaceuticals, petroleum products, and dyes have been reported in water bodies around the world (Hokkanen et al., 2016). Therefore the presence of these toxic contaminants in water poses a high risk to humans as well as to other living creatures (Zabihi et al., 2009). In addition, the shortage of water resources and the production of wastewater in high volume put huge pressure on humankind. There is an urgent need for the treatment of wastewater to eliminate these contaminants. Over the years, several technologies have been developed and utilized for the removal of these contaminants from water, such as reverse osmosis, precipitation, filtration, ion exchange, coagulation, solvent extraction, and adsorption (Lata and Samadder, 2016; Unuabonah and Taubert, 2014). However, most of these methods are highly expensive and ineffective for contaminants removal; therefore it is necessary to develop new treatment methods (Ali, 2012). Among these different wastewater treatment technologies, adsorption has gained considerable attention because of its simplicity, high efficiency, and effectiveness toward a range of pollutants, removal of contaminants even at low concentration, high economic values, ease of operation, and the availability of a broad range of adsorbents such as composites, carbon nanotubes, and nanoparticles (Unuabonah and Taubert, 2014; Ali, 2012; Ghanbarian et al., 2017; Kumari et al., 2019; Xie et al., 2011a,b).

Utilization of biomaterials such as cellulose, starch, gelatin, chitin, alginate, and chitosan for contaminants removal from wastewater is considered more advantageous because of their nontoxicity, biodegradability, biocompatibility, and renewable nature as compared to