# Chapter 10
# Adsorptive Removal of Toxic Dyes Using Chitosan and Its Composites

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## Contents

**Abstract** Adsorption is considered to be one of the most efficient and cost-effective processes for the removal of pollutants including dyes from polluted water bodies. Wide range of materials is being studied for removing dye molecules that impart colour to water. Chitosan has emerged as a low-cost, non-toxic, biodegradable and easily available option for removing dye molecules by adsorption. The functional

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groups in chitosan, e.g. the hydroxyl and the amino groups, are responsible for the adsorption of cationic as well as anionic dyes. Here we have discussed some of the significant cases of cationic and anionic dye adsorption by chitosan. Broadly, chitosan-based adsorbent can be categorized as (a) grafted and cross-linked chitosan to enhance adsorption capacity and also to impart superior mechanical stability so that the adsorbent can be used in harsh condition and (b) composites with wide range of materials, e.g. clay, carbon materials, other polymers and metal oxides. Further sizes and morphologies, e.g. sphere, beads, nanofibres, have effects on the adsorption capacities. In addition, the scope for adsorptive photocatalytic dye degradation has been discussed. For this purpose, ZnO–chitosan nanocomposite is taken as a model adsorbent cum photocatalyst for removing Congo red anionic dye, where chitosan facilitated adsorption while ZnO favoured dye degradation.

**Keywords** Chitosan · Composites · Dye · Adsorption

## 10.1   Introduction

Increased industrialization, urbanization and agricultural activities elevated the concentrations of toxic chemical compounds in water (Jayaswal et al. 2018). Consumption of polluted water is linked with health hazards and can have fatal consequences (Schwarzenbach et al. 2010). These toxic compounds include pesticides, phthalates, polyaromatic hydrocarbon, phenols and its derivatives, industrial dyes and heavy metals (Shahat et al. 2015; Chequer et al. 2013; Dutta et al. 2019). Among these, dye industries are one of the most significant point sources for water pollution. They are toxic in nature and are carcinogenic to human beings and aquatic lives (Sharma et al. 2015; Daneshvar et al. 2017). Dyes are organic compounds that impart colour to water, and therefore, they are widely used for colouring applications in textile, paints, leather, cosmetics, plastic, paper and photographic industries (Christie 2001). Industries are using large amounts of water for dyeing applications, and the unregulated discharge of dye effluent into mainstream water bodies without any treatment process is dangerous for the environment. Also, most of the dyes can persist in the environment for long periods as they are resistant to natural degradation processes such as thermal, biological and photodegradation. These dyes when present in water hinder the photosynthesis process and therefore affect the ecosystem of aquatic plants and animals. In humans, azo dyes can be metabolized into aromatic amines and N-hydroxylamines which cause severe damage to DNA (Rajaguru et al. 1999, Pinheiro et al. 2004, De Aragão Umbuzeiro et al. 2005). Therefore, removal of toxic dyes from wastewater is necessary to avoid any potential hazard to the environment and its creatures.

Adsorption is one of the most widely used decontamination techniques for the removal of dissolved impurities from one phase to another (Naushad et al. 2016). It is a mass transfer phenomenon which involves accumulation of dissolved material
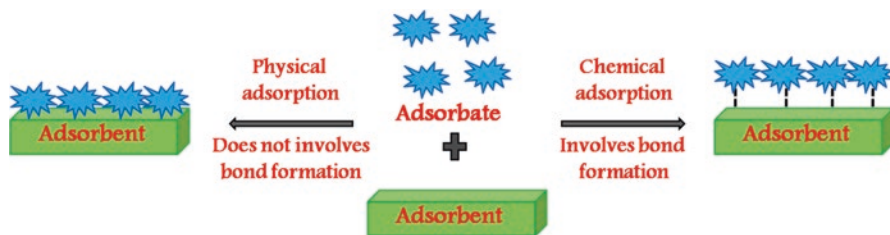
**Fig. 10.1**  Physical and chemical natures of adsorption process

called *adsorbate* on the surface of a solid material called *adsorbent*. It is governed by various physical (does not involve formation of new bonds) and chemical (involves formation of new bonds) forces and depending upon that adsorption can be reversible or irreversible (Fig. 10.1). Several other factors such as pH, temperature, concentration and contact time also affect adsorption phenomenon. Many adsorbents have been developed with an ability to remove toxic organic dyes from aqueous solution via adsorption process. Based on the resources, adsorbents can be classified as either natural or synthetic. Wide range of adsorbents are being explored which include bio-adsorbents like algae and fungi; readily available in nature, e.g. clay, mud and coal; synthetic materials, e.g. activated carbon, graphene and carbon nanotubes; and inorganic adsorbent like silica, alumina, zeolites, zinc oxide, iron oxides, etc. (Rafatullah et al. 2010, Dabrowski 2001). In addition, there have been significant studies on exploring industrial, municipal and agricultural wastes as adsorbent (Gupta 2009). The important features for a material to qualify as a good adsorbent are high adsorption capacities with high selectivity, reusability and low cost. In view of this, polymeric materials, particularly polysaccharides/biopolymers such as starch, chitin, chitosan and cellulose, have gained interest as alternative adsorbents or functionalizing the surface of adsorbents for the removal of dyes (Crini 2005). These are also low-cost natural adsorbent which does not pose any threat to the environment after their usage. These materials contain oxygen and/or nitrogen bearing functional groups which favour adsorption of dyes. The structural and physico-chemical characteristics of these materials provide opportunity of surface modifications which helps in achieving enhanced adsorption properties. Chitosan is one of the most widely studied adsorbents including other polysaccharides like cellulose and starch, due to high abundance and low cost (Crini 2006). Here we will discuss different cases of chitosan and their composites as an adsorbent.

## 10.2   Physico-chemical Properties of Chitosan

Adsorption involves interaction between adsorbate and adsorbent. Therefore molecular structure of the adsorbent would be decisive to explain the adsorption properties of the adsorbent. Chitosan is an acetylated derivative of chitin, which is a
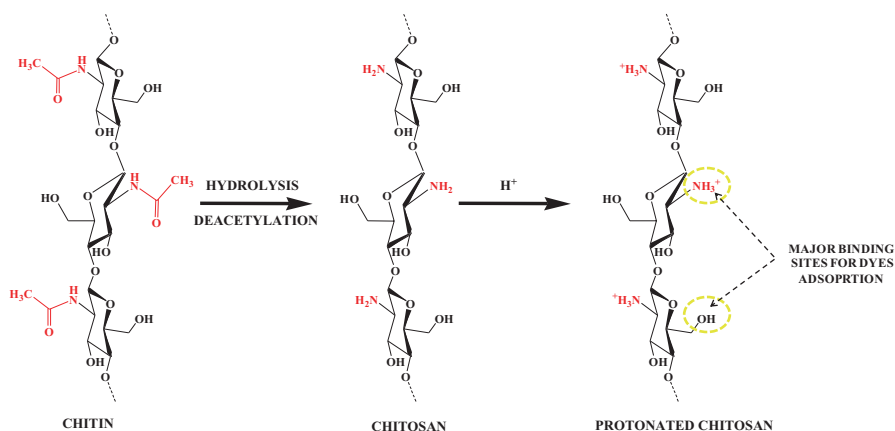
**Fig. 10.2** Chemical structures of chitin, chitosan and protonated chitosan

naturally occurring amino polysaccharide, and it is also known as poly-β-(1→4)-*N*-acetyl-ᴅ-glucosamine. The chemical structure of chitin is given in Fig. 10.2. It is obtained by the alkali treatment of the exoskeleton of crustaceans and shrimp, cartilages of molluscs, cuticles of insects and cell walls of microorganisms (Abdou et al. 2008). Chitosan is a common name of poly-β-(1→4)-2-amino-2-deoxy-ᴅ-glucose, which is deacetylated derivative of chitin. It is derived by the alkaline hydrolysis of chitin, which causes conversion of *N*-acetyl (−NHCOCH₃) groups into amine (−NH₂) groups. The degree of deacetylation of chitosan is the ratio of the total number of deacetylated units to the number of acetylated units. It is also a measure of number of –NH₂ groups which offer sites for binding with adsorbate molecules or ions. It may be remarked here that chitosan has found wide applications in different domains of science and technology, including an important adsorbent due to its low cost and non-toxicity. It should be stressed here that the toxicity of the adsorbent is an important specification as the spent adsorbents are often disposed in landfill.

One of the most important applications of chitosan is in the removal of pollutants such as organic dyes or toxic metal ions from contaminated water (No and Meyers 2000). The presence of hydroxyl and amine functional groups in chitosan plays vital role in the adsorption of pollutants from aqueous solution (Albadarin et al. 2017; Sharma et al. 2017). The most promising characteristic of chitosan is its chemical structure that allows chemical and physical modifications to enhance its adsorption ability. Chitosan with lower degree of deacetylation exhibits superior adsorption capacity towards acidic dyes as compared to chitosan with higher degree of deacetylation (Wong et al. 2008). This is due to the modifications in the internal structure of chitosan during deacetylation process which causes reduction in adsorption capacity. Other factors like crystallinity, weight and distribution of acetyl and amine functional groups also affect adsorption characteristics of chitosan (Jaworska et al. 2003; Guibal and Roussy 2007). For example, high molecular weight chitosan

exhibits poor solubility at basic pH because of intermolecular hydrogen bonding. But at acidic pH, chitosan shows excellent solubility due to the protonation of its amine groups. Similarly, poorly crystalline chitosan displays low adsorbent capacity due to the inaccessibility of amine and hydroxyl groups. Chitosan being a potential adsorbent suffers from many drawbacks, such as its poor thermal and mechanical strength (Guibal 2004), poor stability in acids (Zhou et al. 2009), low porosity and poor surface area (Alhwaige et al. 2013; Crini and Badot 2008). However, unlike several other polysaccharides, chitosan can be transformed into different morphologies like beads (Lee et al. 2014), nanofibres (Schiffman and Schauer 2007), membranes or films (Salehi et al. 2016) and nanoparticles (Shajahan et al. 2017) to increase its chemical functionality and mechanical and acid stability. Mechanical stability and adsorption capacity of chitosan have also been increased by making composites with clay, bentonite, montmorillonite, activated carbon, graphene oxide and metal oxide nanoparticles (Ngah et al. 2011; Zhang et al. 2016a, b; Chen et al. 2013; Reddy and Lee 2013). In subsequent section, we will discuss some selected cases where chitosan was used as adsorbent for dye removal.

## 10.3  Raw Chitosan

Several studies are being reported on the adsorption of dye molecules by pure chitosan. Mostly the researchers attributed the amine and hydroxyl groups in chitosan as binding sites for adsorption of dye molecules. It is important to mention that dye compounds can be broadly categorized as acidic dye, basic dye and reactive dye. The nature of interactions between dye molecules and chitosan depends upon the functional groups in dye. Acidic dyes are water-soluble anionic dyes which contain one or more sulfonic acid groups or other acidic groups. Therefore, adsorption of acidic dyes by chitosan occurs at low pH values where the negatively charged functional groups of dyes can bind electrostatically with the protonated binding sites of chitosan, mainly with $NH_3^+$. On the other hand, basic dyes are cationic water-soluble dyes which contain one or more electropositive centre and therefore exhibit lower adsorption values as compared to acidic dyes with chitosan-based adsorbents. Apart from acidic and basic dyes, chitosan-based adsorbent has been widely studied for the removal of reactive dyes from aqueous solution because these dyes contain a reactive that can form chemical bond with the hydroxyl and amine functional groups of the chitosan. The adsorption of reactive dyes by chitosan is a fast process and often displays very high adsorption capacity values.

In 2015, Pietrelli et al. reported the adsorptive removal of different types of dyes such as Telon B red (acidic dye), astrazon GTLN red (basic dye), Remazol RR gran yellow (reactive dye) and Scarlet red 23 (direct dye) by pure chitosan (Pietrelli et al. 2015). They performed adsorption experiments in batch mode as a function of pH, temperature, contact time, initial dye concentration and grain size. Under similar experimental conditions, the order of dye adsorption by chitosan was acidic > direct > reactive > basic dyes. As compared to basic pH, the adsorption of

dye by chitosan was more at acidic or neutral pH. This is due to protonation of amine group at lower pH which is responsible for electrostatic interactions between chitosan and dye molecules. This led to exploring adsorptive removal of different types of dye molecules by modifying chitosan at suitable pH. The ability of chitosan to get protonated at low pH is therefore expected to favour removal of anionic or acidic dye from wastewater.

Wong et al. conducted studies on the removal of various kinds of acid dyes such as acid green 25, acid orange 10, acid orange 12, acid red 18 and acid red 73 from aqueous system (Wong et al. 2003). For an optimized dose of chitosan as adsorbent and pH of the dye solution, the maximum adsorption capacities were 645.1, 922.9, 973.3, 693.2 and 728.2 mg/g, respectively. These values were determined from Langmuir adsorption isotherm, which implied that the dye interaction with chitosan is largely due to adsorption at the surface of the chitosan. The difference in the adsorption capacities was attributed to the molecular sizes and number of sulfonic acid groups attached to dye molecule. The optimum contact time was 24 h and the dye adsorption followed Langmuir isotherm model. Several other researchers also studied adsorption of anionic dye using chitosan as adsorbent (Pathania et al. 2016; Dos Anjos et al. 2002; Saha et al. 2010; Maghami and Roberts 1988; Kumar 2000). Thermodynamic results further showed that the process of dye uptake by chitosan is a spontaneous and an endothermic process. Though adsorption is primarily an exothermic process, these studies revealed that the adsorption capacity is enhanced at higher working temperature. Such anomalous behaviour is attributable to the need of activation energy for dye adsorption.

In addition, researchers also found it interesting to study adsorption of basic or cationic dyes by chitosan. However, the maximum adsorption capacity achieved in the case of basic dyes is lower as compared to acidic dyes. This is attributable to unfavourable electrostatic interactions between the positively charged chitosan and positively charged dye molecules (Annadurai 2002). In that case the observed order of cationic dye adsorption on chitosan is attributable to other forms of interactions, especially via π–π interaction between the six-membered rings of dye molecules and those in the molecular structure of chitosan. Adsorption of basic dye and reactive dyes occurs at higher pH due to the interaction of free electron pair of nitrogen with the electropositive centre of dye molecules. They have further showed that adsorption of different dyes on chitosan follows Langmuir adsorption isotherm indicating monolayer nature of adsorption.

The adsorption capacity of chitosan is also found to be influenced by the degree of deacetylation (Jóźwiak et al. 2017). Chitosan flakes with three different degrees of deacetylation, i.e. 75, 85 and 90%, were tested for the adsorption of a textile dye reactive black 5 from aqueous solution. It was found that chitosan flake with 90% degree of deacetylation reveals highest adsorption capacity of 1049.6 mg/g. This value is 160 times than more than that of chitosan with 75% degree of deacetylation. Deacetylation of chitosan results into incorporation of more number of amine groups. Therefore the drastic increase in the adsorption capacity of chitosan due to increased deacetylation is attributable to availability of higher number of amine sites on chitosan. Other studies also support the concept of achieving high adsorption

efficiency with chitosan flakes having high degree of deacetylation and vice versa (Kim et al. 1997). Thus, it can be concluded that unmodified chitosan can be used as an adsorbent for different types of dyes. However, adsorption capacity mainly depends on the nature of dye molecule, its molecular structure, degree of deacetylation and other experimental conditions like pH, temperature, contact time, etc.

## 10.4  Modified Chitosan

Chitosan exhibits great potential as adsorbent for toxic dyes, but at the same time it suffers from the drawback of low mechanical strength and poor acid stability. These two criteria are important for translating the use of chitosan as an adsorbent at industrial scale where rigidity of the structure and chemical environment are important considerations. Physical modification of chitosan is known to be an effective way to reinforce improved mechanical property and also acid stability. Chitosan can be physically transformed into various forms like beads, membranes, fibres, hydrogel or granules. Similar to the chitosan flakes, physically transformed chitosan also exhibits excellent dye adsorption properties with enhanced stability. The presence of reactive hydroxyl and amino functional groups in chitosan facilitates the modification process. Physical modifications do not bring any chemical change in the chitosan but bring in different morphological changes such as varying porous structures of chitosan with improved adsorption capacity. Physical modification causes expansion of chitosan chains, reduces crystallinity and increases the rate of diffusion of dye molecules to the internal adsorption sites (Li and Hsieh 2006). Porous chitosan beads can be prepared by the dropwise addition of acidic solution of chitosan into NaOH solution (Bekçi et al. 2008). It is important to thoroughly wash the beads with distilled water to remove any traces of NaOH from the surface. These dried chitosan beads exhibited excellent adsorption characteristics towards removal of cationic malachite green dye at higher pH. The favourable adsorption is attributable to interaction of dye molecules with the lone pair of electron present on nitrogen atom of the dye structure. Furthermore, as the adsorption is better at higher pH, so the surface of the chitosan could be modified by hydroxyl ions and hence favoured electrostatic interaction with the cationic dye. This is corroborated from the adsorption data at lower pH which revealed poor adsorption capacity owing to electrostatic repulsion between cationic dye and protonated chitosan beads. Chitosan beads were also effective in the removal of anionic dyes such as eosin Y, from aqueous solution (Chatterjee et al. 2005). Adsorption studies suggested that the removal of anionic dyes by chitosan beads follows pseudo-second-order kinetics and satisfies Langmuir model with a high adsorption capacity of 80.84 mg/g at 30 °C and at pH 4. Further, it was also illustrated that the 98% of the adsorbed eosin Y can be de-adsorbed from the chitosan beads at pH 11 or 12. The recycled chitosan beads can be reused as adsorbent for eosin Y dye up to five cycles without any significant loss in adsorption capacity.

Physical modification of chitosan in the form of membrane or film is another effective way to increase the adsorptive property by increasing porosity of the material. Different types of chitosan membranes are being developed by simple casting method on glossy paper surface (Mello et al. 2006). These types of chitosan membranes were very efficient in retaining methylene blue dye molecules with 100% efficiency. Similarly, the dye adsorption capacity of chitosan films prepared on plexiglas plates was compared with that of raw chitosan powder (Moura et al. 2016). It was found that chitosan films with 95% degree of deacetylation exhibited 99% adsorptive removal of reactive black 5 dye at pH 4. The advantage of using chitosan films as adsorbent is the ease in the separation and recovery of the adsorbent from the dye solution so that the film can be reprocessed for multiple uses.

Chitosan in the form of fibres is also found to be promising adsorbent for the adsorption of coloured dye stuff as impurities from wastewater. Chitosan fibres are cheaper and exhibit superior adsorption characteristics as compared to activated carbon fibres (Yoshida et al. 1991). Pure chitosan nanofibres of varying diameter were successfully synthesized using electrospinning method (Li et al. 2018a, b). The electrospinning parameters have a significant effect on the specification of the nanofibres. It is found that the average diameter of chitosan fibre was about 100 nm, which increased by about 30% when the operating voltage of the electrospinning unit was decreased from 20 kV to 15 kV. Further, the feed chitosan concentration is also important in controlling the diameter of the fibres. This is attributable to the viscosity of the chitosan feed. For example, the average diameter of the fibres was increased to 164 nm, when chitosan concentration was raised from 6 to 7% w/v. The dye adsorption efficiency of chitosan nanofibres is also influenced by its diameter. It was observed that dye adsorption capacity decreased with increase in the fibre diameter. This can be attributed to increase in surface area due to decreasing fibre diameter. High adsorption capacity of 1377 mg/g was achieved with chitosan fibres with an average diameter of 80–100 nm. The observed adsorption properties are superior to microscale chitosan sample prepared using traditional thermal-induced separation technique. As-prepared microstructures consist of laminar films and inter-connective pores which revealed an adsorption capacity of 412 mg/g only. Hollow chitosan fibres prepared via dry–wet spinning methods were also tested as a suitable bio-adsorbent for the removal of reactive blue 19 dye (Mirmohseni et al. 2012). It was observed that the dye uptake by the hollow fibres follows pseudo-second-order kinetics and obeys Freundlich isotherm. A high adsorption capacity of 454.5 mg/g was achieved at pH 3.5 in 90 min.

Similarly, porous chitosan nanofibers were fabricated by electrospinning method using 82.5 wt% deacetylated chitosan blended with polyvinyl alcohol (PVA) (Li and Hsieh 2006). The chitosan/PVA composition was important factor for obtaining lump less uniform nanofibers of desirable average diameter, which varied in the range of 20–100 nm. Hydrolysis of these chitosan nanofibres with NaOH resulted into nanoporous fibres with non-uniform surface morphology and pores. The porous structure in chitosan nanofibres was achieved by removing PVA matrix by alkali treatment. Further, the stability of the chitosan nanofibres was improved by cross-linking chitosan fibre with Denacol EX841. These types of

cross-linked chitosan nanofibres exhibited efficient adsorptive removal of acid dye (Yoshida et al. 1993). The maximum amount of acid orange II dye was adsorbed at pH 6.9 was10.6 mol/kg on chitosan nanofibres crosslinked with 4.76 wt% Denacol EX841. Chitosan fibres were also employed for the recovery of direct dye and acid dye from dilute aqueous solution. Therefore, it can be affirmed that porous chitosan was an excellent strategy for removing dye via adsorption.

## 10.5   Cross-Linked Chitosan Beads

Though chitosan exhibits great potential as a dye adsorbent, it also suffers from several limitations. High crystallinity and low hydrophilicity and porosity are some of the major shortcomings associated with chitosan. Intra-/intermolecular hydrogen bonding between hydroxyl and amine groups of same/different chains would tend to reduce the dye adsorption capacity of chitosan due to the unavailability of the functional groups for binding with dye molecule. Chemical structure of dyes also affects the adsorption properties of cross-linked chitosan beads (Cestari et al. 2004). The adsorption of dye on the surface of chitosan beads occurs in two steps, i.e. transfer of dye molecules from aqueous phase to the surface of adsorbent followed by the diffusion of molecule into the interior pores and binding sites. Dye removal by chitosan beads depends upon the concentration and nature of binding functional groups on dye. Intramolecular hydrogen bonding between the sulfonic acid and $NH_2$ groups of dye hinders its adsorption on the chitosan beads due to the absence of electrostatic forces. Similarly, more ramified and branched structure of dyes would also suppress the adsorption process at high temperatures. This is because at high temperature desorption is more favourable as compared to adsorption due to bulky dye structure. On the other hand, for linear and small dye molecules, adsorption increases with increase in temperature. This is due to opening of the pores of the adsorbent which helps in the diffusion of dye molecules to the internal binding sites those available on the beads.

Notably, bulky dye molecules might not be favourable to penetrate into the complex porous structure of chitosan due to steric hindrance. In this regard, modification of chitosan into gel beads by cross-linking agent is found to drastically enhance its adsorption capacity. Cross-linking of chitosan resulted in improving some of the important specifications for enhanced dye adsorption, e.g. improving mechanical strength and its stability in acidic medium and increasing porosity as well as increasing surface area. In addition, diffusion of dye molecules into the internal sorption sites of chitosan beads has been accounted for 99% malachite green (cationic) dye removal efficiency at pH 8 (Guibal et al. 2005). Several cross-linking agents, e.g. epichlorohydrin (ECH), sodium tripolyphosphate (TPP), glutaraldehyde (GLA) and ethylene glycol diglycidyl ether (EGDE), revealed better results in preparing chitosan beads.
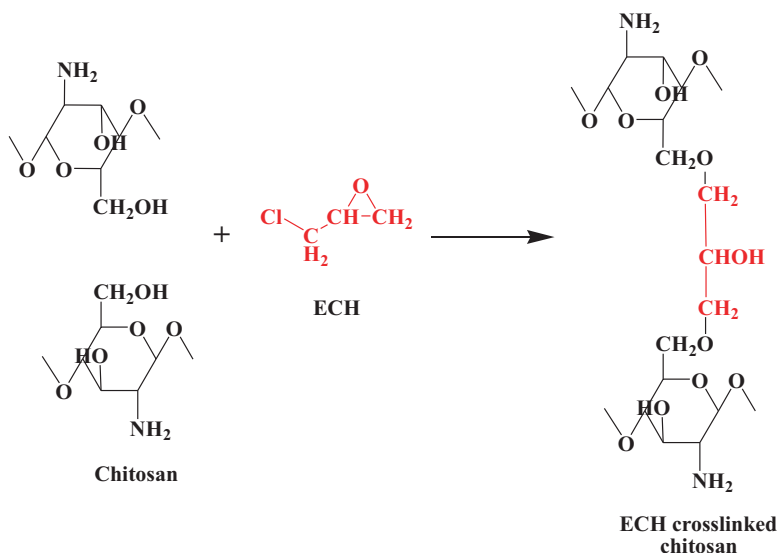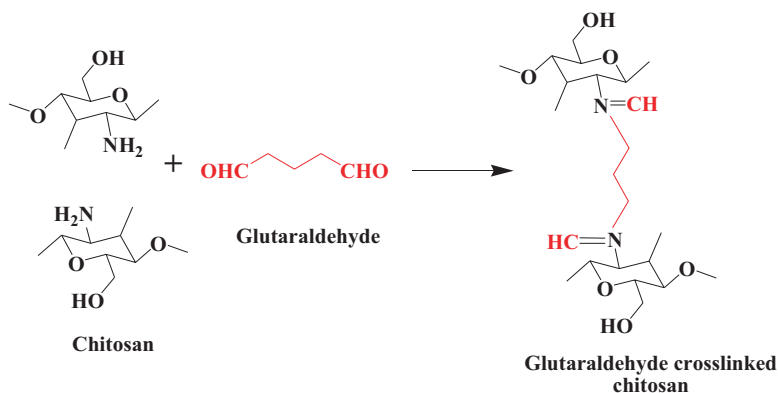
**Scheme 10.1**  Mechanism of chitosan cross-linking by epichlorohydrin (ECH)

## 10.5.1  ECH Cross-Linked Chitosan

The ECH has highly reactive chlorine centre and an oxirane ring. The cross-linking of chitosan by ECH occurs through the hydroxyl group of chitosan, as shown in Scheme 10.1. Because of this the amine group of chitosan remains free for adsorption with dye molecule. It is observed that smaller-sized ECH-linked chitosan beads could remove reactive red 189 dye from aqueous system at acidic pH. The corresponding adsorption capacity was 1936 g/kg, which is much better than pure chitosan as adsorbent at acidic pH (Chiou and Li 2002). Furthermore, successful studies on the removal of several other anionic dyes such as reactive red 222, acid blue 92 and reactive black 5 are also reported using ECH cross-linked chitosan beads as adsorbent (Chiou et al. 2003, Hanh et al. 2007, Kim et al. 2012).

In addition, ECH cross-linked chitosan beads were developed in acidic and basic medium for adsorption of azo dye (Li et al. 2013). Under similar adsorption conditions and at pH 4, strikingly better adsorption of Congo red (anionic azo dye) was found than the cationic dye. This is attributable to electrostatic interactions between positive residual charge at the amine groups of cross-linked chitosan and negatively charged dye molecules. On the same ground, the poor adsorption of cationic dye was due to electrostatic repulsions between the positively charged adsorbent and cationic dye molecules. Further, it is found that ECH cross-linked chitosan prepared in alkaline medium exhibited higher adsorption capacities than the unmodified chitosan.
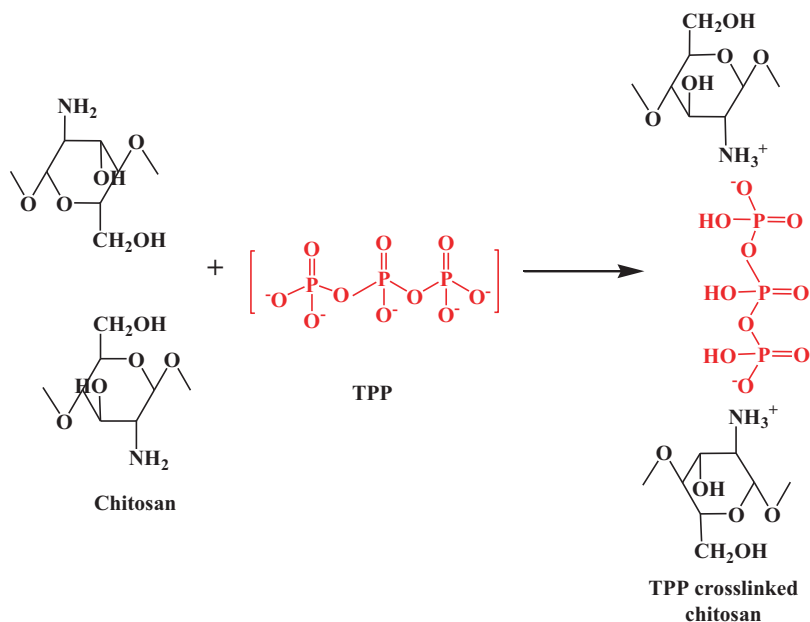
**Scheme 10.2**  Cross-linking mechanism of chitosan by glutaraldehyde

## 10.5.2  GLA Cross-Linked Chitosan

Glutaraldehyde (GLA) has been another interesting cross-linking agent for developing chitosan beads. GLA contains two aldehyde groups which cross-link with the amine group of chitosan through N=C linkages, as shown in Scheme 10.2. Because of this, the hydroxyl groups in chitosan become available for interacting with the dye molecules for adsorption. The effective cross-linking of chitosan with GLA in solution phase takes has been optimized to be a slow process (Guibal et al. 2003). Several studies have been reported on adsorptive removal of dye molecules from aqueous solution by chitosan beads cross-linked with GLA. For example, efficient adsorption of methyl orange (an anionic azo dye) by GLA cross-linked chitosan beads suggested affinity of anionic dye by positive residual charge on chitosan beads via electrostatic interactions (Morais et al. 2008). However, it is observed that GLA cross-linked chitosan beads are less efficient for adsorptive dye removal than other types of chitosan beads (Kamari et al. 2009). This could be attributed to the masking of the active binding sites, i.e. $-NH_2$ groups on chitosan during cross-linking.

## 10.5.3  TPP Cross-Linked Chitosan

Tripolyphosphate is a polyanionic molecule which can cross-link with the protonated amino group of chitosan in acidic condition (Liu et al. 2004). A tentative mechanism of cross-linking is shown in Scheme 10.3. The anionic TPP binds with cationic chitosan polymer via inter-/intramolecularly and resulted in the successful bead formation (Crini and Badot 2008; Bhumkar and Pokharkar 2006). It is noted

**Scheme 10.3** Mechanism of chitosan cross-linking by tripolyphosphate (TPP)

that the TPP cross-linked chitosan beads are more rigid as compared to chitosan beads prepared using ECH as cross-linker. The TPP cross-linked chitosan beads exhibited excellent pH-dependent adsorption of reactive red 189 dye from wastewater using TPP cross-linked chitosan beads (Chiou and Li 2003). The maximum dye adsorption capacity was 1800 mg/g at pH 3 and desorption occurred at pH 10.

Similarly, a comparison study on adsorption of Congo red anionic dye and methylene blue cationic dye was performed on TPP cross-linked chitosan beads (Kyaw et al. 2011). The adsorption efficiency was higher (~82%) for the Congo red dye at an optimum pH of 4. At the same pH and adsorbent dose, only 42% of methylene blue dye (cationic) was removed. This is governed by favourable/unfavourable electrostatic interactions between the charged pairs of adsorbent and dye molecule. Comparative studies of the adsorption of anionic Congo red dye on chitin and TPP cross-linked chitosan beads were performed in a wide pH range of 2–9 (Raval et al. 2016). Gradual decrease in the adsorption capacity values was observed with increased pH values. At high pH value of 7 and above, adsorption of dye on both the adsorbent is suppressed due to the presence of excessive hydroxyl ions which compete for the available adsorption sites. Removal of acid green 27 dye from aqueous solution was achieved using nanometre size TPP cross-linked chitosan beads (Hu et al. 2006). The maximum monolayer adsorption capacity was determined to be 1051.8 mg/g. It was further concluded that the nanosized chitosan beads displayed significantly higher adsorption capacity as compared to micron-sized chitosan beads due to high surface area.

Furthermore, molecular structure of dye also affects the adsorption capacity of TPP cross-linked chitosan beads significantly (Chiou and Chuang 2006). For example, the complexity in the molecular structure of reactive blue 15 dye resulted in its poor adsorption as compared to small linear structure of methanol yellow dye. However, ECH cross-linked chitosan beads revealed better adsorption efficiencies as compared to TPP cross-linked chitosan beads. If we compare the structure of ECH cross-linked and TPP cross-linked chitosan beads, it is evident that amine groups are available for binding in ECH cross-linked beads while hydroxyl groups are available in TPP cross-linked chitosan beads. It is also implied that the amine groups are better sites for dye adsorption than the hydroxyl groups in the chitosan beads.

### 10.5.4   Other Cross-Linking Agents

EDGE is an important cross-linking agent which contains two epoxide functional groups at the edges. EDGE cross-linking provides mechanical strength and acid stability to the chitosan and reduces swelling ability (McCloskey et al. 2009). Comparative study of the adsorption of acid red 37 (AR 37) and acid blue (25) from aqueous solution was performed using chitosan and EDGE cross-linked chitosan as adsorbents. It was found that chitosan exhibits much better adsorption properties for the two dyes as compared to its cross-linked derivative. This could be due to the possible cross-linking of the EDGE with $-NH_2$ groups of chitosan via epoxide groups, which reduces the concentration of available active binding sites. The adsorption profile matched well with the Langmuir and pseudo-second-order models. It has been also shown that both the adsorbents are capable of retaining their adsorption capacities even after three cycles of adsorption–desorption. Other cross-linked used for synthesizing chitosan beads are diglycidyl (7-ethyloctadecane diacid diglycidyl) (Shimizu et al. 2003), dimethyloldihydroxy ethylene urea (Fahmy et al. 2004) and ionic liquids (Naseeruteen et al. 2018).

## 10.6   Grafted Chitosan

Grafting is an effective way of enhancing adsorption capacity of chitosan without altering its properties. Grafting brings physical as well as chemical modifications in chitosan and improves its mechanical strength. As mentioned earlier, chitosan backbone has hydroxyl and amine functionalities which act as reaction centres for grafting. Grafting of different functional groups in chitosan occurs via formation of covalent bonds and has no significant effects on its biocompatibility, biodegradability and mucoadhesivity. On the other hand, grafting could introduce new functional

groups in chitosan structure to enhance the concentration of active sites for binding of dye molecules and also control its diffusion properties (Crini and Badot 2008). There are many routes of synthesizing grafted chitosan, but the most common among them is free-radical polymerization. Ammonium persulfate (APS), potassium persulfate (PPS), ceric ammonium nitrate (CAN), thiocarbonate–potassium bromate (TCPB), potassium diperiodatocuprate (III) (PDC), 2,2-azobisisobutyronitrile (AIBN) and ferrous ammonium sulphate (FAS) are some of the examples of initiators that have been used to initiate grafting copolymerization. In this strategy, the mechanical and adsorptive capability of chitosan was improved by cross-linking, and the grafting further augmented the adsorption capability. It is further noted that the resultant properties of the grafted chitosan depend on the molecular structure, length, concentration and properties of the side chain (Jayakumar et al. 2005). For example, adsorptive removal of reactive dye effluent was enhanced for the batch of chitosan beads prepared by amine-grafted GLA and ECH as cross-linking agents (Kyzas et al. 2011). Adsorption capacity of grafted chitosan is also influenced by the amount of grafting reagent. Therefore, it is necessary to optimize the concentration of grafting agent to achieve maximum number of active binding sites (Kyzas et al. 2013). Acrylamide and poly(ethyleneimine) were successfully employed as reagents for the grafting of amido and imino functional groups, respectively. Furthermore, the adsorption capacity of poly(ethyleneimine)-grafted chitosan was found to be better than that of acrylamide-grafted chitosan. This is attributable to more electropositive character of imino groups as compared to amido groups. The adsorption capacity of chitosan grafted with poly(ethyleneimine) enhanced the adsorption capacity by a factor of 3.5. Similarly, ethylenediamine grafting also increases the amino group concentration on chitosan surface which causes high removal efficiency of anionic dyes from wastewater (Huang et al. 2011).

## 10.7  Chitosan Composites

Chitosan has been widely used for synthesizing composites including those with nanoscale materials. For example, clay, activated clay, charcoal and graphene oxide and different types of metal oxides are only some of the materials with which chitosan composites were made to derive better adsorptive properties. Notably, the materials listed above are also well known adsorbents for removing wide range of hazardous compounds including dyes. Therefore composites of these materials with chitosan have often resulted in achieving improvement in adsorption properties. These types of chitosan-based composites are found to offer improved mechanical and chemical stability with large surface area, which made them desirable adsorbent for large-scale dye removal treatment. Some of the chitosan-based composites as adsorbents are discussed below.

### 10.7.1 Chitosan–Clay Composites

Similar to chitosan, clay minerals have also received much attention in the removal of pollutants from aqueous solution via adsorption mechanism. Integration of chitosan with clay material led to the development of more efficient adsorbent system. The composition of chitosan and clay would play important role in the morphology as well as the adsorption properties of the composites. Chitosan-activated clay beads of diameter 4.42 mm were synthesized using a mixture of NaOH and ethanol (Chang and Juang 2004). These composite beads exhibited better adsorptive removal of methylene blue and reactive red 222 dye from water, as compared to activated clay. The highest adsorption capacities of chitosan-activated clay composites as determined from the Langmuir adsorption isotherm were 330 g/kg and 1912 g/kg for methylene blue and reactive red 222 dyes, respectively. The adsorption capacities of the composites were either better or similar to those of the chitosan beads. Under such circumstances, the advantage of using clay–chitosan beads would limit the use of chitosan which is more expensive than clay. Consequently, the cost of dye removal could be drastically reduced by using optimized composition of clay and chitosan. In addition, the chitosan-clay composite beads exhibit excellent mechanical strength and hence these composites could be repeatedly used under harsher physical conditions. The mechanisms of the dye adsorption were different as the reactive red 222 dye adsorption obeyed pseudo-first-order kinetics, whereas methylene blue dye adsorption followed pseudo-second-order kinetics. The reason for the difference in the adsorption kinetic mechanism is attributed to the difference in the molecular structures of dyes. Small methylene blue dye molecules can easily migrate into the interior pores of the adsorbent beads and thus follow diffusion mechanism. Fixed-bed adsorption of methylene blue dye was carried out using beads composed of modified ball clay and chitosan, of particle size in the range 0.5–20 mm (Auta and Hameed 2014). Beads of modified ball clay and chitosan composite adsorb molecules of methylene blue dye at high pH via electrostatic forces. At high pH value, OH⁻ ions abstract proton from the active sites of the composite adsorbent such as SiOH, COOH, etc. and bind with dye molecules. At low pH values, protonation of these functional groups is not favorable for adsorption of dye molecules on the surface of adsorbent beads. The effect of inorganic salts such as sodium sulphate, sodium chloride and sodium bicarbonate were found to affect the uptake of dye molecules from aqueous solution. It was noted that the dye uptake was greatly hindered in the presence of sodium sulphate as compared to those of sodium chloride and sodium bicarbonate.

Bentonite and montmorillonite are some of the natural clay materials which are abundant in nature. They mainly consist of aluminium phyllosilicate mineral and are widely used as adsorbent for the removal of pollutants from wastewaters due to their low cost. Chitosan/montmorillonite nanocomposites were prepared with varying molar ratios of reactant materials and were explored as adsorbent for the removal of anionic Congo red dye (Wang and Wang 2007). Compared to pure chitosan and

pure montmorillonite, these composites exhibited improved adsorption characteristics over a wide pH range of 4–9. Similarly, chitosan/bentonite composites have been widely used as adsorbent for the adsorption of toxic textile dyes from aqueous system (Dotto et al. 2016). Bentonite is an attractive support material for the immobilization of chitosan and is used to enhance its mechanical stability. Chitosan/bentonite composites also exhibited high adsorption efficiency and excellent acid stability. Chitosan/bentonite composites have been considered as a potential adsorbent for the removal of anionic and cationic dyes with easy phase separation and reusability. The maximum adsorption capacity achieved for anionic amaranth red and cationic methylene blue dyes from coloured effluents were 362.1 mg/g and 496.5 mg/g, respectively. In addition, chitosan/bentonite composites further cross-linked with glutaraldehyde have also been developed as adsorbent for the removal of Amido Black 10B anionic dye (Liu et al. 2015). The maximum adsorption capacity of such composite adsorbent was determined as 323.6 mg/g at 293 K and pH 2. Higher adsorption capacity of 418.4 mg/g was achieved for Amido Black 10B dye by Zr(IV) surface-immobilized, cross-linked chitosan/bentonite composites (Zhang et al. 2016a, b). Adsorption studies were also reported on the removal of weak acid scarlet dye using composites of chitosan and CTAB-modified bentonites (Guo et al. 2012). The active functional groups present in chitosan and bentonite or montmorillonite interact with each other to form grafted copolymer. Since some cross-linking agent is used for the grafting mechanism, the resultant polymer network comprises of free functional moieties at the end of the polymer chain which facilitates dye adsorption.

### 10.7.2   Carbon–Chitosan Composites

Activated carbon and graphene or graphene oxides are interesting carbonaceous materials and are known to be excellent adsorbent owing to high surface area porous structure. Compared to graphene, activated carbon is a low-cost material. But the adsorption capacities of these materials are usually very high and hence the cost of adsorbent can be compensated (Tan et al. 2008). Activated carbon can be prepared from any carbon-rich materials. For example, municipal waste, household kitchen waste and agricultural wastes can be treated to synthesis bulk amount of activated carbon (Ahmed 2016). ECH is found to be an excellent linker agent for developing activated carbon–chitosan composite beads (Auta and Hameed 2013). Fixed-bed adsorption studies of such activated carbon–chitosan composite beads exhibited excellent adsorption properties for the removal of cationic methylene blue dye and anionic acid blue 29 dye. Maximum adsorption capacities achieved in case of cationic methylene blue dye and anionic acid blue 29 dye by cross-linked chitosan beads were 103.64 and 193.4 mg/g, respectively, at 30 °C. This value has been increased to 197.3 and 345.1 mg/g when studies were conducted using activated carbon–chitosan composite beads. It has been demonstrated that microwave heating could reduce the time needed for synthesizing such activated carbon–chitosan beads (Chen and He 2017). The adsorption capacities of the composite bead increases

with increasing activated carbon content attain a maximum adsorption capacity value of 35.4 mg/g with a 10:4 mass ratio of chitosan to activated carbon.

Graphene is a flat two-dimensional allotrope of carbon composed of sp$^2$ hybridized carbon atoms arranged in honeycomb-type structure. However, it is hydrophobic in nature and hence their application in aqueous medium would be challenging. This can be overcome by modifying and by oxidizing the peripheral carbons of the graphene system to synthesis hydrophilic graphene oxide. Essentially graphene oxide is easy to synthesize by Hummer's method or by modified Hummer's method (Verma and Dutta 2015). It should be realized that graphene oxide is highly soluble in water, and hence it may not be very convenient to be used as a heterogeneous adsorbent. It that case, either, graphene oxide can be used for functionalizing any material to be used as an adsorbent, e.g. clay and chitosan, for improving their adsorption property. In addition, graphene oxide can be reduced to amines and then its composite with clay can be more functional for adsorption. These derivatives of graphene systems can be categorized on the basis of different concentrations of oxygen functional groups such as –COOH, −OH and C−O−C in the basal plane and at the edges of graphene skeleton. Graphene surface can be chemically tuned for the removal of metal ions as well as dyes from aqueous solution (Verma and Dutta 2017a, Verma and Dutta 2017b). The composite of graphene oxide and chitosan can be synthesized by the formation of amide bond via reaction between –COOH group of graphene oxide and –NH$_2$ group of chitosan. In addition, glutaraldehyde is also known to act as a linker for synthesizing graphene-chitosan composites (Travlou et al. 2013). The functional groups of graphene derivatives and those in chitosan together act as active binding sites for the removal of dye molecules from solution. The adsorption efficiency of such graphene oxide/chitosan composites against the removal of reactive black 5 dye was very high (277 mg/g) at 25 °C and at pH 2. The dye adsorption was attributed to hydrogen bonding interactions between amine groups of chitosan and oxygen containing functional of graphene oxide. Further, it was noted that the adsorption capacity of the composite was better than those of individual materials used in making the composites. It should be remarked here that different morphologies of graphene oxide/chitosan composites were developed for dye adsorption application. The chitosan/graphene oxide hydrogel nanocomposites prepared by self-assembly and chitosan/graphene oxide fibre nanocomposites revealed excellent dye adsorption properties (Li et al. 2014; Chen et al. 2013). Dye adsorption due to interaction between the sulfonic acid (–SO$_3$H) group of dye molecule and the protonated amines of chitosan at acidic condition is discussed here.

### 10.7.3   Chitosan-Metal Oxide Composites

Metal oxides are versatile materials and some of them have found application as adsorbent. The ease of synthesis and extraordinary physico-chemical properties including high surface area of metal oxide nanoparticles are some of the key features for utilizing these materials as dye adsorbent. In addition, metal oxides exhibiting

magnetic property are useful for the post adsorption magnetic separation from adsorbate medium. Further, it is observed that the adsorption properties of metal oxides are drastically improved when they are made composites with chitosan. For example, magnesium oxide nanoparticles immobilized on chitosan substrate were found to be an excellent adsorbent for the removal of methyl orange dye (Haldorai and Shim 2014). The advantage of immobilizing MgO nanoparticles on chitosan over free MgO nanoparticles is the ease of separation of the adsorbent after adsorption. In addition, the surface charge of chitosan/MgO nanocomposite was +50.7 mV at pH 7, which facilitated the removal of negatively charged dye molecules from solution by electrostatic interaction. It was possible to achieve 98% dye removal efficiency in 30 min with 0.5 g of chitosan/MgO nanocomposite. The scope for reusability of the chitosan/MgO nanocomposite has also been demonstrated up to five cycles without sacrificing its dye removal efficiency.

Similarly, $Fe(OH)_3$-loaded chitosan beads were developed for removal of anionic Congo red and methyl orange dyes from the solution (Li et al. 2018a, b). The adsorption capacities were 445.32 and 314.45 mg/g for Congo red and methyl orange, respectively, at pH 3. Such high adsorption capacities were attributed to positive surface charge on the adsorbent owing to protonation of the amine groups of chitosan. The dye adsorption mechanism was proposed on the basis of physical (electrostatic) and chemical interactions. The chemical interaction was discussed in the light of possible complexation mechanism based on hydrogen bonding or Lewis acid-base mechanism between $Fe(OH)_3$ and the dye molecules. In addition, magnetic composites of chitosan were prepared by incorporating $Fe_3O_4$, $Fe_2O_3$, $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$ particles (Haldorai et al. 2015; Zhu et al. 2010; Sadrolhosseini et al. 2017; Zhang et al. 2014; Ansari et al. 2016; Kumar et al. 2018). These magnetic nanocomposites showed fast dye adsorption properties with high efficiency. Also, presence of magnetic material in the composite provided an easy way of adsorbent separation using an external magnetic. Dye adsorption studies were also reported using ethylenediamine- and glutaraldehyde-modified magnetic chitosan nanoparticles (Zhou et al. 2011; Zhou et al. 2014). Furthermore, magnetic nanoparticles were also introduced in chitosan/graphene oxide composites to induce magnetic properties to the composites. This three-component adsorbent system was investigated for the adsorption of anionic and cationic dyes such as methylene blue (Fan et al. 2012b), methyl blue (Fan et al. 2012a) and methyl violet and alizarin yellow R (Gul et al. 2016). Langmuir adsorption capacities recorded for these studies were 180.83, 95.16, 17.66 and 14.82 mg/g, respectively. It was found that adsorption of anionic and cationic dyes by $Fe_3O_4$ supported chitosan/graphene oxide composite is not affected by the ionic strength of the solution. It was also studied that the as-prepared adsorbent can be reused up to four consecutive cycles without any loss in the adsorption capacity when acetone was used as the desorbing agent (Gul et al. 2016).

It should be remarked here that nanocomposites of chitosan and ZnO or $TiO_2$ or CuO offer very interesting property. These metal oxides are known to be excellent photocatalytic agent (Nenavathu et al. 2018; Fujishima et al. 2008, Sharma and Dutta 2015). So their nanocomposites or beads with chitosan could offer adsorptive photocatalytic degradation. Our ongoing studies on removal of Congo red anionic

**Fig. 10.3** FE-SEM image of ZnO–chitosan nanocomposite
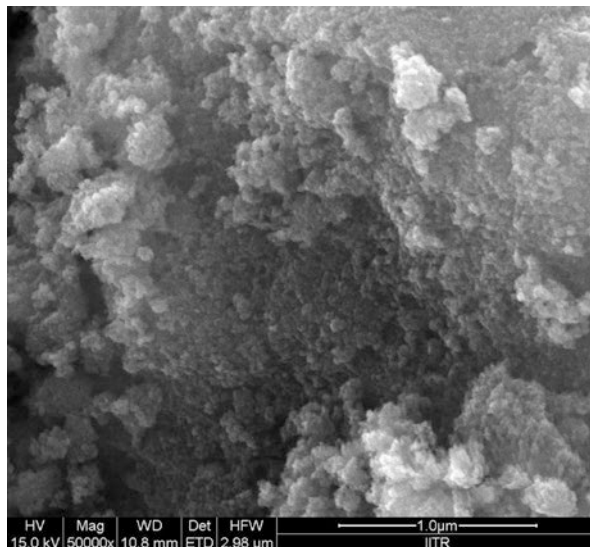


dye by ZnO–chitosan nanocomposites under UV light exposure ($\lambda$ = 365 nm) revealed initial adsorption of the dye on the surface of ZnO–chitosan nanocomposites followed by photocatalytic degradation of the dye. Here the ZnO–chitosan nanocomposite was prepared by hydrothermal method (Liu and Zeng 2003), where the initial chitosan composition taken was 5 wt % of the Zn precursor. The morphological information of the ZnO–chitosan nanocomposite is evident from the FE-SEM image (Fig. 10.3), showing spherical nanoparticles of ZnO adhered to the chitosan polymeric matrix. The synthesis of ZnO–chitosan nanocomposite was confirmed from XRD measurement which revealed formation of wurtzite structure (Fig. 10.4), and our results matched well with the XRD of ZnO reported in literature (Dutta et al. 2012). The band structure of ZnO is revealed from the UV-vis spectrum showing excitonic peak at 367 nm (Fig. 10.5). The dual role of adsorption and photocatalytic dye degradation by ZnO–chitosan nanocomposite was established by following decrease of the dye concentration in reaction medium, as shown in Fig. 10.6a. The decrease in the dye concentration in dark condition is due to adsorption process, where 58% of the dye molecules were adsorbed at equilibrium condition attained in 90 min. In this study, the dye concentration was deliberately kept high with respect to the amount of adsorbent in order to establish both adsorption and photocatalytic processes. The dye removal due to adsorption process and not due to photocatalytic process was ensured by treating the Congo red dye solution with ZnO–chitosan nanocomposite in dark condition. This corresponded to 58% dye removal in 120 min. Subsequently, when the reaction assembly was transferred to UV light exposure, a total of 96% of the dye molecules was removed (Fig. 10.6a). It should be mentioned here that the dye degradation during UV light exposure was not due to photolysis, which was confirmed from negligible decrease in dye concentration in a control study where the dye solution was exposed without treating with ZnO–chitosan nanocomposites. Therefore, the observed decrease in the dye
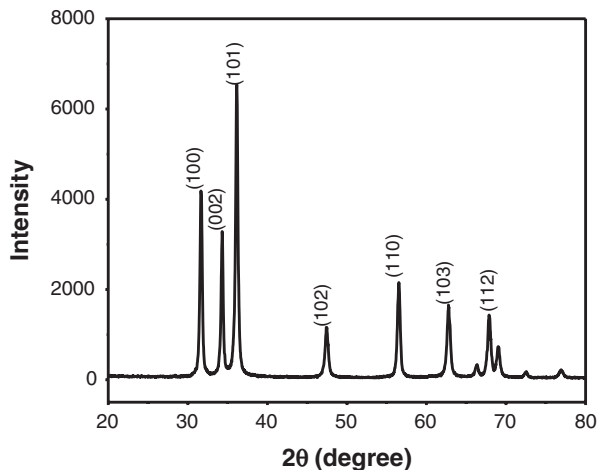
**Fig. 10.4** X-ray diffraction of ZnO nanoparticles used in ZnO–chitosan nanocomposite
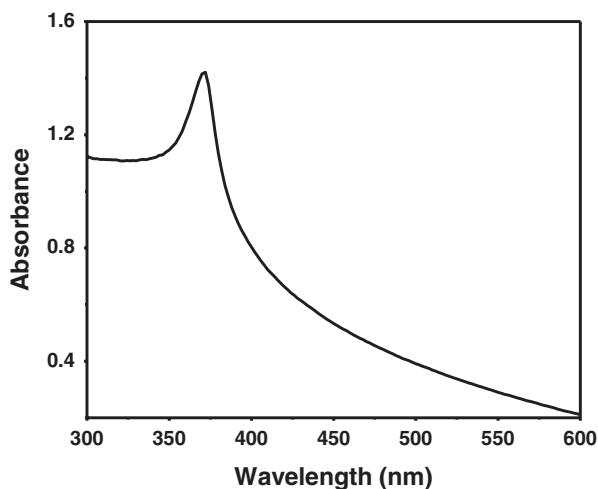


**Fig. 10.5** UV-visible spectrum of ZnO nanoparticles used in ZnO–chitosan nanocomposite showing band structure

concentration under UV light after adsorption process was due to photocatalytic degradation triggered by ROS generation. Under UV light exposure, hydroxyl radicals are generated due to interaction of photoexcited holes at the valence band and moisture at the surface of the ZnO nanoparticles. Such phenomenon is very well documented by our research group (Nenavathu et al. 2013). Because of the degradation, the dye molecules were removed from the surface of the nanocomposites, and hence it was reused without any further dye desorption treatment. The reusability of the nanocomposite for three consecutive cycles of dye removal is shown in Fig. 10.6b.
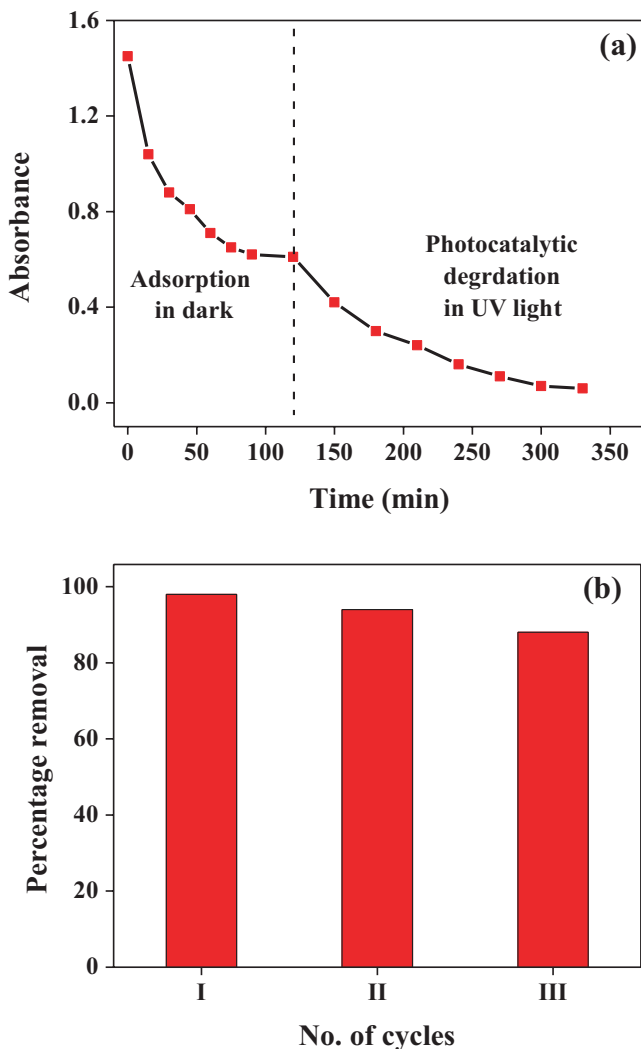
**Fig. 10.6** (**a**) Dye removal efficiency of ZnO–chitosan nanocomposite via adsorption–photocatalytic degradation process and (**b**) reusability studies of ZnO–chitosan for dye removal

## 10.7.4  Other Chitosan-Based Composites

Novel chitosan composites were also prepared with other polysaccharide material such as cellulose which also exhibit great potential towards the removal of dye stuff from aqueous solution. The cellulose/chitosan composite showed a high Langmuir adsorption capacity of 381.7 mg/g at pH 7 and at 303 K for anionic Congo red dye (Wang et al. 2018). Adsorption property of nanofibrillated cellulose/chitosan composites modified with ethylenediamine was also evaluated against cationic and

anionic dyes. The models cationic and anionic dyes considered for this study were methylene blue and new coccine, respectively (Liu et al. 2016). A high adsorption value of 0.67 mmol/g was observed for methylene blue dye at pH 4, whereas a value of 0.172 was observed at pH 2 for anionic new coccine dye. The reusability results showed that the effective desorption of dyes can be achieved using $NH_4OH/NH_4Cl$ as desorbing agent. It was observed that after three cycles, the recycled adsorbent can keep 10% and 98% adsorption capacities for methylene blue and new coccine, respectively. The reason for the different adsorption capacities is attributable to the dissimilar adsorption mechanism of cationic and anionic dyes by ethylenediamine-modified nanofibrillated cellulose/chitosan composites.

Composites of chitosan pyrrole and chitosan aniline were also prepared with agricultural waste material such as rice bran and employed for the adsorption of malachite green dye. The respective adsorption capacities were 122.5 and 55 mg/L for an initial dye concentration of 200 mg/L with an adsorbent dose of 0.05 g/L (Bhatti et al. 2017). Other work also reports successful removal application of dyes by porous chitosan/hydroxyapatite composite membrane (direct blue 15, 369 mg/g) (Shi et al. 2017), cross-linked chitosan/β-cyclodextrin polymer composite (methyl orange, 392 mg/g) (Jiang et al. 2018), fly ash–chitosan–graphene oxide composite (acid red GR, 38.87 mg/g: cationic red X-5GN, 64.50 mg/g) (Sheng et al. 2016) and chitosan–alunite composite (reactive red 2, 462.74 mg/g: acid red 1, 588.75 mg/g) (Akar et al. 2016).

## 10.8   Other Aspects of Dye Adsorption on Chitosan-Based Adsorbents

The nature of the adsorption of adsorbate on the surface of adsorbent material is governed by thermodynamic parameters such as Gibb's free energy ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$). These factors were further used to describe spontaneity, favourability and endothermicity/exothermicity of the adsorption process. Here, in this section, we will only consider the thermodynamic aspects of the dye removal studies using chitosan-based solvents discussed above. It was observed that the adsorptive removal dye by different forms of chitosan and its composites are spontaneous in nature as suggested from the negative $\Delta G°$ and is a favourable process. However, adsorption capacity of the chitosan-based adsorbent may increase or decrease with the rise of temperature. It was observed that the endothermicity/exothermicity of the adsorption process is independent of the chemical nature of dye. Most of the studies discussed above revealed that the adsorption of dyes by unmodified chitosan is an endothermic process. The reason for the enhancement in the adsorption capacity values is the diffusion of dye molecules into the interior of the adsorbent material at high temperature. Thermodynamic studies of the adsorption of acidic dyes on chitosan composites with montmorillonite, bentonite, $Fe(OH)_3$, cellulose and fly ash–graphene oxide are

endothermic in nature (Wang and Wang 2007; Liu et al. 2015; Li et al. 2018a, b; Wang et al. 2018; Sheng et al. 2016). On the other hand, endothermic as well as exothermic adsorption processes were reported for the removal of reactive dye by ECH cross-linked chitosan (Kim et al. 2012; Chiou and Li 2003). The reason for the variation in the adsorption thermodynamics may depend on the structural difference of the adsorbent material.

Kinetics of the adsorption of different types of dyes by chitosan and its composite material follows pseudo-second-order kinetics rather than pseudo-first-order kinetics. However, very few studies report some special conditions where the adsorption kinetics follows pseudo-first-order model or any other kinetic model such as Elovich kinetic model (Chiou and Chuang 2006; Dotto et al. 2016). The kinetics of the adsorption process also depends on the initial dye concentration. It was found that the adsorption of anionic metanil yellow and reactive blue 15 dye on chemically cross-linked chitosan follows pseudo-first-order kinetics at low initial dye concentrations but follows pseudo-second-order model for higher initial concentration of dye (Chiou and Chuang 2006). The reason for the change in the kinetic mechanism lies in the fact that the adsorption driving forces are stronger for higher initial dye concentration. Hence it can be concluded that adsorption of dyes on chitosan-based adsorbent is independent of the nature of dye (cationic/anionic/reactive). But at the same time, its mechanism depends upon the experimental conditions.

## 10.9    Summary

This book chapter deals with the discussions on utilization of chitosan as a versatile adsorbent for removal of organic dyes from aqueous system via adsorption mechanism. A consolidated list of chitosan-based adsorbent for the removal of various types of dyes is presented in Table 10.1. Chitosan is derived by the deacetylation of its precursor material chitin by alkali treatment. The presence of free hydroxyl and amino groups in chitosan is helpful in the adsorption of dye molecules. Adsorption of anionic dyes by chitosan occurs at low pH values due to protonation of its functional groups. Removal of cationic dyes by chitosan yields low adsorption capacity values due to the electrostatic repulsive force between protonated chitosan and positively charged dye molecules. Adsorption capacity of chitosan is greatly affected by the degree of deacetylation, crystallinity and pH of the dye solution. Some other drawbacks associated with chitosan are its low mechanical strength and acid stability.

It is found that the adsorption capacity, mechanical strength and acid stability of chitosan can be improved by performing physical and chemical modifications of chitosan. Raw chitosan can be modified into various morphologies such as beads, fibres, membranes and nano- and microparticles. In addition, physical modifications of chitosan can lead to porous network structure with an advantage of reusability of the adsorbent. However, this type of modification is sometimes accompanied with

**Table 10.1** Consolidated list of chitosan based adsorbent for dye adsorption

| Sl. No. | Adsorbent | Dye | Adsorption capacity | Temperature (°C) | pH | References |
|---|---|---|---|---|---|---|
| 1. | Chitosan | Astrazon GTLN red | 58.82 mg/g | 20 | 6 | Pietrelli et al. 2015 |
| | | Telon B red | 144.9 mg/g | | | |
| | | Remazol RR gran yellow | 98.04 mg/g | | | |
| | | Scarlet red 23 | 142.8 mg/g | | | |
| 2. | Chitosan | Acid green 25 | 645.1 mg/g | 25 | 4 | Wong et al. (2003) |
| | | Acid orange 10 | 922.9 mg/g | | | |
| | | Acid orange 12 | 973.3 mg/g | | | |
| | | Acid red 18 | 693.2 mg/g | | | |
| | | Acid red 73 | 728.2 mg/g | | | |
| 3. | Chitosan 10B | Methyl orange | 30.14 μmol/g | 33 | 4 | Saha et al. (2010) |
| 4. | Chitosan hydrogel (DD = 90%) | Reactive black 5 | 1559.7 mg/g | 22 | 4 | Jóźwiak et al. (2017) |
| 5. | Chitosan beads | Malachite green | 93.55 mg/g | 30 | 8 | Bekçi et al. (2008) |
| 6. | Chitosan hydrobeads | Eosin Y | 80.84 mg/g | 30 | 8 | Chatterjee et al. (2005) |
| 7. | Chitosan powder | Reactive black 5 | 654.3 mg/g | 25 | 4 | Moura et al. (2016) |
| 8. | Chitosan film | Reactive black 5 | 589.5 mg/g | 25 | 4 | Moura et al. (2016) |
| 9. | Chitosan nanofibrous membranes (86 nm) | Acid blue 113 | 1338 mg/g | RT | – | Li et al. (2018a, b) |
| 10. | Chitosan hollow fibres | Reactive blue 19 | 454.5 mg/g | 25 | 3.5 | Mirmohseni et al. (2012) |
| 11. | ECH cross-linked chitosan beads (2.3–2.5 mm) | Reactive red 189 | 1936 mg/g | 30 | 3 | Chiou and Li (2002) |
| 12. | ECH cross-linked chitosan beads | Reactive red 222 | 2252 mg/g | 30 | 3 | Chiou et al. (2003) |
| 13. | ECH cross-linked chitosan beads | Reactive black 5 | 0.68 mol/kg | 35 | 5 | Kim et al. (2012) |

**Table 10.1** (continued)

| Sl. No. | Adsorbent | Dye | Adsorption capacity | Temperature (°C) | pH | References |
|---|---|---|---|---|---|---|
| 14. | GLA cross-linked chitosan beads | Acid blue 25 | 127.06 mg/g | 27 | 4 | Kamari et al. (2009) |
| | | Acid blue 37 | 166.67 mg/g | 27 | 6 | |
| | $H_2SO_4$ cross-linked chitosan beads | Acid blue 25 | 102.53 mg/g | 27 | 4 | Kamari et al. (2009) |
| | | Acid blue 37 | 139.28 mg/g | 27 | 6 | |
| 15. | Chitosan beads | Congo red | 166.67 mg/g | RT | 6 | Raval et al. (2016) |
| 16. | Chitosan nanoparticles | Acid green 27 | 1051.8 mg/g | 25 | 5 | Hu et al. (2006) |
| 17. | Cross-linked chitosan beads | Metanil yellow | 1334 mg/g | 30 | 4 | Chiou and Chuang (2006) |
| | | Reactive blue 15 | 722 mg/g | | | |
| 18. | Chitosan ionic liquid beads A | Malachite green | 8.07 mg/g | RT | 4 | Naseeruteen et al. (2018) |
| 19. | EDA modified chitosan | Eosin Y | 294.12 mg/g | 25 | 5 | Huang et al. (2011) |
| 20. | Chitosan-activated clay composite | Methylene blue | 330 mg/g | 30 | 7.14 | Chang and Juang (2004) |
| | | Reactive dye RR222 | 1965 mg/g | 30 | 6.47 | |
| 21. | Chitosan/ montmorillonite nanocomposite | Congo red | 54.52 mg/g | 30 | 7 | Wang and Wang (2007) |
| 22. | Chitosan/bentonite hybrid composite | Amaranth red | 362.1 mg/g | 25 | 2 | Dotto et al. (2016) |
| | | Methylene blue | 496.5 mg/g | 25 | 10 | |
| 23. | Cross-linked chitosan/ bentonite composite | Amido black 10B | 323.6 mg/g | 20 | 2 | Liu et al. (2015) |
| 24. | Chitosan–CTAB modified bentonites | Weak acid scarlet | 102 mg/g | 25 | – | Guo et al. (2012) |
| 25. | Graphene oxide/ chitosan fibres | Fuchsin acid dye | 175.4 mg/g | 20 | 4.5 | Li et al. (2014) |
| 26. | Ethylenediamine- modified magnetic chitosan nanoparticles | Acid orange 7 | 3.47 mmol/g | 25 | 4 | Zhou et al. (2011) |
| | | Acid orange 10 | 2.25 mmol/g | | 3 | |
| 27. | Glutaraldehyde cross-linked magnetic chitosan nanoparticles | FD&C blue 1 | 475.61 mg/g | 25 | 3 | Zhou et al. (2014) |
| | | D&C yellow 5 | 292.07 mg/g | | | |

**Table 10.1** (continued)

| Sl. No. | Adsorbent | Dye | Adsorption capacity | Temperature (°C) | pH | References |
|---------|-----------|-----|---------------------|------------------|-----|------------|
| 28. | Magnetic chitosan/ graphene oxide composite | Methylene blue | 180.83 mg/g | 30 ± 0.2 | 10 | Fan, Luo, Sun, Li, Lu and Qiu. (2012) |
| 29. | Magnetic chitosan grafted with graphene oxide | Methyl blue | 98.52 mg/g | 30 | 5.3 | Fan, Luo, Li, Lu, Qiu and Sun (2012) |
| 30. | Cellulose/chitosan hydrogel | Congo red | 381.7 mg/g | 30 | 7 | Wang et al. (2018) |

the lowering of adsorption capacity due to the screening of the active binding sites which hinders dye adsorption process. Chemical modifications of chitosan include modifications in its hydroxyl and amine functional groups to achieve high dye removal efficiency.

Another way of increasing adsorption capacity of chitosan is the formation of its composites with other adsorbent materials. Some of the commonly used materials that are used to reinforce adsorption capacity of chitosan include clays, activated carbon, graphene and its derivatives and metal oxide nanoparticles. The incorporation of these materials improves mechanical strength of chitosan and also increases its stability in acids. Incorporation of magnetic nanoparticles in chitosan provides as easier way of the magnetic separation of the adsorbent. Finally, it has been demonstrated that chitosan–metal oxide nanocomposite could be an excellent choice for the removal of dye molecules via adsorptive photocatalytic degradation, which has tremendous scope and future for translating the system to industrial level.

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