REVIEW ARTICLE

Physicochemical modification of chitosan adsorbent: a perspective

Asokogene Oluwadayo Francis[1,2] · Muhammad Abbas Ahmad Zaini[2] ⓘ · Idris Misau Muhammad[3] ·
Surajudeen Abdulsalam[3] · Usman Aliyu El-Nafaty[3]

Abstract

Chitosan is a low-cost natural adsorbent. Its derivatives from chemical and physical modification processes possess superior properties for wide applications to meet the growing demands. The chemical modification includes replacement reactions, chain elongation and depolymerization, while the physical modification is to obtain polymeric forms such as powders, nanoparticles and gels. This paper is aimed to highlight the present trends in chitosan preparation and modification, the enhancement in adsorptive properties and the remarks into future directions. The mechanisms involved in adsorption by chitosan derivatives and how the spent adsorbent can be regenerated were also discussed. Meanwhile, for the adsorption of heavy metals from wastewater, chitosan modified with activated carbon showed a better adsorption capacity of 90.90 mg g^{-1} for Cr(VI) and 50.50 mg g^{-1} for Cd(II), and for dye adsorption, chitosan modified with activated neem leave showed better adsorption capacity of 90.8 mg g^{-1} for methylene blue, and for phenol removal, chitosan modified with salicylaldehyde and β-cyclodextrin polymer showed better adsorption capacity of 179.73 mg g^{-1}.

Keywords Adsorption · Chitosan · Hydrophilicity · Mechanism · Modification · Physicochemical

1 Introduction

Chitosan is a post-deacetylation chitin derivative and one of the most abundant post-cellulose polysaccharides in nature [1, 2]. It has found wide applications in biotechnology, agriculture, medicine and so on, due to growing demands [3–5]. In general, shrimp, crab, crayfish and krill shell can be used to prepare chitosan [6, 7]. However, studies have also shown that alternative sources of chitin (basic raw materials for chitosan preparation) are bees, fungi, coral and crustacean resting eggs [8]. This basic raw material (chitin) for chitosan preparation can be processed through chemical processes involving deproteinization, demineralization and deacetylation [9, 10]. Annually, 2000 tons of chitosan is produced mainly from shrimps and crab shell waste [11, 12].

Crustaceans are found to be more suitable for deacetylation and have different degrees of deacetylation-based solubility and swelling characteristics which are attributable to the parallel arrangement of their main chains due to weak intermolecular hydrogen bonding [13, 14]. This swelling property allows adsorption, floating and chitosan drug diffusion mechanism [15–17]. Chitosan is also one of the most available sustainable products in the natural environment, obtained as a result of the chemical or enzymatic deacetylation of chitin in the biosynthesis process [18]. This method leads to partial or complete elimination of acetyl groups from the chitosan group of acetyl-amino. Chitosan's name is applied to the altered chitin which contains less than 25% of the acetyl groups [19, 20]. Figure 1 presents the chemical structures of chitin and chitosan.

$(1 \rightarrow 4)$-2-Acetamido-2-deoxy-β-D-glucan and $(1 \rightarrow 4)$-2-amino-2-deoxy-β-D-glucan are the basic structures of Chitin and chitosan, respectively (Fig. 1). Nevertheless, the difference between them is the degree of deacetylation and their solubility in dilute acid media [22, 23]. When the chitin degree of deacetylation drops to about 50%, it becomes soluble in aqueous acidic media and is called

✉ Muhammad Abbas Ahmad Zaini
abbas@cheme.utm.my

1 Department of Mineral and Petroleum Resources Engineering, Federal Polytechnic, Auchi, Edo State, Nigeria

2 Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu-Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

3 Department of Chemical Engineering, Abubakar Tafawa Balewa University, Bauchi, Bauchi State, Nigeria

Fig. 1 Chemical structure of chitin and chitosan [21]
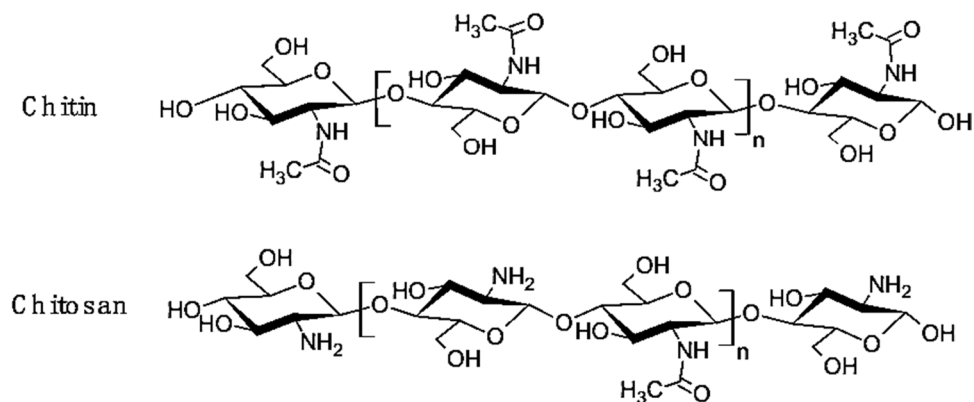
chitosan [24, 25]. Depending on the source, there are three crystalline polymorphic forms of chitin. These include shrimp and crab shell α-chitin, squid pen ß-chitin and cephalopoda stomach cuticles γ-chitin [26].

To improve the sorption potential, resistance to low pH and mechanical strength of chitosan, several physical and chemical modification methods have been applied [27]. Physical modifications include the preparation of chitosan for all applications in various forms such as powder, nanoparticles, gel beads, membranes, sponges, type structure of "honeycomb" and various types of fibre [16]. Chemical modifications include cross-linking with glutaraldehyde,

ß-cyclodextrin oxidized, ethylene glycol diglycidyl ether or epichlorohydrin [28]. Figure 2 presents a schematic representation of the cross-linking reaction of chitosan with glutaraldehyde.

Chitosan has found numerous applications in various industries, such as textiles, paper, cosmetics, pharmaceutical, agricultural, medical and environmental engineering [31–33]. It is primarily used in environmental engineering as an effective biosorbent [34].

The advantages of chitosan over other adsorbents include its abundance as biopolymer in nature, the presence of characteristics free amino and hydroxyl functional

Fig. 2 Schematic representation of the cross-linking reaction of chitosan with glutaraldehyde [29, 30]
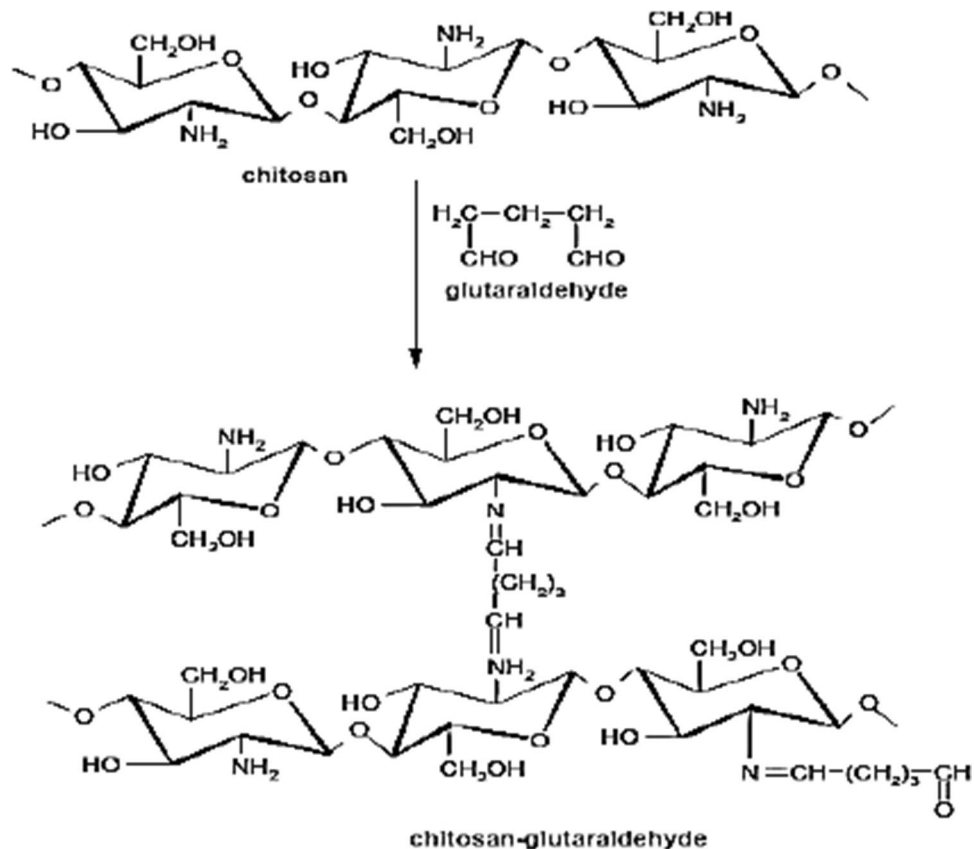
groups which makes it chelate five or more metals than other adsorbents [35] and the presence of positions that can be modified in its chemical structure [36]. In metal sorption, chitosan is selective because it does not take up alkaline and alkaline earth metal ions but transition and post-transition metal ions [17]. These properties of sorption were used for environmental, separation and analytical purposes [16]. Other advantages include its low price, high sensitivity to a variety of contaminants, chemical stability, high reactivity and pollution selectivity [16, 37].

Chitosan modification results in the formation of chitosan derivatives which possess better properties and an increased number of adsorption sites and adsorption capacity [36, 38]. Wang et al. [39] and Kulkarni et al. [40] reported chitosan modification methods to include N-substitution, O-substitution and free radical graft copolymerization. LogithKumar et al. [41] discussed recent research in chitosan modifications by quaternization, carboxyalkylation, hydroxylation, phosphorylation, sulphation and copolymerization for bone tissue engineering. Seedevi et al. [42] showed an increase in the antioxidant property of chitosan from sepia prashadi by chlorosulfonic acid in *N,N*-dimethylformamide. Campelo et al. [43] recorded an increase in the roughness and hydrophilicity and a decrease in calcium deposit of chitosan by sulphation modification for metallic implants when in contact with blood. Galhoum et al. [44] showed an increase in uranyl removal onto chitosan grafted with diethylenetriamine. Vakili et al. [45] reported an improve adsorption capacity of colorant blue 4 by chitosan modified with hexadecylamine and 3-aminopropyl triethoxysilane. Furthermore, chitosan hydrogels used in wastewater treatment have been greatly improved when modified by protonation, carboxylation and grafting with glutaraldehyde, epichlorohydrin, ethylene glycol, diglycidyl ether and sodium tripolyphosphate [46–48]. Stabilization of enzymes like amylase from *Aspergillus carbonarius* was achieved when chitosan was modified with phthalic anhydride [49] and the stabilization of horseradish peroxide was achieved when chitosan was covalently modified using phthalic anhydride [50].

Several review papers have been published on chitosan extraction [15], chitosan and modified chitosan as low-cost adsorbent [20, 36, 37], chitosan application in the industry, agriculture and medical science [3, 31, 41, 51] and chitosan and modified chitosan regeneration [52]. However, this review attempts to discuss the underlying background of chitosan preparation, its inherent properties for industrial applications and life cycle assessment, highlight the physicochemical modifications leading to the enhanced adsorptive properties of chitosan derivatives for water pollutants removal and nutrient recovery, and summarize the adsorption mechanisms and recovery of spent chitosan derivatives with the view to shedding insight into future directions.

2 Life cycle assessment

The environmental impact of most disposable waste has been evaluated and comparison made using life cycle assessment (LCA). This allowed for the quantification and comparison of the environmental impact among or between stages of production or services within their life cycle [53]. Laceta et al. (2013) reported on the environmental assessment of 1 m^2 chitosan-based films after conducting a comparative environmental assessment between polypropylene (PP) commercial food packaging film and developed chitosan-based biodegradable film. Their environmental load in diverse life cycle stages such as material extraction, film manufacture and end of life was studied and a comparison was made. The result revealed that PP films had a higher impact on fossil fuels and carcinogens impact categories. However, chitosan-based films had a higher environmental load in land use, minerals and respiratory inorganic categories. Muñoz et al. (2017) also reported on life cycle assessment of chitosan production from cradle to gate in India and Europe from the viewpoint of the supply chains of their raw materials (snow crab and shrimp waste shells in Canada and India, respectively), their processing in China and India and chitosan manufacture in Europe and India. The result showed a difference in the environmental profiles of both chitosan from crab and shrimp waste shells, which were reflections of the difference in supply chains of raw materials, production location and applications. Beach et al. [54] reported on alternatives for investing microalgae by flocculation using chitosan, ferric sulphate and alum by building a life cycle inventory. The result from the life cycle inventory showed the superiority of chitosan from the viewpoint of the environment as a flocculant for microalgae harvesting.

3 Preparation of chitosan

The process of chitosan preparation involves the deproteinization of autolyzed crustacean shells in 3–5% (w/v) NaOH solution at room temperature for few hours. This is accompanied by demineralization (through processing, extraction of the inorganic minerals) with 3–5% (w/v) HCl aqueous at room temperature to obtain a white to beige coloured chitin. Next, it is treated at 90–120 °C for 4–5 h with 40–60% (w/v) NaOH solution, resulting in chitin deacetylation to form chitosan. The insoluble precipitate is washed with water. The deacetylation conditions determine the molecular weight of the polymer and the degree of deacetylation [13, 55]. Meanwhile, just as chitin undergoes alkaline deacetylation
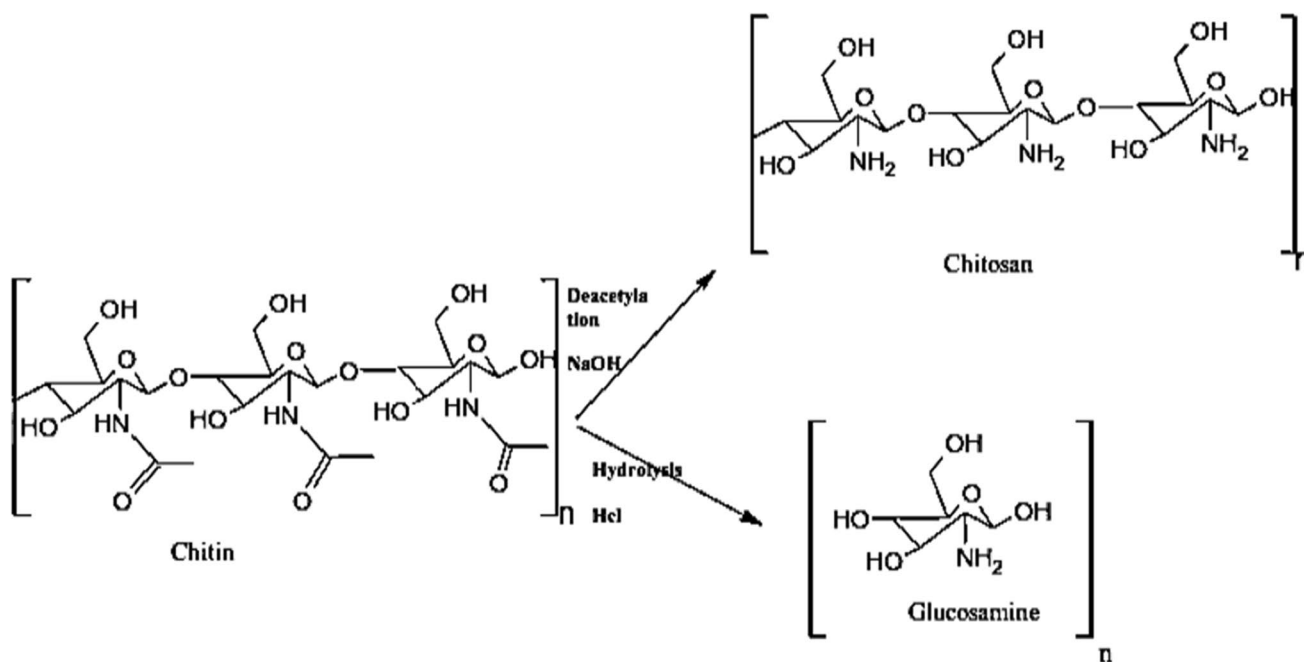
Fig. 3 Molecular reactions between chitin and chitosan with HCl and NaOH [56]

in the presence of sodium hydroxide to give chitosan, it also undergoes hydrolysis in the presence of hydrochloric acid to produce glucosamine as shown in Fig. 3 [56].

4 Properties of chitosan for industrial applications

Different chitosan properties determine their end uses. For example, strong hydrophilicity often due to a large number of highly reactive hydroxyl and amine functional groups, specific surface and stability of polymer chain are favourable attributes of chitosan in water pollutants removal [57, 58].

Chitosan is a large number of biopolymers with different degrees of N-deacetylation (40–98%) and molecular weight (50,000–2,000,000 g mol^{-1}). It is characterized by the presence of amine and hydroxyl functional groups which influence its properties. It is a soft base with a D-glucosamine residue and a pKa value of 6.2–7.0 [57, 59]. Chitosan is nontoxic, biodegradable and in the acidic environment, the amine groups of chitosan are protonated to form soluble, positively charged polysaccharides with a high load density [60, 61].

Viscosity is a property of chitosan that increases as its degree of deacetylation and concentration increases, and temperature decreases [16]. It is often in the range of 60 and 780 cPs. Therefore, concentration and temperature are critical factors in determining the viscosity of chitosan solution. The increase in the degree of deacetylation of chitosan

that results in the increase in viscosity can be attributed to the difference in conformity in an aqueous solution of high- and low-deacetylated chitosan. Chitosan with strong deacetylation has an extended conformation with a more flexible chain due to the load repulsion in the molecule. Meanwhile, low load density in the polymer chain of chitosan molecule results in the formation of rod-like or coiled shape at a low degree of deacetylation [16].

Chitosan materials possess a density in the range of 0.15 and 0.3 g mL^{-1} due to their porous nature as in the case of chitosan from marine crab and squilla and commercial chitosan [55, 62].

Fourier transform infrared (FTIR) analysis of chitosan shows a broad absorption band in the range of 3000 to 3500 cm^{-1} which is attributed to O–H stretching vibrations and the 3263 cm^{-1} to the vibration of N–H [59, 62]. The stretching vibrations of C-H occur at 2854 cm^{-1} and the absorption peak at 1558 cm^{-1} corresponds to the N–H bending vibrations. The amide II band is used as the characteristic band of N-acetylation. The spectra of chitosan show the different vibration that occurs after deacetylation process, which shows that the C=O vibration at 1627 cm^{-1} region associated with chitin has been reduced in chitosan, as well as the emergence of the absorption band at 894 cm^{-1} on chitosan which is the vibration for NH$_2$ [62].

Water binding capacity (WBC) of chitosan is within the range of 138 and 805% as reported by [62] for chitosan from Pessu river crab shell, [63] for chitosan synthesized from fish, crab and shrimp, Sarbon et al. (2015) for chitosan from mud

Table 1 Physicochemical properties of chitosan from different sources

Source of chitosan	Yield (%)	Molecular weight (g mol^{-1})	Moisture content (%)	Ash content (%)	Loss on drying	pH	Solubility	Degree of deacetylation (%)	Reference
Prawn	57.69	159,653	4	1.86	2	6.7	Acetic acid	87	Tarafdae and Biswas [65]
Shrimp	34	1,599,558	-	0.25	9.34	8.5	-	89.79	Puvvada et al. [66]
Fish	7.72	1.01×10^5	0.691*	0.53*	-	-	-	78.2	Sakthivel et al. [67],*Satpathy et al. [68]
Crab	41.37	-	10.8	-	-	-	-	80.8	Abdullin et al. [69]
Fungi	-	-	10.9	0.89	-	-	Acetic acid	85	Kumaresapillai et al. [70]
Bacterial	16/10	-	-	-	-	-	-	-	Kaur et al. [71]
Crayfish	-	-	9.6	-	-	-	-	89.6	Abdullin et al. [69]
Mealworm	31.9	-	-	-	-	-	-	-	da Silva et al. [34, 72]
Leucaena leucocephala pod	70.9	-	-	-	-	-	-	-	Aridi et al. [73]

crab and [64] for commercial chitosan from shrimp and crab. It is hydroscopic in nature with less than 10% moisture content and often reveals a split amide band and crystalline polymorph due to its parallel structure [55]. Table 1 presents the synthesized chitosan materials from different sources and their physicochemical properties.

Chitosan's ability to chelate metal ions has made it a potential natural antioxidant for stabilizing and prolonging the shelf life of lipid foods [74]. The presence of organic diacid anhydride in chitosan is useful in the manufacture of cosmetics like shampoos, hair colourants, styling lotions, hair sprays, hair tonics, moisturizer, nail enamel foundation, mouth washer, chewing gum, lipstick and eye shadow [51]. Furthermore, the inherent characters of morphology, size, non-toxicity and density are important in the release of drugs in chitosan base dosage during drug delivery [75]. The biocompatibility and biodegradability properties of chitosan have made it useful in biomedicine and tissue engineering. Low molecular weight chitosan is used as a carrier for solid drug formulations in the drug delivery system. The cationic property of chitosan has found applications in gene therapy system because it provides strong electrostatic interaction with anionic DNA, thus protecting it from nuclease degradation [51, 76]. The antimicrobial property of chitosan has made its film great potential for food preservation [77].

5 Chitosan modification procedures

Physicochemical modification of chitosan has been a growing interest to improve water-acid solubility and adsorption properties, while broadening its applications. The chemical modification involves replacement reactions, chain elongation (cross-linking, copolymerization of graft and polymer networks) and depolymerization, while the physical modification is generally aimed at obtaining conditioned polymeric forms such as powders, nanoparticles and gels (beads, membranes, honeycombs or hollow fibres) [78].

Repo et al. [79] improved the reactivity of chitosan by ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) functionalization. Chitosan is dissolved in 10% (v/v) acetic acid and diluted with methanol. EDTA anhydride in methanol is added, and the mixture is stirred vigorously at room temperature for 24 h. The precipitate is mixed with ethanol and washed with NaOH solution (pH 11) to remove unreacted EDTA. A similar method was adopted for DTPA-functionalized chitosan. EDTA- and DTPA-modified chitosan exhibit effective adsorption for Co(II) and Ni(II) at 93.0% to 99.5% in 100 mg L^{-1} aqueous solutions. Figure 4 illustrates the synthesis route of EDTA- and DTPA-modified chitosan.

Fig. 4 Synthesis of EDTA- and/ or DTPA-modified chitosan [80]
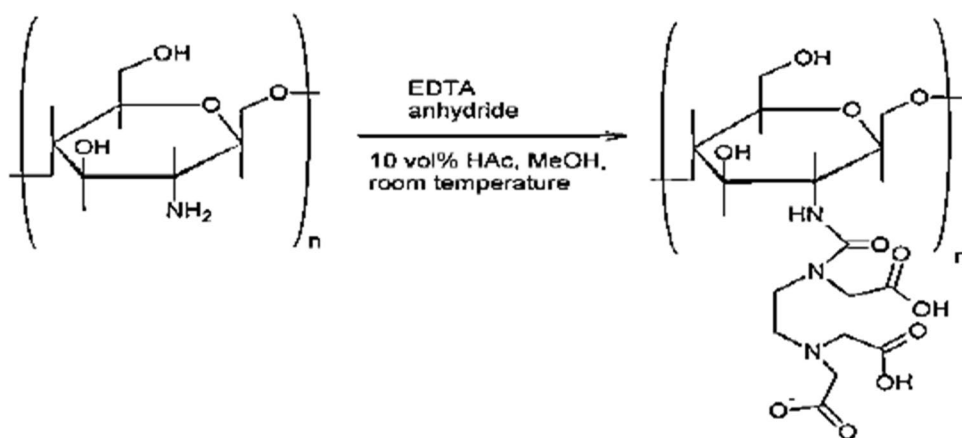
Hariani et al. [81] synthesized bentonite-modified chitosan. Bentonite is added into the chitosan-CH_3COOH solution at pH 4. The mixture was stirred for 2 h. The composite is centrifuged and washed with deionized water to a neutral pH. The calcium-rich bentonite/chitosan composite showed an improved capacity of phenol at 12.5 mg g^{-1} in 125 mg L^{-1} solution at a pH of 7 for 30 min.

Moosa et al. [82] noted chitosan modification using granulated activated carbon. Activated carbon is immersed in chitosan acetic acid solution at a ratio of 10:50 (w/v) at 25 °C for 24 h. The filtrate is soaked in 0.1 mol L^{-1} NaOH for 3 h to precipitate the chitosan on activated carbon. Next, it is washed with distilled water prior to use. The material demonstrates a 95.81% removal of methylene blue as against 85.85% by the unmodified one (Table 3).

Saifuddin and Kumaran [83] encapsulated chitosan onto acid-treated oil palm shell charcoal. The process involves the preparation of chitosan gel using 10 wt% oxalic acid at 50 °C. The charcoal is slowly added to the gel solution, and the mixture is agitated for 24 h to form beads. The process is repeated thrice to form a thick chitosan coating. The material shows an increase in chromium ion removal of 154 mg g^{-1}.

Okoya et al. [84] modified chitosan with cocoa husk char. A 100 mL of the chitosan gel in oxalic acid is diluted with water, wherein cocoa husk char is added. The mixture is agitated for 24 h. Then, the composite is soaked in 0.5% (w/v) NaOH solution for 3 h and rinsed with deionized water. The material depicts the Cr^{6+} and Pb^{2+} adsorption of 333 mg g^{-1} and 263.16 mg g^{-1}, respectively, while the unmodified one records the values of 136.98 mg g^{-1} and 125.0 mg g^{-1}, respectively.

Kyzas and Deliyanni [85] recognized the modification of magnetic chitosan by cross-linking with glutaraldehyde (GLA). GLA-cross-linked chitosan is prepared by adding 15 mL of GLA (approximately 2:1 aldehyde groups (–CHO) of GLA per initial amino group (–NH_2) of chitosan) in a 400 mL of acetic acid solution (2% v/v) bearing 2 g of dissolved purified chitosan. The mixture is stirred at 25 °C for

3 h, and the precipitate is washed with ethanol and distilled water and dried in a vacuum oven at 45 °C. Magnetic nanoparticles are prepared by dissolving 3.5 g of $FeCl_2 \cdot 4H_2O$ and 9.5 g of $FeCl_3 \cdot 6H_2O$ in 400 mL of distilled water at 60 °C for 1 h under nitrogen flow. Ammonia solution is added dropwise to a pH of 10. The precipitate is decanted and freeze-dried. For magnetic cross-linking, 0.75 g of magnetic nanoparticles is added into chitosan solution and the mixture is sonicated for 30 min. This is followed by the same procedures for GLA cross-linking. The modified chitosan derivatives display enhanced reusability upon regeneration. Similarly, GLA-cross-linked chitosan shows an improved Hg(II) capacity of 145 mg g^{-1}, while that with magnetic nanoparticles is 152 mg g^{-1}. Figure 5 illustrates the schematic preparation of cross-linked chitosan with GLA and magnetic nanoparticles and the possible interactions with Hg(II).

Vafakish and Wilson [86] reported the grafting of aniline and acetaldehyde onto chitosan. Aniline renders a light-yellow viscous chitosan solution, while acetone forms a white low-viscous solution. The reaction mixtures are stirred at 70 °C for 18 h. A 3 mol L^{-1} NaOH solution is added gradually under stirring to a pH 7, at which pink precipitate is evolved. The precipitate is separated from the supernatant, washed with water and ethanol, and dried in a vacuum oven at 50 °C for 6 h. The modification enhances the specific surface of chitosan and its capacity towards fluorescein dye to 61.8 mg g^{-1}. Figure 6 presents the synthesis of chitosan by grafting with aniline and acetaldehyde.

Al-Ghamdi et al. [87] noted the modification of chitosan by ρ-bromo-β-ketosulfone. The solvent, ρ-bromo-β-ketosulfone is prepared by refluxing a mixture of 2 mmol sodium benzene sulfinate and 2 mmol ethanolic solution of 4-bromo-4-bromoacetophenone for 6 h, and the solid product is washed with water and recrystallized. The solid is dissolved in chitosan solution, and the residual phase is recovered by evaporated and dried. The modified chitosan exhibits a 122.47 mg/g of Hg(II) removal.
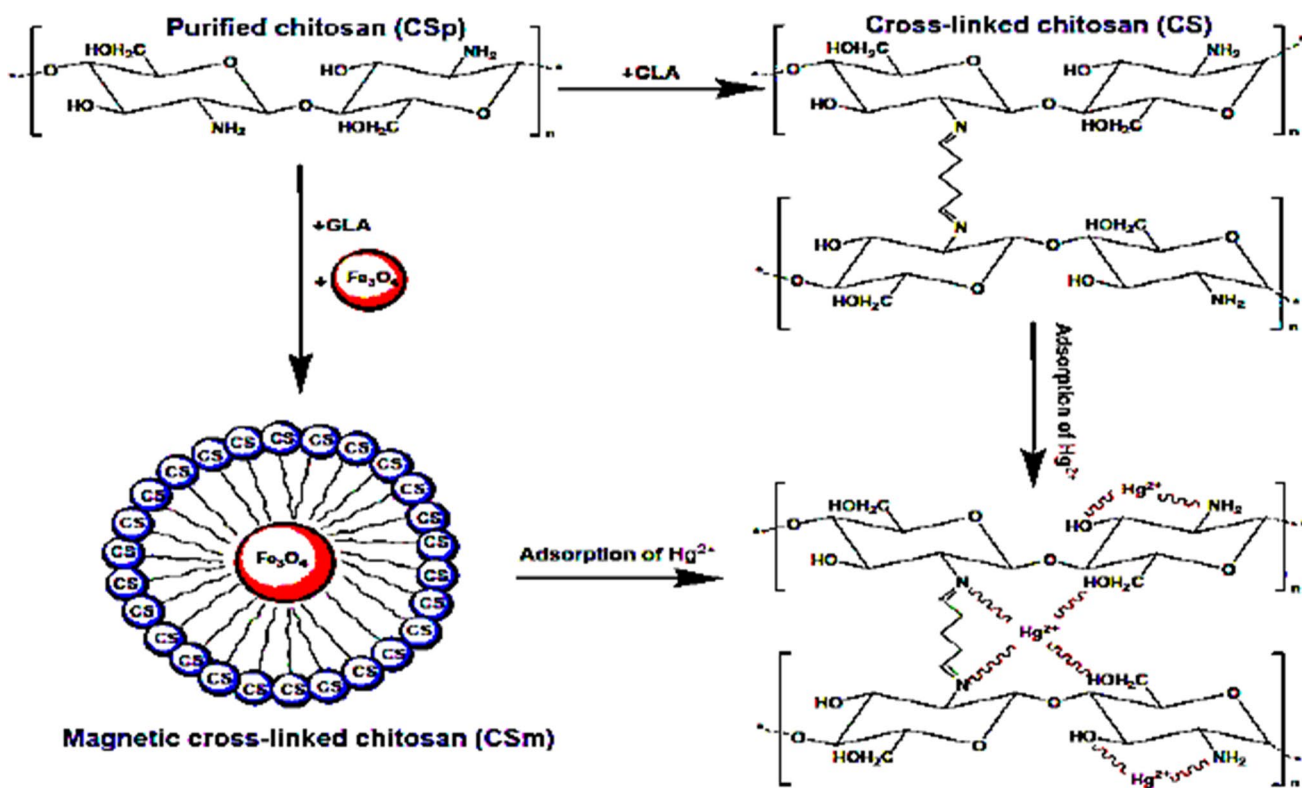
Fig. 5 Preparation of magnetic cross-linked chitosan for Hg(II) removal [85]
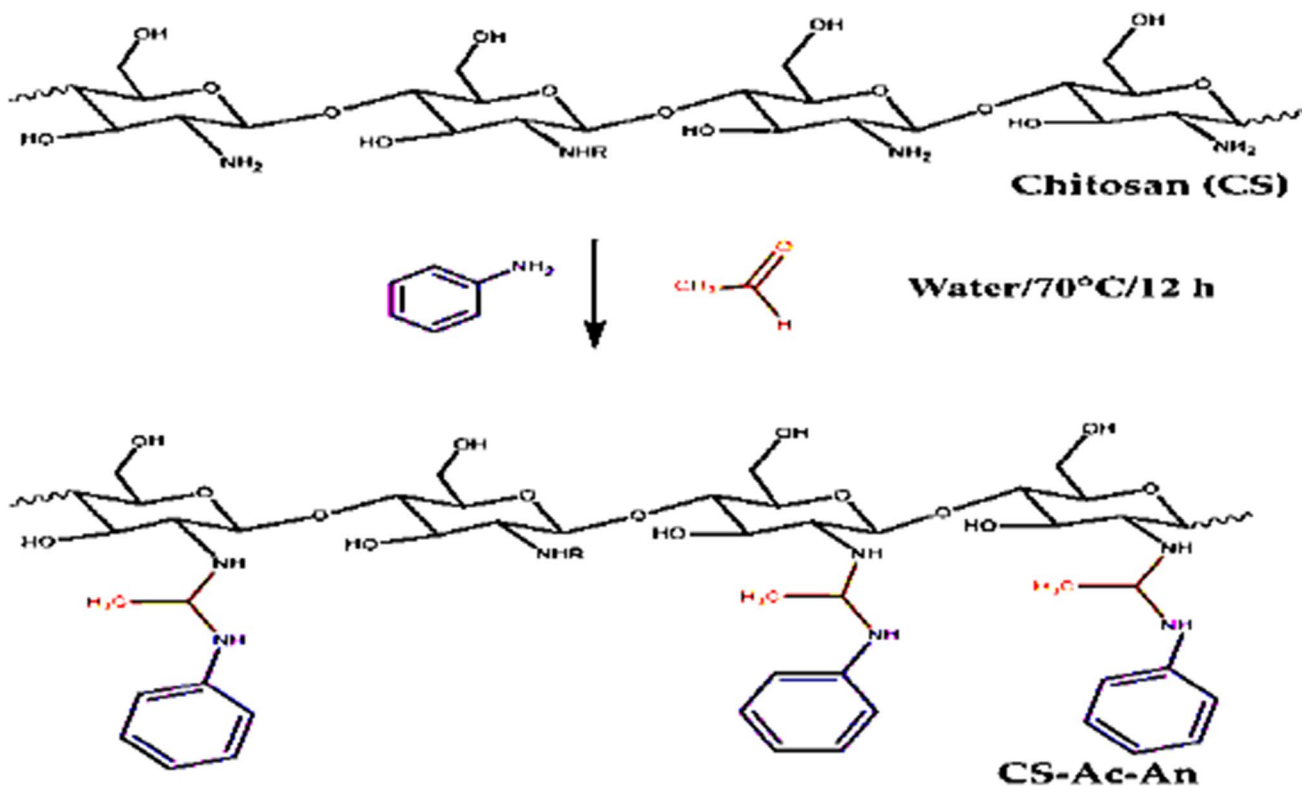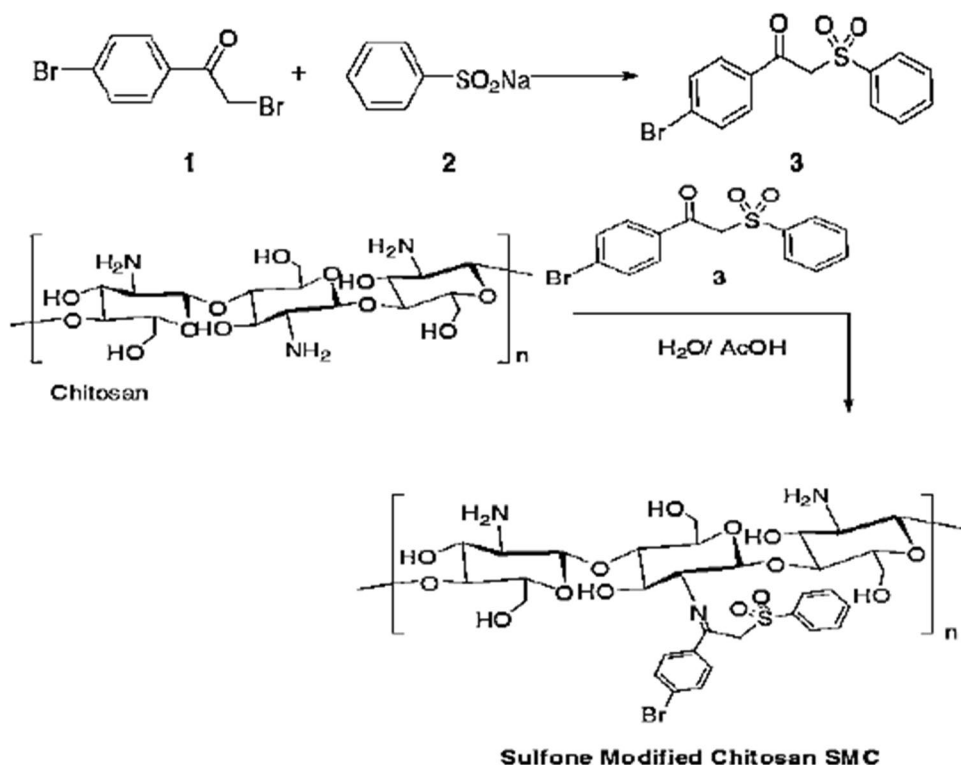

Fig. 6 One-step synthesis of chitosan by grafting with aniline and acetaldehyde [86]

Fig. 7 Preparation of ρ-bromo-β-ketosulfone for chitosan modification [87]

Significant improvement can be observed from the surface morphology as opposed to the pristine chitosan, but the thermal stability decreased. The synthesis routes are shown in Fig. 7.

Hastuti et al. [88] reported the removal of Cr(VI) by epichlorohydrin-modified chitosan. Chitosan gel was prepared by adding NaHCO in chitosan acetic acid solution at ratio of 0.2:2.0 (w/w). The gel is sprayed with 5% NaOH solution to form chitosan beads. The solid is coated in benzaldehyde solution for 2 h. The cross-linking process is carried out by dispersing the beads into dioxane. One mole per litre NaOH solution is slowly added to the stirred solution, followed by epichlorohydrin. The mixture is refluxed for 6 h, and the precipitate is washed with ethanol and water. The modified chitosan demonstrates an improved porosity, increased resistance against acidic medium and enhanced capacity of 89% as compared to 74% by the unmodified one. Figure 8 shows the reaction of chitosan with epichlorohydrin.

Soni et al. [89] disclosed the modification of chitosan-activated carbon composite with tripolyphosphate. A water in paraffin oil emulsion is added into the homogenous chitosan-charcoal suspension in acetic acid. The mixture is agitated for 2 h to form a stable emulsion. A 0.1 mol L^{-1} tripolyphosphate is added dropwise to form nanocomposite particles. The solid is washed with toluene and acetone. The adsorbent exhibits an outstanding phenol adsorption capacity of 409 mg g^{-1}. Similarly, Liu et al. [90] recorded

the effective removal of phenol and Cu^{2+} of over 80% by chitosan-activated carbon membrane composite.

Marrakchi et al. [91] revealed a superior removal of methylene blue and reactive orange 16 at 40.99 mg g^{-1} and 190.97 mg g^{-1}, respectively by epichlorohydrin-cross-linked chitosan-sepiolite composite. Sepiolite powder is dispersed into a chitosan acetic acid solution. The mixture is then added dropwise into a 1 mol L^{-1} NaOH solution. The solid is washed and to a neutral pH and added into epichlorohydrin solution at 50 °C for 6 h.

Sharififard et al. (2016) used 0.2 mol L^{-1} oxalic acid to dissolve chitosan at 40 °C to form a viscous gel. A 20 g of acid-treated activated carbon is mixed with chitosan gel and stirred at 40 °C for 12 h to form a chitosan-activated carbon composite. The composite was added in dropwise into a 0.7 mol L^{-1} NaOH precipitation bath to form beads. The modification has improved its capacity for metal ions, i.e., 90.9 mg g^{-1} for Cr(VI) and 52.63 mg g^{-1} for Cd(II). The pristine one recorded the values of 41.94 mg g^{-1} and 10 mg g^{-1}, respectively. Regunton et al. [92] also attempted similar procedures, where the modified chitosan composite shows a methylene blue removal of 99.77%.

Huang et al. [93] reported the modification of chitosan-activated carbon membrane by cross-linking using epichlorohydrin. Epichlorohydrin-to-membrane ratio is 20 mL g^{-1}, and the cross-linking reaction occurs for 12 h. The cross-linked membrane is treated with concentrated HCl for 90 min for surface protonation and washed with deionized

Fig. 8 Reaction of chitosan with epichlorohydrin [88]
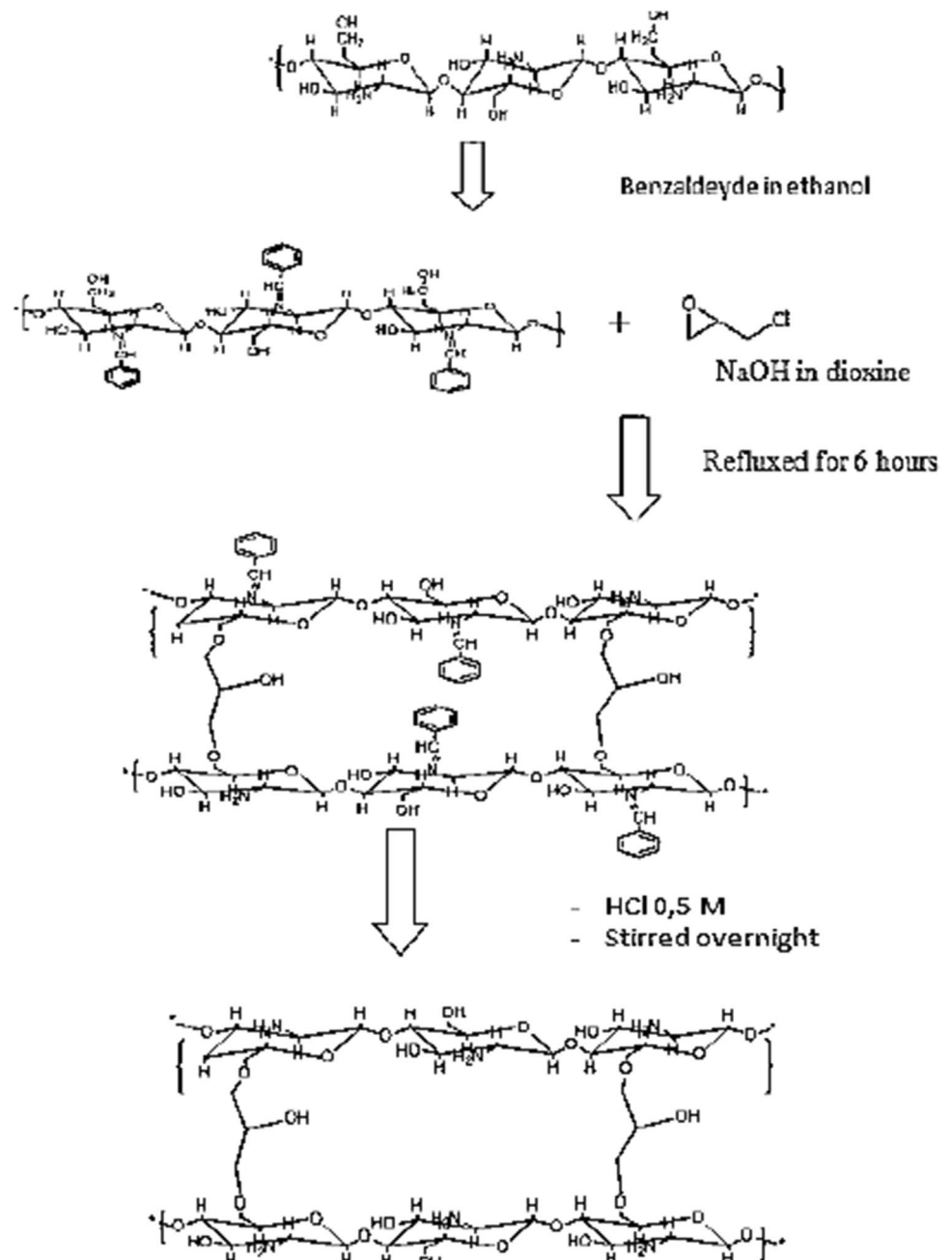
water to a neutral pH. Epichlorohydrin is proven as a suitable cross-linker to boost the phenol and Cr(VI) to 95% at maximum concentrations of 50 mg L^{-1} and 200 mg L^{-1}, respectively.

López-Cervantes et al. [94] modified chitosan beads by glutaraldehyde cross-linking for direct blue 71 removal. The wet chitosan beads from the NaOH bath are suspended in a 0.025 mol L^{-1} glutaraldehyde solution (beads-to-solution ratio of 1:10) at room temperature for 16 h and washed with distilled water and ethanol.

Auta and Hameed [95] showed that the preparation of epichlorohydrin-cross-linked chitosan-activated carbon beads. The chitosan acetic acid solution with dispersed waste tea activated carbon is added dropwise into 0.067 mol L^{-1} NaOH solution to form beads. The beads are cross-linked with epichlorohydrin at 50 °C for 6 h and freeze-dried to preserve the texture. The modified adsorbent is promising for cationic and anionic dyes removal.

Asokogene et al. [62] recognized the synthesis of neem leave-chitosan composite in oxalic acid solution. The activated neem leave is slowly added into the mixture at 50 °C for 2 h. The dried composite is soaked in 0.5% (w/v) NaOH solution for 3 h, rinsed with distilled water and dried. The modified chitosan possesses a better specific surface leading
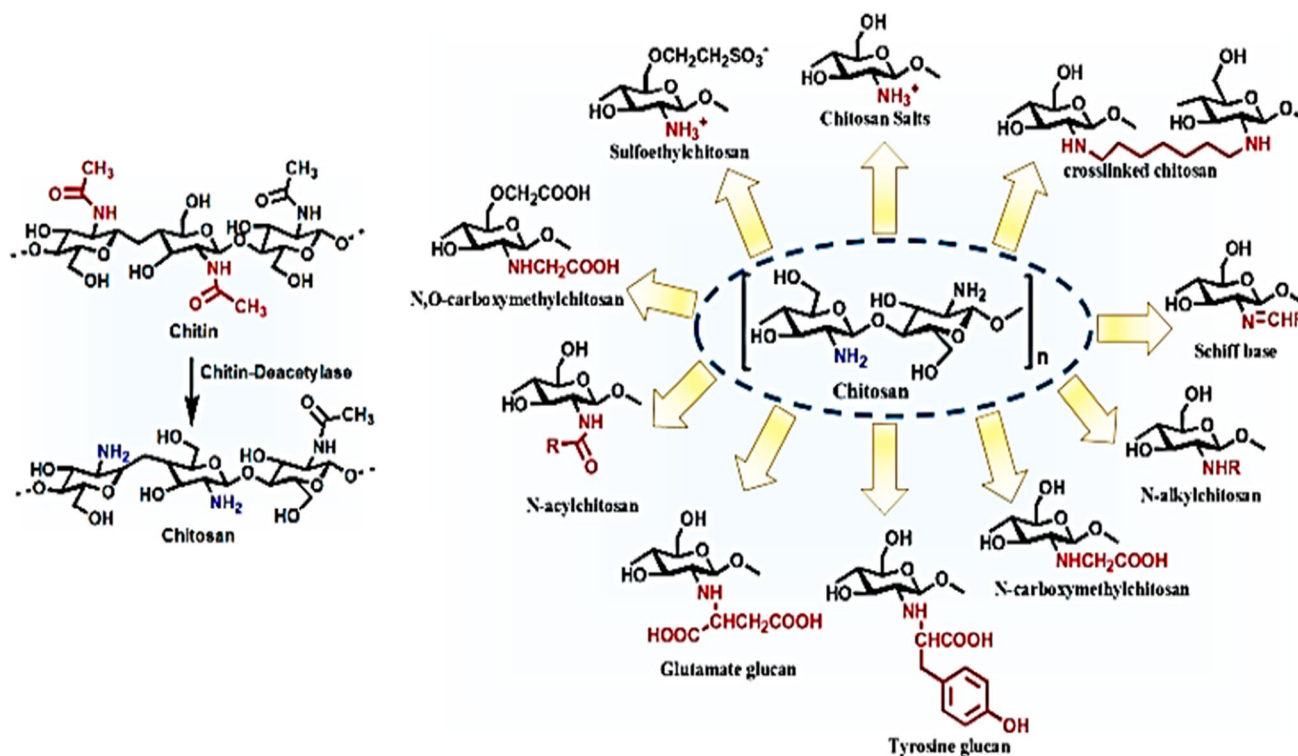
Fig. 9 Chitosan synthesis from chitin and some widely used functionalized chitosan derivatives structures [96]

Table 2 Chitosan modification procedure, some important advantages and limitations

Modification strategy	Description	Advantages	Disadvantages	Reference
Chemical modification	Replacement reaction, chain elongation (cross-linking and copolymerization of graft polymer networks) and depolymerization	1. Formation of chitosan derivatives with superior physicochemical properties 2. Enhancement of chitosan adsorption capacity 3. Resistance in extreme media condition (acidic) 4. Increased number of adsorption sites 5. Improved chemical stability	Cross-linking reaction slightly decrease the adsorption capacity of chitosan because some functional groups of chitosan (–NH_2 or –OH) are bound with the cross-linker and cannot interact with the pollutant in the medium	Vafakish and Wilson [86], Hastuti et al. [88], Marrakchi et al. [91], Kyzas and Dimitrios [36]
Physical modification	Formation of conditioned polymeric materials like powder, nanoparticles and gels (beads membrane, honey comb or hollow fibres)	1. Formation of composite with unique porous structure 2. High specific surface area 3. Improved mechanical strength and heat resistance 4. Enhanced selectivity and regeneration	Low chemical stability in extreme media condition (acidic)	Asokogene et al. [62], Sharififard et al. (2016), Auta and Hameed [95]

to a higher methylene blue capacity of 90.8 mg g^{-1} at a dye concentration of 300 mg L^{-1}.

Nevertheless, chitosan synthesis from chitin and some widely used functionalized chitosan derivatives structures is presented in Fig. 9 [96]. Furthermore, in chitosan

modification procedures, some important advantages and disadvantages are summarized in Table 2.

6 Chitosan derivatives for water pollutants removal

Among the toxic contaminants in water are heavy metals, phenol and dyes. These solutes are harmful if directly ingested, and their accumulation in the food renders a threat during meat, vegetables and fish consumption. Reactive hydroxyl and other functional groups, strong hydrophilicity and stability of polymer chain endow chitosan with a high adsorption ability towards toxic contaminants in water [57, 97, 98].

Sharififard et al. [99] evaluated the adsorption of Cr (VI) and Cd (II) by chitosan adsorbents. The modified chitosan shows an increase of specific surface at 362.30 m^2 g^{-1} as opposed to the pristine one (16.37 m^2 g^{-1}). Similarly, the adsorption capacities for Cr (VI) and Cd (II) improved to 90.90 and 50.50 mg g^{-1}, better than the unmodified one at 41.60 mg g^{-1} and 10.00 mg g^{-1}, respectively (Table 3). The increase in the surface area offers more interaction probabilities between the solutes and active sites for greater removal. Hastuti et al. [88] studied the adsorption of Cr (VI) from batik industrial wastes using chitosan modified with epichlorohydrin. The modified chitosan shows a solubility resistance to acids and an improved capacity from 7.4 mg g^{-1} (unmodified chitosan) to 8.9 mg g^{-1} at 30 min contact time and pH 3. Bahador et al. [100] investigated the effect of chitosan (CS) and iron ore (Fe_3O_4) magnetic nanoparticles on chromium (Cr) removal behaviour of *Moringa leifera* activated carbon (AC). The adsorption capacity showed the following: AC (56.78 mg g^{-1}), CS/AC (114.80 mg g^{-1}), Ac/Fe_3O_4 (121.70 mg g^{-1}) and CS/AC/Fe_3O_4 (130.80 mg g^{-1}). Modified AC and Fe_3O_4 nanoparticles by CS increased Cr removal.

It is very difficult to purify sewage-containing dyes because colouring is generally resistant to biological oxidation and chemical oxidants in some cases. Adsorption at low cost and by means of widely available natural adsorbents is an alternative to the traditional and conventional processes. Advanced oxidation methods are effective but relatively expensive in the degradation of colourants and pigments in wastewater. Chitosan is a promising biosorbent to remove dyes from water [103]. Vafakish and Wilson

Table 3 Adsorptive properties of modified and unmodified chitosan

Modifier	Pollutant	Modified			Adsorption operating parameter	Unmodified			Reference
		Specific surface area(m^2/g)	Total pore volume (cm^3/g)	Adsorption capacity, Q_e (mg/g)		Specific surface area(m^2/g)	Total pore volume (cm^3/g)	Adsorption capacity, Q_e (mg/g)	
Ca-bentonite	Phenol	-	-	12.5	pH 6, 90 min	-	-		Hariani et al. [81]
Granulated activated carbon	MB	795	-	11.99	25 °C, pH 6, 5 h	7.45	-	11.04	Moosa et al. [82]
Acetaldehyde-aniline	Fluorescein dye	-	-	61.8	23 °C, pH 7, 24 h	-	-	1.96	Vafakish and Wilson [86]
Epichlorohydrin	Cr(VI)	-	-	8.9	pH 3, 90 min	-	-	7.4	Hastuti et al. [88]
Activated carbon	Cu^{2+} Phenol	-	-	34.19 74.35	20 °C, pH 7 240 min	-	-	-	Liu et al. [90]
Epichlorohydrin-sepiolite	MB RO 16	45.46	0.10	40.99 190.97	30 °C, 1800 min	-	-	-	Marrakchi et al. [91]
Activated carbon	Cr(VI) Cd(II)	362.30	0.23	90.90 50.50	pH 6 150 min	16.37	0.02	41.60 10.00	Sharififard et al. (2016)
Activated carbon	Cr(VI) Phenol	-	-	50.58 28.15	-	-	-	-	Huang et al. [93]
Oxalic acid-neem leaf	MB	389 351	0.224 0.133	90.8 47.23	30 °C, pH 6, 72 h	226	0.125	29.93	Asokogene et al. [62]
Bentonite nanoclay	NH_4^+N	-	-	82.11%	pH 6	-	-	43.19%	Haseena et al. [101]
Magnetite	Glyphosate	-	-	90%	60 min	-	-	-	Soares et al. [102]

[86] studied the aniline-modified chitosan for the removal of anionic fluorescein dye. The adsorption capacity increased from 1.96 to 61.8 mg g^{-1}. Similarly, Asokogene et al. [62] reported the potential of activated neem leave-chitosan composite for methylene blue removal. The specific surface increased from 226 to 389 m^2 g^{-1}, while the capacity rose from 29.93 to 90.8 mg g^{-1}. Carvalho et al. [104] evaluated the adsorption potential of chitosan films from shrimp waste on anthocyanin pigment from red cabbage with the view to providing information about the immobilization of anthocyanin molecules onto chitosan films. The adsorption capacity of the chitosan film was 140 mg g^{-1}. Pinheiro et al. [105] evaluated the adsorption potential of chitosan from shrimp waste and alginate beads on anthocyanins from *Pinot Noir* grape skin with the view to demonstrating the possibility of concentrating different molecular structures of anthocyanins onto chitosan and alginate beads. The adsorption capacity of chitosan and alginate beads was 216 mg g^{-1} (65%) at pH 8 and 126.4 mg g^{-1} (38%) at pH 4, respectively.

Chitosan has been successfully used to extract anions from water in recent years. Chatterjee and Woo [106] used chitosan beads to remove nitrates. The capacity of 92.1 mg g^{-1} was recorded at pH 3, initial nitrate concentration of 1 g dm^{-3} and temperature of 30 °C. In a related work, the protonated cross-linked glutaraldehyde chitosan gel beads displayed a pH-independent process of nitrate extraction [107]. The protonated chitosan beads had also been applied as defluoridating medium [108]. The presence of other coexisting anions shows that the adsorption varied with pH, whose maximum capacity lies between 4.72 and 7.32 mg g^{-1}. The hydrogen bonds are indicated as the sorption mechanism between the positively charged amino groups of chitosan and fluoride ions. Affonso et al. [109] evaluated fluoride adsorption from fertilizer industry effluent using carbon nanotubes stabilized in chitosan sponge (CNT-CS) as adsorbent. The removal capacity of fluoride was 975.4 mg g^{-1}, which was an indication of the potential of hybrid material to remove fluoride from the real matrix. Further evaluation showed that after 5 cycles of regeneration, the reuse of adsorbent kept similar adsorption capacities in all cycles.

Chitosan has also been used for the adsorption of nutrients from an aqueous solution. Safie et al. [110] carried out an adsorption performance comparison on ammonium ion (NH$_4^+$) of natural zeolite (NZ), activated NZ (ANZ) with high molecular weight chitosan (HMWC) and low molecular weight chitosan (LMWC). The result showed that HMWC, NZ and ANZ attained adsorption equilibrium at 15 h and LMWC at 20 h. However, the removal capacity was 0.769, 0.331, 2.162 and 2.937 mg g^{-1} for LMWC, HMWC, NZ and ANZ, respectively. Haseena et al. [101] also prepared a novel composite adsorbent of chitosan and bentonite nanoclay in the form of thin films and its adsorption potential for

ammonium-nitrogen (NH$_4^+$N) from an aqueous solution was investigated and compared with unmodified chitosan. The removal of ammonium-nitrogen from an aqueous solution of initial concentration of 15 ppm, pH of 6 and adsorbent dosage of 0.5 g was 43.19 and 82.11%, respectively for unmodified and modified chitosan (Table 3). The removal efficiency of modified chitosan was almost twice that of the unmodified chitosan. This was an indication that the modified chitosan possessed more surface area for adsorption.

Zhao et al. [111] fabricated a cost-effective, biomass-derived and novel adsorbent by coating polydopamine on lanthanum-chitosan hydrogel (La-CS@PDA) which is rich in amine groups for the adsorption of phosphate in wastewater. Phosphate adsorption was enhanced by the diffusion structure of the channel-network of La-CS@PDA,hence, the adsorption capacity was 195.3 mg g^{-1} which was superior to other phosphate adsorbent materials in literature. Nevertheless, in the presence of other competitive anions like Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, NO$_3^-$, F$^-$ and HCrO$_4^-$, La-CS@PDA demonstrated distinct selective adsorption for phosphate due to the presence of selective binding sites of La species in the composite.

Phenols are among the most toxic contaminants in water. They are toxic to aqua species even at low concentrations, in addition to the risk of loss of taste and aroma. New alternative methods to remove phenols effectively from water are continuously sought and investigated. The classical approaches using the biological treatment and activated carbon adsorption reveal low efficiency, while the advanced phenol extraction/oxidation methods are satisfactory but costly [112]. Li et al. [113] examined chitosan derivatives by chemical modification using salicylaldehyde and ß-cyclodextrin polymer for phenol, p-nitrophenol and p-chlorophenol removal. The performance of chitosan for phenols removal is initially poor (1.98–2.58 mg g^{-1}), while the modification strategies boost the removal to as high as 179.73 mg g^{-1}. Table 3 generalizes the effects of chitosan modification on its texture and performance as an adsorbent for solutes removal.

7 Adsorption mechanisms

The adsorptive interactions of chitosan depend on pH, crystallinity, water affinity and deacetylation (amino group content) [114]. Adsorption could also govern by complex formation or electrostatic attraction in acid media, ion exchange with protonated amino groups and chelation at amino groups [115]. Chitosan chelates metals in solution five to six times due to the presence of free amino groups in the chitosan chain. This property is widely used for the uptake, separation or recovery of valuable metals and dyes for environmental purposes. The use of chitosan is somewhat limited

in industrial applications due to the cost of materials, the variance of characteristics and the availability of resources, hence the need for its synthesis [16].

The adsorption properties of chitosan are due to its functional groups including improved hydrophilicity by polymer hydroxyl groups, which also helps to increase the diffusion of polymer networks and enables metals and dyes to be adsorbed from the aqueous solution. In several ways, hydroxyl and amino groups can react with aqua solutes. The amino groups are very important for adsorption processes as compared to the hydroxyl groups, for which the degree of deacetylation is an important parameter for assessing the quality of chitosan biopolymer [57]. Figures 10 and 11 illustrate the working mechanisms of methylene blue and chromium, respectively, by chitosan derivatives [116, 117].

Yet, certain challenges can occur in the chemical system, including the susceptibility of chitosan solubility in acidic solution, for which it is not desirable to withstand its insoluble texture [16]. Hence, cross-linking reactions may improve the stability of chitosan under acidic and alkaline conditions,however, this process can reduce the adsorption traits.

High nitrogen content in chitosan works as active sites for several chemical reactions in water. The amine groups in chitosan are weak enough to deprotonate water [57],

$$\text{Chitosan} - \text{NH}_2 + \text{H}_2\text{O} = \text{Chitosan} - NH_3^+ + \text{OH}^+$$
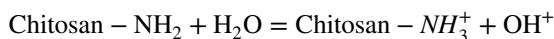
The pKa value of chitosan (6.3) increases its solution pH when in contact with water [57]. Chitosan adsorption is dependent on solution pH due to the direct effect of an acid–base reaction. The amine groups serve as a binding site for metals via chelation mechanisms in the deprotonated form of chitosan. Chitosan may also bear electrostatic properties for ion-exchange mechanisms to adsorb aqua metals [57].

Fig. 10 Adsorption mechanism of methylene blue on chitosan beads [116]
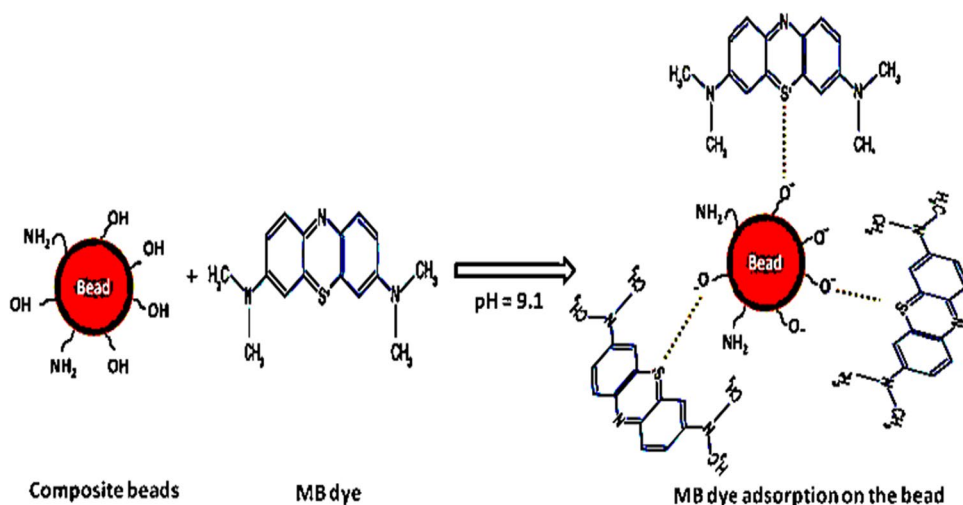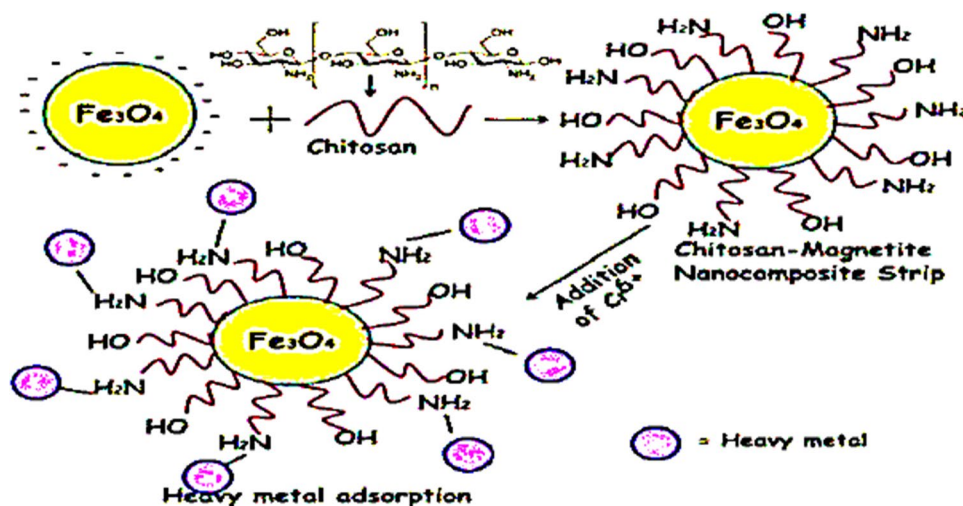

Fig. 11 Mechanisms of chromium ions removal by chitosan-magnetite nanocomposite strip [117]

8 Recovery of spent chitosan

Spent chitosan/chitosan derivatives are in most cases non-biodegradable and toxic after adsorption due to the deposit of adsorbates. The regeneration is carried out by chemical treatment with mineral acids (H_2SO_4, HCl and HNO_3), complexing or chelating, agent (EDTA, EDTA-disodium (Na_2EDTA)), alkaline (NaOH, NH_4OH), salt (NaCl, KNO_3, Na_2CO_3, Na_2SO_4), organic acid (citric acid) solution and distilled water because of the simplicity, convenience, effectiveness and low cost of these desorption agents to restore the properties of chitosan materials [118–121]. Thermal and biological desorption methods for chitosan are not common because chitosan cannot withstand high temperature [122] and the ease of biodegradability due to accessibility for the microorganism in biological desorption [123].

Mineral acids are mostly used as desorption solvents for cationic pollutants because of the favourable adsorption nature in the basic environment of these cationic pollutants and the mechanism involved in their adsorption on chitosan and chitosan derivatives adsorbents. Therefore, in desorption, these mineral acids supply a high number of cation (H^+) which weakens the interaction between the cationic pollutants and their adsorption groups. Meanwhile, the anions from these mineral acids form a complex with the cationic pollutants and are released into the solution [124]. Complexing or chelating agents like EDTA and EDTA-disodium (Na_2EDTA) in desorption of cationic pollutants form complexes because of their high-affinity constant which replace the functional groups on the chitosan and its derivatives adsorbent complexed with ions and complexate with ions [125–127]. Alkali desorption agents are mostly used to desorb the anions in pollutants from chitosan and its derivative adsorbents due to the higher affinity of these anions to react with Na^+ or NH_4^+

than the adsorption sites, thus weakening the adsorbate and adsorbent bonds in alkali conditions [128, 129]. Salt desorption agents are considered as suitable because of their ability to weaken the interaction between cationic pollutants and the binding sites on the chitosan and its derivatives surface in order to form complexes that are stable [130, 131].

The weak or strong adsorptive forces between the sorbent surface and the sorbate molecules in the regeneration media often determine the efficiency of desorption [95, 132]. Therefore, the adsorption of adsorbate after adsorbent regeneration depends on the efficiency of regeneration of adsorbents after adsorbate desorption. Deposited adsorbates are desorbed using a cheap and eco-friendly agent and the adsorbent regenerated for another cycle. Regeneration is important for keeping the adsorption process cost low [133, 134]. Desorption and regeneration of chitosan and its derivatives are found to increase with increased temperature, contact time and agitation speed [135, 136]. Other factors include the increased concentration of desorption and regeneration agents. However, an excessive increase in concentration could lead to the disintegration of the chitosan structure [135]. Meanwhile, the low mechanical and chemical stability of chitosan as well as its biodegradability are factors that affect chitosan-based adsorbent regeneration [52]. Figure 12 shows the schematic representation of the chitosan adsorbent regeneration procedure.

Desorption efficiencies and other parameters affecting the regeneration of chitosan and its derivatives adsorbents using various agents are summarized in Table 4. However, limited data from the literature on desorption agents and their operating conditions, such as adsorbate concentration, pH, temperature and eluent concentration has made it difficult to compare the performance of the eluents.

Fig. 12 Schematic representation of adsorption–desorption in chitosan [52]
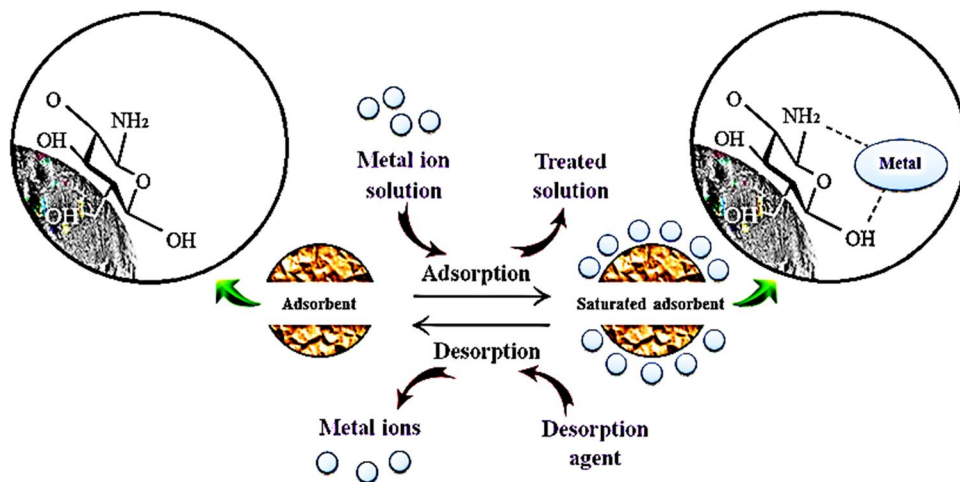
Table 4 Regeneration of chitosan and its derivatives

Adsorbent	Adsorbate	Regeneration agent	Desorption efficiency (%)	Desorption cycle	Reference
Chitosan-coated sand	Cu(II)	1.0 mol L^{-1} HCl, pH 1	99.22	1	Wan et al. [137]
		1.0 mol L^{-1} HCl, pH 3	13.06	1	
Chitosan/clay composite	Rose FRN dye	0.1 mol L^{-1} HCl	87	1	Kausar et al. [132]
Chitosan beads	CU(II)	0.1 mol L^{-1} HCl	94	3	Osifo et al. [138]
		0.0001 mol L^{-1} EDTA	65.24	1	Ngah et al. [139]
Chitosan	Cd(II)	0.01 mol L^{-1} HNO$_3$, pH 1	68	1	Rangel-Mendez et al. [140]
	Cr(VI)	0.01 mol L^{-1} HNO$_3$, pH 3	44.8	1	Bhuvaneshwari et al. [135]
		0.1 mol L^{-1} H$_2$SO$_4$	88	1	
ECH cross-linked chitosan fibre	Pb(II)	2 mol L^{-1} HNO$_3$ thio-urea-1.0 mol L^{-1} HCl	95.6	3	Zhao et al. [141]
Chitosan/sodium silicate	As(V)	L-Cysteine	100	1	Boyaci et al. [142]
Magnetic chitosan nanoparticles/α-ketoglutaric acid	CU(II)	0.1 mol L^{-1} Na$_2$ EDTA	91.5	1	Zhou et al. [143]
Quaternary chitosan-magnetite nanosorbent	Glyphospate	0.1 mol L^{-1} HCl	80	4	Soares et al. [102]
Phosphate chitosan/ethyl hexadecyl dimethyl ammonium bromide	Cr(VI)	5% NH$_4$OH	70	10	Kahu et al. [144]
Ferric hydroxide chitosan beads	As(III)	0.1 mol L^{-1} NaOH	100	5	Padilla-Rodríguez et al. [128]
		1.0 mol L^{-1} NaOH	100	5	
Chitosan/bentonite	Cu(II)	0.1 mol L^{-1} NaCl	36	3	Futalan et al. [130]
	Ni(II)		47	3	
	Pb(II)		13	3	
Magnetic chitosan	U(VI)	1.1 g L^{-1} Na$_2$CO$_3$	94	-	Stopa and Yamaura [145]
GLA-cross-linked chitosan/aminoguanidyl	Ag(II)	2.0 mol L^{-1} KNO$_3$	95	1	Ahamed et al. [146]
	Au(II)		85	5	

9 Conclusion and future prospects

The modification strategies of chitosan have greatly improved the properties of chitosan derivatives for competitive applications especially in water and wastewater treatment and nutrient adsorption/recovery. The existence of amino and hydroxyl groups creates the positions for surface modification either by chemical or physical means. Chitosan derivatives generally hold superior properties of hydrophilicity, mechanical strength and solubility resistance to acids, specific surface, porosity and adsorption. Chitosan also shows superior life cycle assessment from the viewpoint of environmental impact.

A large volume of works may have been published over the years on chitosan and its derivatives for various pollutants removal. Nonetheless, only few of these works clearly presented novel modifications, advantages and limitations, and life cycle assessment of the chitosan structure, while most are still focusing on routine studies by testing the modified adsorbent on different adsorbates. The potential of modifying chitosan is still large and yet to be unlocked and can be significantly developed in the future. Future quest for novel modifiers should ensure that modification strategies are carried out without altering the biodegradability,

antimicrobial and antifungal properties and non-toxicity of the pristine chitosan. Secondly, future research areas should make efforts to employ natural resources as chitosan modifiers because of the safety and health concerns associated with end applications. This development will further promote the use of chitosan derivatives on a larger scale because of the impact it will have on bioprocessing, cosmetics and food industries, among others.

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