Carbon Nanotubes Reinforced Polymeric Hybrid Materials for Water Purification

Anny Leudjo Taka, Michael Klink, Xavier Yangkou Mbianda, Fanyana Mtunzi, and Eliazer Bobby Naidoo

Abstract The accessibility of safe drinking water is currently a critical concern; the challenge is to develop an effective method to remove pollutants to ultra-low levels and recycle wastewater through purification. Among the water purification methods that have already been employed, nanotechnology has been considered the most promising method. This is because the nanomaterials used as adsorbents have been proven to remove different classes of pollutants, including emerging water pollutants, and these nanomaterials can be regenerated and reused. Particularly carbon nanotubes-based polymeric nanocomposite materials have attracted significant research attention because they possess multifunctional properties helpful in removing different types of pollutants from wastewater. Therefore, this chapter reviews recent studies reported on carbon nanotubes modified with natural polymers (biopolymers) such as chitosan, cellulose, and cyclodextrin used in water treatment. The cost and economic value of carbon nanotubes modified with polymeric hybrid materials used as nano-sorbents for water purification are also discussed.

Keywords Nanotechnology · Polymer hybrid · Nanocomposite · Nano-sorbents · Water purification

A. Leudjo Taka (✉) · F. Mtunzi · E. Bobby Naidoo
Institute of Chemical & Biotechnology, Southern Gauteng Science and Technology Park, Vaal University of Technology, Sebokeng Campus, Vanderbijlpark 1983, South Africa
e-mail: lytany04@yahoo.fr

A. Leudjo Taka · M. Klink (✉) · F. Mtunzi · E. Bobby Naidoo
Department of Chemistry, Vaal University of Technology, Vanderbijlpark Campus, Vanderbijlpark 1900, South Africa
e-mail: michaelk1@vut.ac.za; lytany04@yahoo.fr

M. Klink
Department of Biotechnology, Vaal University of Technology, Vanderbijlpark Campus, Vanderbijlpark 1900, South Africa

X. Yangkou Mbianda
Department of Chemical Sciences, University of Johannesburg, Doornfontein, Johannesburg 2028, South Africa

1 Introduction

Nanotechnology has been demonstrated as a promising approach to provide effective nano-sorbent materials for water purification. Among nanomaterials, carbon nanotubes are well known for their excellent chemical, thermal, mechanical, chelating, and many other properties valuable for their use as nano-sorbent for the removal of pollutants from the contaminated water [1–9]. Carbon nanotubes (CNTs) were first described by Iijima [10]; they can be defined as large molecules with cylindrical shapes. They are made up of a hexagonal arrangement of hybridized carbon atoms and can be formed by rolling up a single sheet or multiple sheets of graphene [3, 11]. Therefore, there exist different types of CNTs, such as single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multiwalled CNTs (MWCNTs). In addition, there are three well-established methods used to produce a wide variety of CNTs. These methods are electric arc discharge, laser vaporization, and chemical vapor deposition techniques. Among these methods, chemical vapor deposition (CVD) is one of the most popular used methods [2, 12].

CNTs have attracted tremendous attention in various fields such as electronic, medical, energy, and water purification. CNTs are characterized by their very high surface area to volume ratios, having diameters in the order of a few nanometers and lengths in the range of hundreds of nanometers [3, 13–15]. Besides that, CNTs are versatile materials in the sense that they can be modified with different types of chemical moieties in order to improve their properties and usefulness in various applications, particularly in water purification [3, 13, 14]. For instance, many studies have demonstrated the use of functionalized CNTs as adsorbents for the removal of heavy metal ions and organic pollutants [16–18]. However, using only Functionalized CNTs for water purification is expensive; additionally, there are currently emerging water pollutants that are complex and require efficient nano-sorbent materials with multifunctional properties. In this perspective, special attention has been giving to polymer nanocomposites research, particularly on carbon nanotubes reinforced with polymer hybrid materials [2, 19–21].

Polymer nanocomposites can be defined as multiphase materials with excellent multifunctional properties resulting from the combination of each component in the polymer composite [21]. These multifunctional properties, such as thermal stability, physical, mechanical, organic, inorganic, and antimicrobial properties, are vital in water purification. Furthermore, natural polymer-based nanocomposites are mostly preferred among polymer nanocomposites because natural polymers (or biopolymers) are biocompatible, biodegradable, non-toxic, and possess oxygen-rich functional groups useful for the removal of various classes of water pollutants [21, 22]. Research on CNTs modified with natural biodegradable polymer nanocomposites has attracted a lot of interest. In general, literature has demonstrated that the modification of CNTs with polymer materials usually resulted in nanocomposites and hybrid materials. Therefore, the hybrid material can be defined as a new characteristic different from the original and results from combining different materials (organics and inorganics) at the atomic and molecular levels. In addition, the

nanocomposite refers to a material in which the properties of the original material (e.g., CNTs) are reinforced by combining the original material with a dispersion material (e.g., polymer matrix) [19].

However, one of the key challenges during the synthesis of CNT–polymer nanocomposites is to achieve a proper dispersion of CNTs within the polymer matrix. Many approaches have been reported to achieve the dispersion of CNTs in polymer matrix or composite. Some of these approaches include polymer wrapping, chemical functionalization of CNTs, or the addition of surfactant (in a mixture solution of CNTs and polymer material) [23–27]. Another method could be the interlaying/interleaving method involving a thin layer of CNT/polymer in the laminate's midplane [28, 29]. For instance, previous literature has demonstrated that the dispersion of pristine CNTs was practically impossible because the surface of pristine CNTs is hydrophobic and inert [14, 19, 30–32]. In order to resolve the issue, pristine CNTs must first be chemically functionalized to allow the introduction of oxygen-containing groups on their surface. This will ease their dispersion and chemical reactivity with the polymer matrix [3, 12, 33].

Moreover, the modification of polymer (or biopolymer) with CNTs is advantageous because of the ability of CNTs to enhance the polymer properties to a higher order of magnitude than the non-modified polymer. The properties of polymers which can be improved are their thermal stability, surface area to volume ratio, strength, crystallization, chemical, mechanical, physical properties, and many other properties [14, 19, 30–32]. In this regard, various methods can be employed to achieve the synthesis of CNTs/polymer nanocomposites. These methods include the in-situ approach (e.g., cross-linked polymerization), direct mixing (solution mixing or melt compounding), and film casting-dip coating-physical mixing. However, the melt compounding method is mostly used for the thermoplastic polymer; in this method, CNTs are sheared mechanically, compounded in the molten polymer matrix. On the other hand, the solution mixing method required that the polymer be soluble in the solvent used to disperse the CNTs [34].

Hence, the objectives of this chapter are to deliver a review evaluation on the different methods to modify CNTs with a natural polymer such as chitosan, cyclodextrin, and cellulose and their application for the removal of pollutants from contaminated water. The Cost and economic value of these CNTs reinforced with natural polymeric hybrid materials applied in water purification are also examined.

2 Carbon Nanotubes/Cyclodextrin Polymer Nanocomposites for Water Treatment

Cyclodextrin (CD) are cyclic oligosaccharides derived from enzymatic reactions of starch. They are also known as molecular chelating agents, and they are multipurpose materials because they can be modified to enhance their properties and usefulness in various applications (e.g., drug delivery, food, water purification, cosmetics, textiles).

β-Cyclodextrin is most widely used among the three types of CD (α-CD, β-CD, and γ-CD) because of its good reactivity and it is less costly [35–42]. Additionally, there are many reports on the studies of CDs; this section focuses mainly on the insoluble nanosponge CD polymers modified with CNTs for application as adsorbent material in water purification. The synthesis of insoluble nanosponge CD polymers can be achieved using dehydration, condensation, and deprotonation methods. However, many studies on the modification of CDs with CNTs were conducted by the condensation method [2, 37, 43–45].

The condensation method involves the reaction of CD or CD and CNTs with an excess of the bifunctional linker (cross-linker agent) such as diisocyanates (e.g., diphenylmethane diisocyanate (DPMDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI)) through cross-linking polymerization. The successful reaction can be confirmed by FTIR, proving the disappearance of the cross-linker (isocyanate) peak and the incorporation of the C=O, NH(CO), and other functional groups into the insoluble nanosponge CD polymer or CD/CNT nanocomposite insoluble polymer. The cross-linker agent such as diisocyanate was used to alter the solubility of CD in water resulting in insoluble CD polyurethanes [2, 35, 46, 47].

Insoluble nanosponge CD polymers have demonstrated the capacity to absorb various groups of organic pollutants by forming a host–guest inclusion complex [35, 48–50]. However, these insoluble nanosponge CD polymers have been demonstrated not to be efficient for uptake of complex organic molecules and large inorganic pollutants. Besides that, the literature has shown that the structural integrity of insoluble nanosponge CD polymers was affected after long cycles of regeneration and reuse. Therefore, the development of insoluble nanosponge CD modified with CNTs has been reported to be a valuable way to improve CD polymers' properties and resolve their limitations as adsorbents for water purification [46, 47, 51, 52].

Research studies on the modifications of CD polymers with CNTs to obtain nanocomposite polymers have been reported. These modifications involve mainly the chemical modification of ß-CD with MWCNTs by cross-linking polymerization using HMDI or TDI linker agent. For instance, Salipira et al. have reported on the functionalization of MWCNTs by acid oxidation method and the copolymerization of oxidized-MWCNTs with β-CD. They have demonstrated that oxidized-MWCNTs/β-CD nanocomposite insoluble polyurethane obtained could remove organic pollutants (trichloroethylene and p-nitrophenol) by column studies at 99% [46, 47, 51]. However, in their column studies, Salipera et al. have not conducted detailed column adsorption studies to investigate the effect of pH, contact time, adsorbent dosage, initial concentration, temperature. Additionally, they did not evaluate the performance of their oxidized-MWCNTs/β-CD nanocomposite through column adsorption models. Hence, one can say that this study reported by Salipera and co-workers still presents some limitations.

Lukhele et al. [53] have oxidized MWCNTs, then impregnated the oxidized MWCNTs with Ag nanoparticles; the composite Ag-MWCNTs that they have obtained was copolymerized with β-CD to produce Ag-MWCNTs/β-CD polymer nanocomposite. They have tested the ability of Ag-MWCNTs/β-CD polymer nanocomposite to remove *Escherichia coli* (*E-coli*) in model water solution by a

cell viability counting technique [54]. From the results they have obtained, oxidized MWCNTs impregnated with Ag and copolymerized with CD was able to remove 95% of *E-coli* [53, 54].

Krause and co-workers have prepared Fe–Ni bimetallic nanoparticles embedded on MWCNTs, then through cross-linking polymerization using HMDI as a linker, they have reinforced Fe–Ni–MWCNTs composite with β-CD to obtained a nanocomposite polymer. They have used the synthesized nanocomposite polymer Fe–Ni–MWCNTs/β-CD as an adsorbent to remove trichloroethylene (TCE) from a model pollutant solution by column adsorption. They were able to achieve a 98% reduction of TCE using Fe–Ni–MWCNTs/β-CD polymer nanosponge composite. However, the column adsorption study was not thoroughly conducted; that is, the effect of pH, contact time, adsorbent dose, and other critical parameters affecting the column adsorption study were not investigated. Furthermore, they have not used column adsorption models to establish the mechanism of adsorption of TCE unto their Fe–Ni–MWCNTs/β-CD polymer nanosponge composite.

Moreover, Mamba et al. have reported on the modifications of oxidized MWCNTs (oxi-MWCNTs) and phosphonate-functionalized-MWCNTs (pMWCNT), respectively, by cross-linking polymerization withβ-CDusing HMDI as a linker. Then, they have characterized the oxidized-MWCNTs/β-CD (oxiMWCNT/β-CD) [55] and phosphonate-functionalized-MWCNTs/β-CD (pMWCNT/β-CD) [52] polymer nanocomposites obtained by FTIR, SEM, and Brunauer Teller method (BET) for surface area analysis. FTIR analysis has confirmed the successful polymerization of oxidized-MWCNT and pMWCNT, respectively, with β-CD. SEM analysis revealed that polymers' surface morphologies were non-uniform; they have noted a combination of porous surface and granular appearance. They have also demonstrated the ability of the oxidized-MWCNTs/β-CD polymer nanocomposite to adsorb metal ions pollutants (lead and cobalt) model polluted solutions by batch adsorption study thorough the investigation of the effect of initial concentration, contact time, and competing ions. Oxidized-MWCNTs/β-CD polymer nanocomposite was able to remove both lead and cobalt ions from model polluted solutions with a greater adsorption capacity for lead [55].

Mamba et al. have also demonstrated by batch adsorption study that pMWCNT/β-CD polymer was also efficient for removing of 4-chlorophenol and cobalt ions [52]. They have also shown that isotherms models such as Langmuir best explained the mechanism of adsorption of metal ions, while Freundlich was the good fit model for the adsorption of 4-chlorophenol by pMWCNT/β-CD polymer nanocomposite. However, Mamba et al. reported that the low surface area of oxidized-MWCNTs/β-CD and pMWCNT/β-CD polymer nanocomposites negatively affect the adsorption efficiency at higher concentrations of pollutants in contaminated water. In addition, they have not evaluated the effect of adsorbent dosage, pH effect, desorption, thermodynamics, kinetics, and regeneration studies helping to establish the mechanism of adsorption. They have also not tested the ability of their polymer nanocomposites to remove organics or inorganics (heavy metal ions) from real industrial wastewater samples.

In order to overcome the above limitations on the functionalized carbon nanotubes reinforced with β-CD nanosponge polymer, recent studies have been conducted and published by Leudjo taka et al. [56–58]. They have conducted detailed studies on CNTs reinforced with nanosponge cyclodextrin and metal nanoparticles. They have investigated the synthesis of phosphorylated MWCNTs cross-linked with β-CD and doped with titanium and silver nanoparticles using combined methods of phosphorylation (through amidation reaction), cross-linking polymerization, and sol–gel process. In brief, the pristine MWCNTs were first functionalized by acid oxidation and phosphorylation (Fig. 1). Then the phosphorylated MWCNTs obtained were co-polymerized with β-CD using HMDI as a linker (Fig. 2), and the resulting nanocomposite polymer pMWCNTs-CD was decorated with metal nanoparticles by the sol–gel process to produce pMWCNT-CD/TiO$_2$-Ag (Fig. 3).

Moreover, Leudjo Taka and co-workers have also thoroughly characterized the obtained nanosponge composite polymer, pMWCNT-CD/TiO$_2$-Ag, using thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), BET surface
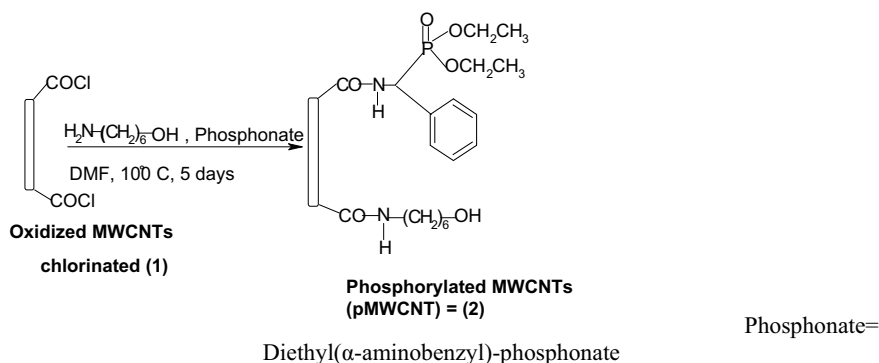
Fig. 1 Functionalization of MWCNTs by phosphorylation method (reprinted with permission from [14])
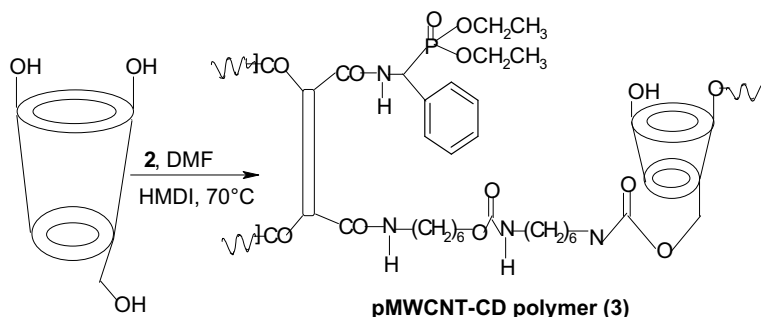

Fig. 2 Cross-linking polymerization of phosphorylated MWCNTs with β-CD (reprinted with permission from [14])
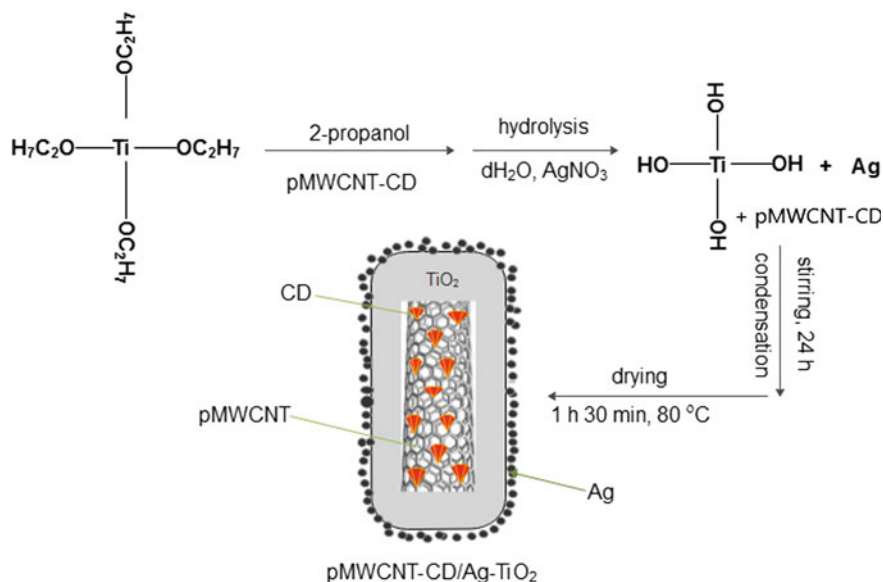
Fig. 3 Modification of pMWCNT-CD with metal nanoparticles using sol–gel process (reprinted with permission from [57])

area analysis, electron microscopy techniques, X-ray diffraction (XRD), and complementary spectroscopy techniques. FTIR spectroscopy confirmed the presence of functional groups (C–H, OH, N–H, O=P–OH, P–O, P=O, Ti–O–C, and NH(CO) of the carbamate linkage and characteristic of the nanosponge polyurethane) on the surface of pMWCNT-CD/TiO_2-Ag nanosponge composite polymer. TGA and DSC analyses were used to assess the thermal stability of the nanosponge composite polymer, which was proved to be stable at a temperature below 100 °C. SEM results revealed that pMWCNT-CD/TiO_2-Ag surface morphology is rough with an aggregation of granular particles, while the native CD and pMWCNT-CD polymers have a porous and sponge-like structure [33]. X-ray photoelectron spectroscopy (XPS) was employed to determine the element composition, binding energy, and respective percentages for each functional group depicted on the surface of the nanosponge composite polymer pMWCNT-CD/TiO_2-Ag. XRD analysis was conducted to confirm the crystallinity in the polymeric chain of developed MWCNT-CD/TiO_2-Ag (due to reinforcement of CD polymer by both pMWCNT and TiO_2 and Ag nanoparticles) and to identify the dominant crystalline phase (TiO_2 anatase) (Fig. 4II). In addition, from the Raman spectroscopy analysis results, the developed pMWCNT-CD/TiO_2-Ag was a clear combination of CD polymer, MWCNTs, rutile, and anatase TiO_2 (Fig. 4I) [57].

Additionally, Leudjo Taka et al. have also proven that the development of pMWCNT-CD/TiO_2-Ag nanosponge composite polymer had could act as a filter
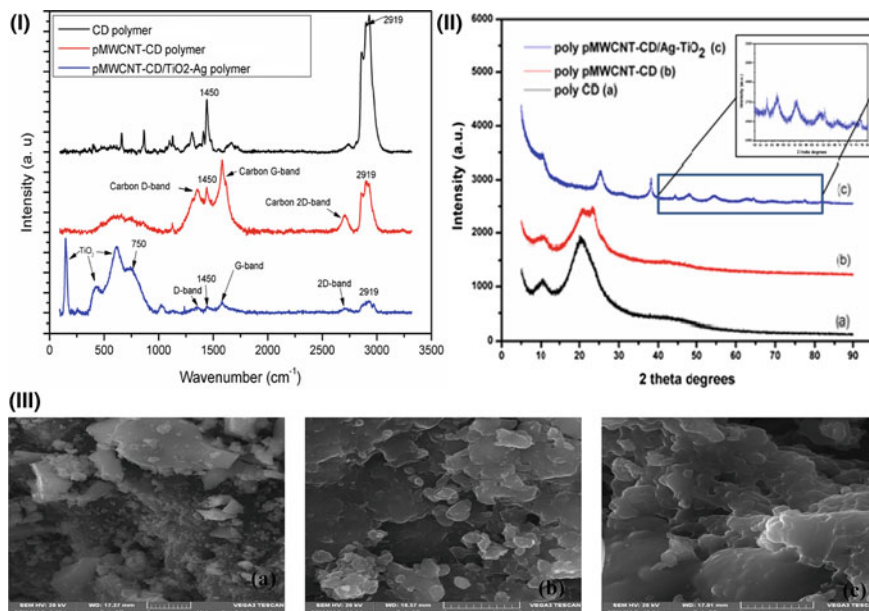
Fig. 4 I Raman spectra, **II** XRD patterns and **III** SEM micrographs (**a** pMWCNT-CD/TiO$_2$-Ag, **b** pMWCNT-CD, **c** CD) of the synthesized nanosponge polymers (reprinted with permission from [14])

to eliminate the organic pollutants (e.g., dyes, chlorinated compounds) [56], inorganic pollutants (e.g., heavy metal ions) [58] and pathogenic microorganism contaminants (e.g., bacteria and fungi) [57]. The batch adsorption studies were conducted to remove organic and metal ions pollutants through the investigation of the factors such as pH, adsorbent dosage, initial concentration, contact time, temperature, and desorption and regeneration studies. The adsorption mechanisms for these pollutants were established through thermodynamic studies and evaluation of the data obtained using various isotherm and kinetic models. Besides that, to prove the efficiency of pMWCNT-CD/TiO$_2$-Ag to act as a disinfectant material, the antimicrobial studies were conducted by microdilution methods and agar platting techniques. Leudjo Taka et al. have also reported that the highest adsorption capacity and potency of pMWCNT-CD/TiO$_2$-Ag against pathogens and other pollutants resulted from the reinforcement of CD nanosponge with both pMWCNTs and metal nanoparticles which help to improve the surface area (352.546 m^2/g), adsorption capacity and antimicrobial efficiency [57].

## 3   Carbon Nanotubes/Chitosan Polymer Nanocomposites for Water Purification

Chitosan is a biopolymer originating from the hydrolysis of chitin (Fig. 5), and it is the N-deacetylated form of chitin with two repeating units bonded together through β-(1,4)-glycosidic bond [34, 59–62]. Chitin is usually obtained from the waste of crustacean shells [59–61, 63]. Chitosan is a biodegradable, environmentally green, and biocompatible polymer. In addition, chitosan is a polycationic and semi-crystalline polymer that is hydrophobic. It has demonstrated excellent chemical and biological properties due to the presence of hydroxyl and amino functional groups, which play an essential role in the reactivity of chitosan [61, 64]. These hydroxyls and amino groups also give the flexibility to chemically alter the structure of chitosan with specific functionalities favoring the introduction of new or improved properties [63, 64]. Besides that, chitosan is hydrophobic in its original form (pristine form), i.e., it is insoluble at neutral pH in water and organic solvents [60, 65]. Hence, it is crucial to improve its solubility in various solvents over a wide pH range through physical and chemical functionalizations useful in further chemical reactions and applications. These chitosan modifications also help introduce the required physical, mechanical, and chemical properties necessary to enhance the reactivity of chitosan
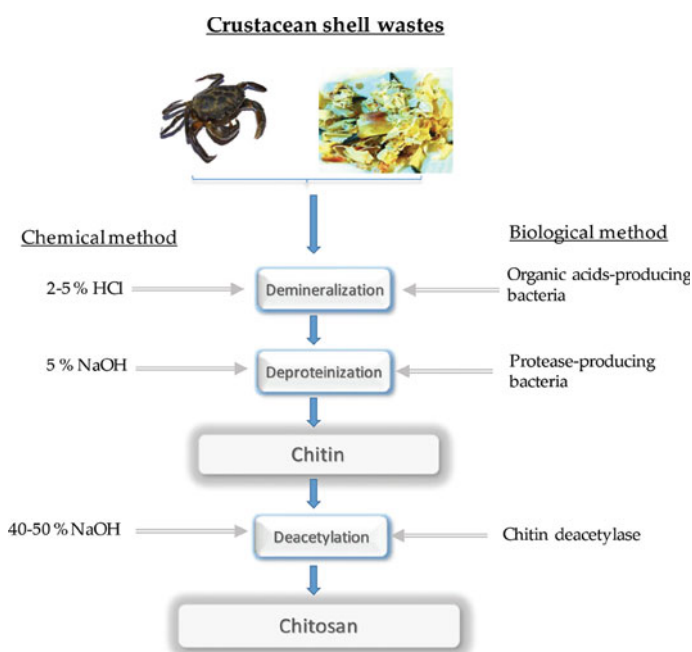
Fig. 5 Extraction methods of chitin and chitosan from crustacean shell wastes (reprinted with permission from [59])

with nanomaterials to produce a chitosan-based nanomaterials composite polymer with high adsorption efficiency and affinity for water contaminants [59–61, 66].

Additionally, chitosan could be chemically functionalized by cross-polymerization, surface grafting, carboxymethylation, internal hydrogen bonding with the aid of solvents, chemical reagents, vapor, coupling agents, and surface-active agents. And, the physical approaches previously used to modify chitosan include sputtering, plasma irradiation, blending, physical mixing, electron beam irradiation, Y-ray irradiation, ultrasounds, and ultraviolet irradiation [60, 61, 66–69]. Figure 6 shows the different methods which can be used for the chemical modifications of chitosan. Chitosan also has different deacetylation degrees, which influences its quality grade, physicochemical modifications, and properties. The degree of deacetylation is the ratio of 2-acetamino-2-deoxy-D-glucopyranose to
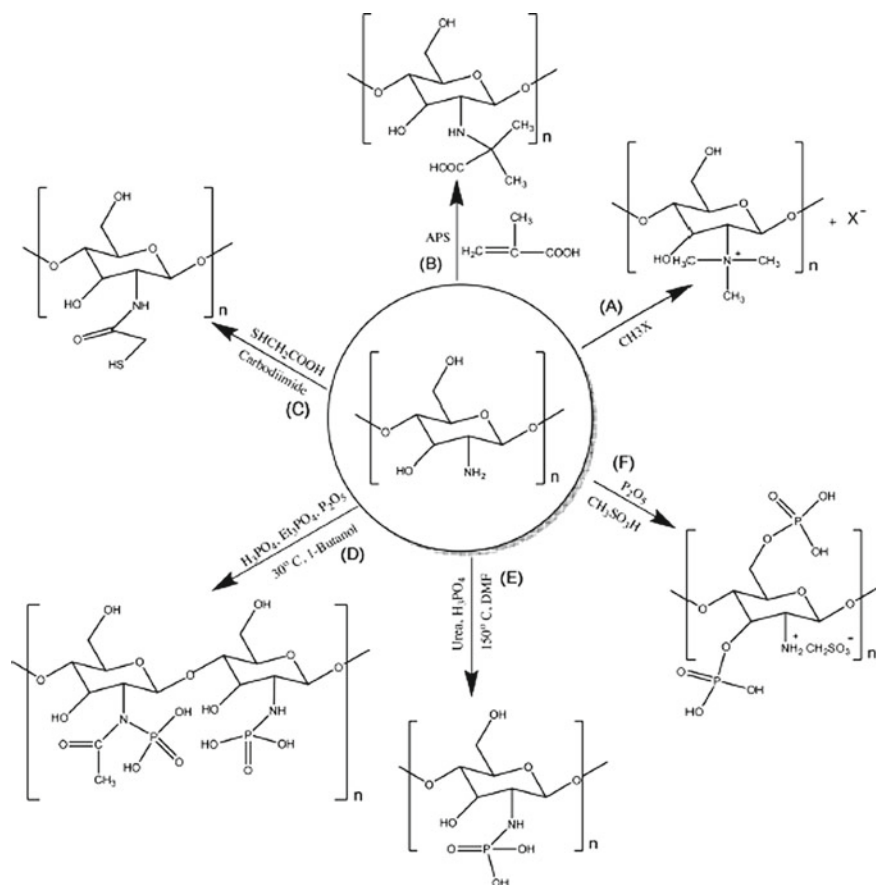
Fig. 6 Schematic representation of the different methods to chemically modify pristine chitosan: methylation (**A**), co-polymerization (**B**), thiolation (**C**), phosphorylation (**D**), (**E**) and (**F**) (reprinted with permission from [20])

2-amino-2-deoxy-D-glucopyranose. Thus, chitosan can be easily soluble in dilute acidic solutions at higher deacetylation's degree (>55%) [59–61, 64].

The research on the synthesis of chitosan-based nanocomposite polymers has drawn a lot of interest because their excellent properties offer a wide range of opportunities for their application [22]. These chitosan-based nanocomposite polymers can be synthesized using various techniques based on *in-situ* or *ex-situ* methods. In the *ex-situ* method, the nanoparticles are first prepared, then added into the polymer matrix solution used as a dispersion medium. On the other hand, the *in-situ* technique includes approaches such as oxidation, cross-polymerization [33, 58], reduction [70–73], precipitation [74], electrospinning methods [75–77], and sol–gel [78]. This *in-situ* technique means that inorganic nanoparticles are directly produced in the polymer matrix solution used as a reaction medium. The *in-situ* technique has been most widely used, and in this technique, the polymer matrix (e.g., chitosan) can act both as a capping agent or stabilizer to prevent the agglomeration of nanoparticles, control the nanoparticles' shape and size during the synthesis [2, 79–81].

In particular, chitosan nanocomposites containing carbon nanotubes and/or nanoparticles fixed into the biopolymer matrix have been developed for their use as nano-sorbents and nanofiltration membranes for the removal of contaminants from wastewater and desalination of water. According to literature, chitosan-based nanocomposite polymers have been demonstrated to enhance the adsorption and degradation of pollutants as well as antibacterial activity [34, 82, 83]. This can be explained by the exceptional mechanical and physicochemical properties resulting from the reinforcement of chitosan with these nanostructured carbons and/or inorganic nanoparticles, which help improve chitosan properties [84–90]. For example, the use of chitosan-based carbon nanotube nanocomposite polymer has been reported by Salam et al. [87] and other researchers to remove toxic metal ions. Salam et al. [87] prepared homogeneous nanocomposites MWCNTs/chitosan through cross-linking polymerization of MWCNTs using glutaraldehyde. The prepared MWCNTs/chitosan was tested for the removal of metal ions pollutants (Cd, Cu, Zn, and Ni) from aqueous solutions by column adsorption. The study proved that MWCNTs/chitosan nanocomposite could efficiently remove metals ions from aqueous solutions [87].

Beheshti et al. [91] have demonstrated the removal of chromium (Cr(VI))using MWCNTs reinforced with both biopolymer chitosan and nanoparticles (Fe_3O_4). The polymer nanocomposite chitosan/MWCNT/Fe_3O_4 was achieved using combined methods of acid oxidation of pristine MWCNTs, then their impregnation with Fe_3O_4 nanoparticles finally dispersion of MWCNTs/Fe_3O_4 composite in chitosan polymer matrix followed by electrospinning process to produce chitosan/MWCNT/Fe_3O_4. The surface morphology and structural analysis were assessed by SEM, TEM, FTIR, and XRD. The performance of chitosan/MWCNT/$Fe_3O_4$was evaluated by batch and fixed-bed column adsorption to eliminate of Cr (VI) from contaminated water solutions. The factors such as pH, initial pollutant concentration, contact time, temperature, and flow rate affecting the adsorption efficiency, were investigated [91].

From the results obtained, the structural analysis and surface morphology analysis had confirmed that chitosan/MWCNT/Fe$_3$O$_4$ was a smooth, uniform nanofibrous (Fig. 7a) and crystalline material with various functional groups (amino, amide, hydroxyl, Fe–O, and C–O) on their surface. Beheshti et al. have shown that in the column system, as the flow rate increase, the adsorption efficiency of chitosan/MWCNT/Fe$_3$O$_4$ also increased (Fig. 7e). The adsorption of Cr(VI) was favorable at high-temperature 45 °C. Langmuir isotherm and pseudo-second-order
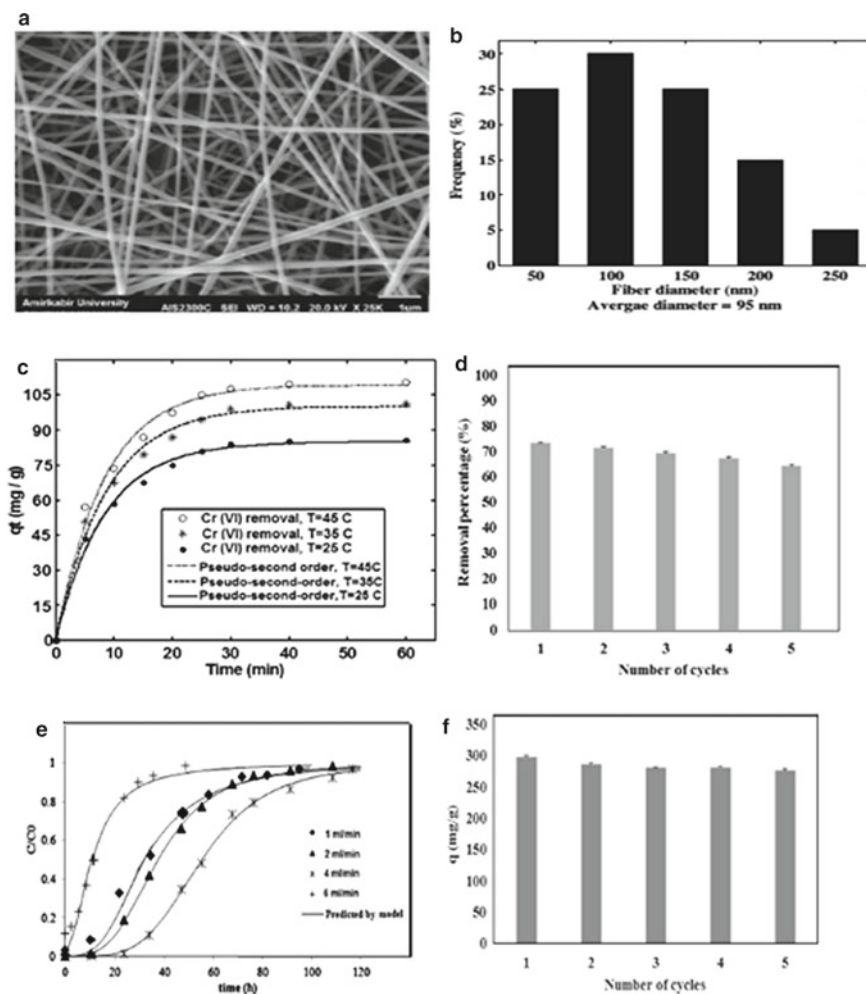
Fig. 7 a SEM image and **b** fiber size distribution of chitosan/MWCNTs/Fe$_3$O$_4$; **c** kinetic and **d** regeneration studies results for the removal of Cr(VI) by chitosan/MWCNTs/Fe$_3$O$_4$ in batch adsorption; **e** column adsorption experiment and predicted breakthrough curves for the removal of Cr(VI) by Chitosan/MWCNTs/Fe$_3$O$_4$; **f** regeneration study by column adsorption (reprinted with permission from [91])

kinetic models (Fig. 7c) best explained the mechanism of Cr(VI) removal in batch adsorption system while Thomas model was the best fit model to predict the sorption of Cr(VI) by chitosan/MWCNT/Fe_3O_4 in column system. After five cycles of desorption and regeneration, the adsorption efficiency was not affected in both column and batch adsorption systems (Fig. 7d and f) [91].

The published work of Alsuhybani et al. [92] revealed that nanocomposite membrane MWCNT/chitosan could be utilized as a nanofiltration membrane for the desalination of water by nanofiltration/reverse osmosis system. The nanocomposite membrane was prepared by evaporative casting method, and the characteristics of the developed membrane were determined through analysis of the surface charge, surface morphology, mechanical properties. From the results obtained, Alsuhybani et al. have shown that the combination of the biopolymer chitosan with MWCNT help to enhance the crystallinity, mechanical properties and increase the flux rate and salt rejection capability during the desalination process. These positive changes were due to incorporating MWCNTs bringing about the packing of hydrophilic chains in the biopolymer matrix. It is also essential to know that nanofiltration is one of the membrane processes which required low pressure and possess the properties such as salt rejection, water permeability, pore size between ultrafiltration and reverse osmosis [92].

Furthermore, Shawky et al. [93] have demonstrated the use of polymer chitosan/CNTs nanocomposite beads for the removal of mercury (Hg(II)) by batch adsorption study. They have synthesized different chitosan/CNTs nanocomposite beads using impregnation and protected cross-linking method, respectively. SEM, FTIR, and TGA techniques were employed to characterize the prepared composite chitosan/CNTs beads nanocomposites. Shawky et al. have shown that the nanocomposite beads prepared by the protected cross-linking technique have good thermal stability and were very effective for removing Hg(II) than the other composite beads prepared using impregnation and normal cross-linking method. The removal of Hg(II) was dependent on solution pH, temperature, and contact time. Langmuir isotherm model was the best fit model to explain the mechanism of Hg(II) sorption onto Chito/CNTs nanocomposite beads. In addition, chitosan/CNTs nanocomposite beads could be considered as cost-effective sorbents for water treatment because they can be recycled several times without any significant loss in adsorption capacity [93].

Zhao et al. [31] have recently developed a new polymer nanocomposite made of chitosan, CNTs, and octa-aminopolyhedral oligomeric silsesquioxanes (POSS) using a self-assembled method. The developed polymer nanocomposite chitosan/POSS/CNTs was characterized using FTIR, TGA, XRD, and TEM techniques. The performance of the developed chitosan-based polymer nanocomposite was tested for the degradation of organic pollutants (Congo red and methyl orange dyes) from model water solutions. Zhao et al. have proven that the intermolecular forces and the modifications of chitosan with both CNTs and POSS enhanced the thermal stability and adsorption capacity of chitosan/POSS/CNTs. The maximum sorption capacities obtained were 314.97 mg/g and 63.23 mg/g for Congo red and methyl orange respectively [31].

Morsi et al. [94] have developed polymer nanocomposites (chitosan/AgNPs, Chitosan/CuNPs, and chitosan/CNTs) and a multifunctional polymer nanocomposite made of chitosan, silver nanoparticles, copper nanoparticles, and CNTs (chitosan/AgNPs/CuNPs/CNTs) (Fig. 8a) which were used as antimicrobial agents to eliminate pathogenic microorganism pollutants from wastewater. The results obtained have shown that the combination of chitosan, nanoparticles, and CNTs produced different dimensional shapes with spherical NPs and CNTs dispersed uniformly into the polymer matrix (Fig. 8b). Additionally, they have depicted that at low concentration of pollutants (microbes) and short contact time (10 min), the antimicrobial activity of the multifunctional polymer nanocomposite was the highest (Fig. 8c) against gram-positive and gram-negative bacteria as well as fungal strain (isolated from wastewater) [94].

4   Carbon Nanotubes/Cellulose Polymer Nanocomposites for Water Decontamination

On earth, cellulose is well known as the most abundant biopolymer (or natural polymer) because it is readily available, and its cost is lower than other natural polymers. Cellulose's surface is rich in functional groups containing oxygen which favor its modifications with various chemical moieties or materials. Cellulose is made of D-anhydroglucopyranose units linked by glycosidic bonds, and it is very biocompatible and hydrophilic [95]. Cellulosecan be found into four types of crystals which include: cellulose I derived from plant, cotton, straw, and wood; cellulose II prepared by alkali treatment from natural cellulose and recrystallization, thus it is regenerated; cellulose III (III$_1$ and III$_2$) is obtained via liquid ammonia treatment of cellulose I and II; cellulose IV is derived from heating of cellulose III with glycerol. Nanocellulose is the smallest structural unit of cellulose, and it is constituted of bacterial nanocellulose, cellulose nanofibers, and cellulose nanocrystals [19, 95, 96]. In addition, literature has demonstrated that nanocellulose (or cellulose) easily aggregate in a reaction medium, to facilitate its dispersibility in water and other solvents, it is important to chemically modify its surface through processes such as sulphonation, oxidation, phosphorylation, and carboxymethylation just to site a few (Fig. 9). These surface chemical modifications of the cellulose significantly improve the properties of the cellulose for their further modifications with other materials to produce polymeric hybrid composite materials [19, 97, 98].

In this regard, the reinforcement of functionalized CNTs (e.g., oxidized CNTs) with cellulose biopolymer has resulted in novel polymeric hybrid nanocomposite materials with many benefits. From previous studies, it has been proved that CNT/cellulose polymeric hybrid nanocomposite materials possess better properties (water wettability, thermal performance or stability, electrical conductivity, mechanical, adsorption efficiency, salt discharge, and permeation flux properties) than each original component present in the polymer nanocomposites [95]. For instance, Chen
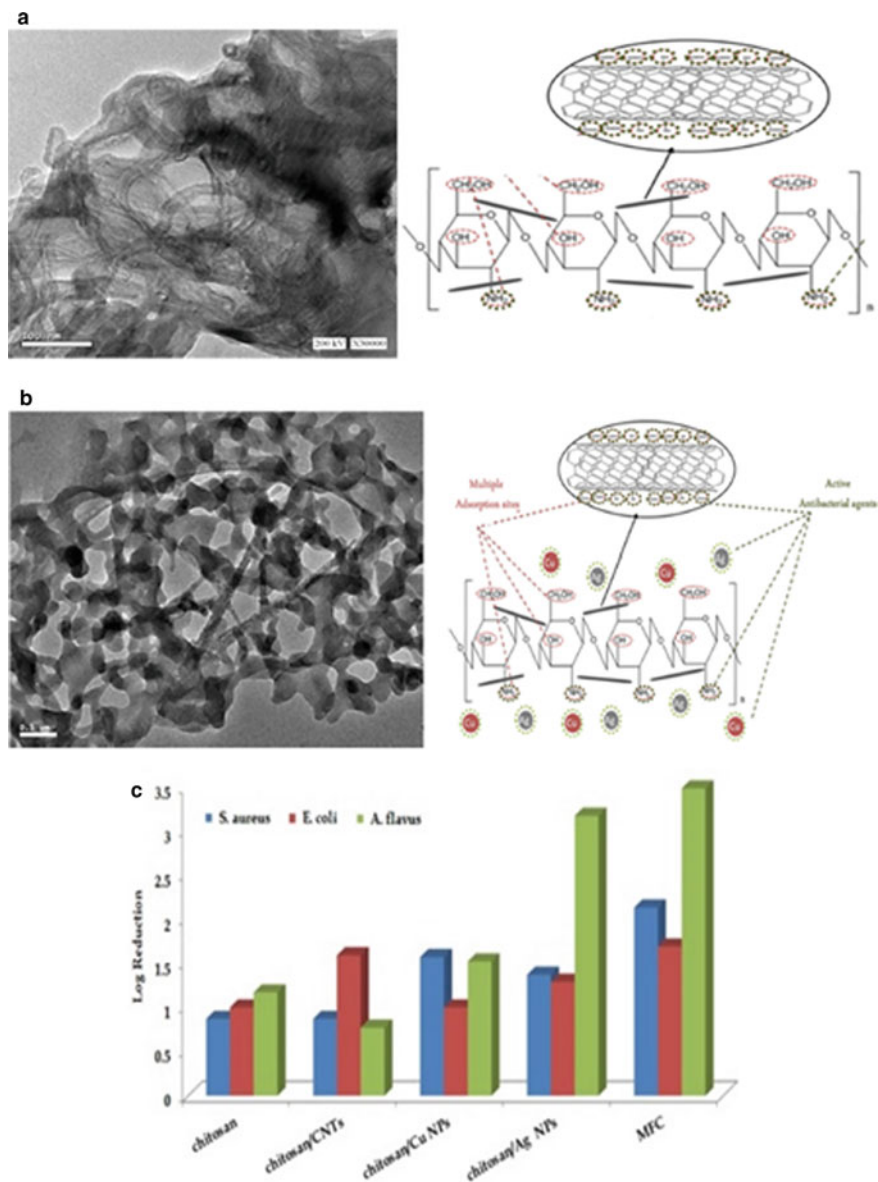
Fig. 8 Illustration of the graphical structural images and TEM micrographs of **a** chitosan/CNTs binanocomposites, **b** Chitosan/AgNPs/CuNPs/CNTs multifunctional nanocomposite and **c** the bar chart summarizing their antimicrobial performance (reprinted with permission from [94])
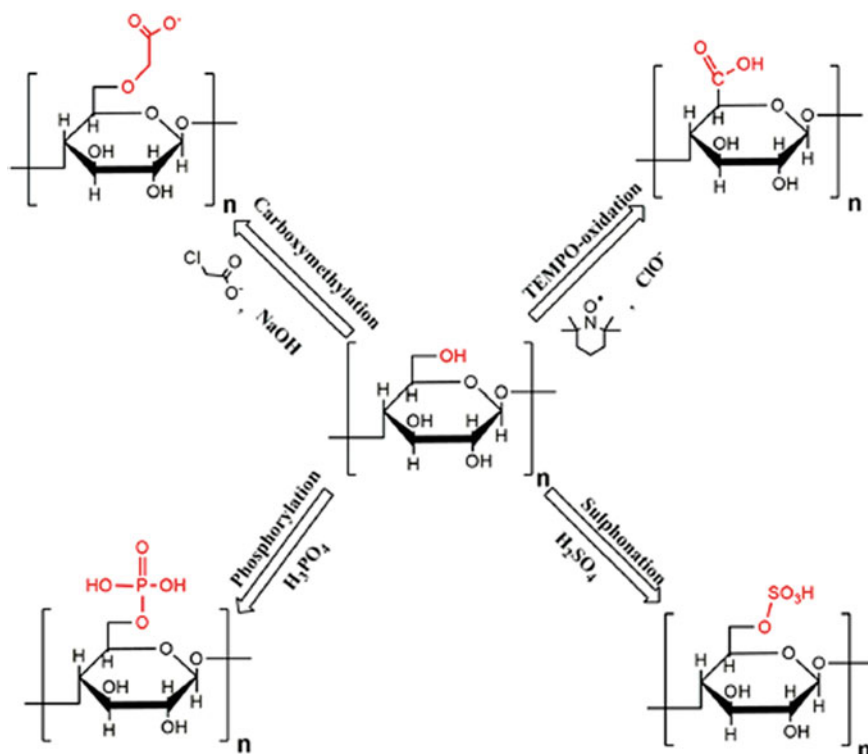
**Fig. 9** Different ways to chemically modify the cellulose surface [19]

et al. [99] have prepared a polymer nanocomposite fiber made of regenerated bacterial cellulose (BC) and 1.0 wt% MWCNTs (BC/MWCNTs) by the dry jet-wet spinning method. The nanocomposite fiber has demonstrated much-enhanced properties than the original bacterial cellulose [99]. Similarly, Lu and Hsieh have used the electro-spinning method to modified MWCNTs with cellulose acetate. They have shown that the obtained MWCNTs/cellulose acetate nanocomposite fiber has improved properties such as higher surface area and mechanical properties than the original cellulose acetate [100]. Hence, it can be noticed that a small amount MWCNTs can be uniformly be loading into cellulose to produce a polymer nanocomposite fiber which has a positive effect on the water wettability, surface structure, and mechanical properties of the composite fiber [95].

Besides, CNTs can be modified with cellulose to obtain polymer nanocomposite membranes which have potential in water purification. In this perspective, Silva et al. [101] have prepared a cellulose-based nanocomposite membrane by mixing pristine MWCNTs with cellulose acetate following the non-solvent induced phase separa-tion method. They have characterized the product obtained using scanning electron microscopy, TGA, and various spectroscopy techniques. SEM analysis confirmed that their developed pristine-MWCNT/cellulose acetate nanocomposite membrane

consisted of a dense layer on top and a porous support layer with a sponge structure. From the TGA result, they have shown that the nanocomposite membrane is very stable up to 320 °C; and the FTIR result confirmed the presence of functional groups resulting from the interaction between the acetate groups of cellulose and CNTs. They have proven that these functional groups were responsible for the effective removal of methylene blue from model wastewater solutions. They have validated that the combination of CNTs with biopolymer cellulose help to adjust the properties of each component in the composite and enhance the properties of polymer nanocomposite membrane, favoring an increase in adsorption capacity [101].

Sabir et al. [102] have also reported on the synthesis of functionalized MWCNTs/Cellulose acetate-polyethylene glycol nanocomposite membrane (Fig. 10) and its application in the desalination of drinking water. To achieve their synthesis, the surface of pristine MWCNTs was firstly engineered (functionalized) by acid oxidation method to introduce oxygen-containing groups helping to facilitated MWCNTs dispersion and reaction with the polymer material. Secondly, the cellulose acetate (CA) was copolymerized with polyethylene glycol 400 (PEG400), then a small amount (0.1–0.5 wt%) of surface engineered MWCNTs (SE-MWCNTs) was
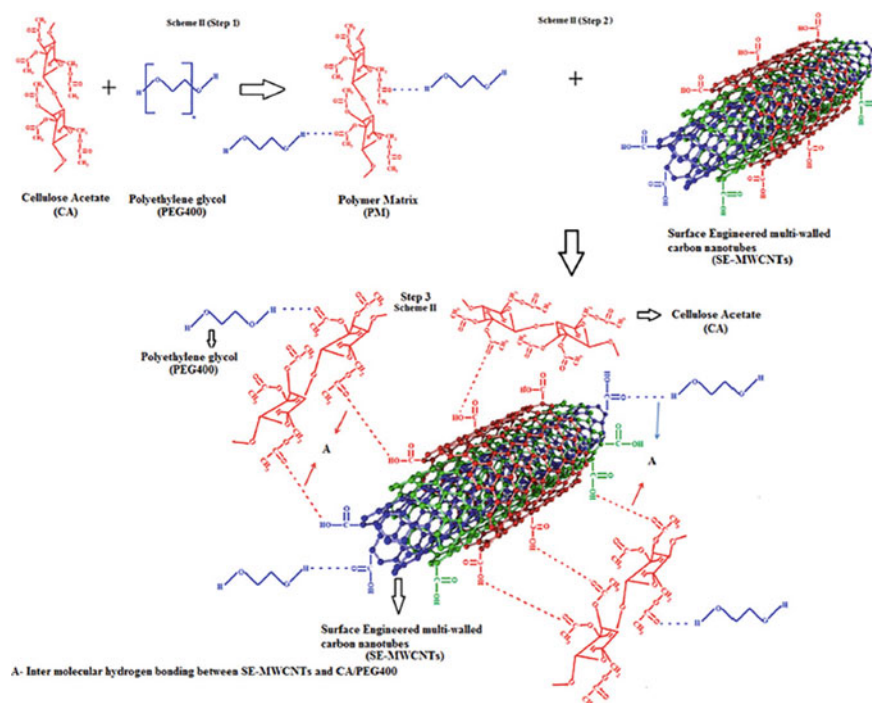

Fig. 10 Schematic illustration of the synthesis of functionalized MWCNTs/cellulose acetate-polyethylene glycol polymer nanocomposite membrane by combined methods of copolymerization and solution casting (reprinted with permission from [102])

dispersed uniformly in CA/PEG400 polymer matrix solution. Finally, the nanocomposite membrane (SE-MWCNTs/CA-PEG400) was obtained by the dissolution casting method. The thermal stability, surface morphology, and structural analysis were investigated by TGA, SEM, and FTIR spectroscopy, respectively. SEM results confirmed the formation of uniform, dense, structured SE-MWCNTs/CA-PEG400 nanocomposite membrane. The performance of the developed nanocomposite membrane was evaluated for removing salt from drinking water by reverse osmosis. From the structural analysis results, Sabir et al. have further reported that SE-MWCNTs/CA-PEG400 polymer nanocomposite membrane had better properties than CA-PEG400 polymer membrane due to the strong interaction between the SE-MWCNTs and CA-PEG400 polymer. This reinforcement of CA-PEG400 polymer with SE-MWCNTs had improved the thermal stability, reduced the permeation flux, increased the desalination and demineralization rates of the SE-MWCNTs/CA-PEG400 nanocomposite membrane [102].

Badawi et al. [103] have also reported on preparing MWCNTs/cellulose acetate, polymer nanocomposite membrane by phase inversion method using deionized water as a non-solvent and acetone as solvent. In their preparation, MWCNTs were first purified and oxidized by acid treatment to introduce functional groups on CNTs' surface, favoring their dispersion into the polymer matrix. They have successfully loaded a small amount of CNTs uniformly into the membranes. They have characterized the MWCNTs/cellulose acetate membrane and demonstrated its capability in desalinating a sodium chloride water solution. They have reported that the lowest MWCNT content in the nanocomposite membrane enhanced the permeation rate and slightly decreased salt retention percentage [103].

CNTs were also modified with biopolymer materials (chitosan, cellulose) and metal nano-photocatalyst to produce polymer nanocomposites, which can be used as photocatalysts to degrade wastewater pollutants. For instance, the synthesis of electrospun cellulose acetate/chitosan/SWCNT/Ferrite/Titanium dioxide nanofiber polymer composite was achieved by Zabihisahebi et al. for the elimination of organic (azo dyes) and inorganic (metal ions) contaminants via photoreduction and adsorption processes. The composite nanofiber was prepared by a combined method of impregnation, sonication, and electrospinning method. The use of the photocatalytic reduction method was adequate to efficiently degrade the azo dyes (e.g., Congo red, methylene blue) at both higher and lower concentrations as well as to remove metal ions (e.g., Cr (VI), As(V)) only at higher concentrations [86].

Furthermore, CNTs reinforced with cellulose or nanocellulose to form polymer nanocomposite hydrogel or aerogels have attracted tremendous attention due to their excellent properties, making them valuable candidates as adsorbent material to resolve the problem of water pollution from oil spillage, chemical leakage, and other water pollutants. For example, Li et al. [104] have fabricated a magnetic cellulose nanofiber (CNF)/polyvinyl alcohol (PVA)/MWCNT carbon aerogel (m-CPMCA) by combined methods of freeze-drying process, carbonization process, and direct immobilization of Fe_3O_4 nanoparticles on aerogel's surface (Fig. 11a). SEM analysis has shown that the nanocomposite polymer aerogel obtained had 3D porous structures piled up by sheet fibers (Fig. 11b). This m-CPMCA aerogel had high porosity and low
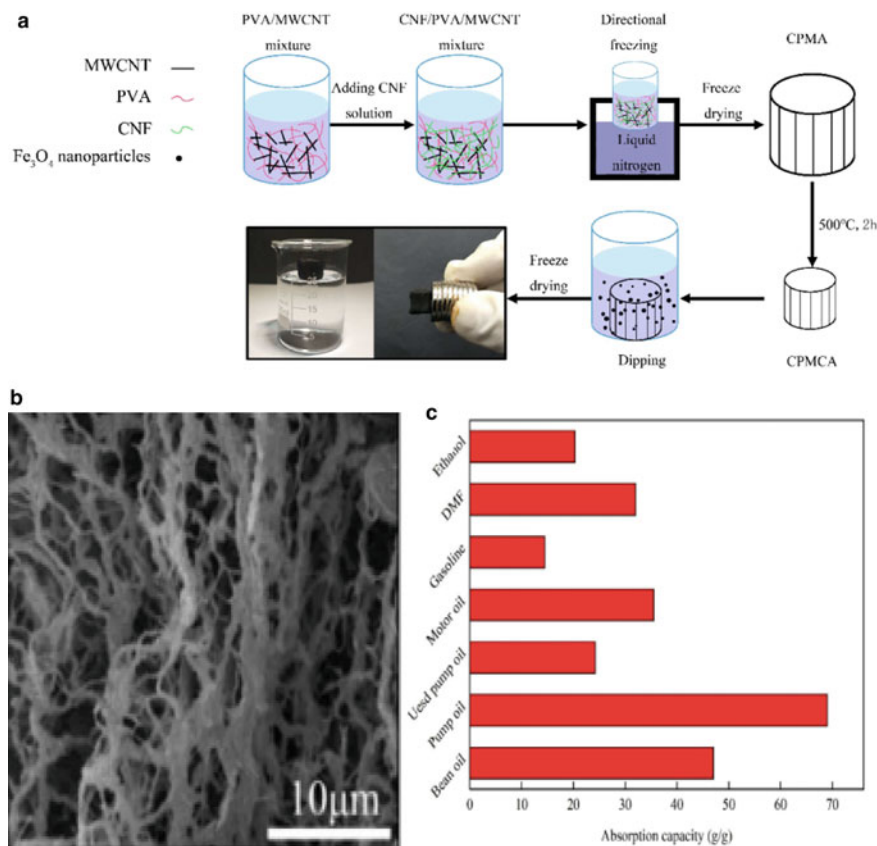
Fig. 11 **a** Complete process for the synthesis of magnetic cellulose nanofiber/polyvinyl alcohol/MWCNT carbon aerogel (m-CPMCA) (the picture also illustrate the ability of m-CPMA to float and trap by a magnet); **b** SEM image of m-CPMCA and **c** absorption performance of m-CPMCA for diverse organic liquids and oils (reprinted with permission from [104])

density. From the water contact angle analysis, Li and colleagues demonstrated that m-CPMCA nanocomposite was super hydrophobic and can always float on the water surface as well as adsorb pollutants. They were also able to demonstrate m-CPMCA's adsorption capacity toward different types of oil or organic liquids commonly found in contaminated water or industrial wastewater (Fig. 11c). Thus, among the organic liquids used for testing, m-CPMA efficiently removed pump oil from contaminated water. They have shown that m-CPMCA can be regenerated by combustion and be reused more than five times [104].

Xu et al. [105] have conducted a study using bamboo powder as a raw material to prepare CNF/MWCNTs carbon aerogel by a simple dipping and carbonization process. From their results obtained, CNF/MWCNTs carbon aerogel (CMCA) had low density, high porosity, and surface morphology similar to 3D sheet-like skeleton

porous structure. Xu et al. have proven that CMCA could absorb oils and organic liquids at 35–110 times its weight. They have reported that this high absorption capacity for different oils or organic liquids' types might be due to the CMCA surface's properties (density, surface tension, hydrophobicity, high porosity) and oils properties. In addition, they have shown that CMCA can be regenerated using distillation and combustion; then reused over 50 cycles. They have also demonstrated the developed CNF/MWCNTs carbon aerogel can be considered as a promising candidate for addressing the problems arising from the spill of oily compounds [105].

Moreover, by grafting and cross-linking polymerization, Khoerunnisa et al. [106] have developed a polymer nanocomposite hydrogel, cellulose/polyvinyl alcohol/CNTs. They have shown that the introduction of CNTs in the polymer matrix significantly changed the morphology and porosity of the composite. They have also depicted from their results that polymer nanocomposite hydrogel (cellulose/polyvinyl alcohol/CNTs) had improved mechanical strength and absorption capacity [106].

Liu and Li [107] have also synthesized a polymer nanocomposite hydrogel made of SWCNTs and tea cellulose. The synthesis was achieved by dispersing a small quantity of SWCNTs (previously oxidized) in a mixture solution of tea cellulose and 1-allyl-3-methylimidazolium chloride, then following by casting techniques to obtain tea cellulose hydrogel-SWCNTs (TCh-SWCNTs) polymer nanocomposite (Fig. 12). They have proved that the prepared TCh-SWCNTs polymer nanocomposite had improved in thermal stability (up to 323 °C) and adsorption capacity for methylene blue [107].
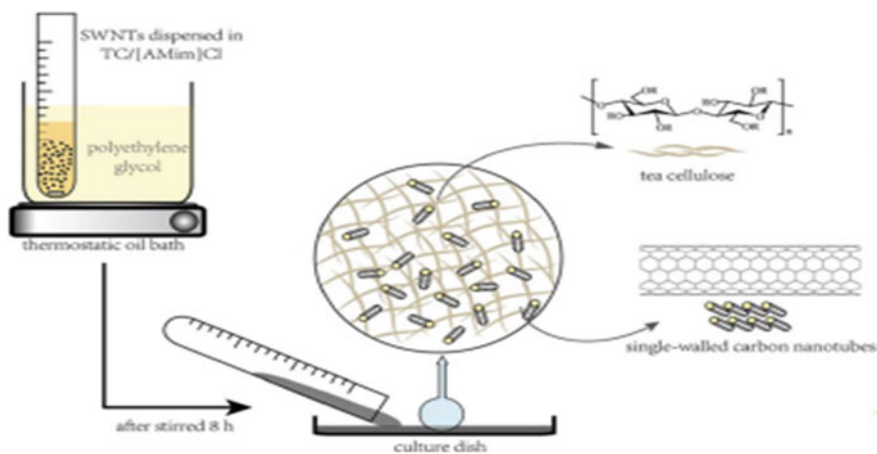
Fig. 12 Illustration of the synthesis process of Tea cellulose hydrogel-SWCNTs (TCh-SWCNTs) polymer nanocomposite (reprinted with permission from [107])

5 Cost and Economy Value of Carbon Nanotubes Modified with Natural Polymeric Materials used as Nano-sorbents for Water Purification

Carbon nanotubes modified with natural polymeric materials are economically valuable because they are environmentally friendly, recyclable, and highly degradable materials that can be considered for water purification. In addition, these green CNTs-based nanocomposite natural polymeric materials are made from renewable resources, and they favor sustainability development because they can be recycled and recovered after every water treatment cycle [34, 95]. The utilization of these CNTs-based nanocomposite natural polymeric materials will also help to avoid secondary pollution because, after many repeating cycles of water purification, they are not the source of waste generation, the spent nano-biosorbents can be applied in other applications such as latent fingerprint detection, biogas, cement, and particleboard production [34, 95, 108, 109]. These CNTs-based nanocomposite natural polymeric nano-biosorbent materials have been demonstrated to possess different shapes, structures, and multifunctional properties that can be applied in other various fields such as biomedicine, electronics, energy, tissue engineering, and drug delivery [34, 95].

On the other hand, to evaluate the total cost from the synthesis of CNTs-based nanocomposite natural polymeric nano-sorbents to their application in water purification is a challenging task; in fact, such evaluation is not often reported. This is because there are many factors to be considered. For instance, Adewale Adewuyi has reported on the cost evaluation of biosorbents and biosorption [109], and Leudjo taka et al. have reported on the cost and the practical aspect of the modification of cyclodextrin nanosponge polyurethanes with CNTs and metal nanoparticles [2]. Therefore, based on their reports one can say that the factors involved in the cost estimation could be the synthesis process including pretreatment, optimization of the process, energy consumption, time required, transportation, maintenance, type of water purification used, desorption process, regeneration process and maybe disposal of the spent nano-biosorbent (unless reused in other application) [2, 109]. Besides, literature has demonstrated that only a very small weight percent of CNTs and/or other nanoparticles were used to reinforced the polymeric materials. Then, the benefits resulting from this reinforcement can reduce some costs. Additionally, if the water purification process used is adsorption, this will help alleviate the overall because the adsorption process is not costly; and it is simple to operate compared to other water purification processes such as membrane filtration, photocatalysis, and reverse osmosis, just to cite a few.

6 Conclusion

To this end, research studies reviewed have proven that carbon nanotubes reinforced with natural polymer possess excellent thermal stability and multifunctional properties (e.g., organic, inorganic antimicrobial properties, mechanical properties) arising from the combination of each component in the polymer nanocomposites. Each of these components present in the polymer nanocomposites has been shown to play an essential role during the water purification process. These CNTs-based natural polymer nanocomposites have been demonstrated to be reused after several cycles of adsorption and desorption without any significant loss in their water treatment performance efficiency. Thus, these CNTs-based natural polymer nanocomposites can be considered as a cost-effective nano-sorbent for water purification. However, it will also be necessary to investigate the nanotoxicity of these CNTs-based natural polymer nanocomposites. Furthermore, the results obtained from these nanotoxicity studies will be crucial to the environment, humans, and the future of nanotechnology for water purification.

References

1. Alonso A, Macanás J, Davies GL, Gun YK (2011) Environmentally-safe polymer-metal nanocomposites with most favorable distribution of catalytically active and biocide nanoparticles. In: Hashim DA (ed) Advances in nanocomposite technology, July 2011. InTech, pp 175–200
2. Leudjo Taka A, Pillay K, Mbianda Yangkou X (2017) Nanosponge cyclodextrin polyurethanes and their modification with nanomaterials for the removal of pollutants from waste water : a review. Carbohydr Polym 159:94–107
3. Aslam MMA, Kuo HW, Den W, Usman M, Sultan M, Ashraf H (2021) Functionalized carbon nanotubes (Cnts) for water and wastewater treatment: preparation to application. Sustain 13:1–54
4. Qu X, Alvarez PJJ, Li Q (2013) Applications of nanotechnology in water and wastewater treatment. Water Res 47:3931–3946
5. Goh K, Karahan HE, Wei L, Bae T-H, Fane AG, Wang R, Chen Y (2016) Carbon nanomaterials for advancing separation membranes: a strategic perspective. Carbon N Y 109:694–710
6. Goh PS, Ismail AF, Hilal N (2016) Nano-enabled membranes technology: sustainable and revolutionary solutions for membrane desalination? Desalination 380:100–104
7. Goh PS, Matsuura T, Ismail AF, Hilal N (2016) Recent trends in membranes and membrane processes for desalination. Desalination 391:43–60
8. Gupta VK, Agarwal S, Saleh TA (2011) Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. J Hazard Mater 185:17–23

9. Santhosh C, Velmurugan V, Jacob G, Jeong SK, Grace AN, Bhatnagar A (2016) Role of nanomaterials in water treatment applications: a review. Chem Eng J 306:1116–1137
10. Lijima S (1991) Helical microtubules of graphitic carbon. Nature 354:56–58
11. Leudjo Taka A (2014) Metal-decorated carbon nanostructures for photocatalytic reduction of CO2. University of Johannesburg
12. Stefanescu EA, Daranga C, Stefanescu C (2009) Insight into the broad field of polymer nanocomposites: from carbon nanotubes to clay nanoplatelets, via metal nanoparticles. Materials (Basel) 2:2095–2153
13. Lee J, Jeong S, Liu Z (2016) Progress and challenges of carbon nanotube membrane in water treatment. Crit Rev Environ Sci Technol 46:999–1046
14. Leudjo Taka A (2018) Phosphorylated carbon nanotube-cyclodextrin/silver-doped titania nanobiocomposites for water purification. University of Johannesburg
15. He H, Pham-Huy LA, Dramou P, Xiao D, Zuo P, Pham-Huy C (2013) Carbon nanotubes: applications in pharmacy and medicine. Biomed Res Int 2013:1–12
16. Ihsanullah AA, Al-Amer AM, Laoui T, Al-Marri MJ, Nasser MS, Khraisheh M, Atieh MA (2016) Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. Sep Purif Technol 157:141–161
17. Ihsanullah A-K, Abu-Sharkh B, Abulkibash AM, Qureshi MI, Laoui T, Atieh MA (2016) Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes. Desalin Water Treat 57:7232–7244
18. Ji L, Zhou L, Bai X, Shao Y, Zhao G, Qu Y, Wang C, Li Y (2012) Facile synthesis of multiwall carbon nanotubes/iron oxides for removal of tetrabromobisphenol A and Pb(II). J Mater Chem 22:15853
19. Miyashiro D, Hamano R, Umemura K (2020) A review of applications using mixed materials of cellulose, nanocellulose and carbon nanotubes. Nanomaterials 10:1–23
20. Leudjo Taka A, Klink MJ, Yangkou Mbianda X, Naidoo EB (2020) Chitosan nanocomposites for water treatment by fixed-bed continuous flow column adsorption: a review. Carbohydr Polym 255:117398
21. Leudjo Taka A, Fosso-Kankeu E, Naidoo EB, Yangkou Mbianda X (2021) Recent development in antimicrobial activity of biopolymer-inorganic nanoparticle composites with water disinfection potential: a comprehensive review. Environ Sci Pollut Res 28:26252–26268
22. Olivera S, Muralidhara HB, Venkatesh K, Guna VK, Gopalakrishna K, Kumar KY (2016) Potential applications of cellulose and chitosan nanoparticles/composites in wastewater treatment: a review. Carbohydr Polym 153:600–618
23. Shariatnia S, Kumar AV, Kaynan O, Asadi A, Asadi A, Asadi A (2020) Hybrid cellulose nanocrystal-bonded carbon nanotubes/carbon fiber polymer composites for structural applications. ACS Appl Nano Mater 3:5421–5436
24. Hersam MC (2008) Progress towards monodisperse single-walled carbon nanotubes. Nat Nanotechnol 3:387
25. Punetha VD, Rana S, Yoo HJ, Chaurasia A, McLeskey JT, Ramasamy MS, Sahoo NG, Cho JW (2017) Functionalization of carbon nanomaterials for advanced polymer nanocomposites: a comparison study between CNT and graphene. Prog Polym Sci 67:1–47
26. Fujigaya T, Nakashima N (2015) Non-covalent polymer wrapping of carbon nanotubes and the role of wrapped polymers as functional dispersants. Sci Technol Adv Mater 16:024802
27. Bekyarova E, Thostenson ET, Yu A, Kim H, Gao J, Tang J, Hahn HT, Chou TW, Itkis ME, Haddon RC (2007) Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites. Langmuir 23:3970–3974
28. Zhou H, Du X, Liu H-Y, Zhou H, Zhang Y, Mai Y-W (2017) Delamination toughening of carbon fiber/epoxy laminates by hierarchical carbon nanotube-short carbon fiber interleaves. Compos Sci Technol 140:46–53
29. White KL, Sue H-J (2012) Delamination toughness of fiberreinforced composites containing a carbon nanotube/polyamide-12 epoxy thin film interlayer. Polymer (Guildf) 53:37–42
30. Motchelaho MAM, Xiong H, Moyo M, Jewell LL, Coville NJ (2011) Effect of acid treatment on the surface of multiwalled carbon nanotubes prepared from Fe-Co supported on CaCO$_3$: correlation with Fischer-Tropsch catalyst activity. J Mol Catal A Chem 335:189–198

31. Zhao H, Wang R, Deng H, Zhang L, Gao L, Zhang L, Jiao T (2021) Facile preparation of self-assembled chitosan-based POSS-CNTs-CS composite as highly efficient dye absorbent for wastewater treatment. ACS Omega 6:294–300

32. Zhang S, Zhang F, Pan Y, Jin L, Liu B, Mao Y, Huang J (2018) Multiwall-carbon-nanotube/cellulose composite fibers with enhanced mechanical and electrical properties by cellulose grafting. RSC Adv 8:5678–5684

33. Leudjo Taka A, Pillay K, Mbianda XY (2018) Synthesis and characterization of a novel bio nanosponge filter (pMWCNT-CD/TiO$_2$-Ag) as potential adsorbent for water purification. In: Ramasami P, Bhowon MG, Laulloo SJ, Li H, Wah K (eds) Emerging trends in chemical sciences. © Springer International Publishing AG, pp 313–343

34. Mallakpour S, Khodadadzadeh L (2018) Biocompatible and biodegradable Chitosan nanocomposites loaded with carbon nanotubes. In: Biodegradable and biocompatible polymer composites. Elsevier Ltd, pp 187–221

35. Mhlanga SD, Mamba BB, Krause RW, Malefetse TJ (2007) Removal of organic contaminants from water using nanosponge cyclodextrin polyurethanes Sabelo. J Chem Technol Biotechnol 82:382–388

36. Li D, Ma M (1998) Cyclodextrin polymer separation materials. Patent WO 9822197

37. Bambo MF (2007) Synthesis, characterization and application of nanoporous cyclodextrin polymers of nanoporous cyclodextrin polymers. University of Johannesburg

38. Villiers A (1891) Sur la fermentation de la fécule par l'action du ferment butyrique. Comptes Rendus l'Académie des Sci 112:536–538

39. Del Valle EMM (2004) Cyclodextrins and their uses: a review. Process Biochem 39:1033–1046

40. Tejashri G, Amrita B, Darshana J (2013) Cyclodextrin based nanosponges for pharmaceutical use: a review. Acta Pharm 63:335–358

41. Buschmann HJ, Schollmeyer E (2002) Applications of cyclodextrins in cosmetic products: a review. J Cosmet Sci 53:575–592

42. Li D, Ma M (2000) Nanosponges for water purification. Clean Prod Process 2:0112–0116

43. Krause RW, Mamba BB, Bambo FM, Malefetse TJ (2010) Cyclodextrin polymers: Synthesis and application in water treatment. In: Hu J (ed) Cyclodextrins: chemistry and physics. Transworld Research Network, Kerala, India, pp 1–25

44. Trotta F, Tumiatti W (2003) Cross-linked polymers based on cyclodextrins for removing polluting agents. WO 03/085002 A1

45. Trotta F, Tumiatti W (2005) Cross-linked polymers based on cyclodextrins for removing polluting agents. Patent US 2005/0154198 A1. 1:1–3

46. Salipira KL, Mamba BB, Krause RW, Malefetse TJ, Durbach SH (2007) Carbon nanotubes and cyclodextrin polymers for removing organic pollutants from water. Environ Chem Lett 5:13–17

47. Salipira KL, Krause RW, Mamba BB, Malefetse TJ, Cele LM, Durbach SH (2008) Cyclodextrin polyurethanes polymerized with multi-walled carbon nanotubes: synthesis and characterization. Mater Chem Phys 111:218–224

48. Mamba B, Krause R, Malefetse T, Sithole S (2015) Degradation studies of β-cyclodextrin polyurethane polymers using soil burial experiments. South African J Chem 61:133–140

49. Mamba BB, Krause RW, Malefetse TJ, Gericke G, Sithole SP (2008) Cyclodextrin nanosponges in the removal of organic matter to produce water for power generation. Water SA 34:657–660

50. Mamba B, Krause R, Malefetse T, Sithole S, Nkambule T (2009) Humic acid as a model for natural organic matter (NOM) in the removal of odorants from water by cyclodextrin polyurethanes. Water SA 35:117–120

51. Salipira KL, Mamba BB, Krause RW, Malefetse TJ, Durbach SH (2008) Cyclodextrin polyurethanes polymerised with carbon nanotubes for the removal of organic pollutants in water. Water SA 34:113–118

52. Mamba G, Mbianda XY, Govender PP (2013) Phosphorylated multiwalled carbon nanotube-cyclodextrin polymer: Synthesis, characterisation and potential application in water purification. Carbohydr Polym 98:470–476

53. Lukhele LP, Krause RWM, Mamba BB, Momba MNB (2010) Synthesis of silver impregnated carbon nanotubes and cyclodextrin polyurethanes for the disinfection of water. Water SA 36:433–436
54. Lukhele L, Krause R, Mamba B Application of silver impregnated carbon nanotubes and cyclodextrin polymers, for the destruction of bacteria in water. In: Water Inst. SA
55. Mamba G, Mbianda XY, Govender PP, Mamba BB, Krause RW (2010) Application of multi-walled carbon nanotube-cyclodextrin polymers in the removal of heavy metals from water. J Appl Sci 10:940–949
56. Leudjo Taka A, Fosso-Kankeu E, Pillay K, Yangkou Mbianda X (2020) Metal nanoparticles decorated phosphorylated carbon nanotube/cyclodextrin nanosponge for trichloroethylene and Congo red dye adsorption from wastewater. J Environ Chem Eng 8:1–11
57. Leudjo Taka A, Doyle BP, Carleschi E, Youmbi Fonkui T, Erasmus R, Fosso-Kankeu E, Pillay K, Mbianda XY (2020) Spectroscopic characterization and antimicrobial activity of nanoparticle doped cyclodextrin polyurethane bionanosponge. Mater Sci Eng C 115:1–15
58. Leudjo Taka A, Fosso-kankeu E, Pillay K, Mbianda XY (2018) Removal of cobalt and lead ions from wastewater samples using an insoluble nanosponge biopolymer composite: adsorption isotherm, kinetic, thermodynamic, and regeneration studies. Environ Sci Pollut Res 25:21752–21767
59. Escudero-Oñate C, Elena Martínez-Francés (2016) A review of chitosan-based materials for the removal of organic pollution from water and bioaugmentation. In: Dongre RS (ed) Chitin-Chitosan—myriad functionalities in science and technology. IntechOpen, pp 71–87
60. Rizeq BR, Younes NN, Rasool K, Nasrallah GK (2019) Synthesis, bioapplications, and toxicity evaluation of chitosan-based nanoparticles. Int J Mol Sci 20:1–24
61. Shukla SK, Mishra AK, Arotiba OA, Mamba BB (2013) Chitosan-based nanomaterials: a state-of-the-art review. Int J Biol Macromol 59:46–58
62. Vafakish W (2019) Surface-modified chitosan: an adsorption study of a "Tweezer-Like" biopolymer with fluorescein. Surfaces 2:468–484
63. Kumar S, Ye F, Dobretsov S, Dutta J (2019) Chitosan nanocomposite coatings for food, paints, and water treatment applications. Appl Sci 9:1–27
64. Wang J, Chen C (2014) Chitosan-based biosorbents: modification and application for biosorption of heavy metals and radionuclides. Bioresour Technol 160:129–141
65. Casettari L, Vllasaliu D, Castagnino E, Stolnik S, Howdle S, Illum L (2012) PEGylated chitosan derivatives: Synthesis, characterizations and pharmaceutical applications. Prog Polym Sci 37:659–685
66. Zhao Y, Guo L, Shen W, An Q, Xiao Z, Wang H, Cai W, Zhai S, Li Z (2020) Function integrated chitosan-based beads with throughout sorption sites and inherent diffusion network for efficient phosphate removal. Carbohydr Polym 230:1–9
67. Chu C-C, Zhong C (2009) Organo-soluble chitosan salts and chitosan-derived biomaterials prepared thereof. pp 1–72
68. Fiorani G, Saoncella O, Kaner P, Altinkaya SA, Figoli A, Bonchio M, Carraro M (2014) Chitosan-polyoxometalate nanocomposites: synthesis, characterization and application as antimicrobial agents. J Clust Sci 25:839–854
69. Gagnon J, Binette A (2008) Chitosan salts, methods of manufacture and uses thereof. pp 50–80
70. Dhanavel S, Manivannan N, Mathivanan N, Kumar V, Narayanan V, Stephen A (2018) Preparation and characterization of cross-linked chitosan/palladium nanocomposites for catalytic and antibacterial activity. J Mol Liq 257:32–41
71. Kemp MM, Kumar A, Mousa S, Park TJ, Ajayan P, Kubotera N, Mousa SA, Linhardt RJ (2009) Synthesis of gold and silver nanoparticles stabilized with glycosaminoglycans having distinctive biological activities. Biomacromol 10:589–595
72. Kemp M, Kumar A, Clement D, Ajayan P, Mousa S, Linhardt RJ (2009) Hyaluronanand heparin-reduced silver nanoparticles with antimicrobial properties. Nanomedicine 4:421–429
73. Travan A, Marisch E, Donati I, Benincasa M, Giazzon M, Felisari L, Paoletti S (2011) Silver-polysaccharide nanocomposite antimicrobial coatings for methacrylic thermosets. Acta Biomater 7:337–346

74. Sambhy V, Macbride MM, Peterson BR, Sen A, Park UV, Pennsyl V (2006) Silver bromide nanoparticle/polymer composites: dual action tunable antimicrobial materials. J Am Chem Soc 128:9798–9808

75. Nthunya LN, Masheane M, Malinga S, Nxumalo E (2017) Greener approach to prepare electrospun antibacterial β-cyclodextrin/cellulose acetate nanofibers for removal of bacteria from water. Sustain Chem Eng 5:153–160

76. Zheng Y, Monty J, Linhardt RJ (2015) Polysaccharide-based nanocomposites and their applications. Carbohydr Res 405:23–32. https://doi.org/10.1016/j.carres.2014.07.016

77. Nthunya LN, Masheane ML, Malinga SP, Edward N, Mamba BB, Mhlanga SD, Nthunya LN, Masheane ML, Malinga SP (2017) Thermally and mechanically stable β-cyclodextrin/cellulose acetate nanofibers synthesized using an environmentally benign procedure. Int J Smart Nano Mater 8:1–19

78. Singh PP, Ambika (2018) Environmental remediation by nanoadsorbents-based polymer nanocomposite. In: New polymer nanocomposites for environmental remediation. Elsevier Inc., pp 223–241

79. Campelo JM, Luna D, Luque R, Marinas JM, Romero AA (2009) Sustainable preparation of supported metal nanoparticles and their applications in catalysis. Chemsuschem 2:18–45

80. Palza H (2015) Antimicrobial polymers with metal nanoparticles. Int J Mol Sci 16:2099–2116

81. Triebel C, Vasylyev S, Damm C, Stara H, Özpınar C, Hausmann S, Peukert W, Münstedt H (2011) Polyurethane/silver-nanocomposites with enhanced silver ion release using multi-functional invertible polyesters. J Mater Chem 21:4377–4383

82. Bui VKH, Park D, Lee YC (2017) Chitosan combined with ZnO, TiO$_2$ and Ag nanoparticles for antimicrobialwound healing applications: a mini review of the research trends. Polymers (Basel) 9:1–24

83. Masheane ML, Nthunya LN, Sambaza SS, Malinga SP, Nxumalo EN, Mamba BB, Mhlanga SD (2017) Chitosan-based nanocomposite beads for drinking water production. IOP Conf Ser Mater Sci Eng 195:1–8

84. Byrne JA, Fernandez-ibanez PA, Dunlop PSM, Alrousan DMA, Hamilton JWJ (2010) Photocatalytic enhancement for solar disinfection of water: a review. Int J Photoenergy 2011:1–13

85. Yu Z, Day D, Ciston S (2012) Improving solar water disinfection (SODIS) with a photoreactive TiO2/SWCNT composite on plastic PET bottles. J Exp Second Sci 1:40–43

86. ZabihiSahebi A, Koushkbaghi S, Pishnamazi M, Askari A, Khosravi R, Irani M (2019) Synthesis of cellulose acetate/chitosan/SWCNT/Fe$_3$O$_4$/TiO$_2$ composite nanofibers for the removal of Cr(VI), As(V), Methylene blue and Congo red from aqueous solutions. Int J Biol Macromol 140:1296–1304

87. Salam MA, Makki MSI, Abdelaal MYA (2011) Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution. J Alloys Compd 509:2582–2587

88. Zhang L, Zeng Y, Cheng Z (2016) Removal of heavy metal ions using chitosan and modified chitosan: a review. J Mol Liq 214:175–191

89. Keshvardoostchokami M, Babaei S, Piri F, Zamani A (2017) Nitrate removal from aqueous solutions by ZnO nanoparticles and chitosan-polystyrene–Zn nanocomposite: Kinetic, isotherm, batch and fixed-bed studies. Int J Biol Macromol 101:922–930

90. Moridi Z, Mottaghitalab V, Haghi AK (2011) A Detailed review of recent progress in carbon nanotube/ chitosan nanocomposites. Cellul Chem Technol 45:549–563

91. Beheshti H, Irani M, Hosseini L, Rahimi A, Aliabadi M (2016) Removal of Cr (VI) from aqueous solutions using chitosan/MWCNT/Fe$_3$O$_4$ composite nanofibers-batch and column studies. Chem Eng J 284:557–564

92. Alsuhybani M, Alshahrani A, Haidyrah AS (2020) Synthesis, characterization, and evaluation of evaporated casting MWCNT/chitosan composite membranes for water desalination. J Chem 2020:1–9

93. Shawky HA, El-Aassar AHM, Abo-Zeid DE (2012) Chitosan/carbon nanotube composite beads: preparation, characterization, and cost evaluation for mercury removal from wastewater of some industrial cities in Egypt. J Appl Polym Sci 125:E93–E101

94. Rania E Morsi, Alsabagh AM, Nasr SA, Zaki MM (2017) Multifunctional nanocomposites of chitosan, silver nanoparticles, copper nanoparticles and carbon nanotubes for water treatment: Antimicrobial characteristics. Int J Biol Macromol 97:264–269

95. Dong YD, Zhang H, Zhong GJ, Yao G, Lai B (2021) Cellulose/carbon composites and their applications in water treatment—a review. Chem Eng J 405:126980

96. Tapia-Orozco N, Ibarra-Cabrera R, Tecante A, Gimeno M, Parra R, Garcia-Arrazola R (2016) Removal strategies for endocrine disrupting chemicals using cellulose-based materials as adsorbents: a review. J Environ Chem Eng 4:3122–3142

97. Bejoy T, Midhun CR, Athira KB, Rubiyah MH, Jithin JA, MooresGlenna LD, Clément S (2018) Nanocellulose, a versatile green platform: from biosources to materials and their applications. Chem Rev 118:11575–11625

98. Eyley S, Thielemans W (2014) Surface Modification of Cellulose Nanocrystals. Nanoscale 6:7764–7779

99. Chen P, Kim HS, Kwon SM, Yun YS, Jin HJ (2009) Regenerated bacterial cellulose/multi-walled carbon nanotubes composite fibers prepared by wet-spinning. Curr Appl Phys 9:e96–e99

100. Lu P, Hsieh Y-L (2010) Multiwalled Carbon Nanotube (MWCNT) reinforced cellulose fibers by electrospinning. ACS Appl Mater Interfaces 2:2413–2420

101. Silva MA, Hilliou L, de Amorim MTP (2020) Fabrication of pristine-multiwalled carbon nanotubes/cellulose acetate composites for removal of methylene blue. Polym Bull 77:623–653

102. Sabir A, Shafiq M, Islam A, Sarwar A, Dilshad MR, Shafeeq A, Butt MTZ, Jamil T (2015) Fabrication of tethered carbon nanotubes in cellulose acetate/polyethylene glycol-400 composite membranes for reverse osmosis. Carbohydr Polym 132:589–597

103. Nouran El Badawi, Ramadan AR, Esawi AMK, El-Morsi M (2014) Novel carbon nanotube–cellulose acetate nanocomposite membranes for water filtration applications. Desalination 344:79–85

104. Li J, Zhou L, Jiang X, Tan S, Chen P, Zhou H, Xu Z (2019) Directional preparation of superhydrophobic magnetic CNF/PVA/MWCNT carbon aerogel. IET Nanobiotechnol 13:565–570

105. Xu Z, Jiang X, Tan S, Wu W, Shi J, Zhou H, Chen P (2018) Preparation and characterisation of CNF/MWCNT carbon aerogel as efficient adsorbents. IET Nanobiotechnol 12:500–504

106. F. Khoerunnisa, Sonjaya Y. Hendrawan ODP (2015) Superabsorbent hydrogel composite based on copolymer cellulose/poly(Vinyl Alcohol)/CNT. In: Mart T, Triyono D (eds) International symposium on current progress in mathematics and sciences. AIP Conference Proceedings, p 17292016

107. Liu Z, Li D (2021) Preparation and characterization of cellulose composite hydrogels from tea residue and single-walled carbon nanotube oxides and its potential applications. Front Chem 9:1–8

108. Fouda-Mbanga BG, Prabakaran E, Pillay K (2020) Synthesis and characterization of CDs/Al_2O_3 nanofibers nanocomposite for Pb^{2+} ions adsorption and reuse for latent fingerprint detection. Arab J Chem 13:6762–6781

109. Adewuyi A (2020) Chemically modified biosorbents and their role in the removal of emerging pharmaceutical waste in the water system. Water (Switzerland) 12:1–31