We are IntechOpen,
the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Biopolymer-Based Materials from Polysaccharides: Properties, Processing, Characterization and Sorption Applications

Rohan S. Dassanayake, Sanjit Acharya and Noureddine Abidi

Abstract

Biopolymers are polymeric materials derived from biological sources. Due to their renewability, abundance, biodegradability and other unique properties such as high adsorption capabilities and ease of functionalization they have been investigated for several industrial applications including sorption. Polysaccharides especially cellulose, chitin and chitosan are important biopolymers because of their high abundance, wide distribution and low cost of production. This chapter provides an overview of properties, common processing methods, and material characterization of three commonly studied biopolymers namely cellulose, chitin and chitosan. It provides a thorough review on recent developments on utilization of cellulose, chitin, and chitosan-based materials for various sorption applications. Specifically, their application and efficiency in organic dye removal, heavy metals removal, oil and solvent spillage cleanup, and CO_2 adsorption are presented and discussed.

Keywords: cellulose, aerogels, chitin, functionalized cellulose aerogels, biopolymer-based materials

1. Background

1.1 Biopolymers

As the name suggests, biopolymers are polymers synthesized by living organisms. Therefore, they are polymeric biomolecules i.e. long chain biomolecules comprised of covalently linked repeating monomeric units [1]. Living organisms (plants, animals, bacteria, fungi and yeast) synthesize a wide range of biopolymers such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins, cellulose, chitin, starch, etc. Biopolymers carry out countless number of vital functions, such as storage of energy, preservation and transmittance of genetic information, and cellular construction, in vivo. DNA and RNA are the hereditary materials for the storage and passage of the genetic information in all living organisms, and thus making perpetuation of life possible in the planet. Proteins not only catalyze reactions (e.g. enzymes) and take part in cell signaling (e.g. hemoglobin) but also

provide structural support (e.g. collagen). Cellulose is the major structural component of the plant cell walls.

There are three main classes of biopolymers owing to their universal occurrence and abundance: (i) polynucleotides, (ii) polypeptides/poly amino acids, and (iii) polysaccharides. Polynucleotides (DNA and RNA) are long polymers composed of 13 or more nucleotide monomers [1]. Polypeptides are the short polymers comprised of amino acids as monomeric units and amide bonds link the monomeric units together [2]. Polysaccharides are composed of monomeric sugars linked together by O-glycosidic linkages. Among hundreds identified polysaccharides, cellulose, starch, chitin, chitosan are some of the important examples [3–5]. In contrast to the often simpler and more random structure of the synthetic polymers, biopolymers, in their natural states, are complex molecular assemblies that assume defined 3D structure and shapes, often known as hierarchical levels of structure.

Since biopolymers possess material properties suitable for various industrial and medical applications, they have garnered a great deal of interest both in academia and industry. Primarily, the interest and increasing trend of application of biopolymers as commodity products stems from their renewability, biodegradability and, often, their biocompatibility. Even though traditional plastics (petroleum based polymer products) are still indispensable in our daily life, there is a growing concern about their environmental impacts as they are non-biodegradable and as a consequent, accumulate in the environment. Furthermore, petroleum is not a renewable resource and its reserve is dwindling at a fast pace. Thus, biopolymers derived from renewable resources possess competitive advantage over synthetic non-renewable polymers. However, the cost of production of biopolymers and biopolymer based commodity products is of prime importance if they are to compete with oil-based synthetic polymers in the market.

Exploiting biopolymers, which are abundant and can be obtained from source material at lower cost, as a main component of biopolymeric products can be a smart strategy in the first place to mitigate the cost related issues. To that end, polysaccharides, the biopolymers comprised of monosaccharides (sugars) linked together by O-glycosidic linkages are of obvious choice. Both the most abundant natural resource, cellulose, and the second most abundant biopolymer, chitin, are polysaccharides [3, 6]. Additionally, polysaccharides are widely distributed in nature as they can be derived from plants, animals and microorganisms. Furthermore, variation in physicochemical properties, such as mechanical properties, solubility, viscosity, gelling potential, surface and interfacial properties, governed by monosaccharide composition, chain length (degree of polymerization), linkage types and patterns, provide polysaccharides versatility in preparation of materials with diverse applications. In fact, polysaccharides based materials in different forms including fibers, films, food casing, membranes, hydrogels, aerogels and sponges, with applications in several important commercial areas such as food, pharmaceuticals, biomedical, electronics, and adsorption have been developed [7–13]. Thus, polysaccharide-based biopolymers are promising candidates in the preparation of materials that can meet the much coveted dual requirements of environmental friendliness and economic sustainability. In this book chapter we focus on three important polysaccharide based biopolymers: cellulose, chitin, and chitosan.
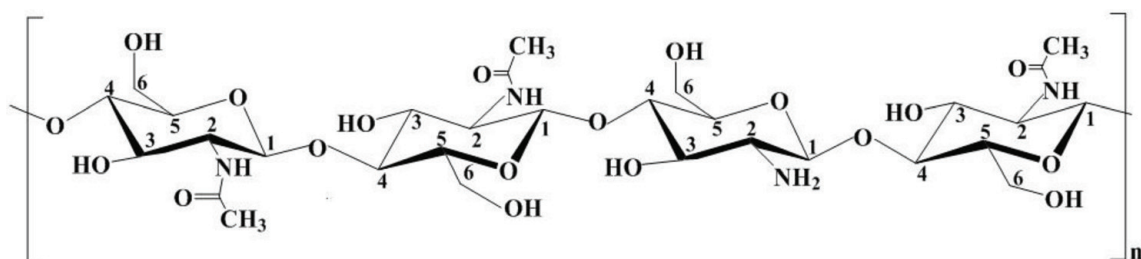
1.2 Cellulose

Cellulose, the most abundant renewable resource in the planet with an annual yield of 1.5×10^{12} tons, is the major structural component in plant cell walls. Besides plants, some species of bacteria, algae also biosynthesize cellulose. Tunicates are the only known animals capable of biosynthesizing cellulose [3, 14]. Because of its abundance, cellulose can serve as a virtually inexhaustible source of raw material in production of

sustainable bioproducts, the so called "green products" [3]. It is a linear homopolymer of β-D glucose monomers covalently linked together by 1→4 glycosidic bonds i.e. the ringed glucose monomers are joined together via polycondensation reaction between hydroxyl groups at C1 of a glucose unit and C4 of the neighboring glucose unit. Since, every glucose unit is rotated 180° with respect to its neighbors along the fiber axis, dimer of glucose, called cellobiose, is considered as a repeating unit of cellulose polymer (**Figure 1a**) [15]. However, the convention of considering cellobiose as a repeating unit has been challenged and a recent review in this regard makes a cogent argument that glucose is the repeating unit rather than the cellobiose [16]. Cellulose is a long chain molecule and the degree of polymerization (DP) differs with source and the treatments employed during its extraction. The DP of cellulose is reported to be as high as 10,000 and 15,000 in wood and cotton fibers [14, 17].

Cellulose in nature is not found as an isolated molecule, but rather possesses an intriguing multi-level assembly, popularly known as hierarchical structure [18]. It is usually agreed that, during biosynthesis, approximately 36 individual cellulose molecules are assembled together to form elementary fibrils, which have dimensions in nano-scale (a square cross section, 3–5 nm in size). Elementary fibrils further undergo packing into a larger entity called microfibrils with a cross section of ∼20 nm × 8 nm. These microfibrils further assemble into macro sized cellulose fibers (e.g. wood fiber, cotton fiber) [14, 15]. However, specific packing of cellulose may be different based on the source.
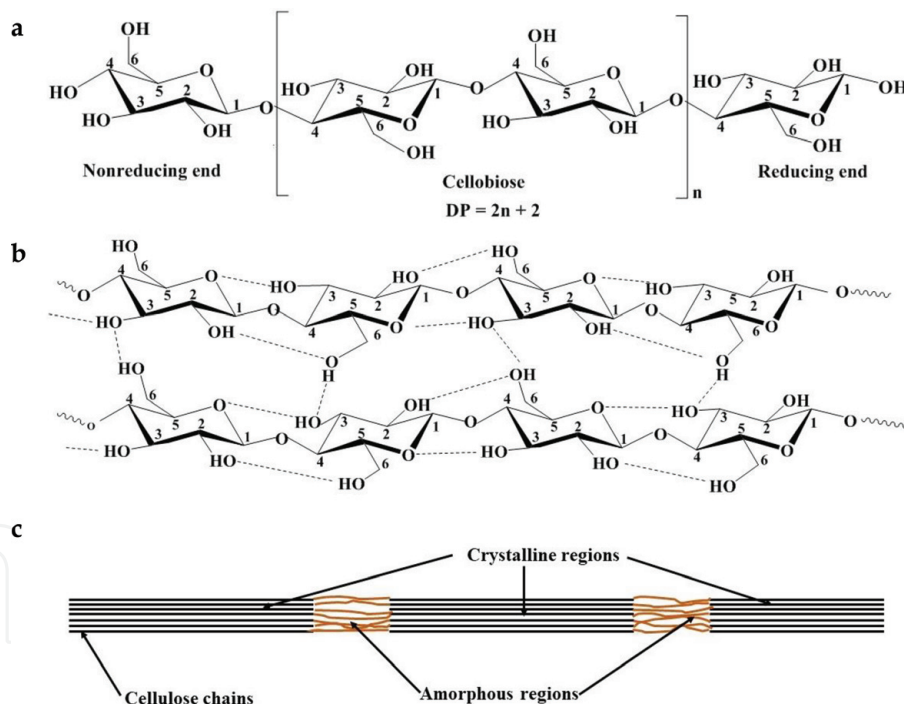
Figure 1.
Chemical structure and hydrogen bonding in cellulose: (a) chemical structure of cellulose, (b) hydrogen bonding in cellulose, and (c) schematic of cellulose microfibrils showing crystalline and amorphous structure.

Figure 2.
Chemical structure chitin.

Prevalence of hydroxyl groups in cellulose (three hydroxyl groups per glucose monomer) results in extensive intra-and interchain hydrogen bonding in cellulose (**Figure 1b**). Intra-and interchain hydrogen bonding and the stacking interactions mainly originating from Van der Waals forces facilitate highly ordered arrangement (crystalline regions) of cellulose fibrils although there are also amorphous regions present (where arrangement of cellulose chains is disordered) as depicted in **Figure 1c** [19]. In general, cellulose, regardless of the source, is highly crystalline and high molecular weight biopolymer and is, usually, a fibrous, tough and hydrophilic but insoluble in water and other common solvents [20]. However, important properties such as DP, crystallinity and fibrillar organization are dependent on the source. For example, cellulose from cotton fiber is more crystalline (~80% crystallinity) as compared to wood cellulose (~50% crystallinity). Similarly, quite different from plant derived cellulose, bacterial cellulose has ultrafine nanofibrous network structure, high hydrophilicity, and moldability [21].

1.3 Chitin

Chitin is another important polysaccharide and the most abundant biopolymer on the planet after cellulose. It is a structural biopolymer, contributing in strength and reinforcement, present in the exoskeleton of arthropods (i.e., in the shells of shrimps and crabs), and the cuticle of insects. It is also found in the cell walls of fungi, yeast and other organisms in lower plant and animal kingdoms [4]. Structurally, it is similar to cellulose except the presence of acetamide or amine functional groups at C2 position of the glucose monomer unit. Therefore, chitin is a linear polymer of 2-acetamido-2-deoxy-D-glucopyranose linked together by β(1→4) glycosidic bond [22] (**Figure 2**). The degree of acetylation (DA) which is the share of nitrogen sites occupied by acetyl group is typically ~90% in chitin after extraction and purification from source material since alkali treatment applied for the removal of protein also lowers DA [23].

Similar to cellulose, native chitin is arranged in highly crystalline microfibrils because of the extensive hydrogen bonding among the polymer chains. It is tough, hydrophobic, and insoluble in water and other common organic solvents. Chitin is even more recalcitrant to solubilization and consequently harder to process than cellulose [6].

1.4 Chitosan

Chitosan is the most important partially deacetylated derivative of chitin with degree of acetylation (DA) <50%. Typically chitin has DA <35% [24]. Chitin can be deacetylated by treating it with concentrated alkali at elevated temperature. Enzymatic hydrolysis in the presence of chitin deacetylase can also be employed for deacetylation purpose [21]. Therefore, chitosan can be represented by the same chemical structure as chitin. While chitin is insoluble in common solvents, chitosan can be dissolved in weak acidic solutions (aqueous solutions with pH < 6.5). It is soluble in hydrochloric acid and aqueous organic acids such as formic, acetic, oxalic and lactic acids. Protonation of the free glucosamine in acidic condition facilitates chitosan solubility [25, 26]. Chitin and chitosan are reported to have inherent antimicrobial properties.

2. Processing of cellulose, chitin and chitosan

2.1 Derivatization of cellulose, chitin and chitosan

Because of the abundance of hydroxyl (OH) groups present in cellulose, it can be derivatized through esterification, etherification, and other reactions to produce

cellulose derivatives such as acetylated (e.g. cellulose acetate), carboxy methylated (e.g. carboxymethyl cellulose), and phosphorylated (e.g. cellulose diphenyl-phosphate) and cationized cellulose [27–30]. Cellulose acetate (CA) is one of the most important commercially available cellulose derivatives with many applications such as fiber, film, and osmotic membrane. CA is a cellulose ester in which hydroxyl groups in cellulose are esterified with acetate groups to varying degrees [31]. Similarly, chitin and chitosan can be derivatized through O- and N-substitution to obtain carboxyalkyl derivatives such as O-carboxymethyl chitin, O-carboxymethyl chitosan and N,N-dicarboxymethyl chitosan [21, 24]. Derivatization not only eases the processing of these biopolymers since derivatives can be solubilized in common solvents and even in water based on degree and type of substitution [21, 29, 32], but also imparts some novel chemical and physical properties to cellulose. For instance, phosphorylation of cellulose can impart enhanced flame retardancy and bioactivity [21, 32]. Similarly, carboxyalkylation of chitosan enhances its affinity towards metal ions and has application in metal ions collection [24].

2.2 Dissolution of cellulose, chitin and chitosan

Due to their high molecular weight and complex biopolymeric network (extended hydrogen bonding and crystallinity), processing of cellulose and chitin into desirable forms, such as films, membranes, fibers, and gels, via dissolution is generally considered as nontrivial task as they are insoluble in water and other common organic solvents [13, 33]. Therefore, although studied for a long time, cellulose and chitin dissolution in cost effective and environmentally friendly manner remains an active area of research. A number of solvents/solvent systems have been developed over the course of time. Derivatizing solvent (carbon disulfide/aqueous sodium hydroxide used in "Viscose" process), and other non-derivatizing solvents such as aqueous alkali solution (e.g. aqueous solution of 7% sodium hydroxide/12% urea), *N,N*-dimethylacetamide/lithium chloride (DMAC/LiCl), *N*-methylmorpholine-*N*-oxide (NNMO) (used in "Lyocell" process), and ionic liquids (ILs) have been some of the important cellulose solvents [34–38]. Aqueous sodium hydroxide/urea solution, DMAc/LiCl and ILs such as 1-allyl-3-methylimidzolium bromide, 1-butyl-3-methylimidzolium chloride and 1-butyl-3-methylimidazolium acetate have been reported to be capable of dissolving chitin [33]. Although they are yet to find significant industrial breakthrough, ionic liquids are thought to have advantages over other solvents due to their chemical and thermal stability, tunability, non-flammability, negligible low vapor pressure, high efficiency in dissolution of both cellulose and chitin. Regenerated cellulose products such as fibers, film, aerogels and beads have been prepared from biopolymer solutions in different solvents [39–42].

2.3 Aerogels

Aerogels are broadly defined as sol–gel derived materials, which are highly porous, low density and predominantly mesoporous (pore diameter: 2–50 nm) [43]. They are derived from hydrogels followed by the removal of liquid component using super critical point drying or freeze-drying to avoid damage to the original gel micro-structure prepared from biopolymers solution. Because of their very low density, high porosity and high specific surface area, aerogels have potential applications in separation, adsorption, catalyst, photo-electricity, and biomedicine [13]. High surface area aerogels from cellulose (400–500 $m^2\ g^{-1}$) [44], chitin (560 $m^2\ g^{-1}$) [45], and chitosan (248 $m^2\ g^{-1}$) [46] have been prepared.

2.4 Nanofibrillation/nanoparticles (nanocellulose, nanochitin, nanochitosan)

The term "nanocellulose"/"nanochitin"/"nanochitosan" encompasses various materials derived from respective biopolymers, which possess at least one dimension in the nanometer range [14, 47]. Nanoparticles from cellulose and chitin are usually prepared by destructing the native hierarchical structure of these biopolymers [48]. Cellulose and chitin nanofibers, in general, are obtained by subjecting purified cellulose and chitin substrates to multiple mechanical shearing actions, which disintegrate the native microfibril structure and release enmeshed individual or bundle of fibrils. Chitosan nanofibers are typically produced by electrospinning [49].

Highly crystalline elongated rod like (or needle-like) nanoparticles called nanocrystals can be obtained when cellulose and chitin substrates are subjected to a strong acid hydrolysis treatment due to preferential dissolution of amorphous domains. For acid hydrolysis to produce nanocrystals, sulfuric acid and hydrochloric acid are usually employed [50, 51]. Biopolymer nanoparticles can be directly processed into films and aerogels by drying from the suspension or they can be utilized as reinforcement agents in other polymer matrices.

3. Characterization of biopolymers

The most widely used characterization techniques of biopolymers include Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). In this section, we discuss the characterization of polysaccharides: cellulose, chitin, and chitosan using FTIR, XRD, TGA and SEM.

3.1 Materials

Microcrystalline (MCC) was provided by FMC Biopolymer (Newark, DE). Chitosan (75–85% deacetylated) and chitin from shrimp shells were used as received from Sigma-Aldrich (Saint Louis, MO).

3.2 Instrumentation

3.2.1 X-ray diffraction (XRD) analysis

The wide-angle powder X-ray diffraction patterns of the samples were recorded on a SmartLab XRD system (Rigaku Corporation, ModelHD2711N) with CuK$_\alpha$ radiation (λ = 1.541867 Å). The accelerating voltage and tube current used were 40 kV and 44 mA, respectively. A continuous scanning was performed at a scan speed of 2°/min and the 2θ ranged from 10° to 60°.

3.2.2 Thermogravimetric analysis (TGA)

Thermogravimetric (TG) analyses of cellulose, chitin and chitosan samples were obtained using a PerkinElmer Pyris1TGA instrument (PerkinElmer, Waltham, MA) furnished with a 20-sample auto-sampler. TG profiles were recorded in an inert nitrogen atmosphere (20 ml/min) from 37 to 600°C with a constant a heating rate of 10°C/min using a high-resolution mode. All data were analyzed using Pyris Data Analysis software.

3.2.3 Scanning electron microscopy (SEM)

The morphology of cellulose, chitin and chitosan samples was studied on a Hitachi S-4700 field emission scanning electron microscope (TM-100, Hitachi, Japan) with an accelerating voltage of 15 kV.

### 3.2.4 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the cellulose, chitin and chitosan samples were recorded using a PerkinElmer Spectrum-400 FTIR spectrometer equipped with a universal attenuated total reflectance (UATR) accessory (PerkinElmer, Waltham, MA). All FTIR spectra were collected at a spectral resolution of 4 cm^{-1}, with 32 co-added scans in the wavenumber range of 4000 to 650 cm^{-1}. The spectra were analyzed using PerkinElmer Spectrum software.

All samples were conditioned in an environmentally-controlled laboratory maintained at a relative humidity of 65 ± 2% and temperature of 21 ± 1°C for at least 48 h prior to their characterization.

4. Characterization of cellulose, chitin and chitosan

4.1 X-ray diffraction (XRD) analysis

Wide-angle X-ray diffraction measurements were collected for raw cellulose, chitin, and chitosan powder samples. **Figure 3** shows the X-ray diffraction curves for cellulose, chitin, and chitosan. The XRD pattern of cellulose exhibits five major diffraction peaks at 14.9 (101), 15.8 (10ī), 21.8 (021) 22.5 (002) and 34.6 (004) which are in agreement with the literature values reported for cellulose I$_\beta$ [52]. The XRD patterns of chitin showed two strong reflections at 9.2° (020) and 19.1° (110) and minor reflections at 12.6° (021), 22.9° (130) and 26.2° (013) corresponding to α-chitin [53]. Chitosan shows two distinct peaks at 10.67 (020) and 19.92° (110) [54]. Our results suggest that chitin has the highest crystallinity as compared
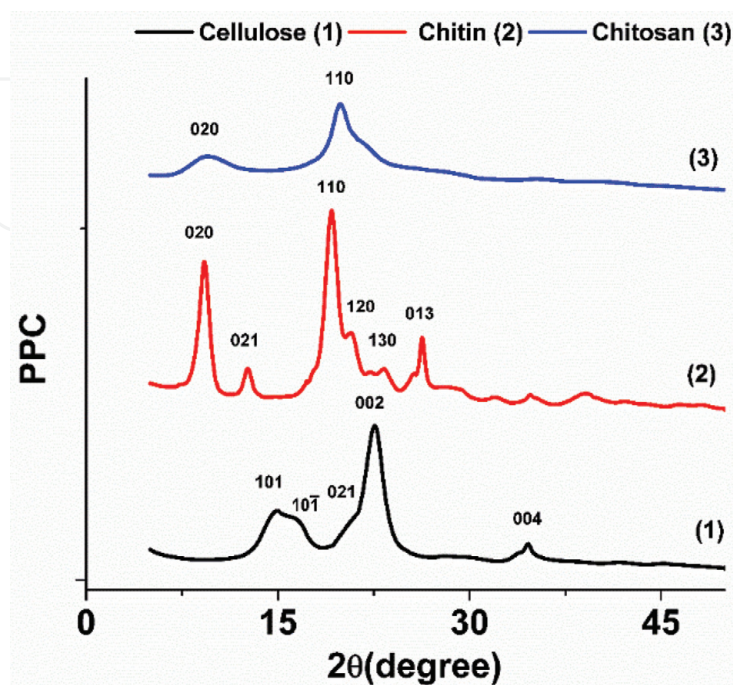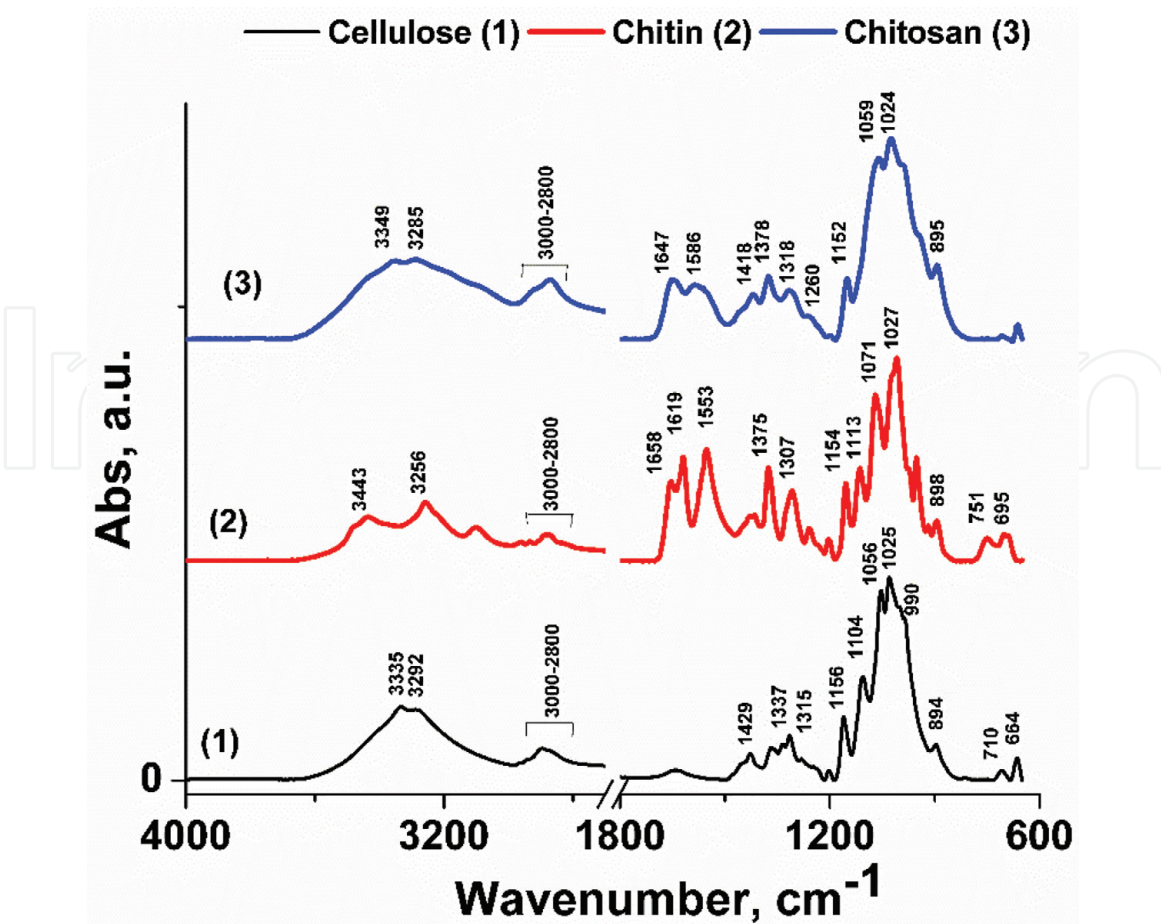

Figure 3.
Wide angle X-ray diffraction curves for cellulose, chitin and chitosan powder.

to cellulose and chitosan. The low crystallinity of chitosan is the result of the deacetylation process.

4.2 FTIR characterization

FTIR studies were performed on cellulose, chitin and chitosan powders. **Figure 4** shows the UATR-FTIR spectra of cellulose, chitin, and chitosan collected in the wavenumber range of 4000–600 cm^{-1}. The peaks of cellulose at 3335 and 3234 cm^{-1} are attributed to the O-H stretching vibrations and the extensive inter- and intra-molecular hydrogen bonding network [55]. For chitin, the vibrations attributed to O-H and N-H stretching are visible at 3434 and 3256 cm^{-1} and for chitosan those peaks appear at 3434 and 3256 cm^{-1} [56, 57]. The bands in the region of 3000–2800 cm^{-1} correspond to the -CH$_2$ symmetrical and asymmetrical stretching vibrations of polysaccharides [55–57]. Chitin exhibits the doublet amide I band at 1658 and 1619 cm^{-1} representing the presence of H-bonding in a C=O group with the NH group of the adjacent chain and the O-H group of the inter-chain [58]. The amide II band of chitin and chitosan is located at 1553 and 1586 cm^{-1}, respectively [56, 57]. The peak at 1307 cm^{-1} corresponds to the amide III band (in-plane mode of CONH$_2$ group) of chitin. Respective, amide I and C-N stretching of amide III of chitosan appear at around 1647 and 1318 cm^{-1}. The vibrations at ~1152 and ~1110 cm^{-1} are attributed to the anti-symmetrical bridge of C-O-C stretching and anti-symmetric in-plane stretching. The peaks at ~1060 and ~1025 cm^{-1} correspond to the C-O stretching of the polysaccharide [55–57]. The band at ~895 cm^{-1} is assigned to β-linkage of the polysaccharide [55–57].

Figure 4.
FTIR spectra of cellulose, chitin, and chitosan in the wavenumber region of 4000–600 cm^{-1}.

4.3 TG and DTG analysis

High-resolution thermogravimetry (TG) profiles recorded in flowing nitrogen (N_2) were used to investigate the thermal stability of cellulose, chitin and chitosan, see **Figure 5(a)**. All samples display two main weight loss regions at 35–150 and 250–450°C. In the first region, approximately, 5.1–9.0% of the weight loss was observed, which is attributed to the removal of physically adsorbed water. The second region represents the largest weight loss of 90.4, 86.6 and 63.4% for cellulose (1), chitin (2) and chitosan (3), respectively, corresponding to the degradation of polysaccharide structure of the biopolymer. The differential thermogravimetric (DTG) profiles generated from TG data are shown in **Figure 5(b)**. The DTG curves for cellulose, chitin, and chitosan exhibit the main decomposition peaks at 371, 391 and 300°C, respectively. These results suggest that among three biopolymers, chitin has the highest thermal stability while chitosan has the least thermal stability.

4.4 SEM studies

The morphological characteristic of cellulose, chitin and chitosan was investigated and **Figure 6** shows the comparison of typical surface morphologies for cellulose, chitin and chitosan. As it can be seen, all samples exhibited more irregular, flat, rough nanofiber surface with no porosity.
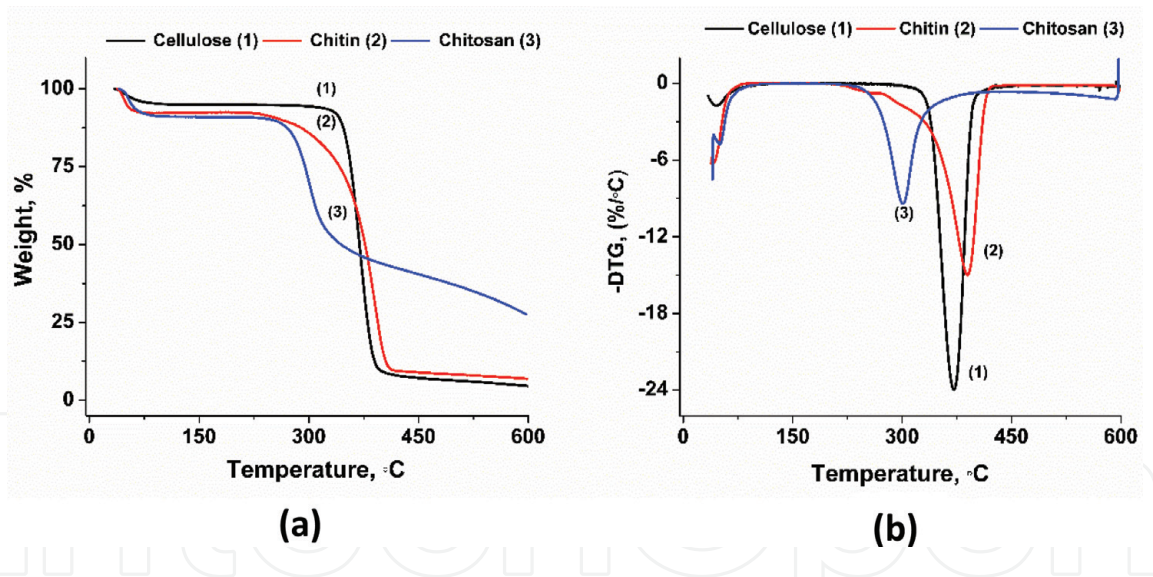

Figure 5.
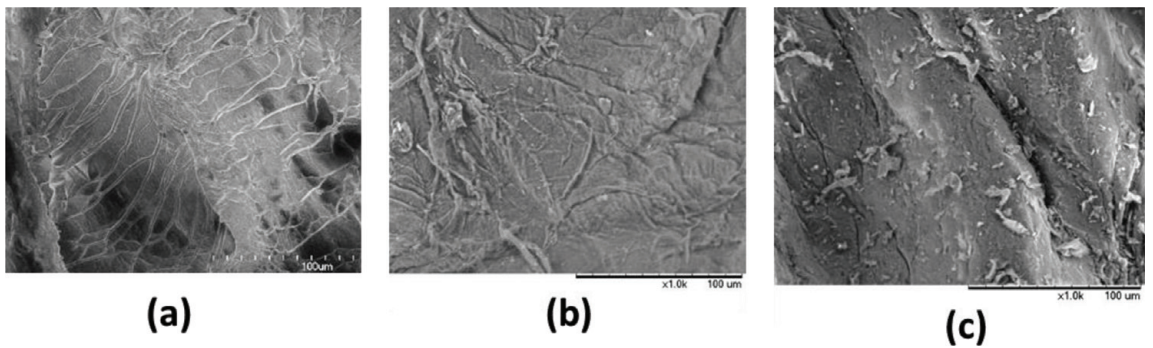*(a) TG and (b) DTG profiles of cellulose, chitin and chitosan.*

Figure 6.
SEM images of (a) microcrystalline cellulose, (b) chitin and (c) chitosan at 100 um magnification.

5. Applications of biopolymer-based materials in sorption

With the rapid industrialization, more environmental concerns (such as industrial discharge of organic dyes and heavy metal ions, oil and solvent spillage, and emission of greenhouse gases including carbon dioxide (CO_2)) have emerged as a critical worldwide issue, imposing detrimental damages to the environment, economy and human health. Recently, biopolymer-based materials being sustainable, readily available, biodegradable, economical, and environmentally-friendly, they are widely investigated both in industry and research as a green approach in remediating those issues. In this section, we discuss the use of cellulose-, chitin-, and chitosan-based materials as sorbents for four different applications including removal of organic dyes and heavy metals, oil and solvent spillage cleanup and CO_2 adsorption.

5.1 Dye removal

Industries including textile, leather, paper, printing, and paint utilize large amounts of water for processing have the potential to contaminate waterways through the discharge of organic dyes into natural water resources and water treatment systems. Over 10,000 different textile dyes with an estimated annual production of over 7×10^5 tons are available commercially [59, 60]. Most of these organic dyes are excessively used and 10–20% is directly discharged as aqueous effluents into different water bodies [61]. Most problematic ones are the brightly colored, water-soluble reactive and acid dyes as these dyes cannot be removed through conventional treatment systems. Discharging of organic dyes into water bodies has raised acute and chronic concerns to the ecosystems and human health. For example, the release of those organic dyes can lead to eutrophication, non-esthetic pollution and imbalance in the aquatic biological systems and also causes chronic toxicity, carcinogenicity and neurotoxicity towards humans and animals. Commonly applied technologies for removing organic dyes from wastewater include chemical precipitation and adsorption [62, 63], electrochemical oxidation and reduction [64], aerobic and anaerobic treatment [65, 66], coagulation and flocculation [67, 68], membrane separation [69], ultra-filtration [70], H_2O_2/ultra-violet (UV) and photocatalysis [71–73], ion exchange [74], sonochemical degradation [71], Fenton and heterogeneous Fenton-like catalysis [75–77], electrolysis [78], and advanced oxidation processes (AOPs) [56, 79]. At present, there is a critical need for research that enables new means of inexpensive, reusable, environmentally and energetically sustainable wastewater management systems for wastewater treatment. Recently, biopolymer-based materials have attracted interests as emerging alternative techniques for the removal of organic dyes from industrial effluents due to their relative abundance, eco-friendly, high thermal and mechanical stability, low cost, nontoxicity, easy functionalization, and excellent sorption capacities. Here, we report the roles of biopolymer-based materials mainly derived from cellulose, chitin, and chitosan as sorption materials for the removal of organic dyes from industrial wastewater.

Liu et al. investigated the porous cellulose-based bioadsorbent for the removal of anionic dye acid blue 93 (AB93) and cationic dye methylene blue (MB) from single and binary dye solutions by grafting acrylic acid and acrylamide onto cellulose surface [80]. They reported maximum sorption capacity of 1372 mg/g at an initial absorbent concentration of 2500 mg/L for both of AB93 and MB with a reusability up to three consecutive cycles. The adsorption process followed the pseudo-second-order kinetic model and the Freundlich isotherm model. Jiang and coworkers

prepared ultralight aerogels from cellulose nanofibrils (CNFs) derived from rice straw [81]. These ultra-lightweight aerogels have been studied as adsorbents for the removal of cationic dye malachite green (MG) dye from aqueous media. The highest adsorption capacity of MG was found to be 212.7 mg/g. They also reported a 100% MG removal via four consecutive adsorptions at a 1:5 mg/mL aerogel/MG ratio and 10 mg/L dye concentration and 92% MG adsorption in a single batch at 10:5 mg/mL aerogel/MG ratio and 100 mg/L dye concentration. The adsorption process obeyed a pseudo-second-order kinetic model and monolayer Langmuir adsorption isotherm. The dye desorption was also achieved by increasing ionic strength, leading to the recovery of both dye and CNF aerogel. Ruan and coworkers prepared porous 2,3-dialdehyde cellulose-chitosan (DAC-CS) beads and their applications in the removal of Congo red dye [82]. DAC-CS beads showed 100% dye removal at a capacity of 200 mg/g at pH. 2 in 100 g/L dye solution. About 93% of the adsorbed Congo red in DAC-CS beads could be desorbed at pH. 12 NaOH solution. A similar trend was observed in the second cycle with the adsorption and desorption of 100 and 89%, respectively. Cross-linked quaternized cellulose nanofibrils (Q-CNFs) have been investigated as adsorbents for removal of three different anionic dyes by Maatar and Boufi [83]. They reported the adsorption capacity of approximately 160, 230, and 560 mg/g for red 180, blue CR19, and orange 142 dye, respectively. The authors also confirmed the main contribution of electrostatic interactions between positive sites and the CNF surface and dye sulfonate groups by zeta potential measurements. The regeneration of the Q-CNF sorbent could be achieved by extraction with KCl solution in ethanol-water mixture.

Kinetics of the adsorption of reactive yellow 2 (RY2) and reactive black 5 (RB5) by chitin was investigated by Akkaya et al. [84]. They concluded that the adsorption of RY2 by chitin from aqueous solution is favorable at low temperature and pH and the adsorption of RB5 by chitin is favorable at high temperature and pH. Cao and coworkers studied the adsorption isotherms and kinetic analysis of methylene blue (MB) onto porous chitin sorbents (PChs) with different content of chitin, ranging from 0.9 to 3.5% [85]. The maximum adsorption capacity of 384 mg/g with 79.8% MB removal was observed for PChs containing 3.5% chitin. The same adsorption capacity with 65% removal ratio was observed after six repetitive cycles. The adsorption equilibrium followed Freundlich isotherm model. Xu and coworkers reported the synthesis and efficient removal of MB by nanocomposite microspheres fabricated from chitin and clay [86]. These chitin/clay microspheres (CCMs) showed a maximum adsorption capability of 156.7 mg/g. A dye removal of 99.99% was observed within 20 at a low MB concentration of 10 mg/g. They also demonstrated a stability over five adsorption/desorption cycles for CCMs. Their kinetic data fitted well with the pseudo-second-order and monolayer Langmuir isotherm models. Gopi et al. prepared a chitin nanowhisker (*ChNW*)-functionalized polyvinylidene fluoride (PVDF) membrane using electrospinning technique [87]. They reported a maximum adsorption capacity of 72.6 mg/g and 88.9% removal efficiency of indigo carmine (IC) dye with their *PVDF/ChNW* (15%:1% wt.) composite membrane as compared to neat PVDF.

Xu and coworkers synthesized poly(2-acrylamido-2-methylpropane sulfonic acid grafted magnetic chitosan microspheres (PMCMs) for MB adsorption [88]. They investigated the effects of initial solution pH (1.0–10.0), temperature (30–50°C), contact time (0–660 min) and initial concentration (50–1600 mg/L) on dye adsorption kinetics. At pH. 9, PMCMs exhibited maximum MB sorption capacity of 1000, 1250 and 1428 mg/g at 30, 40 and 50°C, respectively. They also showed that the adsorption capacity increased with increasing of the initial solution pH and temperature. The adsorption kinetic and adsorption equilibrium

data followed the pseudo-second-order kinetic model and monolayer Langmuir isotherm model, respectively. PMCMs could also be separated under external magnetic field and regenerated under acidic conditions. Naseeruteen et al. exhibited the removal of Malachite Green (MG) by mesoporous chitosan ionic liquid beads prepared from chitosan and 1-butyl-3-methylimidazolium based ionic liquids [89]. The effects of initial pH, adsorbent dosage, agitation time and initial MG concentration have also been investigated. The optimum conditions reported were pH 4.0, 0.008 g of adsorbent dosage and 20 min of agitation time. The data obtained at pH 4 fitted well to a pseudo-second order kinetic model and followed the Langmuir model. The maximum adsorption capacity obtained for two chitosan beads prepared from 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium was 8.07 and 0.24 mg/g respectively.

5.2 Removal of heavy metals

The surge in energy production and the increasing use of heavy metals in various industrial processes have led to the generation of large quantities of industrial waste containing heavy metals. Therefore, heavy metals are released into the environment including air, water, soil, and biosphere in excessive amounts on daily basis. Heavy metal ions are mainly elements from the fourth period of the periodic table including chromium (Cr), arsenic (As), cobalt (Co), copper (Cu), nickel (Ni), zinc (Zn), lead (Pb), and mercury (Hg) and have a high atomic weight and a density at least 5 times higher than that of water [90]. Heavy metals are typically toxic, persistent, non-biodegradable and bioaccumulative. Due to the high solubility, heavy metals are easily absorbed by plants and aquatic species and subsequently enter the food chains and then the human body. The presence of high levels of heavy metals in the human body may cause various health effects including skin irritations, stomach cramps, vomiting, multiple organ damage, birth defects, nerve system damage and development of autoimmunity. Most commonly used techniques for the removal of heavy metals include membrane filtration, adsorption, coagulation, chemical precipitation, ion-exchange, electrochemical, biological treatments and advanced oxidation processes [91]. However, adsorption technologies are widely considered as cheap and energy efficient solutions for removal of heavy metals. Biopolymers including cellulose, chitin, and chitosan have been widely investigated as sorbents for remediation of heavy metals due to their excellent sorption properties and environmental benignity [92–94]. Here we present, recently reported applications of biopolymer-based materials for the removal of heavy metals.

d'Halluin et al. prepared a chemically modified cellulose filter paper with ethylenediaminetetraacetic acid (EDTA) for heavy metal remediation in water [95]. Cellulose-EDTA composite showed 90–95% removal efficiency for various heavy metal ions including Ag(I), Pb(II), Cd(II), Ni(II), Zn(II), Sn(II), and Cu(II). They also investigated the adsorption kinetics using Langmuir, Freundlich, and Temkin isotherms and the recyclability of their material. Fakhre and coworkers synthesized a supramolecular polysaccharide composite material from cellulose (CEL) and dibenzo-18-crown 6 (DB18C6) using ceric ammonium nitrate as initiator [96]. They studied the removal of five different heavy metal ions including Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} by [CEL + DB18C6] composites. They reported adsorption capacities and percentage of metals removal of (197 mg/g, 98%), (180 mg/g, 94%), (186 mg/g, 93%), (194 mg/g, 97%), and (192 mg/g, 96%) for Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+}, respectively. The regeneration of the material is dependent on the type and concentration of regenerating solution (NH_4Cl, HNO_3, NaCl and $CaCl_2$). Shao et al. studied the removal of Cu^{2+} ions by a porous waste paper (WP)-chitosan adsorbent (CSA) [97]. WP-CSA exhibited adsorption capacity of 156.3 mg/g for Cu^{2+} and

98.3% desorption efficiency in 0.1 M H_2SO_4 solution. This adsorption equilibrium followed the pseudo-second order model and the Langmuir monolayer model.

Duan and coworkers presented the fabrication of lignin/chitin films from a binary solvent system composed of the ionic liquid 1-butyl-3-methylimidazolium acetate and γ-valerolactone and their application as an adsorbent for Fe(III) and Cu(II) cation uptake from aqueous solutions [98]. Lignin/chitin film showed the adsorption capacity of 84 and 22 wt% for Fe(III) and Cu(II) cations within 48 h. During the regeneration process up to 12 and 46 wt%, respectively, could be desorbed. The adsorption isotherms for both Fe(III) and Cu(II) obeyed the Langmuir model. Ethylenediaminetetraacetic acid (EDTA) modified β-cyclodextrin/chitosan (CDCS-EDTA) composite was prepared and applied for the removal of Pb(II) and anionic dye acid red 73 (AR) by Wu and coworkers [99]. They also investigated the effects of adsorbent dose, contact time and pH value on the CDCS-EDTA adsorption efficiency. The maximum adsorption capacities reported were 114.8 and 754.6 mg g^{-1} for Pb(II) and AR under optimal conditions with adsorption efficiently of 93.4 and 92.1%, respectively. Both adsorption processes followed the pseudo-second-order adsorption kinetic model and the Langmuir isotherm model. Kwok et al. studied the sorption of anionic species arsenite, As(III) ions and arsenate, AS (V) ions onto chitosan and nanochitosan [100]. The equilibrium adsorption capacity of chitosan and nanochitosan for As(III) and As(V) ions were (0.5 and 8 mg/g) and (6.1 and 13 mg/g), respectively.

5.3 Oil and solvent spillage cleanup

An oil or a solvent spill is the accidental or intentional discharge of petroleum hydrocarbons into the environment, especially the aquatic ecosystem. Oil and solvent spills have become a serious environmental problem due to the increasing use, exploration, production and transportation of oils and solvents worldwide by various petrochemical and chemical industries. Those spillages lead to the pollution of aquatic ecosystems and natural water resources including underground water streams and coastal waters and affect both human and animal health through inhalation, skin, digestion, and eye irritation. Therefore, efficient and rapid removal of oil and solvent spills on the surface of water is imperative for protecting the aquatic environment, water resources, and subsequently human and animal health. Currently available oil and solvent spill techniques include physical diffusion, in-situ burning, bioremediation, and mechanical recovery [101, 102]. Among those technologies, cleaning the spilled oil and solvents by physical adsorbents is an attractive approach because of their ease of use and simplicity. Biopolymer-based adsorbents have been widely investigated for cleanup of oil and solvents due to their relative abundance, sustainability, low-cost, selectivity, fast adsorption kinetics, reusability and environmental benignity. Some recent developments in the use of biopolymer-based materials in oil and solvent spillage cleanup processes are discussed below.

Ao et al. reported the synthesis and separation of different oil/water mixtures using a cellulose hydrogel-coated mesh (CHM) [103]. They reported selective separation of a series of mixtures including hexane, cyclohexane, petroleum ether, liquid paraffin, pump oil and xylene with a high separation efficiency of over 98.9% and a high flux of 12,885 L/ m^2 h. Their material also showed high reusability, anti-salt properties, and stability after 60 successive cycles of separation with a separation efficiency of >98.2%. Magnetic hydrophobic polyvinyl alcohol (PVA)-cellulose nanofiber (CNF) aerogels (MHPCA) were prepared and used as effective oil absorbents by Xu and coworkers [104]. A series of oils including soybean oil, corn germ oil, pump oil, used pump oil, gasoline, motor oil, ethanol, and dimethylformamide

(DMF), were tested and MHPCA showed oil absorption capacity in the range of 59–136 g/g. MHPCA exhibited magnetically driven oil absorption and elasticity after 30 compression-release cycles, showing its reusability and durability. Cheng and coworkers investigated the use of pure cotton and cotton/cellulose aerogels derived from pure cotton and cellulose fiber from paper waste for the removal of oil and organic solvents [105]. The cotton/cellulose aerogels exhibited better performance over pure cotton aerogels because of the synergetic effects of two different cellulose fiber sources. The sorption capacity of the cotton/cellulose composite aerogel was 72.3 and 94.3 g/g for machine oil and dichloromethane, respectively [105].

Duan and coworkers prepared hydrophobic and oleophilic methyltri-chlorosilane (MTCS) coated-chitin sponges and showed their ability to absorb a wide range of oils and nonpolar organic solvents including chloroform, gasoline oil, hexane, pump oil, silicon oil and toluene from the surface and bottom of the polluted water [106]. They reported that low viscosity organics such as chloro-form, gasoline oil, hexane, and toluene could be absorbed to equilibrium within 8 min, whereas higher viscosity oils, such as pump oil and silicon oil could reach the absorption equilibrium within 13 min. MTCS-coated chitin sponges displayed recyclability with at least 10 times with approximately 93% adsorption capacity. Li et al. prepared porous chitosan-oxidized cellulose aerogel as an oil and organic solvent absorbent [107]. They reported the adsorption capacity in the range of 13.77–28.20 g/g for various oils and organic solvents including carbon tetrachlo-ride, ethylene glycol, silicon oil, ethylene acetate, pump oil, crude oil, acetone, ethanol, diesel, and gasoline. Their material was stable over 50 absorption-desorption cycles following a pseudo-second-order kinetic model. The utilization of N,O-carboxymethyl chitosan for the adsorption of Marine Diesel, Diesel and Marine-2T oil for oil spill treatment has been reported by Doshi and coworkers [108].

5.4 Carbon dioxide adsorption

Carbon dioxide (CO_2) is the primary greenhouse gas (GHG) emitted through human activities and also considered as one of the major contributors to the green-house effect and global warming. CO_2 emissions, primarily from fossil fuel based power plants account for over 87% of the global annual emission of CO_2 [109]. According to the Intergovernmental Panel (IPCC) Fifth Assessment Report, the industrial revolution has significantly contributed to the raised atmospheric CO_2 levels from 280 to 400 parts per million (ppm) in the last 150 years [110]. It is estimated that by the end of year 2030, the global GHG emission could rise by 25–90% as compared to the GHG level in 2000, reaching CO_2 atmospheric levels in the range of 600–1550 ppm [111]. Some long-term effects of global warming include higher temperatures, changing rainfall patterns, rising sea levels, severe weather events ranging from flash floods, high intense hurricanes, freezing winters, severe droughts and heat waves. Therefore, many approaches including improved energy efficiency and energy conservation, increased utilization of low carbon fuels such as natural gas, hydrogen or nuclear power, usage of renewable energy such as solar, wind and hydropower and bioenergy, application of geoengineering processes such as afforestation and reforestation and use of carbon dioxide capture, storage and utilization (CCSU) techniques are extensively considered and adopted by various countries to mitigate CO_2 emissions [112, 113]. Among those, CCSU technologies have received a significant interest due to their ability to control in-situ CO_2 emis-sions from both industrial sources and natural sources. CCSU technologies mainly accompany separation of CO_2, transportation of captured and compressed CO_2, and

underground storage of CO_2 for reuse. However, the success of these CCSU technologies relies on the CO_2 adsorption efficiency, manufacturing cost, and ease of handling and regeneration. Solid adsorbents include carbonaceous materials, covalent organic frameworks (COFs), porous organic frameworks (POPs) and metal–organic frameworks (MOFs), metal oxides (alkaline, alkaline earth and transition metals) and mesoporous silica-based materials and amines have been proposed for CCSU technologies [114–116]. Solid adsorbents derived from biopolymers are attracting interest for CCSU technologies because of their unique properties. Recently reported applications of biopolymer-based materials in capturing CO_2 gas are discussed in this section.

Biopolymers/biopolymers based composites	Pollutants	References
Cellulose	Acid blue 93 and methylene blue	[80]
	Malachite green	[81]
	Congo red	[82]
	Red 180, Blue CR 19, and Orange 142	[83]
	Ag(I) and Sn(II)	[95]
	Pb(II), Cd(II), Ni(II), and Zn(II)	[95, 96]
	Cu(II)	[95–97]
	Hexane, cyclohexane, petroleum ether	[104]
	Liquid paraffin, pump oil, and xylene	
	Machine oil and dichloromethane	[105]
	CO_2	[115, 117–119]
Chitin	Reactive yellow 2 and Reactive black 5	[84]
	Methylene blue	[85, 86]
	Indigo carmine	[87]
	Fe(III) and Cu(II)	[98]
	Chloroform, gasoline oil, hexane, toluene,	[106]
	silicon oil, pump oil	
	CO_2	[39]
Chitosan	Methylene blue	[88]
	Malachite green	[89]
	Acid red 73 and Pb(II)	[99]
	As(III) and As(IV)	[100]
	Carbon tetrachloride, ethylene glycol, silicon oil,	[107]
	Ethylene acetate, pump oil, crude oil, acetone, ethanol, and gasoline	[107]
	Diesel	[107, 108]
	Marine diesel	[108]
	CO_2	[120, 121]

Table 1.
Polysaccharide based biopolymers used in sorption of different pollutants.

Dassanayake et al. investigated the preparation of activated carbon monoliths derived from cellulose-based aerogel (aerocellulose) and its CO_2 adsorption properties at low and ambient temperatures [117]. The activated carbon prepared from aerocellulose exhibited a specific surface area of 753 m^2/g, a total pore volume of 0.72 cm^3/g, and a micropore volume of 0.27 cm^3/g. The physical CO_2 uptakes for these materials were 5.8 mmol/g of CO_2 at 0°C and 1 atm and 3.7 mmol/g of CO_2 at 25°C and 1.2 atm. They also reported the synthesis and CO_2 adsorption of a series of amidoxime (AO)-functionalized microcrystalline (MCC) and nanocrystalline cellulose (NCC)-mesoporous silica composites at ambient and elevated temperatures [115, 118]. They reported the CO_2 sorption capacities of MCC-AO composites in the range of 0.40–1.27 and 2.84–3.85 mmol/g at ambient (25°C, 1.2 atm) and elevated temperatures (120°C, 1.0 atm), respectively. Whereas, NCC-AO composites which showed highest CO_2 uptakes of 3.30 mmol/g at 25°C (1.2 atm) and 5.54 mmol/g at 120°C (1 atm), respectively. Both MCC-AO and NCC-AO composites displayed a good recyclability and stability after 10 successive adsorption/desorption cycles with negligible losses of the sorption capacity. Shehaqui et al. reported the direct CO_2 capture from air onto nanofibrillated cellulose (NFC)-polyethylenimine (PEI) foams [119]. They demonstrated the impact of both PEI and relative humidity (RH) on the CO_2 capture under atmospheric conditions with CO_2 concentration of $\sim$400 ppm. At 80% RH and PEI content of 44 wt%, a CO_2 uptake of 2.22 mmol/g was achieved with a stability over five repetitive cycles.

Dassanayake and coworkers also studied the CO_2 adsorption on activated carbon prepared by carbonization and KOH activation of chitin aerogels [39]. Their material showed CO_2 adsorption capacities of 5.02 mmol/g at 0°C and 3.44 mmol/g at 25°C under ambient pressure of 1 atm. Eftaiha et al. investigated the CO_2 adsorption by a chitin-acetate (CA)/dimethyl sulfoxide (DMO) binary system and reported the CO_2 uptake of 3.63 mmol/g at 3.95 atm and 0°C [120]. Fujiki and Yogo investigated CO_2 adsorption capacities of nitrogen-doped activated carbons prepared from chitosan at two different pressure conditions; namely 0.15 and 0.99 atm at 25°C [121]. They reported CO_2 adsorption capacities of 1.6 mmol/g at 0.15 atm and 4.9 mmol/g at 0.99 atm for their material. Alhwaige et al. reported the preparation of montmorillonite (MMT) reinforced bio-based chitosan-polybenzoxazine (CTS-PBZ) composite carbon aerogels and their ability to capture CO_2 [122]. MMT-CTS-PBZ composite carbon aerogels showed a maximum CO_2 adsorption of 5.72 mmol/g with multi-cyclic adsorption-desorption stability.

Table 1 summarizes the main applications of biopolymer-based materials for pollutants removal from water and sorption of CO_2.

6. Conclusion

Biopolymers and biopolymer-based materials have been widely investigated for various sorption applications due to their excellent adsorption capacities, easy functionalization, relative abundance, green, sustainable, biodegradable, low cost, and environmental benign properties. In this chapter, we presented the properties, processing, characterization and sorption applications of three most commonly studied natural polysaccharides, namely cellulose, chitin and chitosan. Recent developments of cellulose, chitin and chitosan-based materials in organic dye removal, heavy metals removal, oil and solvent spillage cleanup, and CO_2 adsorption have been extensively discussed.

Author details

Rohan S. Dassanayake, Sanjit Acharya and Noureddine Abidi*
Department of Plant and Soil Science, Fiber and Biopolymer Research Institute,
Texas Tech University, Lubbock, TX, USA

*Address all correspondence to: noureddine.abidi@ttu.edu

IntechOpen

References

[1] Pattanashetti NA, Heggannavar GB, Kariduraganavar MY. Smart biopolymers and their biomedical applications. Procedia Manufacturing. 2017;**12**:263-279

[2] Numata K. Poly(amino acid)s/polypeptides as potential functional and structural materials. Polymer Journal. 2015;**47**:537

[3] Klemm D. et al. Cellulose: Fascinating biopolymer and sustainable raw material. Angewandte Chemie International Edition. 2005;**44**(22):3358-3393

[4] Rinaudo M. Chitin and chitosan: Properties and applications. Progress in Polymer Science. 2006;**31**(7):603-632

[5] Lenz DM et al. Multiple reprocessing cycles of corn starch-based biocomposites reinforced with Curauá fiber. Journal of Polymers and the Environment. 2018

[6] Chen X et al. Effect of treatment methods on chitin structure and its transformation into nitrogen-containing chemicals. ChemPlusChem. 2015;**80**(10):1565-1572

[7] Hu Y, Abidi N. Distinct chiral nematic self-assembling behavior caused by different size-unified cellulose nanocrystals via a multistage separation. Langmuir. 2016;**32**(38):9863-9872

[8] Hu Y, Catchmark JM. In vitro biodegradability and mechanical properties of bioabsorbable bacterial cellulose incorporating cellulases. Acta Biomaterialia. 2011;**7**(7):2835-2845

[9] Hu Y, Catchmark JM, Vogler EA. Factors impacting the formation of sphere-like bacterial cellulose particles and their biocompatibility for human osteoblast growth. Biomacromolecules. 2013;**14**(10):3444-3452

[10] Hu Y et al. Engineering of porous bacterial cellulose toward human fibroblasts ingrowth for tissue engineering. Journal of Materials Research. 2014;**29**(22):2682-2693

[11] Hu Y et al. Preparation, characterization, and cationic functionalization of cellulose-based aerogels for wastewater clarification. Journal of Materials. 2016;**2016**:10

[12] Hu Y et al. Bioabsorbable cellulose composites prepared by an improved mineral-binding process for bone defect repair. Journal of Materials Chemistry B. 2016;**4**(7):1235-1246

[13] Wang S, Lu A, Zhang L. Recent advances in regenerated cellulose materials. Progress in Polymer Science. 2016;**53**:169-206

[14] Moon RJ et al. Cellulose nanomaterials review: Structure, properties and nanocomposites. Chemical Society Reviews. 2011;**40**(7):3941-3994

[15] Habibi Y, Lucia LA, Rojas OJ. Cellulose Nanocrystals: Chemistry, self-assembly, and applications. Chemical Reviews. 2010;**110**(6):3479-3500

[16] French AD. Glucose, not cellobiose, is the repeating unit of cellulose and why that is important. Cellulose. 2017;**24**(11):4605-4609

[17] George J, Sabapathi SN. Cellulose nanocrystals: Synthesis, functional properties, and applications. Nanotechnology, Science and Applications. 2015;**8**:45-54

[18] Gibson LJ. The hierarchical structure and mechanics of plant

materials. Journal of the Royal Society Interface. 2012;**9**(76):2749-2766

[19] Parthasarathi R et al. Insights into hydrogen bonding and stacking interactions in cellulose. The Journal of Physical Chemistry A. 2011;**115**(49): 14191-14202

[20] Peresin MS et al. Nanofiber composites of polyvinyl alcohol and cellulose nanocrystals: Manufacture and characterization. Biomacromolecules. 2010;**11**(3):674-681

[21] Khan F, Ahmad SR. Polysaccharides and their derivatives for versatile tissue engineering application. Macromolecular Bioscience. 2013;**13**(4):395-421

[22] Tanaka K, Yamamoto K, Kadokawa J-I. Facile nanofibrillation of chitin derivatives by gas bubbling and ultrasonic treatments in water. Carbohydrate Research. 2014;**398**:25-30

[23] Van de Velde K, Kiekens P. Structure analysis and degree of substitution of chitin, chitosan and dibutyrylchitin by FT-IR spectroscopy and solid state ^{13}C NMR. Carbohydrate Polymers. 2004;**58**(4):409-416

[24] Ravi Kumar MNV. A review of chitin and chitosan applications. Reactive and Functional Polymers. 2000;**46**(1):1-27

[25] Kurita K. Controlled functionalization of the polysaccharide chitin. Progress in Polymer Science. 2001;**26**(9):1921-1971

[26] Di Martino A, Sittinger M, Risbud MV. Chitosan: A versatile biopolymer for orthopaedic tissue-engineering. Biomaterials. 2005;**26**(30):5983-5990

[27] Acharya S et al. Chemical cationization of cotton fabric for improved dye uptake. Cellulose. 2014; **21**(6):4693-4706

[28] Pinkert A et al. Ionic liquids and their interaction with cellulose. Chemical Reviews. 2009;**109**(12): 6712-6728

[29] Wu J et al. Homogeneous acetylation of cellulose in a new ionic liquid. Biomacromolecules. 2004;**5**(2): 266-268

[30] Xiao P et al. Synthesis, characterization and properties of novel cellulose derivatives containing phosphorus: Cellulose diphenyl phosphate and its mixed esters. Cellulose. 2014;**21**(4):2369-2378

[31] Rana S et al. Regenerated cellulosic fibers and their implications on sustainability. In: Muthu SS, editor. Roadmap to Sustainable Textiles and Clothing: Eco-Friendly Raw Materials, Technologies, and Processing Methods. Singapore: Springer Singapore; 2014. pp. 239-276

[32] Heize T, El Seoud OA, Koschella A. Cellulose derivatives: Synthesis, structure, and properties. In: Springer Series on Polymer and Composite Materials. Springer International Publishing; 2018

[33] Duan B et al. Recent advances in chitin based materials constructed via physical methods. Progress in Polymer Science. 2018;**82**:1-33

[34] Budtova T, Navard P. Cellulose in NaOH–water based solvents: A review. Cellulose. 2016;**23**(1):5-55

[35] Potthast A et al. The cellulose solvent system N,N-dimethylacetamide/ lithium chloride revisited: The effect of water on physicochemical properties and chemical stability. Cellulose. 2002; **9**(1):41-53

[36] Sen S, Martin JD, Argyropoulos DS. Review of cellulose non-derivatizing solvent interactions with emphasis on activity in inorganic molten salt

hydrates. ACS Sustainable Chemistry & Engineering. 2013;**1**(8):858-870

[37] Vitz J et al. Extended dissolution studies of cellulose in imidazolium based ionic liquids. Green Chemistry. 2009;**11**(3):417-424

[38] Wang H, Gurau G, Rogers RD. Ionic liquid processing of cellulose. Chemical Society Reviews. 2012;**41**(4): 1519-1537

[39] Dassanayake RS et al. Activated carbon derived from chitin aerogels: Preparation and CO_2 adsorption. Cellulose. 2018;**25**(3):1911-1920

[40] Duan B et al. High strength films with gas-barrier fabricated from chitin solution dissolved at low temperature. Journal of Materials Chemistry A. 2013; **1**(5):1867-1874

[41] Acharya S. et al. Preparation and characterization of transparent cellulose films using an improved cellulose dissolution process. Journal of Applied Polymer Science. 2017;**134**(21)

[42] Acharya S, Hu Y, Abidi N. Mild condition dissolution of high molecular weight cotton cellulose in 1-butyl-3-methylimidazolium acetate/N,N-dimethylacetamide solvent system. Journal of Applied Polymer Science. 2018;**135**(9):45928

[43] Zhao S et al. Biopolymer aerogels: Chemistry, properties and applications. Angewandte Chemie International Edition. 2018;**57**:7580-7608

[44] Cai J et al. Cellulose aerogels from aqueous alkali hydroxide–urea solution. ChemSusChem. 2008;**1**(1–2):149-154

[45] Robitzer M, Renzo FD, Quignard F. Natural materials with high surface area. Physisorption methods for the characterization of the texture and surface of polysaccharide aerogels. Microporous and Mesoporous Materials. 2011;**140**(1):9-16

[46] Primo A, Quignard F. Chitosan as efficient porous support for dispersion of highly active gold nanoparticles: Design of hybrid catalyst for carbon-carbon bond formation. Chemical Communications. 2010;**46**(30): 5593-5595

[47] Lin N, Dufresne A. Nanocellulose in biomedicine: Current status and future prospect. European Polymer Journal. 2014;**59**:302-325

[48] Ifuku S. Chitin and chitosan nanofibers: Preparation and chemical modifications. Molecules. 2014;**19**(11): 18367-18380

[49] Dutta AK et al. Simple preparation of chitin Nanofibers from dry squid pen β-chitin powder by the star burst system. Journal of Chitin and Chitosan Science. 2013;**1**(3):186-191

[50] Kalia S et al. Nanofibrillated cellulose: Surface modification and potential applications. Colloid and Polymer Science. 2014;**292**(1):5-31

[51] Tzoumaki MV, Moschakis T, Biliaderis CG. Metastability of nematic gels made of aqueous chitin nanocrystal dispersions. Biomacromolecules. 2010; **11**(1):175-181

[52] Park S et al. Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance. Biotechnology for Biofuels. 2010;**3**:10-10

[53] Liu S et al. Extraction and characterization of chitin from the beetle *Holotrichia parallela* Motschulsky. Molecules. 2012;**17**(4): 4604-4611

[54] Li L-H et al. Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes. Carbohydrate Research. 2010;**345**(8): 994-998

[55] Abidi N, Cabrales L, Haigler CH. Changes in the cell wall and cellulose content of developing cotton fibers investigated by FTIR spectroscopy. Carbohydrate Polymers. 2014;**100**:9-16

[56] Dassanayake RS et al. One-pot synthesis of MnO_2–chitin hybrids for effective removal of methylene blue. International Journal of Biological Macromolecules. 2016;**93**:350-358

[57] Queiroz MF et al. Does the use of chitosan contribute to oxalate kidney stone formation? Marine Drugs. 2014;**13**:141-158

[58] Kumirska J et al. Application of spectroscopic methods for structural analysis of chitin and chitosan. Marine Drugs. 2010;**8**(5):1567-1636

[59] Chequer FMD et al. Textile dyes: Dyeing process and environmental impact. In: Günay M, editor. Eco-Friendly Textile Dyeing and Finishing. Rijeka: InTech; 2013. p. Ch. 06

[60] Yagub MT et al. Dye and its removal from aqueous solution by adsorption: A review. Advances in Colloid and Interface Science. 2014;**209**:172-184

[61] Zhou Y et al. Removal of methylene blue dyes from wastewater using cellulose-based superadsorbent hydrogels. Polymer Engineering & Science. 2011;**51**(12):2417-2424

[62] Li Y et al. Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. Chemical Engineering Research and Design. 2013;**91**(2):361-368

[63] Zhu MX et al. Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud. Journal of Hazardous Materials. 2007;**149**(3):735-741

[64] Alaoui A et al. Activity of Pt/MnO_2 electrode in the electrochemical degradation of methylene blue in aqueous solution. Separation and Purification Technology. 2015;**154**:281-289

[65] Chan YJ et al. A review on anaerobic–aerobic treatment of industrial and municipal wastewater. Chemical Engineering Journal. 2009;**155**(1):1-18

[66] Işık M, Sponza DT. Biological treatment of acid dyeing wastewater using a sequential anaerobic/aerobic reactor system. Enzyme and Microbial Technology. 2006;**38**(7):887-892

[67] Patel H, Vashi RT. Removal of Congo red dye from its aqueous solution using natural coagulants. Journal of Saudi Chemical Society. 2012;**16**(2):131-136

[68] Teh CY et al. Recent advancement of coagulation–flocculation and its application in wastewater treatment. Industrial & Engineering Chemistry Research. 2016;**55**(16):4363-4389

[69] Ciardelli G, Corsi L, Marcucci M. Membrane separation for wastewater reuse in the textile industry. Resources, Conservation and Recycling. 2001;**31**(2):189-197

[70] Huang J et al. Evaluation of micellar enhanced ultrafiltration for removing methylene blue and cadmium ion simultaneously with mixed surfactants. Separation and Purification Technology. 2014;**125**:83-89

[71] Zhang K et al. Comparison of catalytic activities for photocatalytic and sonocatalytic degradation of methylene blue in present of anatase TiO_2–CNT catalysts. Ultrasonics Sonochemistry. 2011;**18**(3):765-772

[72] Dariani RS et al. Photocatalytic reaction and degradation of methylene blue on TiO_2 nano-sized particles. Optik—International Journal for Light and Electron Optics. 2016;**127**(18):7143-7154

[73] Rosario-Ortiz FL, Wert EC, Snyder SA. Evaluation of UV/H$_2$O$_2$ treatment for the oxidation of pharmaceuticals in wastewater. Water Research. 2010;**44**(5):1440-1448

[74] Raghu S, Basha CA. Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater. Journal of Hazardous Materials. 2007;**149**(2):324-330

[75] Zhuang L et al. A novel bioelectro-Fenton system for coupling anodic COD removal with cathodic dye degradation. Chemical Engineering Journal. 2010;**163**(1):160-163

[76] Lim H et al. Highly active heterogeneous Fenton catalyst using iron oxide nanoparticles immobilized in alumina coated mesoporous silica. Chemical Communications. 2006;(4):463-465

[77] Hsueh CL et al. Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. Chemosphere. 2005;**58**(10):1409-1414

[78] Matheswaran M, Raju T. Destruction of methylene blue by mediated electrolysis using two-phase system. Process Safety and Environmental Protection. 2010;**88**(5):350-355

[79] Dassanayake RS, Rajakaruna E, Abidi N. Preparation of aerochitin-TiO$_2$ composite for efficient photocatalytic degradation of methylene blue. Journal of Applied Polymer Science. 2018;**135**(8):45908

[80] Liu L et al. Adsorption removal of dyes from single and binary solutions using a cellulose-based bioadsorbent. ACS Sustainable Chemistry & Engineering. 2015;**3**(3):432-442

[81] Jiang F, Dinh DM, Hsieh Y-L. Adsorption and desorption of cationic malachite green dye on cellulose nanofibril aerogels. Carbohydrate Polymers. 2017;**173**:286-294

[82] Ruan C-Q, Strømme M, Lindh J. Preparation of porous 2,3-dialdehyde cellulose beads crosslinked with chitosan and their application in adsorption of Congo red dye. Carbohydrate Polymers. 2018;**181**:200-207

[83] Maatar W, Boufi S. Microporous cationic nanofibrillar cellulose aerogel as promising adsorbent of acid dyes. Cellulose. 2017;**24**(2):1001-1015

[84] Akkaya G, Uzun İ, Güzel F. Kinetics of the adsorption of reactive dyes by chitin. Dyes and Pigments. 2007;**73**(2):168-177

[85] Cao Y-L et al. Modification of chitin with high adsorption capacity for methylene blue removal. International Journal of Biological Macromolecules. 2018;**114**:392-399

[86] Xu R et al. Chitin/clay microspheres with hierarchical architecture for highly efficient removal of organic dyes. Carbohydrate Polymers. 2018;**188**:143-150

[87] Gopi S et al. Chitin nanowhisker (ChNW)-functionalized electrospun PVDF membrane for enhanced removal of indigo carmine. Carbohydrate Polymers. 2017;**165**:115-122

[88] Xu B et al. Poly(2-acrylamido-2-methylpropane sulfonic acid) grafted magnetic chitosan microspheres: Preparation, characterization and dye adsorption. International Journal of Biological Macromolecules. 2018;**112**:648-655

[89] Naseeruteen F et al. Adsorption of malachite green from aqueous solution by using novel chitosan ionic liquid beads. International Journal of Biological Macromolecules. 2018;**107**:1270-1277

[90] Tchounwou PB et al. Heavy metals toxicity and the environment. EXS. 2012;**101**:133-164

[91] Carolin CF et al. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. Journal of Environmental Chemical Engineering. 2017;**5**(3): 2782-2799

[92] Jamshaid A et al. Cellulose-based materials for the removal of heavy metals from wastewater—An overview. ChemBioEng Reviews. 2017;**4**(4): 240-256

[93] Anastopoulos I et al. Chitin adsorbents for toxic metals: A review. International Journal of Molecular Sciences. 2017;**18**(1):114

[94] Zhang L, Zeng Y, Cheng Z. Removal of heavy metal ions using chitosan and modified chitosan: A review. Journal of Molecular Liquids. 2016;**214**:175-191

[95] d'Halluin M et al. Chemically modified cellulose filter paper for heavy metal remediation in water. ACS Sustainable Chemistry & Engineering. 2017;**5**(2):1965-1973

[96] Fakhre NA, Ibrahim BM. The use of new chemically modified cellulose for heavy metal ion adsorption. Journal of Hazardous Materials. 2018;**343**:324-331

[97] Li Z et al. Converting untreated waste office paper and chitosan into aerogel adsorbent for the removal of heavy metal ions. Carbohydrate Polymers. 2018;**193**:221-227

[98] Duan Y et al. Lignin/chitin films and their adsorption characteristics for heavy metal ions. ACS Sustainable Chemistry & Engineering. 2018;**6**(5): 6965-6973

[99] Wu D et al. EDTA modified beta-cyclodextrin/chitosan for rapid removal of Pb(II) and acid red from aqueous solution. Journal of Colloid and Interface Science. 2018;**523**:56-64

[100] Kwok KCM et al. Adsorption/desorption of arsenite and arsenate on chitosan and nanochitosan. Environmental Science and Pollution Research. 2018;**25**(15):14734-14742

[101] Doshi B, Sillanpää M, Kalliola S. A review of bio-based materials for oil spill treatment. Water Research. 2018; **135**:262-277

[102] Tu L et al. *Calotropis gigantea* fiber derived carbon fiber enables fast and efficient absorption of oils and organic solvents. Separation and Purification Technology. 2018;**192**:30-35

[103] Ao C et al. Reusable, salt-tolerant and superhydrophilic cellulose hydrogel-coated mesh for efficient gravity-driven oil/water separation. Chemical Engineering Journal. 2018; **338**:271-277

[104] Xu Z et al. Preparation of magnetic hydrophobic polyvinyl alcohol (PVA)–cellulose nanofiber (CNF) aerogels as effective oil absorbents. Cellulose. 2018; **25**(2):1217-1227

[105] Cheng H et al. Cotton aerogels and cotton-cellulose aerogels from environmental waste for oil spillage cleanup. Materials & Design. 2017;**130**: 452-458

[106] Duan B et al. Hydrophobic modification on surface of chitin sponges for highly effective separation of oil. ACS Applied Materials & Interfaces. 2014;**6**(22):19933-19942

[107] Li Z et al. Excellent reusable chitosan/cellulose aerogel as an oil and organic solvent absorbent. Carbohydrate Polymers. 2018;**191**: 183-190

[108] Doshi B et al. Effectiveness of N,O-carboxymethyl chitosan on

destabilization of marine diesel, diesel and marine-2T oil for oil spill treatment. Carbohydrate Polymers. 2017;**167**: 326-336

[109] Le Quéré C et al. The global carbon budget 1959–2011. Earth System Science Data. 2012;**5**(2):1107-1157

[110] McHale G, Shirtcliffe NJ, Newton MI. Contact-angle hysteresis on super-hydrophobic surfaces. Langmuir. 2004;**20**(23):10146-10149

[111] Cassie ABD, Baxter S. Wettability of porous surfaces. Transactions of the Faraday Society. 1944;**40**:546-551

[112] Wang Q et al. CO_2 capture by solid adsorbents and their applications: Current status and new trends. Energy & Environmental Science. 2011;**4**(1): 42-55

[113] Leung DYC, Caramanna G, Maroto-Valer MM. An overview of current status of carbon dioxide capture and storage technologies. Renewable and Sustainable Energy Reviews. 2014; **39**:426-443

[114] D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: Prospects for new materials. Angewandte Chemie (International Ed. in English). 2010; **49**(35):6058-6082

[115] Dassanayake RS et al. Amidoxime-functionalized nanocrystalline cellulose-mesoporous silica composites for carbon dioxide sorption at ambient and elevated temperatures. Journal of Materials Chemistry A. 2017;**5**(16): 7462-7473

[116] Gregor S, Ganin AY, Yiu HHP. Sustainable CO_2 adsorbents prepared by coating chitosan onto mesoporous silicas for large-scale carbon capture technology. Energy Technology. 2015; **3**(3):249-258

[117] Dassanayake RS et al. Preparation and adsorption properties of aerocellulose-derived activated carbon monoliths. Cellulose. 2016;**23**(2): 1363-1374

[118] Gunathilake C et al. Amidoxime-functionalized microcrystalline cellulose-mesoporous silica composites for carbon dioxide sorption at elevated temperatures. Journal of Materials Chemistry A. 2016;**4**(13):4808-4819

[119] Sehaqui H et al. Fast and reversible direct CO_2 capture from air onto all-polymer nanofibrillated cellulose—polyethylenimine foams. Environmental Science & Technology. 2015;**49**(5): 3167-3174

[120] Eftaiha AF et al. Chitin-acetate/DMSO as a supramolecular green CO_2-phile. RSC Advances. 2016;**6**(26): 22090-22093

[121] Fujiki J, Yogo K. The increased CO_2 adsorption performance of chitosan-derived activated carbons with nitrogen-doping. Chemical Communications. 2016;**52**(1):186-189

[122] Alhwaige AA, Ishida H, Qutubuddin S. Carbon aerogels with excellent CO_2 adsorption capacity synthesized from clay-reinforced biobased chitosan-polybenzoxazine nanocomposites. ACS Sustainable Chemistry & Engineering. 2016;**4**(3): 1286-1295