A Review on Green Porous Composites Made of Cellulose and Chitosan Derivatives for Water Treatment

Viet Thanh Tran, Luon Nguyen, Nga Nguyen Hoang Do, Phung Thi Kim Le*
Refinery and Petrochemical Technology Research Centre, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam
phungle@hcmut.edu.vn

Water pollution is one of the alarming issues with many common cases such as oil spills from oil tankers on the sea, and wastewater containing high levels of heavy metals and dyes, especially in the textile industry. These situations seriously affect the development of the water ecosystem and the health of the surrounding population, flora, and fauna. Recently, porous materials have been considered an effective solution in dealing with water problems because of their ability to absorb large amounts of pollutants when properly activated. In this study, we provide an overview of the porous composites made of cellulose and chitosan, which are the two huge resources in agricultural and fishery by-products in developing countries. The foams, hydrogel beads, membranes, and aerogels blending cellulose and chitosan, illustrate the efficient absorption of oils, solvents, dyes, and heavy metals in wastewater. This review introduces the status of the mentioned water pollution problems; the abundance of the two natural ingredients extracted from the bio-wastes; analysis and comparison of different methods to synthesize the cellulose/chitosan porous composites along with their physico-chemical characteristics. Finally, applications and a forward-looking view of the porous composites in water treatment are discussed to show a promising research direction in developing advanced and functional materials.

1. Introduction

Water may be an important role in facilitating life's basic activities. Through industrial, agricultural, and domestic activities, water pollution is more serious (Begum et al., 2021). The reality of water pollution has drawn the most attention from all countries, which primarily consists of oil spills, organic chemicals (dyes and detergents), fertilizer and pesticides, and inorganic chemicals like heavy metal ions (Wei et al., 2019). Many reports on the status of water pollution in many parts of the world have been published. For example, the heavy metal levels in various Chinese metropolitan regions are over World Health Organization (WHO) limits due to fast urbanization and industry (Li et al., 2015). Although many efforts have been performed, these levels still exceed the standard, especially the Three Gorges Reservoir (Wang et al., 2021). Oil-contaminated water is hazardous to aquatic and terrestrial living forms, as well as being unattractive and disagreeable in odor, and possibly destructive to human health and the economy, particularly the tourism sector (Liu et al., 2017). More than 7.3 M barrels of oil have been spilled in urban and industrial natural aquatic ecosystems, as well as natural and accidental maritime transit (Karatum et al., 2016). The hazardous effects of dye pollution are related to their degradability into carcinogetic amine compounds, while the dark color of dyes hinder to marine plants' photosynthetic activities (Vu et al., 2022). Methylene blue is a cationic dye causing poison at over-concentration (greater than 100 mg/kg), it is difficult to break down under normal conditions, and existing in water can be harmful to living species and human health (Phuong et al., 2021). The efficient methods for removing oils, heavy metals, and dyes from wastewater are critical.

Some of the general approaches are used such as physical adsorption, chemical treatment, in situ combustions, and biotechnology to deal with the oil spill (Yu et al., 2019). To remove the heavy metal ions from aqueous solutions, many methods such as ion exchange, reverse osmosis, membrane filtering, phytorextraction, traditional coagulation, precipitation, and electrochemical treatment have been applied. And removing the dye from effluent, different methods have been tried such as sonochemical treatment, electrochemical treatment, photocatalytic oxidation, and adsorption (Li et al., 2016). Among them, adsorption is the common method with
several benefits, including environment-friendliness, inexpensive processing costs, simple production processes, regeneration capabilities, and the ability to remove trace concentrations of contaminants (Ihsanullah et al., 2022).

Recently, porous materials such as foams, hydrogel beads, membranes, and aerogels have been reported as efficient adsorbents for wastewater treatment because of their unique properties including high specific surface area, high porosity, and lightweight (Ganjali et al., 2017). Porous materials could be made of both synthetic and natural sources to produce advanced products having individual characteristics. For synthetic sources, traditional polymers such as polystyrene (PS), polyurethane (PU), polyvinyl chloride (PVC), and polyolefin, are commonly employed as the matrix of porous materials for foaming (Zhang et al., 2020). Natural polysaccharides such as cellulose, chitin, starch, alginate, and pectin have received a lot of attention over the years because of the potential benefits of low cost, storage stability, non-toxicity, biocompatibility, and biodegradability. Cellulose and chitosan which are the most abundant raw materials in nature have been utilized to fabricate high-value engineering materials such as foams, hydrogel beads, membranes, and aerogels, exhibiting for adsorption pollutants. Due to the high mechanical properties, efficiently separates oil/water, but absorption capacity of dyes and heavy metal ions is rather poor, and inactive molecular structure limits applicability of cellulose. Chitosan has low mechanical strength and promotes acidic conditions, as well as chelating characteristics. The combination of cellulose and chitosan binding force to heavy metal ions with porous structure and chemical affinity of wet cellulose. These polysaccharides are regarded as great resources for sustainable development due to their natural abundance and cheap overall cost (García-González et al., 2011). In most cases, the materials are synthesized from either cellulose or chitosan associated with other reagents to enhance their adsorption capability. Cellulose acts as the supporting framework of the material while chitosan consists of numerous adsorption sites. Taking advantage of both cellulose and chitosan, the resulting porous composites show better efficiency in eliminating the pollutants, indicating the requirement to blend them. To the best of our knowledge, there has been no study reviewing the published works regarding the synthesis of advanced porous composites from cellulose and chitosan for water treatment. This review summarizes the characteristics and adsorption behaviour of different porous composites mainly fabricated from cellulose and chitosan to highlight their potential in dealing with contaminated water. Moreover, this study provides a comprehensive view of the efficiency of cellulose and chitosan combination in the synthesis of high-performance materials as well as research direction on solutions to enhance water treatment performance.

2. Different sources of cellulose and chitosan in nature

2.1 Cellulose

Cellulose is one of the common polysaccharides in nature, structures of β-d-glucose monomers are linked by 1,4-β-glycosidic bonds. With plenty of hydroxyl groups at the C2, C3, and C6 positions on the surface, there are hydrogen bonds between cellulose chains (Chen et al., 2021). In the form of microfibrils in the cell walls of the plant, algae tissues, and membrane of epidermal cells of tunicate, cellulose is also synthesized by bacteria with nanofiber networks. The properties of cellulose include superior mechanical properties (tensile strength of 300-1,240 MPa), low density (0.085 g/cm³), and biodegradability, while biomaterials with renewable, low-cost, and efficient adsorbents for wastewater treatment because of their unique properties including high specific surface area, high porosity, and lightweight (Ganjali et al., 2017). Porous materials could be made of both synthetic and natural sources to produce advanced products having individual characteristics. For synthetic sources, traditional polymers such as polystyrene (PS), polyurethane (PU), polyvinyl chloride (PVC), and polyolefin, are commonly employed as the matrix of porous materials for foaming (Zhang et al., 2020). Natural polysaccharides such as cellulose, chitin, starch, alginate, and pectin have received a lot of attention over the years because of the potential benefits of low cost, storage stability, non-toxicity, biocompatibility, and biodegradability. Cellulose and chitosan which are the most abundant raw materials in nature have been utilized to fabricate high-value engineering materials such as foams, hydrogel beads, membranes, and aerogels, exhibiting for adsorption pollutants. Due to the high mechanical properties, efficiently separates oil/water, but absorption capacity of dyes and heavy metal ions is rather poor, and inactive molecular structure limits applicability of cellulose. Chitosan has low mechanical strength and promotes acidic conditions, as well as chelating characteristics. The combination of cellulose and chitosan binding force to heavy metal ions with porous structure and chemical affinity of wet cellulose. These polysaccharides are regarded as great resources for sustainable development due to their natural abundance and cheap overall cost (García-González et al., 2011). In most cases, the materials are synthesized from either cellulose or chitosan associated with other reagents to enhance their adsorption capability. Cellulose acts as the supporting framework of the material while chitosan consists of numerous adsorption sites. Taking advantage of both cellulose and chitosan, the resulting porous composites show better efficiency in eliminating the pollutants, indicating the requirement to blend them. To the best of our knowledge, there has been no study reviewing the published works regarding the synthesis of advanced porous composites from cellulose and chitosan for water treatment. This review summarizes the characteristics and adsorption behaviour of different porous composites mainly fabricated from cellulose and chitosan to highlight their potential in dealing with contaminated water. Moreover, this study provides a comprehensive view of the efficiency of cellulose and chitosan combination in the synthesis of high-performance materials as well as research direction on solutions to enhance water treatment performance.

2.2 Chitin and chitosan

Chitin is one of the most naturally plenty biopolymers behind cellulose and it has been found in different sources such as crustaceans, fungi, insects, annelids, Mollusca, Coelenterata, etc. (Shepherd et al., 1997). The raw materials constitute approximately 20 – 30 % chitin, 20 – 40 % proteins, 30 – 60 % minerals, and nearly 14 % lipids (Begum et al., 2021). Chitin is an insoluble crystalline in water, common solvents that has limitations in commercial applications but its derivatives such as chitosan, chitoooligosaccharides, and glucosamine have solubility in diluted acid and modified biological properties. Chitosan is obtained by deacetylation partially N-acetyl glucosamine after the demineralization with HCl, deproteinization with NaOH, and decolorization on chitosan-based materials at 60 – 100 °C for 12 – 48 h. Recently, ionic liquid extraction has been utilized for chitin extraction to control the higher quality, which has a higher degree of acetylation along with no polymer
degradation. Minerals and proteins in raw materials must be removed in advance for chitin extraction (Li and Bai, 2005).

Because of its diverse biological activity, outstanding biocompatibility, and full biodegradability, in addition to its low toxicity, chitosan has been exploited as a one-of-a-kind polymer with a wide range of capabilities. Among them, the plenty of free amino groups in chitosan readily interact with a wide range of negatively charged surfaces and form water-insoluble complexes spontaneously. Chitosan is an adsorbent of pollutants for oils, dyes, and metals from wastewater (Zhang et al., 2021).

3. Porous composites from cellulose and chitosan

3.1 Foam composites

Foams are defined as porous materials with 50 % porosity in the structure and a diameter of pore more than 50 nm (Kim et al., 2018). Morphology of porous structure, especially the organization of pores, and physical parameters such as pore size, pore volume, and surface area affect significant adsorption ability of the foams (Andrieux et al., 2019). The high adsorption of cellulose/chitosan foam reaches 1,170.2 mg/g congo red compared to cellulose foam, which is at 623.2 mg/g (Kim et al., 2018). As seen in Table 1, cellulose and chitosan with different specifications such as degree of polymerization (DP), degree of deacetylation (DD), and fiber size were used as precursors. The foam composites could be developed by a facile preparation of nanofiber cellulose derived from trees and crab/shrimp shells-based chitosan via the sol-gel process (Wang et al., 2016). The other method was illustrated by solvent exchange (water → ethanol → t-butyl alcohol) and followed by freeze-drying to prepare foams (Kim et al., 2018). An advanced method of foam templating and microfluidics was performed to achieve a higher structural order of solid foam and adjust the bubble sizes. Briefly, the monodisperse chitosan/cellulose nanofiber foams are cross-linked by genipin to form a foam structure, that is afterward freeze-dried to receive monodisperse nanocomposite foams (Andrieux et al., 2019). Later, a foam gel material with a macroporous structure and a pore size ranging from 0 to 170 nm was fabricated by the physical foaming without a catalyst. Microcrystalline cellulose and chitosan are blended and sodium dodecyl sulfonate as a foaming agent to obtain foam gel (Zhao et al., 2020). Generally, foam composites from cellulose/chitosan are fabricated by uncomplicating methods without harmful waste, which possesses a high porous, lightweight, and good mechanic due to cellulose as a reinforcement.

<table>
<thead>
<tr>
<th>Specifications of cellulose</th>
<th>DD of chitosan (%)</th>
<th>Synthesis method</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Compressive modulus (kPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofiber (2 - 5 nm)</td>
<td>95</td>
<td>Sol-gel process</td>
<td>0.006-0.014</td>
<td>99.6-99.7</td>
<td>5 - 60</td>
<td>Wang et al. (2016)</td>
</tr>
<tr>
<td>Nanofiber (10 - 20 nm)</td>
<td>80</td>
<td>Solvent exchange</td>
<td>0.044-0.065</td>
<td>95-96.7</td>
<td>50 - 375</td>
<td>Kim et al. (2018)</td>
</tr>
<tr>
<td>Nanofiber (1.6 - 2.1 nm)</td>
<td>90.56</td>
<td>Foam templating and microfluidics</td>
<td>0.0115-0.0162</td>
<td>98.8-99.1</td>
<td>171 - 174</td>
<td>Andrieux et al. (2019)</td>
</tr>
</tbody>
</table>

3.2 Hydrogel bead composites

Hydrogel beads are a form of the gel prepared aimed to lower the degree of crystallinity to improve the adsorption capacity of chitosan. Cellulose/chitosan hydrogel beads have a low degree of crystallinity allowing the high heavy metal adsorption capacity to be achievable due to the positive affinity between the metal ions and amorphous regions of chitosan. The hydrogel beads can be regenerated and reused after accomplishing their mission in metal adsorption (Li and Bai, 2005). Because of the low mechanical strength and promoted acidic conditions of hydrogel beads, chemical cross-linking in the presence of cross-linking agents are used on the hydrogel bead surfaces to enhance their practical applications (Li et al., 2016). In the past, the beads were crosslinked by using glutaric dialdehyde (GA), ethylene glycol diglycidyl ether (EGDE), and epichlorohydrin (Li and Bai, 2005).

Extruding and regenerating method was commonly applied to synthesize the hydrogel beads as seen in Table 2. For example, the homogeneous mixture of cellulose and chitosan in ionic liquid 1-ethyl-3-methylimidazolium acetate was extruded from a syringe tip into a coagulating bath of absolute ethanol. The hydrogel beads obtained after that be used to remove dye pollution from wastewater (Li et al., 2016).
Table 2: Summary of hydrogel beads derived from cellulose and chitosan

<table>
<thead>
<tr>
<th>Specifications of cellulose</th>
<th>DD of chitosan (%)</th>
<th>Synthesis method</th>
<th>Dimension (mm)</th>
<th>Pore size (µm)</th>
<th>Specific surface area (m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose (20 µm)</td>
<td>85</td>
<td>Extruding and regenerating</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td>Li and Bai (2005)</td>
</tr>
<tr>
<td>Cellulose (filter paper)</td>
<td>90</td>
<td>Extruding and regenerating</td>
<td>3</td>
<td>0.01 - 0.02</td>
<td>2.28377</td>
<td>Li et al. (2016)</td>
</tr>
<tr>
<td>Cellulose (DP=1,100)</td>
<td>84</td>
<td>Extruding and regenerating</td>
<td>2-3</td>
<td>100 - 300</td>
<td>-</td>
<td>Twu et al. (2003)</td>
</tr>
</tbody>
</table>

3.3 Membrane composites

Membranes have been used for removing toxic substances in wastewater. The membranes could be fabricated from cellulose and chitin via the freezing/thawing method, using the NaOH/urea aqueous system (Tang et al., 2011). The fabrication of composite membranes resulted in a nanoporous structure with a thickness of 250 - 270 nm that could be further stabilized by crosslinking with glutaraldehyde vapours (Karim et al., 2014). The characteristic of membrane composites as seen as in Table 3. With the hardy interaction between cellulose and chitin/chitosan, the membranes with a microporous structure, a great surface area, and metal affinity, resulting in an excellent absorption capacity of heavy metal ions.

Table 3: Summary of membrane composites derived from cellulose and chitosan

<table>
<thead>
<tr>
<th>Specifications of cellulose</th>
<th>DD of chitin/chitosan (%)</th>
<th>Synthesis method</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
<th>Specific surface area (m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose (20 - 30 µm)</td>
<td>Chitin (97)</td>
<td>Freezing/thawing method</td>
<td>0.14</td>
<td>10 - 80</td>
<td>55</td>
<td>Tang et al. 2011</td>
</tr>
<tr>
<td>Cellulose nanocrystals (6 - 10 nm)</td>
<td>Chitosan (≥ 75.5)</td>
<td>Freeze drying</td>
<td>-</td>
<td>13 - 17</td>
<td>2.9 - 3.1</td>
<td>Karim et al. 2014</td>
</tr>
</tbody>
</table>

3.4 Aerogel composites

Aerogels are porous materials with a 3D network filled with a porosity of 95 %, lightweight (3 – 150 mg/cm³), low thermal conductivity, and large surface area (500 – 1,000 m²/g. The vegetable oil absorption capacity of cellulose nanofiber/chitosan-based aerogel is up to 253 g/g, more than three times of cellulose nanofiber aerogel at 87 g/g (Zhang et al., 2021). The common fabrication of aerogels is using the sol-gel method and freeze-drying, the process of co-dissolution and regeneration is also using an inorganic ionic liquid (solution of lithium bromide) (Liao and Pan, 2021). The specific properties of aerogels derivate form cellulose and chitosan are listed in Table 4 below.

Table 4: Summary of aerogel composites derived from cellulose and chitosan

<table>
<thead>
<tr>
<th>Specifications of cellulose</th>
<th>Specifications of chitosan</th>
<th>Synthesis method</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline (45.8 - 257 µm)</td>
<td>DD &gt; 75 %</td>
<td>Sol-gel process</td>
<td>0.05 - 0.11</td>
<td>62.30 - 80.34</td>
<td>Ozen et al., 2021</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Medium molecular weight</td>
<td>Co-dissolution and regeneration process</td>
<td>0.0211 - 0.0501</td>
<td>-</td>
<td>Liao and Pan, 2021</td>
</tr>
<tr>
<td>Nanofiber</td>
<td>DD &gt; 90 %</td>
<td>Sol-gel process</td>
<td>0.0084 &gt; 96</td>
<td>-</td>
<td>Zhang et al., 2021</td>
</tr>
<tr>
<td>Cellulose</td>
<td>DD 90 %</td>
<td>Sol-gel process</td>
<td>0.065 95</td>
<td>-</td>
<td>Meng et al., 2017</td>
</tr>
</tbody>
</table>

4. Applications of porous composites from cellulose and chitosan for wastewater treatment

The different adsorption capacities of porous composites are illustrated in Table 5. The oil absorption capacity of aerogels can reach 125 - 253 g/g attributed to the regular alignment of pores that can absorb rapidly and provide a large volume for repositing liquids (Zhang et al., 2021). Recently has proven its ability to clean oil spills thanks to its outstanding adsorption of nearly 40 times its weight (Ho et al., 2021). The adsorption of congo red (CR) as an anionic dye onto foam surface could approach to 1,170.2 mg/g attributed to the hydrogen bonding between the sulfonate groups (-SO3-) of CR and the hydroxyl groups (-OH) of cellulose, the amino (-NH₂) or azo (-N=N-) groups of CR and the acetal oxygens (C-O-C linking) of cellulose, and Van Der Waals interaction of ring structures between CR and cellulose molecules (Kim et al., 2018). The removal of heavy metal ions such
as Cu$^{2+}$, Pb$^{2+}$, and Hg$^{2+}$ from wastewater by porous composites can be up to 252.6 mg/g by chelating effect and the amino group performs as an electron-rich donor (Li and Bai, 2005).

Table 5: Adsorption capacity of porous composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>Oil/solvent</th>
<th>Heavy metal ions</th>
<th>Dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foam</td>
<td>-</td>
<td>-</td>
<td>1,170.2 mg/g (Congo red)</td>
</tr>
<tr>
<td>Hydrogel bead</td>
<td>-</td>
<td>53.2 mg/g (Cu$^{2+}$)</td>
<td>40 mg/g (Congo red)</td>
</tr>
<tr>
<td></td>
<td>Li and Bai, 2005</td>
<td>3.85 mmol/g (Hg$^{2+}$)</td>
<td>88 % (Victoria Blue 2B)</td>
</tr>
<tr>
<td>Membrane</td>
<td>-</td>
<td>2.44 mmol/g (Pb$^{2+}$)</td>
<td>13 %* (Rhodamine 6G)</td>
</tr>
<tr>
<td>Aerogel</td>
<td>7 - 10 g/g (mineral oil, petroleum ether, methylbenzene, hexane, cyclohexane)</td>
<td>252.6 mg/g (Pb$^{2+}$)</td>
<td>31.56 mg/g (methylene blue)</td>
</tr>
<tr>
<td></td>
<td>Meng et al., 2017, 125 - 253 g/g (motor oil)</td>
<td>Li et al., 2019</td>
<td>136.64 mg/g (methyl orange)</td>
</tr>
<tr>
<td></td>
<td>Zhang et al., 2021</td>
<td>2.0 mmol/g (Cu$^{2+}$)</td>
<td>48 % (Methyl Violet 2B)</td>
</tr>
</tbody>
</table>

* Percentage removal of Victoria Blue 2B, Methyl Violet 2B, Rhodamine 6G at 10 mg/L initial concentration.

5. Conclusions

A summary of the top concern about water pollution and effective solutions utilizing natural sources is presented to provide a highlighted potential of cellulose/chitosan porous composites. They are considered a kind of green material because of their excellent adsorption stability, eco-friendliness, biocompatibility, and biodegradability. The as-fabricated absorbents like foams, hydrogel beads, membranes, and aerogels can remove oils, heavy metals, and dyes from wastewater via the porous structure and hydrophobic surface, which is a result of the modification through silanization, and carbonization of cellulose. The high adsorption of chitosan according to an abundance of amino groups forms a negative charge surface. The combination of cellulose and chitosan enhances the properties of materials compared to individual ones.

Acknowledgments

We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

References


Li H., Li Y., Lee M.-K., Liu Z., Miao C., 2015, Spatiotemporal Analysis of Heavy Metal Water Pollution in Transitional China, Sustainability, 7(7), 9067-9087.

Li M., Wang Z., Li B., 2016, Adsorption behaviour of congo red by cellulose/chitosan hydrogel beads regenerated from ionic liquid, Desalination and Water Treatment, 57(36), 16970-16980.


Liao Y., Pan X., 2021, Self-indicating and high-capacity mesoporous aerogel-based biosorbert fabricated from cellulose and chitosan via co-dissolution and regeneration for removing formaldehyde from indoor air, Environmental Science: Nano, 8(5), 1283-1295.


Yu C., Lin W., Jiang J., Jing Z., Hong P., Li Y., 2019, Preparation of a porous superhydrophobic foam from waste plastic and its application for oil spill cleanup, RSC Advances, 9(65), 37759-37767.

