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# Emerging environmentally friendly bio-based nanocomposites for the efficient removal of dyes and micropollutants from wastewater by adsorption: a comprehensive review

 Wafa Al-Gethami,<sup>a</sup> Muhammad Azam Qamar,<sup>ID</sup> \*<sup>b</sup> Mohammad Shariq,<sup>\*c</sup> Abdel-Nasser M. A. Alaghaz,<sup>d</sup> Ahmad Farhan,<sup>ID</sup> <sup>e</sup> Ashwaq A. Areshi<sup>f</sup> and M. Hisham Alnasir<sup>g</sup>

Water scarcity will worsen due to population growth, urbanization, and climate change. Addressing this issue requires developing energy-efficient and cost-effective water purification technologies. One approach is to use biomass to make bio-based materials (BBMs) with valuable attributes. This aligns with the goal of environmental conservation and waste management. Furthermore, the use of biomass is advantageous because it is readily available, economical, and has minimal secondary environmental impact. Biomass materials are ideal for water purification because they are abundant and contain important functional groups like hydroxyl, carboxyl, and amino groups. Functional groups are important for modifying and absorbing contaminants in water. Single-sourced biomass has limitations such as weak mechanical strength, limited adsorption capacity, and chemical instability. Investing in research and development is crucial for the development of efficient methods to produce BBMs and establish suitable water purification application models. This review covers BBM production, modification, functionalization, and their applications in wastewater treatment. These applications include oil–water separation, membrane filtration, micropollutant removal, and organic pollutant elimination. This review explores the production processes and properties of BBMs from biopolymers, highlighting their potential for water treatment applications. Furthermore, this review discusses the future prospects and challenges of developing BBMs for water treatment and usage. Finally, this review highlights the importance of BBMs in solving water purification challenges and encourages innovative solutions in this field.

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## 1. Introduction

Rapid economic development and fast-growing industrialization have resulted in an increase in the volume of contaminants in the water supply from various processes, including electroplating, leather tanning, mining, paper, batteries, and pesticides.<sup>1</sup> Because of this, there is an urgent need for specialized materials and technology for both water recycling and waste

water treatment. The ideal properties of the material would be a high adsorption capacity, reusability, low cost, and the ability to adjust the porosity. With the ability to optimize different qualities, including mechanical strength, surface area, porosity, hydrophobicity, and dispersibility, bio-based materials are one of the potential possibilities made from diverse polymeric materials for water purification. Dyes, pharmaceutical wastes, heavy metals, and other pollutants have been accumulated in water sources in the last several years due to increased industrialization.<sup>2</sup> For example, the presence of lead (Pb(II)) ions in ponceau red, a synthetic red azo dye made from tar that causes hypersensitive allergic responses and led to the growth of colon, stomach, and rectal associated malignancies, has led to its classification as a possible human urine carcinogen. High concentrations of suspended particles, dyes, and chemicals, as well as a high chemical oxygen demand (COD), may be found in water bodies polluted by dye effluents. The textile industry uses more than 8000 chemicals in the development of 3600 dyes.<sup>3</sup> This is a severe threat to human health, as ingestion of dyes can have extremely carcinogenic or mutagenic effects.<sup>4</sup> Thus, before

<sup>a</sup>Chemistry Department, Faculty of Science, Taif University, Al-Hawiah, PO Box 11099, Taif City, Saudi Arabia

<sup>b</sup>Department of Chemistry, School of Science, University of Management and Technology, Lahore 54770, Pakistan. E-mail: qamariub@gmail.com

<sup>c</sup>Department of Physics, College of Science, Jazan University, Jazan 45142, Saudi Arabia

<sup>d</sup>Department of Chemistry, College of Science, Jazan University, Jazan 45142, Saudi Arabia

<sup>e</sup>Department of Chemistry, University of Agriculture Faisalabad, Faisalabad 38040, Pakistan

<sup>f</sup>Samtah General Hospital, Ministry of Health, Jazan, 86735, Saudi Arabia

<sup>g</sup>Department of Physics, RIPHAH International University, Islamabad, 44000, Pakistan



their disposal in any water bodies, the dyes and chemicals must be treated using extremely efficient adsorbent materials. Similarly, exposure to oil spills may cause irritation of the skin and eyes as well as neurological and respiratory issues. Although the long-term consequences of oil spills are unknown, it is nevertheless necessary to clean them up as soon as possible.<sup>5</sup>

As a result of the high demand for potable and industrial water, wastewater treatment has become an essential process in recent times. Complexation,<sup>6</sup> precipitation,<sup>7</sup> ion exchange,<sup>8</sup> advanced oxidation processes (AOPs),<sup>9</sup> membrane filtration,<sup>10</sup> reverse osmosis,<sup>11</sup> activated carbon adsorption,<sup>9</sup> ultraviolet (UV) photolysis/photocatalysis,<sup>12</sup> and electro dialysis<sup>13</sup> are all examples of conventional technologies used to treat wastewater. Clean water can be produced sustainably *via* wastewater processing and desalination.<sup>14</sup> Current research studies are focused on enhancing the existing wastewater purification systems, and creating new energy-efficient and cost-effective technologies. Protein nanofibrils,<sup>15,16</sup> covalent organic frameworks (COFs),<sup>17</sup> metal-organic frameworks (MOFs),<sup>18,19</sup> graphene,<sup>20</sup> carbon nanotubes,<sup>21</sup> fluorinated oligoamide nanorings and artificial water channels (AWCs)<sup>22,23</sup> are just some of the advanced materials used in water treatment. These materials, however, have significant production costs and complicated synthesis processes.

Owing to their abundance in the environment and use as a bio-source in the fabrication of bio-based nanofibers, biopolymers have recently attracted significant attention. They have unique properties, including being hydrophilic to avoid fouling, being mechanically and chemically stable, and being easily modifiable with chemicals. Biopolymers have been studied for their possible use in removing a wide variety of contaminants from water.<sup>24</sup> There has been a lot of research into various polymers for this purpose, including cellulose, chitosan, hemicellulose, polylactic acid, cellulosic biopolymer, and alginate.<sup>25</sup> Due to their biocompatibility, disinfection capability, non-toxicity, and adsorption behavior, chitosan and cellulose have received the greatest research attention as biopolymers for use in water purification processes, like membrane filtration, micropollutant removal, degradation of dyes and oil-water separation.<sup>26</sup>

BBMs offer many significant benefits over more traditional water treatment materials, such as metal oxides, activated carbon, clays, metal sulfides, carbon-based nanomaterials, zeolites and mesoporous silica.<sup>27,28</sup> BBMs have the following vital benefits: (i) naturally occurring in large amounts, (ii) able to selectively remove trace impurities like heavy metals, (iii) readily biodegradable, and (iv) inexpensive and efficient in terms of both power consumption and heat production. These qualities make them excellent candidates for use as water filtration materials and adsorbents.<sup>29</sup> Although bio-based materials have many benefits, they have a few problems that need to be addressed. The cost of BBMs cannot be brought down to a reasonable level for high-volume manufacturing because of the insufficient efficiency and effective exploitation of widely accessible inexpensive feedstocks, *i.e.*, lignocellulosic bio-based materials. The inherent features of the resulting BBMs need to be tailored to the target chemicals. However,

suitable production and modification procedures have not yet been discovered.<sup>30</sup> The nature of the contaminants, kinetics, and removal mechanism, the green synthesis techniques of BBMs and their efficient and effective applications, and bio-material recyclability are all important concepts and criteria for studying these materials.<sup>31–34</sup>

Bio-based nanomaterials like chitosan, cellulose, and other plant-based nanofibers are discussed in this study as potential solutions for the remediation of various pollutants such as dyes, heavy metals, pharmaceutical toxins and organic pollutants. Micropollutants may be removed using a variety of traditional techniques, *i.e.*, adsorption, membrane filtering, coagulation, ion exchange, flocculation, and chemical precipitation. Electrospinning, chemical modification and phase inversion are one of the many processes for generating natural nanofibers, and it has the benefits of being cost-effective, highly reproducible, and efficient.<sup>35</sup> Functionalization of plant-based materials with other groups results in enhanced properties, which is comprehensively discussed. Therefore, we conduct an in-depth evaluation of the many bio-based materials currently on the market, as well as bio-based nanofibers made by various manufacturing techniques, surface changes, and adsorption behavior for use in water purification. In this review, we have provided an overview of the capabilities and structural features of BBMs. In order to remove diverse contaminants from water systems, this article discusses the construction and modification procedures of BBMs to permit distinct chemical and physical features. The most recent developments in the design of BBMs for use in water purification are highlighted in this article. The reason for using BBMs is comprehensively evaluated. The impact of various functionalizations on the water purification process is also the main focus of this review. In conclusion, we review the key ideas and obstacles encountered while working to improve the BBMs with superior water treatment capabilities. Our study not only adds to the growing body of knowledge on BBMs, but also serves as a comprehensive theoretical foundation upon which to build more sophisticated BBMs.

## 2. Polysaccharides as a precursor of biomaterials

The harmful effects of using fossil fuels and petrochemicals are increasingly becoming a growing concern. It is predicted that by 2050, synthetic polymers will be manufactured using 20% of all fossil fuels.<sup>27,36,37</sup> Therefore, it is critical to discover replacements for petroleum-based goods, moving from hydrocarbon energy to a more desirable renewable fuel. Fossil-based materials, often acquired through environmentally deteriorating processes, might be replaced with bio-based feedstock. Biopolymers may be made from renewable resources in three different ways:

- (1) Through fractionation and extraction, as with cellulose, starch, lignin, protein, chitin, and sodium alginate.<sup>38</sup>
- (2) Polymerization of bio-monomers derived from renewable biomass sources, as with polylactic acid.<sup>39</sup>



(3) Through direct production by microorganisms, as with polyhydroxyalkanoates (PHAs).<sup>40</sup>

Different hydroxyl, carboxyl, amino, acetal, and ester functional groups in these biopolymers allow for various chemical and physical properties in bio-based materials (Fig. 1).<sup>41</sup> BBMs have shown promising commercial applications in water treatment in recent years after being developed into a wide range of products, including fibers, membranes, hydrogels, foams, particles, and powders, *via* various modification and fabrication routes.

## 2.1 Lignin

Naturally occurring lignin is a complicated heterogeneous biopolymer made up of 3 different kinds of monomeric phenolic substructures, syringyl (S) units, guaiacyl (G) units, and *p*-hydroxyphenyl (H) units, that originate from coniferyl alcohol, coumaryl alcohol, sinapyle alcohol, and monolignols.<sup>42</sup> Several different forms of ether linkages and carbon-carbon bonds, including biphenyl (5-5'), aryl ether (-O-4'), phenylcoumaran (-5'), and resinol, are used to randomly join the three subunits during biosynthesis. S and G units, together with less H units, make up the bulk of hardwood lignin, whereas G units make up the vast majority (92–95%) of softwood lignin. All three components are grass lignin. The chemical and physical properties of lignin, *i.e.*, its reactivity, functionality, and hydrophilicity, are analyzed by the presence of different functional molecules within the macromolecules of lignin, including phenolic and aliphatic hydroxyls, carbonyl, methoxyl groups, and carboxylic.<sup>43–46</sup>

As an alternative to costly commercial sorbents, lignin-based biosorbents have been recently created using crosslinking, grafting, copolymerization, and hybridization modification procedures. Gao *et al.*<sup>47</sup> devised and produced a variety of lignin-based adsorbents that used lignin as grafted and essential poly(acrylic acid) (PAA) as the tentacles. Better adsorption selectivity correlates with a larger PAA branched chain distribution density, as predicted by a binary non-linear model based on Pearson correlation analysis and phenomenological theory. Theoretical and fundamental advice for creating and designing innovative high-efficiency lignin-based biosorbents is provided, with improved structural connections of graft-modified surface

adsorbents in binary pollutants. Using cyanuric chloride as a chemoselective crosslinker, lignin was chemically bonded to amine-functionalized magnetic nanoparticles.<sup>48</sup> Good selectivity of Pb(II), regeneration, and outstanding stability characterizes the lignin-based adsorbent synthesized using a temperature-controlled synthetic approach. Lignin-based magnetic materials have the ability to be used as cheap and ecological adsorbents in water decontamination due to their efficient removal and quick recovery capabilities. A nano-trap made of a bendable lignin-based material was developed to sequester metal ions ( $M^+$ ) and inhibit bacteria growth. The lignin-based nano-trap (LBNT) was effective because of the robust  $M^+$  binding on the surface of the functionalized lignin. Interestingly, Ag loaded with LBNTs was employed as a novel antimicrobial material, and it showed extraordinary efficacy against *E. coli* and *S. aureus* (99.68% and 99.76%, respectively).<sup>48,49</sup> To get rid of the As(v) in the water, lignin was treated with triethylenetetramine (TETA) using the Mannich procedure. The As(v) adsorption capacity was best for activated lignin at 25 °C and 9.0 pH, with As(v) > Cr(vi) > P being the order of selectivity (v). Biosorbents made from lignin show promise for widespread use in the industry.<sup>50,51</sup>

## 2.2. Cellulose

Cellulose is primarily made from lignocellulosic biomass, which is the most common and widespread source of cellulose in nature. The linear biopolymer comprises  $\beta$ -D-glucopyranose units connected by  $\beta$ -1,4 glucosidic linkages. The cellulose degree of polymerization (DP) ranges from around 100 to over 10 000, depending on the plant type.<sup>52</sup> An anhydroglucose cellulose unit has three hydroxyl groups (-OH), one each at carbons 2, 3, and 6. These OH<sup>-</sup> groups establish intra- and intermolecular hydrogen bonds inside the macromolecules, giving them their stiffness and crystallinity. For cellulose to be effective as a biosorbent, it must be in its most basic form, both small and porous, with plenty of active binding sites.<sup>53</sup> Because of the abundance of OH<sup>-</sup> groups, cellulose has been the subject of extensive study.<sup>54–58</sup>

There are two primary classes of cellulose modification techniques. Sulfation,<sup>59</sup> etherification,<sup>60</sup> carbanilation,<sup>61</sup> silylation,<sup>62</sup> esterification,<sup>63</sup> and amination<sup>64</sup> are all examples of

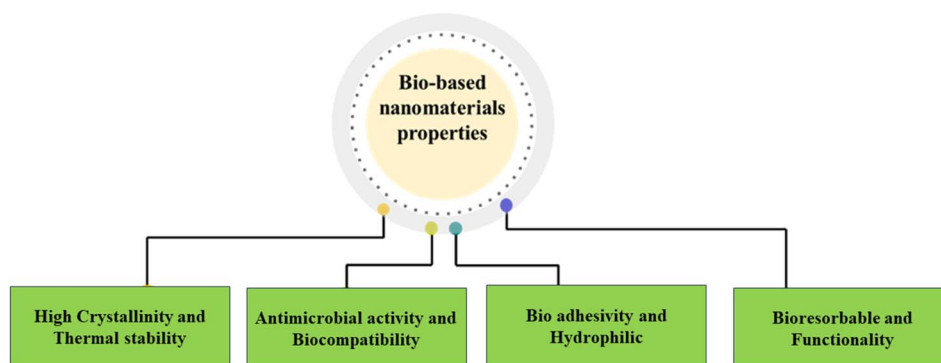


Fig. 1 Fundamental physicochemical characteristics of bio-based materials.



functional groups that are linked directly to the OH radical of cellulose molecules, a process known as a direct modification. The other class contains free radical polymerization, ring-opening polymerization, and controlled radical polymerizations to graft monomers onto cellulose chains in homogeneous and heterogeneous solutions.<sup>65</sup> The cellulose components that undergo these modifications significantly aid water decontamination and the elimination of harmful organic and metal chemicals.<sup>66</sup>

As a consequence of their high aspect ratio, high hydrophilicity, low density, and remarkable mechanical properties, natural cellulose-based resources such as wood and cotton-generated cellulose nanocrystals (CNCs) are good nanostructures in membrane processes for ecological sciences and environmental engineering fields. Boosting the antifouling capabilities of CNCs membranes is made easier by removing cellulose at the nanoscale, eliminating major flaws related to the layered structures. Thin film composite nanofiltration membranes made from CNCs were developed by Huang *et al.* for increased water flow and chlorine resistance.<sup>67</sup> A significant improvement in salt removal of  $\text{MgSO}_4$  (96.1%) and  $\text{Na}_2\text{SO}_4$  (98.3%) and water penetration flow ( $106.9 \text{ L m}^{-2} \text{ h}^{-1}$ ) was seen in CNCs thin film composite (TFC) membranes compared to TFC membranes without CNCs. Bai *et al.*<sup>68</sup> inserted cellulose nanocrystals into a polyamide (PA) layer while manufacturing a TFC membrane to improve antifouling and separation performance (Fig. 2a). Compared to PA TFC without CNCs, the penetration of synthesized CNC-TFC membranes was 60.0% greater with just 0.02 wt% CNCs. Because of their exceptional hydrophilicity and permeability, CNC-TFC membranes show promising desalination and purifying applications for water. CNCs membranes offer more fouling resistance and recovery capabilities than commercial membranes (Fig. 2b).

### 2.3. Chitosan

Partial deacetylation of chitin is the principal source of chitosan, the only naturally occurring cationic polysaccharides. The hydroxyl group and free amino on the CS chains achieve an effective chelation effect or electrostatic adsorption of anionic organic and metal ion contaminants. Chitosan-based materials

display various limitations that prevent their broad use in water treatment, including acidic solubility, poor mechanical strength, and insufficient absorption capacity, despite their major benefits in adsorbents.<sup>69</sup>

Crosslinking, grafting, carboxymethylation, and acetylation are just a few chemical modifications used during the last several decades to boost adsorption capacity and chemical stability. A water purification strategy using a heterostructure chitosan multilayer membrane by layer-by-layer self-assembly design route was modeled after the layered structure of wood. The sieve effect, hydrophobic and strong van der Waals forces effect shown by the biomimetic membrane provided the required removal of diverse contaminants. Meanwhile, this multilayer membrane has demonstrated great durability under constant use and high recycling rates when getting rid of oil droplets.<sup>70</sup> The adsorption capacity of Chitosan (CS)-based adsorbents for industrial dyes and heavy metal ions has been improved by incorporating different nanoparticles into CS matrices, which has increased their specific surface areas. By combining electrospraying and freeze-casting, radially-oriented microchannel and honeycomb-cobweb designs were used to construct graphene oxide-aerogel microspheres by Yu *et al.* Higher adsorption capacities of the aerogel for the anionic dyes eosin Y and rhodamine B, the cationic dyes methylene blue and methyl orange (MB), and micropollutants result from the creation of a variety of interactions between the contaminants, including complexation, conjugation, coordination and chelation.<sup>71</sup> The developed CS-based nanofiber membrane has a penetration flux of  $1533.26 \text{ L m}^{-2} \text{ h}^{-1}$ , and can efficiently filter out dyes and heavy metals from pure water. Green chemistry and sustainable development are supported by the fact that no VOCs were utilized to manufacture the nanofiber membrane. The research might lead to a more efficient and cost-effective method for creating high-tech membranes for water filtration in the near future.

### 2.4 Starch

Starch is an adaptable and common natural polymer that has gained a lot of interest as a potentially useful ingredient in the pharmaceutical, nutritional, and chemical industries. Starch

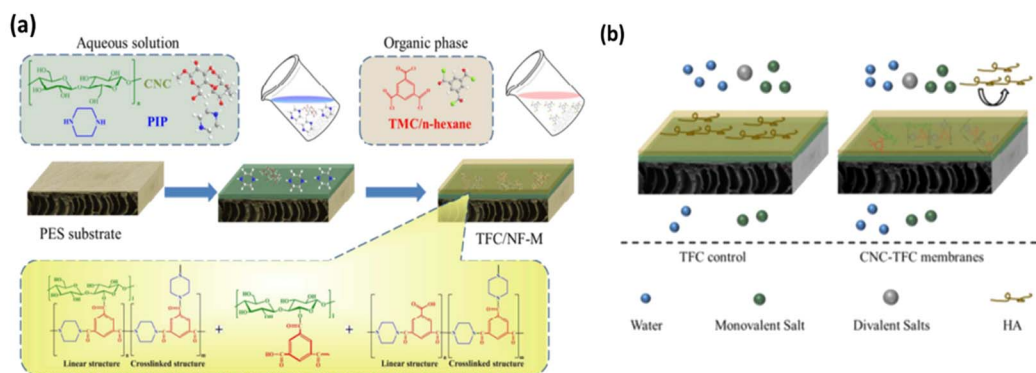


Fig. 2 (a) Synthetic scheme of the CNC-TFC membrane. (b) Adsorption mechanism of CNC-TFC membranes for metal ions. Reproduced with permission.<sup>68</sup> Copyright (2018), ACS.



has two different types of polysaccharides, amylopectin and amylose.<sup>72</sup> Twenty to thirty percent of starch is amylose, which is insoluble in water and consists of a linear chain of D-glucose components with  $\alpha$ -1,6 glycosidic linkages (1%) and 1.4 glycosidic connections (99%). Amylopectin is mostly composed of a branching chain of D-glucose components joined by  $\alpha$ -1,4 glycosidic connections (70–80%) and  $\alpha$ -1,6 glycosidic linkages (20–50%). Amylopectin is two to three times as large as amylose, with a molecular weight of 1–2 million daltons.<sup>73,74</sup> Amylopectin is actually the water-soluble component of starch, which makes up around 80% of starch.<sup>75</sup> Starch has many benefits, including its biocompatibility, low cost, availability, and biodegradability. Nevertheless, natural starch has low adsorption capacity because it lacks necessary functional groups like carboxyl, amino, or ester. Chemical techniques such as crosslinking, grafting, oxidation, irradiation, and esterification have been used to alter starch and enhance its utility beyond these parameters.<sup>76</sup> The ability of this hydrogel to soak up anionic and cationic dyes suggests it might be used in wastewater treatment. By reacting starch with (3-chloro-2-hydroxypropyl trimethyl) ammonium chloride, cationic starch-containing ammonium groups were formed, which were then used to make starch-based nanocomposites for cationic dyes adsorption.<sup>77</sup> The produced quaternary starch has the ability to absorb the nitrate group from wastewater with a maximum adsorption capacity of 205 mg g<sup>-1</sup>. This effect was sustained at 78.5% after eight sorption-desorption cycles. There are several studies on removing heavy metals and dyes using modified starch, but far less research on the removal of ammonia and phenol. New methods of modifying starch with a high affinity for these poisonous chemicals need to be investigated in future studies.<sup>78</sup>

## 2.5 Alginate

Natural polysaccharide alginate is harvested from brown seaweeds and is a sustainable resource of bio-based materials. It is composed of  $\alpha$ -L-guluronic acid (S unit) and  $\beta$ -D-mannuronic acid (M Unit) in the form of heteropolymeric (GMGMGMGM blocks) and homopolymeric (GGGG or MMMM blocks) sequences, respectively. As a polymer, alginate has many carboxyl and hydroxyl groups, giving it a high affinity for radionuclides and metals.<sup>79</sup> However, scientists are very interested in learning more about synthesizing alginate derivatives *via* surface functionalization to advance their stability and mechanical strength for use in environmentally friendly applications. In most cases, you can functionalize alginate in one of two ways.<sup>80</sup> One method involves chemical functionalization, whereby covalent connections are formed between alginate and functional groups *via* processes, *i.e.*, oxidation, esterification, copolymerization, amination, and phosphorylation. Alginate may also be physically functionalized *via* ionic crosslinking or blending, which generates relatively weak interactions, *i.e.*, hydrogen bonds, electrostatic contacts, van der Waals forces, and coordination bonds.<sup>81</sup> As a means of increasing the adsorption capacity of U(VI) ions and enhancing the material's mechanical, thermal, and radiation resistance, Khajavi *et al.*<sup>82</sup> utilized crosslinking and grafting procedures to effectively

construct the new amidoximated modified calcium alginate beads with entrapped functionalized SiO<sub>2</sub> nanoparticles for the removal of U(VI) ions from aqueous solutions (Fig. 3a). To improve the mechanical, thermal, and radiative resistance of alginate and the uranium adsorption capacity, we have introduced modified SiO<sub>2</sub> nanoparticles with a -SH group into the calcium-alginate gel beads for the first time. Adsorption capability of U(VI) ions onto the produced beads was studied as a function of SiO<sub>2</sub> (Fig. 3b) and TMPTMS (Fig. 3c) weight percentages. At 5 weight percent SiO<sub>2</sub> and 30 weight percent TMPTMS (relative to the alginate weight), the alginate/SiO<sub>2</sub>/TMPTMS/PAO beads had 3.6 times the adsorption capacity of the blank one (alginate/PAO) for U(VI) ions. The findings demonstrated that U(VI) ions may be effectively removed from aqueous solutions by using a composite adsorbent composed of alginate, SiO<sub>2</sub>, TMPTMS, and PAO. Nanoparticles, in addition to SiO<sub>2</sub>, may be used to raise the alginate resistance, and various functional groups, in addition to amidoxime and -SH, can be used to boost the adsorption capacity of uranium ions, all of which can contribute to future progress in the field of uranium removal from aqueous solutions.

To create a dispersive magnetic solid-phase extraction adsorbent, Orachorn *et al.*<sup>83</sup> integrated metal-organic frameworks (MOFs), graphene oxide (GO<sub>x</sub>), and iron oxide (Fe<sub>3</sub>O<sub>4</sub>) into alginate fiber. Hydrogen bonding and hydrophobic interactions facilitated by combining GO<sub>x</sub> with MOF improved the phthalate ester extraction. Ca<sup>2+</sup> is the most common cation employed during the alginate hydrogel synthesis. Ca<sup>2+</sup> forms a three-dimensional network with the G-block regions through coordinated interactions. By constructing FeCl<sub>3</sub>-activated seaweed carbon and then crosslinking with calcium chloride,<sup>84</sup> researchers were able to produce an alginate hydrogel composite for the effective removal of blue (BB) dye, plasticizer, and bisphenol A (BPA). These studies show that alginate may be used as a long-term absorbent to filter out pollutants in industrial wastewater, which has motivated scientists to investigate this polymer further to evaluate its efficiency.

## 2.6 Gelatin

Collagen is an important protein found in many different types of biological connective tissue, including bone, cartilage, skin, and tendon. Its partial hydrolysis yields the water-soluble biopolymer known as gelatin. Gelatin has many functional groups (*i.e.*, COOH, <sup>-</sup>NH<sub>2</sub>, and <sup>-</sup>OH) in its structure, which might operate as binding points to adsorb contaminants in wastewater channels through ionic or polar interactions. Nevertheless, the limited application of gelatin is due to its limitations, such as its quick degradation and low mechanical strength in moist environments. Therefore, nanomaterials (CNT, Fe<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, and TiO<sub>2</sub>) may improve the material, degradation rate and mechanical stability. Moreover, chemical modification was used to create constituents with high elimination efficiency of pollutants from contaminated water by putting different functional groups onto the gelation molecular chains.<sup>85</sup>



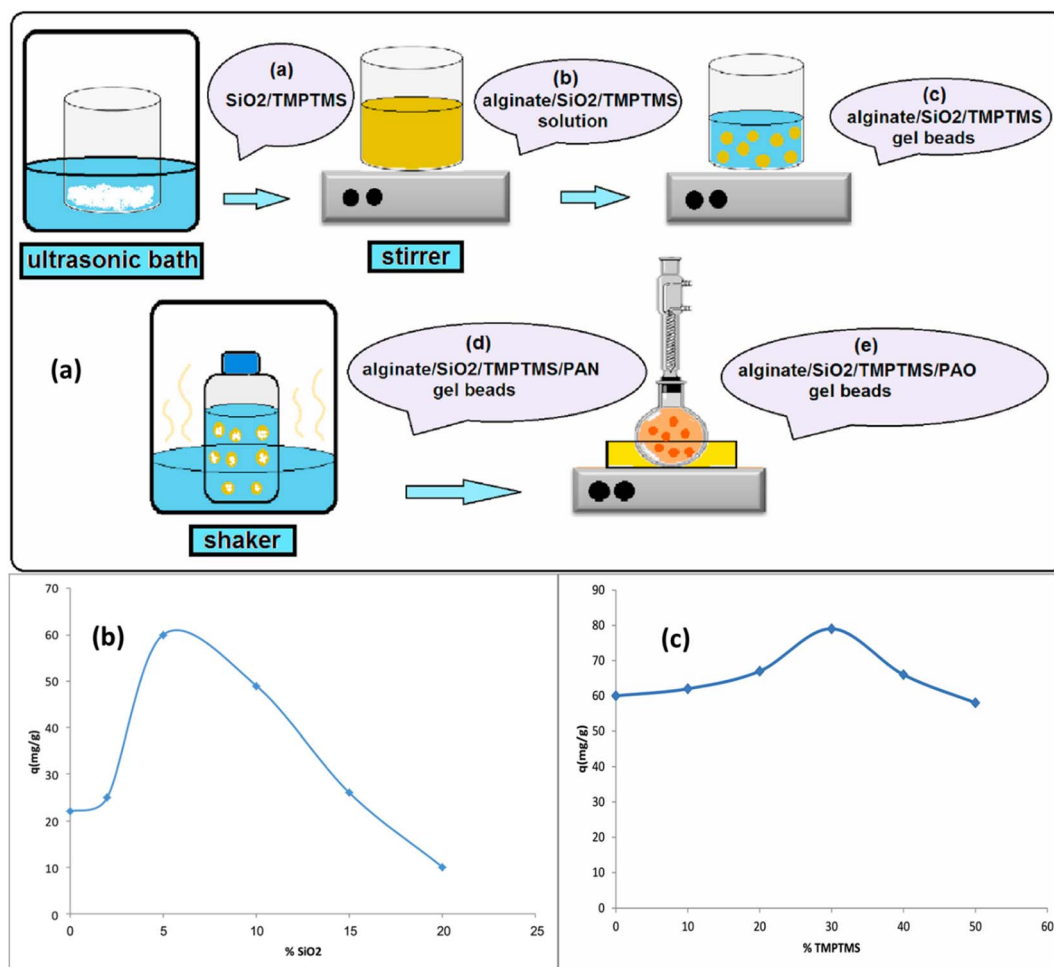


Fig. 3 (a) The adsorbent (alginate/SiO<sub>2</sub>/3-mercaptopropyltrimethoxysilane/amidoxime) fabrication scheme (a–e). (b) The adsorption of U(VI) ions at pH 4 with an initial uranium solution concentration of 120 mg L<sup>-1</sup> and an adsorbent dose of 1 g L<sup>-1</sup> is affected by the SiO<sub>2</sub> content of alginate/SiO<sub>2</sub>/PAO beads. (c) The adsorption of U(VI) ions at pH 4 with an initial uranium solution concentration of 120 mg L<sup>-1</sup> and adsorbent dose of 1 g L<sup>-1</sup> was affected by the amount of TMPTMS present in the alginate/5% SiO<sub>2</sub>/TMPTMS/PAO mixture. Reproduced with permission.<sup>82</sup> Copyright (2021), Elsevier.

Ethylene glycol di-glycidyl ether has been used to manufacture xylan and gelatin-based hydrogels. Good methylene blue adsorption and shear thinning behavior were observed, and the gel was stable under high strain and temperature variations without losing its crosslinked structure (MB). To remove anionic and cationic dyes from an aqueous medium, magnetic nanoparticles of iron oxide and multi-walled carbon nanotubes were treated with carboxylic acid to create a novel adsorbent developed by Samaneh *et al.*<sup>86</sup> A hybrid composite of amine-grafted magnetic gelatin has been produced by Kumar *et al.* that can efficiently remove phosphate (PO<sub>4</sub><sup>3-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) from wastewater. The gelatin hybrid composite interacted with NO<sub>3</sub><sup>-</sup>/PO<sub>4</sub><sup>3-</sup> through electrostatic attraction and a surface complexation process.<sup>87</sup> By combining TiO<sub>2</sub> mixing, polyethyleneimine (PEI) crosslinking, and freeze-drying, Jiang *et al.* developed a multipurpose organic-inorganic composite aerogel based on gelatin. Because of their super amphiphilic surface and hierarchical porous structure, the resultant aerogels showed remarkable selectivity for oil/water separation in

both aqueous and O/W combinations.<sup>88</sup> Adsorbent composites based on gelation show significant potential for use in water purification. Gelation composites with high mechanical strength are thus being developed by scientists for applications, such as the adsorptive elimination of multi-component and pharmaceutical solutions.

## 2.7 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs), a type of hydrophobic aliphatic polyester manufactured by microbes, have material qualities similar to those of typical plastic goods while providing improved biocompatibility and biodegradability. Since PHAs may be entirely decomposed into innocuous compounds in their natural environment, they are important emerging biopolymers to replace traditional petrochemical plastics. Two distinct classes of PHAs have been discovered: short-chain PHAs (with three to five C-atoms in the monomer) and medium-length PHAs (with 6 to 14 C-atoms in the monomers).<sup>89</sup> Changing the feed, the strain, and the fermentation process



allows for simple manipulation of the PHA composition. This structural variety makes PHA useful for various applications since they may be rigid bodies or elastomers, two classes of biomaterials currently unavailable.<sup>90</sup>

Mannina *et al.*<sup>91</sup> presented a new procedure for removing polyhydroxyalkanoates from a contaminated mixed microbial culture to improve the economic and environmental sustainability in wastewater treatment. The underlying premise that scaling up the process from a laboratory to a large-scale ability within the plant might make (mixed microbial cultures) MMC-PHA manufacturing economically and ecologically viable has led to the expansion of the process from the laboratory to the pilot-scale facility. The pilot-scale production of PHAs as final high-value bio-based material yields from municipal solid waste (MSW) and sewage sludge mixes was studied by Valentino *et al.*<sup>92</sup> utilizing a three-step MMC method. This method streamlines the conversion of municipal bio-waste to PHAs using a single basic technology. It significantly reduces the waste that must be disposed of in the end. Samori *et al.*<sup>93</sup> used a combined thermochemical and biotransformation process to extract PHAs and crotonic acid from anaerobically digested sludge, maximizing the sludge's content and chemical energy utilization.

Through a transdisciplinary four-step process (Fig. 4a), the potential of this waste to be used as feedstock for the coproduction of biopolymers and platform chemicals has been evaluated by combining two “tool-boxes,” one based on thermochemical treatments and the other on biological conversions. Fig. 4b shows the microbial fermentation microscale laboratory experiment design. The feedstock's (then its COD's) chemical energy must be transformed into a particular

class of organics, namely VFA, excellent substrates for MMC growth/adaptation during feast and famine cycles, in order to exploit the MMC system for PHA generation. Fig. 4c shows the acidogenic fermentation experiments performed on HTC<sub>ap</sub> obtained at 150, 200, and 250 °C using the same ADSS as the acidogenic inoculum. To measure the HTC fermentation's durability over time, a larger-scale semicontinuous test was conducted. The test was conducted on HTC slurry created at 200 °C without any solid-liquid separation (Fig. 4d), which was chosen to maximize the VFA yield and process dependability (less severe conditions are simpler to accomplish and cost less energy). The approach is to reduce the waste volumes and eliminate material and energy losses by managing the anaerobically digested sewage sludge to acquire high-value-added commodities and chemicals. High manufacturing costs are now the biggest barrier to the mass production and broad use of PHAs. Thus, it is important to investigate other low-cost and readily accessible raw materials for PHAs synthesis. Second, PHAs need to have their qualities, such as machinability and hydrophilicity, increased to fulfill the demands of various applications.

## 2.8 Polylactic acid

Starch feedstock from natural bio-based resources like cassava, corn, and sugarcane is the primary source for the commercially promising biopolymer polylactic acid (PLA). High-purity lactic acid (LA) is produced by microbial fermentation.<sup>94</sup> Lactic acid is a starting material for the chemical synthesis of polylactic acid (PLA) of a predetermined molecular weight from abundant and renewable raw materials like starch. Moreover, PLA is produced

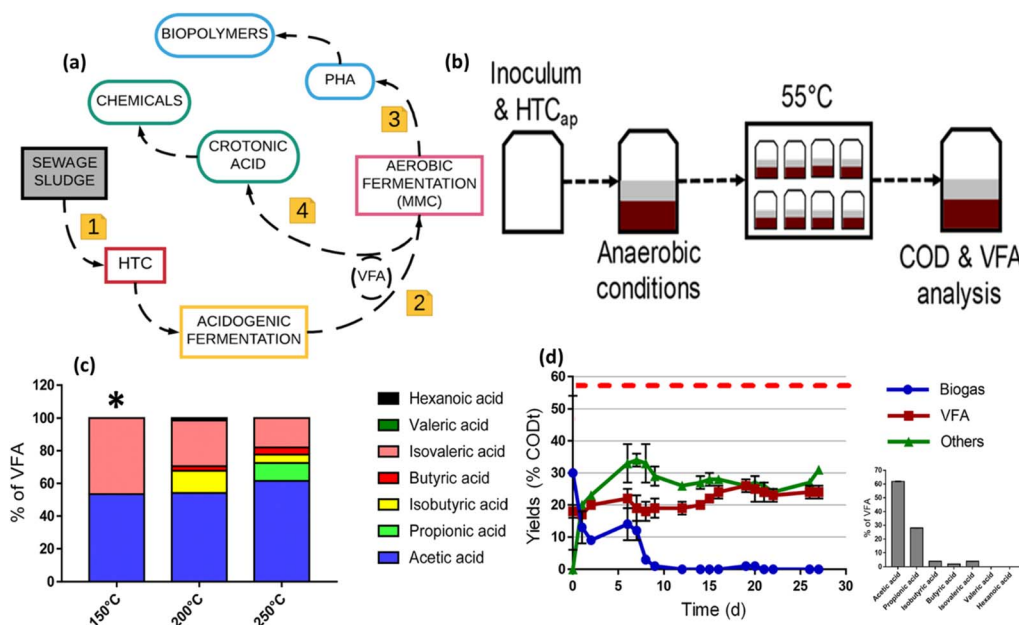


Fig. 4 (a) From wastewater sludge to biopolymers and platform chemicals: a transdisciplinary four-step process. (b) Acidogenic microbial fermentation microscale laboratory test depiction. (c) After fermenting HTC<sub>ap</sub> at 150, 200, and 250 °C for 60 minutes, the relative VFA content (percent). (d) Anaerobic fermentation in semicontinuous test yields of biogas, VFA, and other fermentable compounds (percent, based on total COD, CODt). Reproduced with permission from<sup>93</sup> Copyright (2019), ACS.



in a zero-waste manner and can be broken down entirely by microorganisms in the natural environment after its use, effectively recycling itself in the process.<sup>95,96</sup>

Numerous methods are available today for porous PLA, including foaming, electrospinning, freeze drying, thermally induced phase separation, and 3D printing. Using *in situ* oxidative polymerization, researchers have synthesized PLA electrospun nanofibers covered with chloride-doped polyaniline. Weak electrostatic interactions between the adsorbent and adsorbate was facilitated by combination of the conductive polyaniline (PANI) coating with the porous PLA, leading to good adsorption characteristics of the membranes.<sup>97</sup> Preparing porous PLA materials presents several challenges that include finding the optimal solvent and process parameters and preventing the porous structure from collapsing, which would lead to shrinkage and cracking. Drying porous materials with supercritical carbon dioxide prevents shrinkage and fragmentation, allowing the materials' high open porosity and original structure to be preserved. Supercritical CO<sub>2</sub> drying can produce porous PLA materials with a permeability of up to 73%, which is ideal for treating wastewater efficiently. The structure and morphology of PLA can be adjusted depending on the drying and solvent method.<sup>118</sup> Although PLA materials are used in various wastewater applications, most current research focuses on oily and colored wastewater treatment. Future studies will concentrate on developing highly porous PLA materials for disinfecting water tainted with chemicals like pesticides, surfactants, and bacteria.

## 2.9 Pectin

Pectin is a linear polysaccharide that occurs naturally, and may be obtained from the cell walls of higher plants. It is important because of its flexible, biocompatible, high-molecular weight, nontoxic, and anionic nature. Most plant cells include pectin in the intercellular layer between their major cell walls. Pectin has seen increasing interest in recent years due to its potential uses in the healthcare and biotechnology sectors, among others. Like many other complex polysaccharides, the composition of pectin varies depending on its source and the isolation conditions used. Pectin is mostly composed of chains of d-galacturonic acid molecules connected by a  $-(1\rightarrow4)$  glycosidic bond, with some neutral sugars present along the side chains.<sup>98</sup> Certain COOH groups occur naturally as methyl esters, whereas other may react with NH<sub>3</sub> to make carboxamide groups. They form complexes with metal ions in solutions, and reduce them to metallic nanoparticles without the use of dangerous reducing/stabilizing chemicals.

Palladium nanoparticles were stabilized on polysaccharide materials including Pd/gelatin, Pd/chitosan, and Pd/starch as the easiest greener ways for the synthesis of organically recyclable Pd nanocatalysts. Because of its versatility, which is achieved by the hybrid inclusion of both organic and inorganic nanocomposites, there is a great deal of interest in these materials.<sup>99</sup> Because of its great temperature durability, strong covalent bonding, and highly active surface area, the agar/pectin composite was developed as a stabilizer. Subsequently,

under safer, environmentally preferable circumstances, palladium nanoparticles were produced by *in situ* reduction of palladium ions and immobilized on a membrane surface. The biopolymer composites demonstrated catalytic activity in reduction processes, suggesting their potential use as stabilizers for a wide range of noble metallic NPs. 1,2-Benzenediamine was produced by reduction of *O*-nitroaniline, and recycling tests showed a drop in reaction yield from 100% to 83% after eight cycles of using the nanocomposite. Hybrid pectin/titanium oxide nanobeads were created by Bok-Badura *et al.*, and utilized as an effective nano-adsorbent for the elimination of ionic heavy metals. This study investigated the impact of pH on the adsorption behavior of copper, cadmium, zinc, and lead ions within different pH ranges. Specifically, pH levels ranging from 1 to 5 were considered for Cu(II) and Pb(II), pH levels ranging from 1 to 6 were considered for Cd(II), and pH levels ranging from 1 to 7 were considered for Zn(II). These hybrid nanobeads were capable of binding 0.83 mmol g<sup>-1</sup> of Pb<sup>2+</sup> and 0.68 mmol g<sup>-1</sup> of Cu<sup>2+</sup>.<sup>100</sup>

## 2.10 Agarose

Red algae produce agarose, 3,6-anhydrous- $\alpha$ -D-galactose, and a linear polymer made up of D-galactose. It may create hydrogen bonds with hydrogen atoms already present in its structure, or with water molecules because of the presence of several hydroxyl groups distributed throughout the structural unit.<sup>101</sup> Typically, the molecular weight is between 80 and 140 kilodaltons. Hydrogels made from agarose have the potential to be controlled, stable, and hysteretic.<sup>102</sup> The outcome is a translucent solution formed when the agarose molecules disperse into the surrounding water medium and assume a random coil shape. A tightly organized gel structure typified by a double helix shape is formed at temperatures between 30 and 40 °C as a consequence of hydrogen bonding between agarose molecules. Current research indicates that the global agarose market will continue to show growth over the next five years. By 2022, experts predict that the global agarose market will be worth USD 83.35 million; by 2028, that number is expected to rise to USD 99.35 million. Over the course of the anticipated time frame, this increase is anticipated to occur at a CAGR of 2.97%.<sup>103</sup>

Felipe Melo Lima Gomes *et al.* demonstrated that in order to remove Cd(II) and methyl violet from water, an agar-graphene oxide hydrogel was created for this experiment. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to create images and data describing the hydrogel's composition and structure. Studies were conducted across several disciplines, including kinetics, equilibrium, and regeneration. Langmuir, Freundlich, and Sips isotherm models were used to match the equilibrium experimental data. With an  $R^2$  of 0.968 and  $\chi^2 = 0.176$ , the Sips model provided a very good match to the Cd(II) data. With an  $R^2$  of 0.993 and  $\chi^2 = 0.783$ , the Sips model likewise showed a very good match to the MV data. Maximum adsorption capacities of 76.65 mg g<sup>-1</sup> for monovalent mercury ions and 11.70 mg g<sup>-1</sup> for divalent cadmium ions were found. With  $R^2$  values over 0.90, the pseudo-order models provided a good description of the kinetics of the





Cd(II) and MV adsorption. Regeneration tests showed that the adsorbent could be reused after three cycles of adsorption and desorption for both Cd(II) and monovalent mercury, which is quite an impressive feat. The study demonstrated the feasibility of a practical adsorbent for the repeated removal of Cd(II) and MV from water.<sup>104</sup>

de Araujo *et al.* analyzed the A-GO biocomposite's morphology, and showed that the lyophilized hydrogel had a three-dimensional porous structure. The Sips (Safranin-O) and Freundlich (Chloroquine) adsorption isotherms showed a good match ( $R^2 > 0.98$ ) in the batch experiments. The kinetic data were successfully modelled using driving force models and Fick's diffusion equation, with good results in both cases. Experiments with batch selective adsorption showed that competitive adsorption occurred in the presence of both components in water. This was demonstrated by a reduction in the adsorptive capabilities of around  $10 \text{ mg g}^{-1}$  for each component. Adsorptive capacities for safranin-O were determined to be  $41 \text{ mg g}^{-1}$ , whereas those for chloroquine were determined to be  $31 \text{ mg g}^{-1}$ . The fixed-bed adsorption column breakthrough curves showed that the adsorption capabilities for chloroquine and safranin-O were  $63 \text{ mg g}^{-1}$  and  $100 \text{ mg g}^{-1}$ , respectively.<sup>105</sup>

de Araujo *et al.* introduced hydrogels made with graphene oxide and agar, and have shown evidence of graphene oxide-polymer interactions in their investigation. An irregularly shaped, three-dimensional material formed as a result of this interaction. Adjusting the pH of the BF and MG solutions had a minor effect on the adsorptive capacity, as shown by the batch testing. A constant increase in MB's adsorptive capacity was seen, whereas NB's action was more prominent until the pH approached 8. For the MG, BF, and MB isotherms, the Freundlich model was the best fit, whereas the Sips model was the best fit for the NB isotherm. Successful fits were found for the kinetic data using the equations of Lattice Diffusion Flux, Quasi-Dynamic Flux, and Fickian Diffusion. The fixed-bed experiments showed that the individual dry adsorption capacities of the dyes were as follows: methylene blue  $79.51 \text{ mg g}^{-1}$ , malachite green  $58.25 \text{ mg g}^{-1}$ , and Brilliant blue FCF  $38.11 \text{ mg g}^{-1}$ , Nile blue  $224.46 \text{ mg g}^{-1}$ . These results demonstrated the regenerative capability of the adsorbents. Positive findings regarding the adsorbent's selective separation of colors from synthetic textile effluent were found in an evaluation of the effectiveness of an agar-GO hydrogel-packed column.<sup>106</sup>

### 3. Synthetic strategy to fabricate bio-based materials

As techniques for creating nanomaterials and fabricating thin films have advanced rapidly, a number of novel BBMs have been recently published. In this article, we focus on some of the most modern, widely applicable, and highly efficient methods for preparing BBMs. Molecular imprinting, phase inversion, electrospinning, and chemical modification are only some of the manufacturing processes detailed here (Fig. 5), along with discussions of their respective benefits and drawbacks.

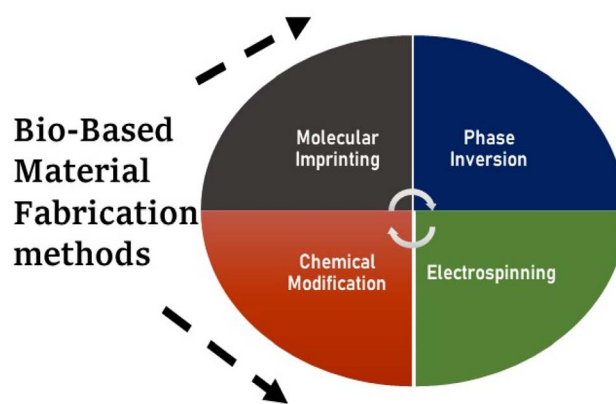


Fig. 5 Various fabrication strategies for bio-based materials.

#### 3.1 Molecular imprinting (MIPs)

The emergence of molecular imprinting has allowed synthetic polymers to be engineered with built-in recognition sites for specific target molecules. Functional cross-linkers and monomers are copolymerized with a template molecule to produce bio-based materials. Extracting the template groups from the polymeric networks requires forming recognition cavities that are equivalent to the template molecules in structure, dimensions, configuration and chemical functional groups. This allows for the selective rebinding and recognition of the original templates from a mixture of closely related compounds. Because of their low cost, excellent selectivity, high stability, physical robustness, and ease of manufacturing, a broad range of molecular imprinting polymers have been developed and used as adsorbents for the efficient and effective separation of carcinogenic organic pollutants and harmful metal ions in wastewater treatment and water purification.<sup>107–113</sup>

There has been substantial progress in the use of bio-based polymeric MIPs in the wastewater treatment sector due to their various advantages. Among these advantages are their potency in selective adsorption, high affinity, lack of toxicity, ease of manufacture, and cheap cost. A photo-responsive cellulose-based intelligent imprinted adsorbent for the specific adsorption of common pesticides material utilizing surface-initiated atom transfer radical polymerization was investigated and synthesized by a group of researchers. The PR-Cell-binding MIP's capacity was able to reach  $11.039 \text{ mg g}^{-1}$  due to its great adsorption specificity, amazing reusability, and outstanding stability for the target 2,4-D. The cellulose adsorbent was easily regenerated by exposure to UV light by incorporating an azobenzene (Azo) function monomer.<sup>114</sup> Chitosan (CS) is a commonly known polysaccharide used in molecular imprinting because it has a high concentration of hydroxyl and amino groups. These groups provide higher affinity to diverse chemicals through different sorts of specialized interactions. In order to selectively remove cadmium from aqueous solutions, Rahangdale *et al.* prepared a dual surface imprinted acrylamide functionalized chitosan-based polymer using epichlorohydrin as a crosslinker, chitosan (CS) as a substrate, 4-hydroxy benzoic acid (4HBA) as a mimic template, and cadmium (Cd) as



a template. For Cd and SA, the highest adsorption capabilities in AGDMIP were 53.42 and 45.77 mg g<sup>-1</sup>, respectively.<sup>115</sup> In order to create ion-imprinted cryo-composites from chitosan, Dinu *et al.* demonstrated an ice-templating and ion-imprinting method using *N,N'*-methylenebisacrylamide (BAAm) and acrylamide (AAM) as monomers, glutaraldehyde (GA) as a cross-linker and Cu<sup>2+</sup> as a template ion. Due to a chelating reaction between the OH and NH<sub>2</sub> groups and Cu<sup>2+</sup> ions from the CS matrix, the II-CCs showed remarkable specificity adsorption ability for the Cu<sup>2+</sup> ions.<sup>116</sup> With the right microscopic recognition cavities, bio-based polymeric MIPs can efficiently remove trace pollutants from water in real-world applications. This is because these MIPs rely on and enhance the formation of bonds between individual recognition sites.

### 3.2 Phase inversion

Currently, phase inversion is the most adaptable, cost-effective, low maintenance and versatile method for fabricating polymeric filtering membranes. This process involves the controlled transition of an initially homogenous polymer solutions to a solid phase. Flat sheets and spinning fibers can be made from membranes with asymmetric and hollow fibers. Different methods of phase inversion include thermally-induced phase separation (TIPS), vapor-induced phase separation (VIPS), and non-solvent-induced phase separation (NIPS). The physical and chemical interactions between the membrane and its environment are influenced by a number of factors, including the additives, solvent interaction, polymer concentration, and bath temperature utilized in the casting solutions. In this method of membrane synthesis, it yields two distinct membrane morphologies and structures *via* finger-like and a sponge-like structures. Structures resembling fingers or macrovoids form when demixing occurs instantly, while structures resembling sponges form when demixing is delayed.<sup>117</sup> Conversely, the sponge-like structure has much greater mechanical strength than the finger-like structure because its tiny pores are surrounded by solid walls, allowing for the production of an entire thin active layer. Conversely, the flow resistance is lowest in the figure-like pores because they are the least twisted. Therefore, optimal support with a thin layer of sponge-like material placed on top of a finger-like sublayer is required to fabricate high-performance filtering membranes.<sup>118–121</sup>

A considerable quantity of cellulosic membranes was produced using the phase inversion method. Cellulose acetate (CA) has been used in a variety of separation techniques, including nanofiltration, microfiltration, ultrafiltration, and reverse osmosis.<sup>122</sup> Asymmetric CA membranes have much promise as a desalination and water purification technique due to their high water porosity and salt retention. The CA-based composite films endured a phase inversion due to the presence of water vapor at room temperature and pressure. With a separation flow of 667 L m<sup>-2</sup> h<sup>-1</sup> and an efficiency of 99.99%, the resultant composite film successfully separated nano-sized surfactant-stabilized W/O emulsions.<sup>123</sup> The TiO<sub>2</sub> photocatalytic activity was also responsible for the bio-film potent photocatalytic destruction of organic molecules under UV

irradiation, which is encouraging news for the industrial and domestic water treatment sectors.

The toxic solvents formerly used in membrane preparation by phase inversion have been replaced with environmentally friendly alternatives. This category includes solvents like dimethyl sulfoxide (DMSO),<sup>124</sup> triethyl phosphate (TEP),<sup>125</sup> dimethyl isosorbide (DMI),<sup>117</sup> and ionic liquids (ILs).<sup>126</sup> Using NIPS and bio-based green solvents like glycerol derivatives and  $\gamma$ -valerolactone (GVL), it is now possible to create permeable membranes. The manufactured membranes with the related  $\gamma$ -valerolactone may be used for microfiltration, ultrafiltration, and nanofiltration if the pore sizes are small enough.<sup>127</sup> Additionally, the cellulose acetate nanofiltration membrane was produced by phase inversion using the green solvents, methyl lactate and 2-methyltetrahydrofuran. A highly porous and permeable morphology, characterized by finger-like macrovoids, was generated at low concentrations of CA. Increasing the CA content in the casting solution decreased the permeance from 32.0 to 2.4 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> and enhanced the rhodamine B dye removal from 31.1% to 99.5%.<sup>128</sup>

Antifouling, permeation flux, and highly specific and selective separation are just a few areas where membrane performance might be improved with the use of nanomaterials into the phase inversion process used to manufacture BBMs nanofiltration membranes. The key limitations of the organic nanoparticles are their lack of thermal stability and deficiency in acid-base tolerance. These limitations may be mitigated by controlling the structure of the organic nanoparticles. The basic limitations of the use of loose nanofiltration membranes include the incompatibility of inorganic nanoparticles with the biopolymer matrices and their tendency to agglomerate, which results in the development and creation of defects and imperfections at the bipolymer interface. Improving the correlation between the inorganic nanoparticles and biopolymers, modifying the surface morphology and structure, and improving the distribution of inorganic nanomaterials are necessary steps in the development and manufacturing of high-performance, reliable and advanced inorganic hybrid loose nanofiltration membranes. The permeability and selectivity of loose nanofiltration membranes are compromised due to the above-mentioned reasons. For this reason, researchers are largely focused on the creation of novel matrix materials that allow for high permeation flux without reducing separation fidelity.

### 3.3 Electrospinning

Producing polymer nanofibers with good structure–property relationships in the submicron range (5–500 nm) inexpensively and in large quantities is now possible by electrospinning. As a consequence of their high permeability, large surface area, high water permeability, and good stability, electrospun polymer nanomaterials have immense capability as filtration materials in the wastewater purification process. Electrospun polymeric nanofibers are created by uniaxially stretching and elongating a viscoelastic polymeric solution in a high voltage field. A syringe pump, a grounded metal collector, a high voltage power supply, and a spinneret are its four components. By



applying a voltage between the needle tip and the grounded collector, the polymer solution is transformed during the electrospinning process from a spherical shape into a conical one (known as Taylor cone). When the electric field strength is strong enough, the surface charges' electrostatic repulsion will overcome the droplet's surface tension. The needle tip's Taylor cone will eject the fluid jet towards the grounded collection. The droplet's surface tension will overcome the surface charges' electrostatic repulsion when the electric field strength is low. The solvent has swiftly evaporated, and the jet has stretched and curved to generate nonwoven membranes.<sup>129–131</sup> This nanofibrous membrane may function as an adsorbent or as a filter membrane in separation processes, including ultrafiltration (UF), microfiltration (MF), and nanofiltration, due to its high permeability (>90%), densely interrelated pores, and multi-channeled architectures (NF).

Recently, a new chitosan/polyvinyl alcohol/polyvinylpyrrolidone membrane was developed using electrospinning for the elimination of organic pollutants and heavy metal ions in polluted water.<sup>132</sup> With pure water permeability of  $4518.91 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and an average diameter of 160 nm, the CS/PVP/PVA nanofiber membrane generated under ideal electrospinning conditions demonstrated permeability and a consistent biocompatible structure. Maximum removal rates for malachite green, methylene blue, Cd(II), Pb(II), Ni(II), and Cu(II) are 94.20, 69.91, 83.33, 90.35, 80.12, and 84.01%, respectively. The large specific surface area and open pore structure of the electrospun cellulose acetate (CA) membranes have made them a promising water filtering material. Using an electrospinning technique, Goetz *et al.* developed a hydrophilic cellulose nanofibrous membrane with an anti-fouling surface structure property. As a result, CA fibers tend to arrange themselves in a disorderly fashion, with some fibers preferentially oriented vertically, horizontally, or diagonally with sizes between 0.5 and 2.0  $\mu\text{m}$ , which results in a nanofiber membrane that has the ability to degrade dyes by 80–99%.<sup>133</sup> The use of electrospun chitosan (CS) membranes for heavy metal ion elimination has become widespread due to their superior metal biodegradability, high hydrophilicity, and chelation ability.<sup>134</sup>

Due to their high flux, improved reduction, low operating pressure, and antifouling capabilities, electrospun nanofiber membranes are potential options for advanced filter media. Nonetheless, there are some drawbacks to electrospinning technology, *i.e.*, a lack of structural stability, needle clogging, high electric field requirements, a time-consuming process, low productivity, and inapplicability to all biopolymers. The development of needleless electrospinning technology has allowed for the resolution of these limitations. High levels of safety and productivity may be achieved in continuous systems *via* the use of needle-free electrospinning for the manufacturing of nanofiber membranes. While the large-scale production of electrospun nanofiber membranes is still in the research and development phase, a few medium-sized manufacturers already exist. Electrospun nanofibrous membranes are the newest generation of filtration materials, and they bring with them important benefits that will help in the creation of cutting-edge viable filtration systems.<sup>135</sup>

### 3.4 Chemical modification

Chemical modification is the process by which the structures of biopolymers are changed chemically to produce derivatives with unique or improved physicochemical features. Chemical modifiers improve chemical stability by covalently attaching to the substrate. By decreasing the impacts of membrane fouling, chemically altering water treatment membranes to enhance their hydrophilicity has the potential to dramatically improve water permeability. Ahn *et al.* transformed ordinary A4 printer paper into multifunctional cellulose membranes by performing a chemical alteration. Calcium carbonate filler in the A4 paper was dissolved using a hydrochloric acid solution, and then alkoxide functional groups were added to the cellulose fibers. After treating the A4 membrane with acid and base, trichlorooctylsilane (COS) was selected to alter the OH groups on the cellulose network.<sup>136</sup> With this chemical modification technology, commercial A4 paper might be utilized in the future as a multifunctional cellulose-based membrane, with a simple procedure and low chemical costs.

Amine is electrophilically substituted by active hydrogen in a process known as the Mannich reaction, which results in aminated lignin. The Mannich approach aminolation of lignin was followed by chelation of Fe(III) onto the aminated lignin to produce novel lignin-based adsorbents for the very efficient phosphate elimination from wastewater. When it comes to phosphate ( $5 \text{ mg L}^{-1}$ ), the newly discovered materials have a removal effectiveness of more than 90%. The adsorption mechanism relies on Fe(III) and phosphate complexation on the lignin-based adsorbent. The findings of this work suggest a realistic and cost-effective way for building low-cost BBMs for the treatment of low-phosphate wastewater, reducing the eutrophication of bodies of water.<sup>137</sup> Chaudhary *et al.* created a highly porous chitosan-based aerogel barrier for rescuing potable water from an oil spill in a ship-breaking yard using genipin as a cross-linking agent. Fig. 6a and b graphically depicts the steps required to make a CS aerogel membrane with a superhydrophilic agarose inner wall coating. The shells of crustaceans like shrimp, lobsters, and crabs are mined for the plentiful natural resource chitosan. The CS's  $-\text{NH}_2$  functionality allows it to be chemically cross-linked, and its fibrous nature means it may be employed in a variety of ways after undergoing chemical and physical modification. Additionally, by regulating the degree of crosslinking, CS may be converted into a robust scaffold-like structure. Agarose was utilized as a gelling agent, and it contributed to the development of a highly porous aerogel membrane that could accommodate a wide range of pore sizes. Interestingly, agarose also played a role in enhancing the hydrophilic property by interacting with chitosan through H-bonding during lyophilization. At 80 degrees Celsius, as shown in Fig. 6c, genipin rapidly crosslinks chitosan, whereas agarose forms a stable gel by H-bonding interaction with the  $-\text{OH}$  of chitosan, allowing the gel to be used at room temperature. Water with a purity of >99% and a flow rate of  $600 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  may be obtained by modifying the genipin cross-linking process, and changing the chitosan-based aerogel into a column-like and stiff scaffold-like structure.<sup>138</sup>

The location, amount, and spatial conformation of the groups utilized to alter the biopolymer are intricately connected



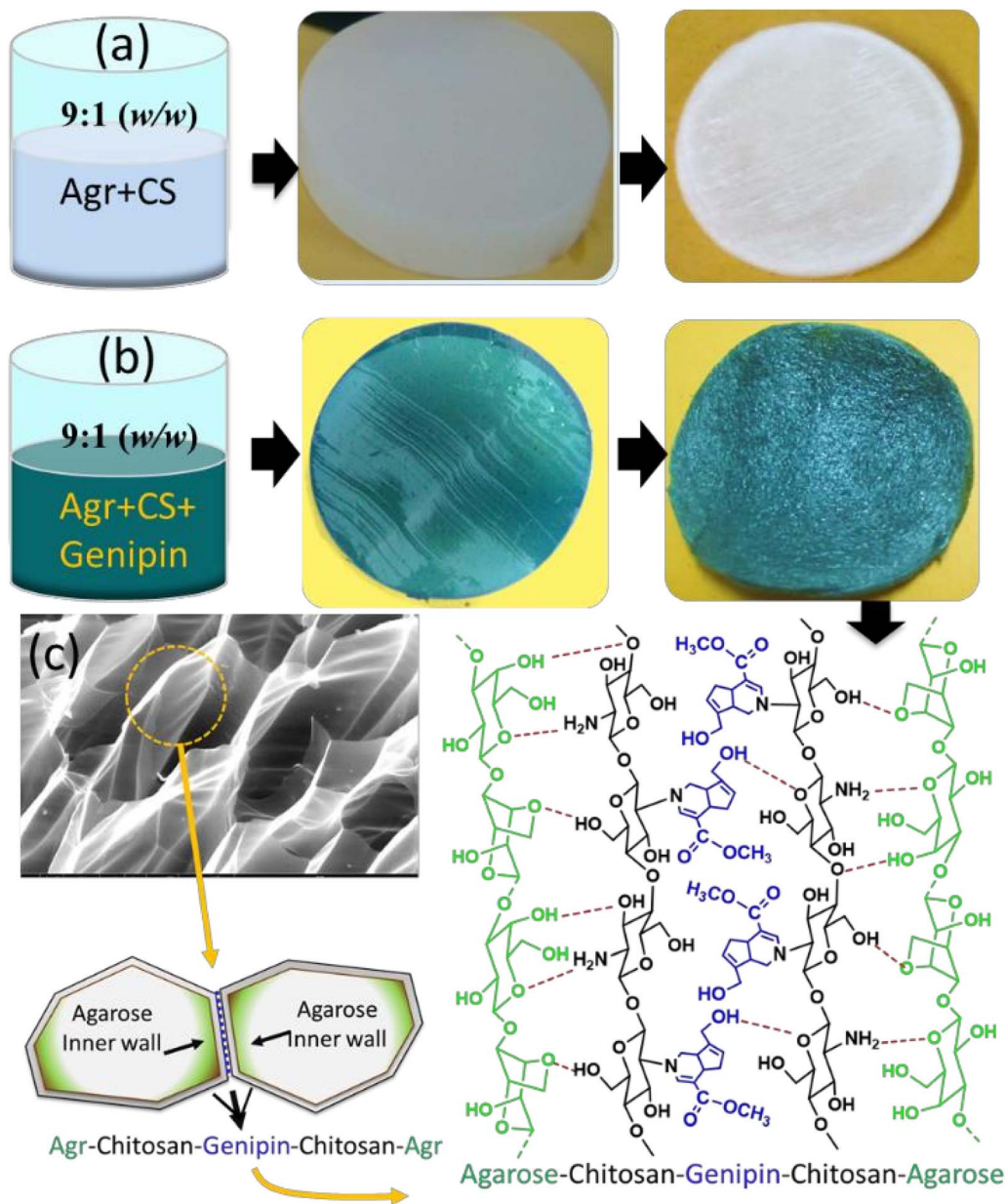


Fig. 6 Aerogel membrane preparation schematics: (a) uncrosslinked chitosan, (b) genipin-crosslinked chitosan, and (c) genipin-crosslinked chitosan with agarose H-bonding to the inner walls of CS. Reproduced with permission from<sup>138</sup> Copyright (2015), ACS.

to the physicochemical features of BBMs. In order to understand more about the structure–function link, scientists must perform extensive research on modified biopolymers. Furthermore, if current techniques for chemical modification are developed and the optimal modification conditions are discovered, the structure and stability of BBMs may be determined more accurately.

#### 4. Benefits of eco-friendly green synthesis over conventional chemical synthesis

There are various benefits to green material production *versus* chemical synthesis.<sup>139</sup> Because biological components are

already accessible, production costs are dramatically reduced.<sup>140</sup> Natural, biocompatible capping and reducing agents found in biology may aid in lowering production costs. Nanoparticles may be made from low-value byproducts of agriculture and industry. Chemical synthesis procedures, on the other hand, need the use of hazardous, dangerous, and/or expensive ingredients that are harmful to the environment.<sup>141</sup>

Commercially available activated carbon and iron or iron oxide nanoparticles are anticipated to be 50 times more expensive than green produced iron-based nanomaterials. The use of bio-based materials in the synthesis process accounts for the remarkable price drop.<sup>142</sup> Because of its quicker kinetics, several investigations favor plant-based bio-based material synthesis over chemical preparation.<sup>143</sup> Furthermore, the



biomimetic green synthesis technique demonstrates the interface between biomolecules and inorganic materials, as well as the underlying biological processes. Because the biomolecules utilized have well-defined structures, chemical properties, and compositions, the metal nanoparticles generated by this method have chemical purity, well-defined geometry, and dimension.<sup>144,145</sup>

## 5. Reasons to remediate the environment with eco-friendly materials

Since the beginning of the industrial age, environmental remediation has been one of the most important tenets of sustainable practice. Notably, the continual discharge of high volumes of synthetic chemicals might surpass natural degradation capability, leaving behind persistent pollutants that have severe effects on the ecosystem and human health.<sup>146</sup> Concentrating pollutants, removing them from environmental matrices, and treating them sequentially to eliminate them are standard steps in any remediation process. The materials' adsorption capacities, which enrich pollutants through chemical and physical interactions between adsorbents and adsorbates,<sup>147,148</sup> are crucial to the concentration of environmental contaminants. The adsorption and treatment of environmental contaminations have been studied using various materials created by non-biological processes. Natural mineral clays,<sup>149</sup> resins,<sup>150</sup> metal-organic frameworks,<sup>151,152</sup> and mesoporous silica<sup>153</sup> are all examples that have been thoroughly explored in the past as potential candidates. However, there are frequently monetary and environmental issues with the production process for these adsorption materials. Researchers in the field of techno-economic analysis have shown that the production of traditional remediation materials is quite labor- and resource-intensive.<sup>154</sup> It is also common for processes like pyrolysis used in the synthesis of certain materials to generate corrosive waste products or hazardous gases. Costs and possible secondary environmental risks are further increased by the post-adsorption and rejuvenation process.

Biomaterials, particularly those made from lignocellulosic biomass, provide an eco-friendly, renewable alternative. When used in conjunction with various functionalities, these biomaterials may be used for effective absorption and remediation.<sup>155</sup> Heavy metals and persistent organic pollutants (POPs) have been examined for their ability to adsorb onto biochar, chitosan, microbial biomass, and a wide variety of agricultural wastes.<sup>156</sup> Biomaterial, and specifically biomass-based material for environmental restoration, has the advantages of being inexpensive, renewable, and non-toxic.<sup>157</sup> Engineering these biomaterials with the use of various functionalities has resulted in increased adsorption capacity, more effective pollutant degradation, and lessening the risk of secondary contamination from the leaching of organic compounds. The conventional treatment train approach to environmental cleanups may be avoided with the use of modern biodegradable adsorptive

materials, which allow for the degradation and removal of the pollutants to be treated in the same system.<sup>158</sup>

## 6. Functionalization of bio-based materials

Biopolymer alterations, in addition to heat processing, have resulted in a more sophisticated material structure design and broader spectrum of environmental cleaning capabilities.<sup>159</sup> Adsorption biomaterials have recently concentrated on the development of 3D materials, as well as the achievement of a high surface area *via* biomaterial design (Table 1). A few of the advantages of functional bio-based materials goods include biodegradability, cost-effective, biocompatibility, environmental friendliness, and renewable resources. These newly advanced biomaterials have shown exceptional functional features, such as improved complexation, chelation, flocculation, adsorption and separation.<sup>159</sup> The reactive carboxymethyl groups, cellulose, lignin and alginate functional materials in biomass have enhanced its adsorbent ability owing to their chemical reactivity, good solubility, and significant chelating ability.

## 7. Environmental remediation by using bio-based materials by adsorption

Adsorption is widely utilized to remove contaminants from water supplies in the water treatment industry.<sup>170</sup> Contaminants are trapped on the surface of an adsorbent material, and then removed from the water by this procedure. Adsorbents might be in the shape of grains, pellets, or powder, all of which provide a large surface area and boost adsorption efficiency. Many types of commercial adsorbents are used in water treatment applications. Activated carbon's high adsorption capacity and ability to remove a wide variety of contaminants, including organic compounds, disagreeable smells, and substances that contribute to poor taste,<sup>171</sup> make it a popular adsorbent. Silica gel, zeolites, and clay minerals are a few more examples of commercial adsorbents. These adsorbents feature diverse adsorption characteristics that make them suitable for the removal of various pollutants.<sup>172</sup> Despite their shown efficacy, commercial adsorbents are not without their drawbacks. Limitations include the high costs of implementing such systems, which become especially problematic in large-scale implementations. Adsorbent regeneration may be a costly and time-consuming procedure, depending on the specific circumstances.

Significant progress in using bionanocomposites as adsorbents has been made in recent years.<sup>173</sup> Hybrid materials known as bionanocomposites combine biopolymers with nanoparticles to enhance their adsorption properties.<sup>174</sup> Nanoparticles, with their huge surface area and functional capabilities, are combined with biopolymers, which are biocompatible and renewable, in these composite materials. The scientific community is very interested in chitosan-clay



Table 1 Functionalized bio-based materials for effective water remediation

Bio-based materials	Primary component	Pollutant	Efficiency	Removal time	Mechanism of removal	Synthesis method	References
Poly(ethyleneimine)-graft-alkali lignin/lanthanum hydroxide	Lignin	Phosphate ion	95%	60 min	Ligand exchange and surface precipitation	Facile fabrication	159
Poly(ethyleneimine)-functionalized cellulose microcrystals	Cellulose	Per-and polyfluoroalkyl substances	80–85%	120 min	Physical adsorption and electrostatic interaction	Oxidation and ion exchange followed by amine-functionalization	160
Cross-linking cellulose nanocrystals	Cellulose	Methylene blue	86%	—	Electrostatic attraction	Freeze-drying	161
Carbonized loofah/tin(IV) sulfide	Loofah plant	Cr	99.7%	120 min	Physical adsorption and photocatalytic	Scalable method	162
Crosslinked carboxymethyl cellulose grafted carboxymethyl polyvinyl alcohol	Cellulose	Cu <sup>+2</sup>	95%	240 min	Ion exchange	Casting method	163
Carboxymethyl cellulose/sodium styrene sulfonate gels	Cellulose	Cr, Pb, Mn and Fe	68.0%, 41.4%, 35.2% and 33.5%	—	Electrostatic attraction	Radiation grafting	164
Lignin sulfonate-based mesoporous materials	Lignin	Malachite green	97%	240 min	Electrostatic interaction	Grafting method	165
Carboxycellulose nanofibers	Cellulose	Cadmium(II)	84%	—	Electrostatic interaction	Nitro-oxidation method	166
Graphene oxide/esterified cellulose nanofibers	Cellulose	Ofloxacin and ciprofloxacin	96.9% and 97.8%	240 min	$\pi$ - $\pi$ interactions, and hydrogen bonding, electrostatic interaction	Chemical treatments followed by esterification	167
Cellulose nanofibers/PVA blend	Cellulose	Cationic and anionic dyes	84%	—	Electrostatic interaction	<i>In situ</i>	168
TEMPO-oxidized cellulose nanofibers	Cellulose	Cooper ions	100%	—	Electrostatic interaction	Grafting method	169

nanocomposites because they are cheap, easy to produce, and effective adsorbents. This class of composites has been found to successfully remove up to 99% of hazardous anionic ions, metals, and dyes from water.<sup>175</sup> Additionally, the effectiveness of graphene oxide-potato starch composites in the adsorption of MB dye from industrial effluents has been investigated. The composite material's adsorption capacity was rather high, at around 90%.<sup>176</sup> The composite material formed a structure similar to plywood, with nanocages, from the combination of GO nanosheets and polysaccharide long chains. According to the study, this structural configuration greatly enhanced the material's ability to absorb organic colors. Electrostatic interactions between graphene oxide and cationic dyes (a) play a role in the adsorption process, and (b) – stacking interactions between the aromatic part of the dye and the delocalized  $\pi$ -electron system of GO play a role in the adsorption process.<sup>177</sup>

Graphene oxide shows surface complexation with heavy metal ions, enhancing their adsorption. When used in the adsorption treatment of wastewater, graphene oxide-chitosan composites demonstrate remarkable stability and mechanical qualities. Chitosan is able to efficiently coagulate pollutants out of aqueous solutions because it is a positively charged

biopolymer with amino and hydroxyl groups. However, challenges such as the high synthesis costs, the necessity for pH adjustment, and decreased efficacy at low concentrations prevent their widespread application. The adsorption properties of the specific heavy metal ions are the primary focus of the current research. However, studies on the treatment of wastewater containing a combination of heavy metal ions are lacking.<sup>178,179</sup> Water contamination by a wide variety of organic and inorganic compounds has been effectively adsorbed by AP-g-3D GO composites.<sup>180</sup> Adsorption capacities for the dyes rhodamine B and Congo red were found to be particularly high in a chitosan-poly(vinyl alcohol)-graphene oxide cross-linked sponge.<sup>181</sup> The adsorption – interaction of the aromatic rings of the dye molecules was enhanced by the 3D porous structures of the biopolymer sponge and the composite sponge.

According to a recent study, the amalgamation of a geopolymer and a biopolymer has been proven to improve the adsorption effectiveness of Ni(II) and Co(II) ions in wastewater. Synergy between lateritic geopolymer and the Tiliaceae family's *Grewia* biopolymer led to the effective removal of almost 80% of Ni(II) and Co(II) ions from the wastewater samples. Iron, aluminium, and silica oxides are concentrated in the



geopolymer produced from laterite clay. The *Grewia* plant biopolymer, on the other hand, is made up of simple sugars, including mannose, xylose, glucose, glucuronic acid, and arabinose. Kaolinite platelets make up the structure of the laterite-clay geopolymer, whereas open holes of varying sizes are seen in the *Grewia* biopolymer. The improved adsorption capabilities of the *Grewia* biopolymer are thought to result from these structural properties.<sup>182</sup>

An extensive study was done on the use of graphene oxide/chitosan composites in the treatment of wastewater *via* adsorption. Biodegradable and cationic biopolymer chitosan has been shown to efficiently remove pollutants from liquid solutions *via* its coagulation properties. However, their use is limited because of the high manufacturing costs, the requirement for pH regulation, and the inefficiency when employed in low concentrations. The research studies presented here give helpful insights into the contaminant adsorption capacities of various graphene oxide/chitosan composites. The adsorption capacity of the GO-cl-potato starch bio-composite for MB dye was remarkable at 500 mg g<sup>-1</sup> (90%).<sup>176,183</sup>

### 7.1 Dye removal by BBMs

Because of their high specific surface area, three-dimensional network structure, sorption capacity, and recyclability, BBMs have been suggested as very efficient adsorbents for the removal of dangerous chemical substances. Recent research has focused on the use of BBMs to remove organic dyes from wastewater because of their cheap operating cost and high efficiency. Mutations, skin irritation, and allergy in humans are only some of the effects that have been linked to dye pollution in water. Consequently, it is crucial to treat dyes using different processes, including oxidation, adsorption, coagulation, reverse osmosis, biodegradation, and so on. Researchers have been interested in developing BBMs for the degradation of organic dyes without negatively impacting the environment from the production of harmful byproducts. The adsorbents are designed to promote electrostatic contact between the dyes *via* their ionic charges. Electrospinning generates the ultrapure chitosan nanofibrous membranes used in acid blue-113 dye removal. The optimal conditions for nanofiber structure and morphology were determined to be a reduction in the nanofiber diameter, which led to an increase in the adsorption capacity owing to the increased surface area, and a maximum adsorption capacity of 1338 mg g<sup>-1</sup>.<sup>184</sup> Hydrophilicity, biocompatibility, and biodegradability were all enhanced when chitosan and polyamide-6 were combined and electrospun the resulting nanomaterials. Tests were developed utilizing response surface methods to select the optimal filtering parameters to remove 95% of Polar Yellow GN and 96% of Solophenyl Red 3BL. The purpose of fusing SiO<sub>2</sub> nanoparticles onto the polyvinyl alcohol (PVA)/chitosan composite was to make the fiber highly stable and more efficient for a longer period of time. Due to the increased surface area (60.76 m<sup>2</sup> g<sup>-1</sup>), higher compaction resistance, and decreased degradation rate (2.65) brought about by the incorporation of nanoparticles, the electrostatic affinity between the anionic dyes and amine resulted in 98%

elimination of the DR23 dye at a flux rate of 1711 L m<sup>-2</sup> h<sup>-1</sup>.<sup>185</sup> In a separate investigation, Mahmoodi and colleagues tested the efficacy of PVA-chitosan nanofibers in removing dye from a colored effluent. Decreases in pH improved the dye removal efficiency because protonation was decreased. On the other hand, at high pH, desorption is preferred, with release efficiencies of 85–90%.<sup>186</sup> Dye recovery performance was also produced by the functionalization of chitosan fibers with ethylenediamine. The thermogravimetric curves showed that ethylenediamine's low boiling point caused functionalization to lower the degradation temperature. A rise in pH allowed for the recovery of both cationic and anionic dyes on the fibers, with enhanced adsorption of MB and reduced adsorption of coccine owing to the protonation-preferred adsorption of anionic dyes.<sup>187</sup> Following this, fibers were electrospun, and chitosan hydrogels were coated to increase their density. Hydrocarbon bonds have a binding energy of 284.32 eV; the carbon–oxygen bond has a binding energy of 286.83 eV; ester groups and alcoholic hydroxyl groups both have a binding energy of 289.31 eV; and the carbon–oxygen bond has a binding energy of 289.31 eV. Numerous carbonyl and alcoholic OH<sup>-</sup> point to the introduction of (multi-walled carbon nanotubes) MWCNTs onto cellulose. Coated materials were able to eliminate 90% of the dye with a molecular mass greater than 600 g mol<sup>-1</sup> at an operating pressure (0.5 MPa) and significant high flux rate (150.72 L m<sup>-2</sup> h<sup>-1</sup>).<sup>188</sup>

Electrospinning between the shoulders is also used to create chitosan nanofibers functionalized with carboxylated CNTs for the removal of methyl orange and methylene blue. Fabrication of clay-based nanofibers for dye removal makes use of montmorillonite's hydrophilicity through a thermally induced sol-gel transition. Water flow (1765 L m<sup>-2</sup> h<sup>-1</sup>), compaction resistance (0.4 bar), dye removal (95% of BB41), resistance to fouling, and reusability potential were all improved by the addition of 2.0 wt% of CNTs.<sup>189</sup> Xu *et al.* decorated clay nanosheets onto the chitin nanofibrous matrix, resulting in the construction of hierarchical architectures. Dyestuffs having a large specific surface area and a high cationic exchange capacity were adsorbed onto the microsphere surface, transported *via* the chitosan channels, and subsequently interacted with clay sheets. Surprisingly, methylene blue's adsorption behavior showed very minor changes depending on pH. Active adsorption sites were not completely exposed when chitosan fibers were dissolved into the solution of binary solvents.<sup>189</sup> Xing *et al.* created sponges by means of thermally induced phase separation, by utilizing tetrahydrofuran in the water/acetic acid solvent system. THF is not the best solvent, but it did an excellent job of opening up more room for the lean phase to develop and showing off the sponge's porous, interconnected structure. The sample with 1 : 79 : 20 (AA : water : THF) and 0.5 wt% chitosan was quenched at 196 °C, and had the highest adsorption capacity of 604.7 mg g<sup>-1</sup>.<sup>190</sup>

Hydrogels resistant to disintegration in water were fabricated by scaling up the process of making adsorbents based on the physical entanglement and hydrogen bonding of nanofibrils. Because of their high specific surface area and surface carboxyl groups, aerogels prepared from cellulose nanofibrils



through a freezing-thawing process are able to remove 92% of MG at a 10 : 5 mg mL<sup>-1</sup> aerogel/MG w/v ratio, and the adsorbed dye is rapidly released when the ionic strength of the solution is increased up to 200 mM NaCl.

Sajab *et al.* added Fe(III) ions to graphene oxide-cellulose nanofibril aerogels. As a result of the Fenton oxidation process, methylene blue was degraded in the presence of hydrogen peroxide, and the loaded fibers were able to remove the dye at a rate that was 30.4% greater than that of the unloaded fibers.<sup>191</sup>

Chemically crosslinked cellulose/graphene oxide nanofibers containing photocatalytic TiO<sub>2</sub>-NH<sub>2</sub> nanoparticles (NPs) have remarkably improved dye-degradation. Titanium dioxide (TiO<sub>2</sub>), when exposed to ultraviolet light, generates an active oxidation species (hydrogen peroxide), which in turn degrades indigo carmine and methylene blue. Power density, pH, duration, and starting dye concentration all had significant impacts on the degradation efficiency.<sup>192</sup> Due to its unique conical shape that is both hydrophobic on the inside and hydrophilic on the outside, the oligosaccharide cyclodextrin is favored. Enhanced adsorption and improved mechanical strength owing to hollow cavity were achieved by incorporating the B-cyclodextrin polymer into poly-caprolactone during electrospinning. Upon the completion of up to eight cycles of re-adsorption, the maximum efficiency was 24.1 mg g<sup>-1</sup> adsorbing 78%.<sup>193</sup>

Researchers have successfully adsorbed crystal violet and rhodamine B (RB) onto graphene oxide nanosheet-coated dialdehyde starch nanocrystals in aqueous solutions (CV). There was a maximum adsorption capacity of 539 mg g<sup>-1</sup> for RB and 318 mg g<sup>-1</sup> for CV in aerogels.<sup>194</sup> Dye-mediated interaction between the CS-based polyelectrolyte and organo-montmorillonites allowed for the effective and quick removal of cariogenic industrial dyes in an employed CS-based polyelectrolyte/organoclay hybrid. Using a CS/organoclay hybrid with a weight ratio of 10/90, researchers were able to completely remove a wide range of hydrolyzed anionic dyes.<sup>195</sup> Polycyclic aromatic hydrocarbons (PAHs) may be extracted from wastewater with the use of magnetic nanoparticles encased in chitosan and pyrolyzed chitosan. The chitosan-based polymer has a good adsorption capacity for both naphthalene and anthracene.<sup>196</sup> In their production of a bifunctional alginate-based composite hydrogel, Qian *et al.* accomplished synergistic photocatalytic and adsorption degradation and decomposition of organic contaminants. Malachite green crystal violet, and methylene blue each had very high adsorption abilities of 3000.08, 993.29, and 1610.34 mg g<sup>-1</sup> in the alginate-based hydrogel, respectively.<sup>197</sup>

Corn starch, 3-chloro-2-hydroxypropyl trimethylammonium chloride, and epichlorohydrin were used in the production of crosslinked cationic starch by Guo *et al.*<sup>198</sup> A maximum adsorption capacity of 208.77 mg g<sup>-1</sup> at 308.15 K was obtained by crosslinking cationic starch when it was employed to remove reactive golden yellow dye from wastewater channels. Crosslinking PVA functionalized with chlorosulfonic acid-based vinyl acetate onto crude starch to provide functionality led Pourjavadi *et al.*<sup>199</sup> to create the MNPs@Starch-g-poly(vinyl sulphate) nanomaterial. After five adsorption-desorption cycles, the

regenerated adsorbent is able to remove up to 90% of MG and MB dyes from solution, demonstrating its effectiveness against these cationic dyes in water. Adsorption capabilities of 567 and 621 mg g<sup>-1</sup> were established initially.

Table 2 provides a quick overview of the many bio-based materials that may be utilized to effectively remove dyes.

## 7.2 Micropollutants removal

A variety of procedures have been used to remove micropollutants (heavy metals pharmaceutical and textile effluents) from water supplies, since their accumulation in humans may be very dangerous if it exceeds acceptable limits. BBMs are viewed as beneficial in this context for micropollutant removal due to their malleability, highly selective surface area, and improved adsorption rates (Table 3).

Micropollutant removal from wastewater at a reasonable cost has emerged as a major area of study. Micropollutants may be selectively removed at low concentrations, and the source materials are the most common biopolymers, making BBMs a promising option for separating and recycling these micropollutants and preventing secondary contamination. Specifically, the highest adsorption capacity of pure chitosan nanofibers was found to be 30.8 mg g<sup>-1</sup> at acidic pH, which is equivalent to the widely testified CS adsorbents for As(III) elimination. Doping iron (Fe) into chitosan nanofibers improved the specific surface area, exposing a higher number of potential active adsorption sites on the adsorbent substrate and improving As(III) selectivity in the metal ion. It is revealed that the presence of CN(CC) groups on the adsorbent surface facilitates As(III) removal.<sup>222</sup> Crosslinking glutaraldehyde and immersing epichlorohydrin resulted in amine grafted on the chitosan nanofiber membranes for electrospinning removal of copper ion from wastewater (Fig. 7a and b). Incorporating amine groups through diethylenetriamine gave the nanofibers an increased stability (with just 6% weight loss after 24 h), which may have been induced by the imine and amine synthesis (Fig. 7c). Fig. 7d shows the loss in weight at varying temperature. Higher quantities of active nitrogen groups in AGNFs result in a stronger chelation adsorption of Cu(II), with maximum adsorption capacities of 166.67 mg g<sup>-1</sup> and 166.67 mg g<sup>-1</sup> from aqueous solution, respectively.<sup>223</sup>

Thiol-functionalized cellulose nanocrystals/PVA/chitosan nanofibrous films displayed improved mechanical characteristics for the adsorption of Cu(II) and Pb(II) ions, with recovery efficiencies of the cellulose nanocrystals (CNC)-containing films reaching 90.58% and 90.21%, respectively.<sup>224</sup> The high surface area of SNC combined with the selectivity of the thiol groups towards the mercuric ions resulted in an 86% improvement in efficiency when compared to untreated nanocellulose.<sup>224</sup> Then, a cellulose acetate nanofibrous membrane hybridized with bio-based silk fibroin was studied for its ability to adsorb heavy metals. Adsorption was generated by the binding of an electronegative COOH group and an amino group in creating a coordination covalent bond with Cu(II) ions. The crosslinked fibers containing 20% CA recovered 75.91 mg g<sup>-1</sup> of copper ions after 60 minutes of adsorption.<sup>225</sup> It was observed that adding





Table 2 Bio-based composites for the effective removal of organic dyes

Bio-based composites	Pollutant	Contact time	pH	Adsorption capacity	Synthesis method	References
Hemicellulose-based adsorbent	Malachite green (MG) dye	60 min	6.5	456.23 mg g <sup>-1</sup>	Periodate oxidation and acetylation	200
Cellulose-based flexible carbon aerogels	Methylene blue	60 min	8	—	Hydrothermal	201
Cellulose-based adsorbents	Congo red, Eriochrome blue	200 min and 100 min	7	380.084, 349.284 mg g <sup>-1</sup>	Free radical polymerization method	202
Cellulose and gelatin-based hydrogel	Ethidium bromide and eosin	30 min	10	—	Grafting of poly(acrylic acid)	203
Copolymerizing acrylic acid (AA)-hydroxyethyl methacrylate (HEMA)-sodium alginate	Brilliant cresyl blue	100 min	—	94%	Free radical polymerization method	204
Magnetic lignin	Titan yellow Congo red	180 min	7	192.51 and 198.24 mg g <sup>-1</sup>	—	205
Starch/activated carbon composite	Methylene blue	90 min	10.5	90%	Carbonization	206
Pd supported on nanocellulose-alginate hydrogel	Methylene blue	5 min	—	—	CNCC and sodium alginate combination solution drops gradually added to CaCl <sub>2</sub> solution	207
Bacteria on polycaprolactone/polylactic acid fibers	Setazal blue BRF-X	—	—	95%	Electrospun	208
Polyvinyl alcohol-chitosan	Direct red 80	1.5 h	2.1	151 mg g <sup>-1</sup>	Electrospun	186
Chitosan/zeolite/polyvinyl alcohol	MO	14 min	8–11	153 mg g <sup>-1</sup>	Electrospun	209
Silica-sand/cationized-starch composite	Acid green 25, methyl orange	20 min	6.8 and 5.8	912.6, 458.7 mg g <sup>-1</sup>	One-step etherification reaction	210
Gelatin/activated carbon composite beads	Rhodamine B	45 min	4	256.41 mg g <sup>-1</sup>	Facile method	211
Cellulose acetate/graphene oxide nanofibers	Indigo carmine	150 min	2	99.8%	Electrospinning	192
Cassava starch-based hydrogel	Methylene blue	45 h	—	2000 mg g <sup>-1</sup>	—	212
Chitosan/polyamide	Reactive black 5	4 h	1	456.9 mg g <sup>-1</sup>	Force-spinning technology	213
Chitosan-gelatin hydrogel loaded with ZnO	Congo red	8 h	10	—	Grafting of acrylamide	214
Polyvinyl alcohol/silica/chitosan composite	Direct red 80	1.5 h	2	322 mg g <sup>-1</sup>	Electrospinning	215
Starch-coated Fe <sub>3</sub> O <sub>4</sub> NPs	Optilan blue textile dye	—	2	50 mg L <sup>-1</sup>	Green synthetic approach	216
Fe <sub>3</sub> O <sub>4</sub> NPs/pectin	MO	—	—	—	Co-precipitation	217
CNCs grafted with acryloyloxyethyltrimethyl ammonium chloride	Neutral reactive blue 19	—	7	80%	Polymerization	218
Starch-doped Fe <sub>2</sub> O <sub>3</sub> nanostructures	Methylene blue	120 min	4, 7	—	Co-precipitation	219
Bacterial cellulose@CdS nanocomposite	Methylene blue	180 min	—	77%	An “anchoring-reacting-forming” pathway	206
Polyamide-6/chitosan	Solophenyl red	—	3	91%	Electrospinning	220
Cellulose aerogel/trimethyl-ammonium chloride	Blue dye 19	30 min	7	160 mg g <sup>-1</sup>	Freeze drying and chemical crosslinking	221



Table 3 Bio-based composites for the effective removal of micropollutants

Bio-based composites	Pollutant	Contact time	pH	Adsorption capacity	Synthetic method	References
Graphene/lignin/sodium-alginate nanocomposite	Pb(II) and Cd(II)	90 min	6	226.24 mg g <sup>-1</sup> and 79.88 mg g <sup>-1</sup>	Hydrothermal polymerization	235
Nanocellulose/poly(vinyl alcohol-co-ethylene) Graphene oxide microcrystalline cellulose	Pb(II) Metformin	24 h	4, 4.5, 6.5 and 8.5	471.55 mg g <sup>-1</sup> 132.10 mg g <sup>-1</sup>	Melt blending extrusion Acid hydrolysis, chemical oxidation cum exfoliation	236 237
Polyethyleneimine functionalized chitosan-lignin	Hg(II)	120 min	5.5	663.5 mg g <sup>-1</sup>	Crosslinking	238
Dual heteroatom NB-co-doped lignin-based biochar	4-NP	12 h	11	—	One-pot carbonization	239
Poly vinylalcohol/chitosan/zinc oxide-NH <sub>2</sub>	Cd(II)	240 min	6	1.239 mmol g <sup>-1</sup>	Cast and electrospun method	240
γ-Fe <sub>2</sub> O <sub>3</sub> @starch	As(III)	120 min	9	96 &	Co-precipitation	241
Chitosan/PVA	Tetracycline	300 h	6	102 mg g <sup>-1</sup>	Electrospun method	232
Starch, CMC-stabilized nano zero-valent iron	Sulfamethazine	60 min	5 & 9	83%	Reduction method	242
Phosphate-decorated carboxymethyl and phosphorylated chitosan (CSP) cellulose	U(VI)	—	5	977.54 mg g <sup>-1</sup>	Crosslinking	243
TiO <sub>2</sub> supported on chitosan scaffolds	Amoxicillin	180 min	7	50%	Sol-gel transition	244
Lignin nanofibers	Fluoxetine	120 min	4.5	185 mg g <sup>-1</sup>	—	231
Ethylenediamine modified pectins	Pb	—	4	94%	—	245
Magnetic starch-based composite adsorbent	Hg(II)	1.5 h	4–7	324.42 mg g <sup>-1</sup>	Co-precipitation	246
Thiolated-spherical nanocellulose	Hg(II)	20 min	5.6	98.6 mg g <sup>-1</sup>	Acid hydrolysis	247
Starch/Fe–Mn binary oxide	As(V) and As(III)	120 min	7	160.63 and 284.64 mg g <sup>-1</sup>	Redox and coprecipitation reaction	243
Cellulose acetate/silk fibroin	Cu(II)	2 h	—	75.91 mg g <sup>-1</sup>	Electrospinning	248
Chitosan/polyethylenimine	Pb and Cd	—	7	341 mg g <sup>-1</sup> and 321 mg g <sup>-1</sup>	—	249
Crosslinked starch polymer	Acetophenone	—	7	180.2 mg g <sup>-1</sup>	Facile one-pot synthetic route	250
Sodium alginate/graphene oxide composite beads	Ciprofloxacin	48 h	4	86.12 mg g <sup>-1</sup>	Magnetic stirring	251
3D alginate-based MOF hydrogel	Tetracycline	—	8	364.89 mg g <sup>-1</sup>	One step method	252
Alginate–protein cryogel beads	Immunoglobulin G (IgG)	90 min	5	175 mg g <sup>-1</sup>	Extrusion dripping method	253
Chitosan/alginate/Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> hydrogel	Pb	120 min	6	234.77 mg g <sup>-1</sup>	—	254
Tricarboxylic cellulose nanofiber	Cu(II)	2 h	—	92.23 mg g <sup>-1</sup>	—	255
f-MWCNTs/FeCl <sub>3</sub> ·4H <sub>2</sub> O	Ibuprofen	120 min	7	1.15 and 11.8 mg g <sup>-1</sup>	Solvothermal	256
Chitosan, hemicellulose, TiO <sub>2</sub>	Ni(II)	—	4	370.4 mg g <sup>-1</sup>	Self-assembly, sol-gel method and polymerization	257
UV-cured chitosan and gelatin hydrogels	Pb <sup>2+</sup> , As <sup>5+</sup>	—	6	—	Microwave-assisted method	258

carboxyl groups and MnO<sub>2</sub> nanoparticles to the tree-shaped cellulose nanofibers increased the surface area by a factor of 2.3 and enhanced the adsorption of the Cu(II) ions to 399.14 mg g<sup>-1</sup>. To create nanofibers, waste pulp with a low cellulose and chitosan content was physically disintegrated before being oxidized with TEMPO to enhance the COO<sup>-</sup> groups for superior adsorption. Both pH (up to 6.2) and oxidation level (26%) were shown to promote adsorption. Bio-based nanofibers can recover about 90% of their original mass after five cycles, which is similar to commercially available montmorillonite nanoclay adsorbents (57 mg g<sup>-1</sup>). Over 94% of the metal ions were captured in the fibers, demonstrating the enormous ability of using CS mixed PVA nanofibers for heavy metal elimination polluted water channels.<sup>226</sup> Carbon-based polyacrylonitrile nanofibers had their carboxyl groups functionalized with chitosan and citric acid. Stability was achieved in adding functional groups to the fibers through pretreatment, peroxidation, and hydrothermal carbonization. When citric acid was added in increments of 0.5 g, the adsorption capacity increased until it

reached 1.0 g, and then it began to decrease. Therefore, incorporation during fiber preparation is optimal. After 5 cycles of adsorption and desorption, the removal efficiency decreased from 80% to 70%. The adsorption of Pb(II) ions was increased by 500% and that of Cd(II) ions by 3000% due to the larger surface area when BBMs was functionalized with oxolane-2,5-dione. Because of this modification to the surface, the efficiency of removal is greatly enhanced while reusability is not compromised.<sup>227</sup>

The dumping of chromium ion into water streams from textile industries has been increasing at an alarming pace, demanding the use of highly effective and selective adsorbents. To combat this issue, researchers have developed aerogels made of cellulose nanofibers grafted with quaternary ammonium. The gel capacity (17.66 mg g<sup>-1</sup>) is very close to that of commercially available quaternary ammonium anion exchangers.<sup>227</sup> A synthetic polymeric material, *i.e.*, polyurethane (PU) was utilized as a matrix to bind carboxymethylated cellulose nanofibrils to avoid accumulation and enable the fibrils to



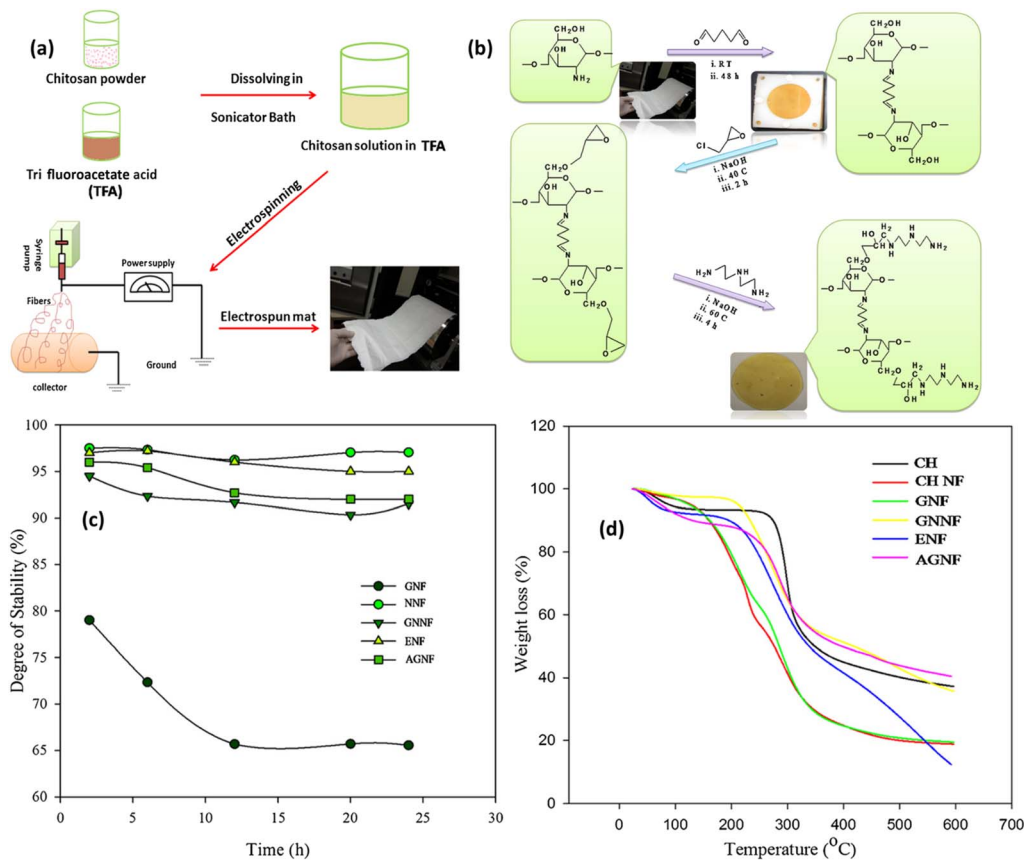


Fig. 7 (a) Methodology for optimizing the electrospinning parameters and preparing the NFs membrane. (b) Fabrication steps for the synthesis of novel AGNFs. (c) Stability curve of the functionalized membrane. (d) TGA thermograms of the prepared novel membrane.<sup>223</sup> Copyright (2018), Elsevier.

freely interrelate with adsorbate, which surprisingly influenced the adsorption rates. Because of the improved malleable strength of the PU combined CMCNFs, the strain-to-failure ratio rose, revealing the interfacial contacts between the matrix and the fibrils. The metal ions Cu(II), Pb(II), and Cd(II) adsorption efficiencies on the PU/CMCNFs were 40.2%, 95.1%, and 61.3%, respectively, while neat-PU adsorption efficiencies were extremely low (1%), demonstrating that the  $\text{NH}_2$  groups on polyurethane did not contribute to the adsorption.<sup>227</sup>

Using a spiral wound module to sustain electrospun chitosan nanomaterials improved both membrane surface area to packing density and volume ratio. Adsorption of heavy metal ions is proportional to the density of the chitosan nanofiber input flow rate and the deposition. The flow rate of  $0.9 \text{ L h}^{-1}$  is similar to that of commonly available nanofiltration membranes, and the nanofibers were able to retain over 90% of chromium ( $\text{Cr(VI)}$ ). The specific adsorption of chromium(VI) over other heavy metal ions was also shown, with peak desorption occurring in less than 2 minutes in both alkaline and acidic conditions, indicating a high regeneration potential.<sup>228</sup> In another study a poly(ethylene oxide)/chitosan complexed permutit was developed for treatment of metal ions. In this case, PEO is meant for enhanced blending, chitosan is meant for chelation, and permutit is meant for adsorption; each

polymeric fiber is unique and may provide a combinatory effect. They concluded that the initial chromium concentration and integration of low-quantity permutit are suitable for adsorption. It involves exchanging  $\text{Na}^+$  in the solution for  $\text{H}^+$ , which prevents the formation of  $\text{H}_2\text{CrO}_4$  and the electrostatic interactions of the ionized ( $\text{NH}_3^+$ ,  $\text{OH}^{2+}$ ) molecules with  $\text{HCrO}_4$ . The BBMs were 90.44% effective in removing water from a solution containing  $50 \text{ mg L}^{-1}$ .<sup>229</sup> The same team of scientists used chitosan, polyvinyl alcohol, and polyethylene glycol to generate several nanofibrous layers. By integrating the aminated  $\text{Fe}_3\text{O}_4$  nanomaterial into the BBMs, they improved their water resistance and thermomechanical properties. As the amount of bio-based material increased, the number of active sites inside the nanofibers capable of chelating metal ions for removal subsequently increased. Maximum adsorption capabilities of 525.8 and  $509.7 \text{ mg g}^{-1}$  for Pb(II) and Cr(VI) ions were determined, respectively. Regeneration cycles showed the membranes to be highly reusable for industrial adsorption applications.<sup>230</sup>

To combat these problems, researchers reported on the synthesis of chitosan nanofibers by a thermally-induced phase separation method at low temperatures. Nanofibers were produced at relatively high concentrations of chitosan solutions, and hole growth in the membrane was induced by a solution of water, acetic acid, and ethanol. An



ethylenediamine tetraacetic acid (EDTA) solution was used to remove heavy metal chelation by amine groups on the fiber surface. After six washings in water, the chitosan nanofibers still managed to hold on to 90% of the Cu(II) that had been dissolved in the water. The method of production not only improved productivity, but also showed remarkable recyclable potential.<sup>230</sup>

Biopolymer adsorbent development lessened some of the risks associated with the aforementioned pollutants, but new contaminants continue to be a challenge for water preservation. Human waste was a major factor in the overall pollution problem. Electrospun lignin nanofibers were characterized by the presence of functional groups, such as ethers, alcohols, and aromatic rings by Camera and colleagues, who found that they removed 70% of the pharmaceuticals pollutant fluoxetine from wastewater (van der Waals forces, electrostatic interactions, –stacking and hydrogen bonds).<sup>231</sup> Chemical crosslinking by glutaraldehyde successfully removed tetracycline, another significant pharmaceutical contaminant, from chitosan combined with PVA nanofibers. A strong adsorption capacity (102 mg g<sup>-1</sup>) was discovered when the various concentrations were adjusted to a volumetric ratio of PVA/chitosan (25 : 75). Ultraviolet (UV) light degrades bisphenol A and diclofenac from TiO<sub>2</sub> nanoparticles immobilized on PVA nanofibers/electrospun gum karaya.<sup>232</sup> Methane plasma-treated TiO<sub>2</sub> membranes had increased sorption and hydrophobicity capacity because of the development of water droplets on their surface, which resulted in the reduction of 20% of diclofenac and 18% of bisphenol A because of the formation of free radicals in response to UV light.<sup>233</sup> Water beaded up on cellulose nanofibers treated with trichloro(heptadecafluorodecyl) silane because of the resultant hydrophobicity. This property is the subject of investigation as a possible means of extracting oil from water. Nanofiber membranes that have been modified in this way have a 99% effectiveness rate at separating oil and water merely by utilizing gravity.<sup>234</sup> Increases in hydrophobicity and penetration fluxes for a broad range of oils were achieved using silver nanoparticles, polydopamine, and -cyclodextrins on PLA nanofibers, with a separation performance of 95% being considered satisfactory.

### 7.3 Oil spills

Worldwide interest in water–oil separation has been inspired by the serious environmental contamination caused by the discharge and leakage of organic compounds from crude oil. The Deepwater Horizon oil disaster in 2010 released an estimated 5 million barrels of crude oil into the Gulf of Mexico.<sup>259</sup> The oil and gas sectors create over 0.250 billion barrels of sludgy sewage per day. In light of this, there has been a lot of focus on developing new, more eco-friendly oil-absorbing materials at lower costs for use in oil spill cleaning. BBMs are the greatest raw material choice for making water–oil separation products that are cheap, efficient, and safe for the environment. Oil–water separation materials developed from BBMs with hydrophobic/hydrophilic interface structures have been intensively researched and used by scientists in recent years, with positive results (Table 4). The dopamine-cellulose surface was

modified by fabricating a stimulus-responsive azeobenzene-fluorosilane compound and grafting it onto the surface. The hydrophilic surface of the cellulose-based substance was brought about by the isomerization impact of UV radiation. The biomaterial's ability to resist organic pollutants, bacteria, and fungi, and its impressive capability for adsorbing oil from O/W combinations make it an attractive choice for wastewater treatment. Ejeta *et al.* developed a cotton-based superwetting material with superoleophilicity (oil-loving) and superhydrophobicity (water contact angle > 150°) to separate water-in-oil emulsions (oil contact angle 5°). Extremely high infiltration fluxes of 10 400 L m<sup>-2</sup> h<sup>-1</sup> and 867 500 L m<sup>-2</sup> h<sup>-1</sup> for W/O emulsion were observed in the resulting SCM after filtering by gravity and external pressure, respectively.<sup>260–262</sup> Since they are durable in chemically aggressive conditions and recyclable, superwetting materials for water–oil emulsion separation are a practical choice for widespread industrial application.

Epoxidized soybean oil was impregnated into cellulose aerogels (GA) so they could soak up oil (ESO). The water contact angle of the cellulose-based aerogels was increased to 132.6 degrees after hydrophobicity adjustment by ESO. An aerogel that has been adsorbed maintains almost 90% of its adsorption capacity after 30 absorption–desorption cycles, proving its use in W/O separation of industrial wastewater and oil spill removal.<sup>263</sup> Recently, researchers working on BBMs for water–oil separation shifted their attention to how to control the surfaces of hydrophilic and hydrophobic interfaces.

### 7.4 Membrane filtration

The membrane separation technique is well established and effective for wastewater treatment due to its comfortable working conditions, size-sieving ability, and fuel efficiency. Water filtering membranes composed of bio-based nanoparticles have a lot of untapped potential because of their high surface-to-volume ratio, extraordinary mechanical capabilities, low ecological effect, and sustainable development. Polymer matrices, including poly(ether sulfone) (PES), poly(vinyl alcohol) (PVA) and poly(vinylidene fluoride) (PVDF), were often used with BBM nanocomposite-based membranes to increase the membrane characteristics like selectivity, permeability, tensile strength, and anti-biofouling.<sup>275–278</sup>

Recently, a vacuum filtration approach was employed to synthesize graphene oxide nanocolloid (nanoGO) biohybrids and TEMPO-mediated oxidative cellulose nanofibers for the purpose of developing self-assembled bio-based membrane for water purification. In the biohybrids, TOCNF has a large amount of CCOH groups that facilitated Cu(II) adsorption, while NanoGO acted as nodes and joints, vastly enhancing the BBM membranes' flexibility, mechanical strength, hydrolytic stability and water flux.<sup>279</sup> By constructing an ultrathin GO barrier layer on a cellulose nanofiber (CNF) membrane without the use of any crosslinker, high-flux water purification membranes may be made with a water flux rate of 18 124 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> and a dye infiltration rate of 90 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>.<sup>280,281</sup> Meanwhile, 2-methyltetrahydrofuran and glycerol derivatives were used to create asymmetric CA full-bio-based NF membranes *via* non-



Table 4 Bio-based composites for the effective adsorption of oils

Bio-based materials	Oil	Hydrophobic modification	Adsorption capacity	Method	References
Carboxymethyl chitosan	Marine diesel	Monochloroacetic acid	—	Partial carboxymethylation	264
H-Oleoyl-carboxymethyl chitosan	Wastewater of oil extraction	Oleoyl chloride	95%	Carboxymethylation and acylation	265
Modified activated carbon aerogel	Gasoline, organic solvent	Polydimethylsiloxane	4.06–12.31 g g <sup>-1</sup>	Polymer coating	266
Sodium salt of oleoyl carboxymethyl chitosan	Marine diesel	Oleoyl chloride	75–85%	Carboxymethylation and acylation	267
Chitosan-silica hybrid (nano-sized)	Toluene, cyclohexane, <i>n</i> -heptane, chloroform	Tetraethyl orthosilicate, 3-(triethoxysilyl)propyl isocyanate	90%	Sol-gel encapsulation	268
Cellulose nanocrystals (nano-sized)	Marine diesel	Choline chloride and oxalic acid dihydrate	—	Deep eutectic solvents	269
Polyvinylpyrrolidone-coated magnetite nanoparticles (nano-sized)	MC252 oil	—	~100	Hydrothermal method	270
Cellulose nanofibril and polyvinyl alcohol	Crude oil	Span-80	54–140 g g <sup>-1</sup>	Emulsification and freeze drying	271
Blends of poly(vinyl alcohol) nanoparticles with chitosan or starch (nano-sized)	Toluene, kerosene and hydraulic oil	—	48.7 g g <sup>-1</sup> , 39.3 g g <sup>-1</sup> and 22.7 g g <sup>-1</sup>	Emulsion polymerization	272
Polyurethane/chitosan foam	Castor oil	Chitosan and ricinoleic acid	267.24 mg g <sup>-1</sup>	Polymerization	273
H-PAA-T	Insoluble oil	Chitosan and polyacrylic acid	135.9 mg g <sup>-1</sup> and 990.1 mg g <sup>-1</sup>	Thermal cross-linking	274

solvent induced phase separation. Increasing the concentrations of 2-MeTHF and CA led to the highest performance, with porosity between 12.8 and 5.5 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> and RB removal of >90%.<sup>282</sup>

The cost-effective membrane developed by BBMs has vast possible applications and promising future growth in the area of wastewater resource recovery. The BBMs membrane has low strength, which results in a limited life, and is readily polluted by waste during the industrial reaction process, which further reduces its usefulness. Therefore, high-strength, green chemistry and antifouling thin film materials should be explored as part of future research into BBMs filtering membrane for industrial wastewater treatment.

## 8. Conclusion and future perspective

The next wave of readily available resources is undoubtedly going to be made up of natural biopolymer-based resources (especially polysaccharides) produced from various derivatives. Many researchers have been drawn to the study of natural biopolymers because of their many desirable characteristics, including their abundance, nontoxicity, renewability, adaptability, low cytotoxicity, and potential for a wide range of applications. Importantly, biopolymer-supported Ag, Cu, Pd, ZnO, TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, and carbon-based materials (GO, CNTs and nanotubes) are among the most successful techniques in nanotechnologies, and the abovementioned polysaccharides are regarded as substitute renewable bio-resources and excellent supports for the nanocatalysts manufacturing.

Natural or biopolymeric-based nanomaterials, such as the conventional adsorbents, require more research to improve

their manufacture in order to be practical and long-lasting for use in industry. It has been proven possible to use nanomaterials based on natural/biopolymeric substances to aid in the flocculation/coagulation of solid compounds in wastewater treatment. Polysaccharides, such as starch, cellulose, chitosan, and pectin, show promise as natural/biopolymers due to their ability to compete with conventional activated carbon in terms of sustainability, reactivity, excellent physicochemical attributes, chemical stability, and significant specificity towards dyes, aromatic compounds and toxic metals.

Concerns about the quality of the environment and the wellbeing of its inhabitants have long made wastewater treatment a top priority for public health officials. The use of evolving nanostructured materials has the potential to improve industrial water remediation, as pollutants can be eliminated while using fewer resources than traditional methods. However, more research is needed in this area, as a major technical barrier is their inflexibility for engineering processes and lack of competitiveness compared to conventionally deployed existing water treatment options. The creation of bio-based nanomaterials using traditional procedures is fairly easy, facile, and innocuous to the environment. Nevertheless, new studies have discovered considerable promise for numerous applications of the biopolymer-based nanomaterials across varied study disciplines. From the perspectives of both ecological remediation and resource management, they thus have the capability to develop as a successful, cost-efficient, and environmentally friendly alternative to current water treatment technologies.

Despite significant progress in the catalytic and synthetic uses of natural biopolymer-based nanomaterials, the following should be given special attention in the next investigations:



- A low-cost, scalable method of producing nanomaterials from polysaccharides.
- Synthesis of biopolymers and its utilization in the wastewater purification process using a wide variety of bio-waste nanomaterials.
- For the production of nano membranes and their use in the wastewater treatment process, it is advantageous to make use of naturally occurring supports such as clays, zeolites, and montmorillonite since they are inexpensive, non-toxic, and readily accessible.
- Processing of animal and agricultural waste, such as bristles, bone, and eggshells, to create biopolymer-based nanomaterials for use in water purification.
- Utilization of greener biological procedures to lower the price of producing bio-based nanomaterials under moderate settings and boost their nano-catalytic efficacy.
- Enhanced magnetic nanoparticles based on polysaccharides for water/wastewater purification.

## Conflicts of interest

There are no conflicts to declare.

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