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Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano) materials for sustainable water treatment: A review

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Abstract

Natural biopolymers, polymeric organic molecules produced by living organisms and/or renewable resources, are considered greener, sustainable, and eco-friendly materials. Natural polysaccharides comprising cellulose, chitin/chitosan, starch, gum, alginate, and pectin are sustainable materials owing to their outstanding structural features, abundant availability, and nontoxicity, ease of modification, biocompatibility, and promissing potentials. Plentiful polysaccharides have been utilized for making assorted (nano)catalysts in recent years; fabrication of polysaccharides-supported metal/metal oxide (nano)materials is one of the effective strategies in nanotechnology. Water is one of the world's foremost environmental stress concerns. Nanomaterial-adorned polysaccharides-based entities have functioned as novel and more efficient (nano)catalysts or sorbents in eliminating an array of aqueous pollutants and contaminants, including ionic metals and organic/inorganic pollutants from wastewater. This review encompasses recent advancements, trends and challenges for natural biopolymers assembled from renewable resources for exploitation in the production of starch, cellulose, pectin, gum, alginate, chitin and chitosan-derived (nano)materials.

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Declaration of Competing Interest

The authors report no declarations of interest.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2020.116986.

Keywords

Polysaccharides; Sustainable nanomaterials; Wastewater treatment; Degradation; Organic dyes; Heavy metals; Pollutants

1. Introduction

Water is one of the world's foremost environmental stress concerns; the supply of safe, affordable drinking and/or clean water is a massively challenging proposition throughout the world. Rapidly escalating environmental contamination of natural resources is an emerging issue in recent years that needs to be tackled on priority basis for sustaining the earth and its inhabitants for future generations. Indeed, resources of freshwater are limited and they are deteriorating fast due to the discharge of untreated or inadequately-treated wastewaters. Traditionally, coagulation/flocculation, ion exchange, floatation, reverse osmosis, oxidation, adsorption, membrane separation, ultra-filtration, sedimentation, electro-precipitation, and advanced oxidation processes are mainly resorted to as the accessible technologies in treating waste-water. Conventional methods of wastewater treatment and purification cannot possibly yield the desired extent of purification to attain accurate or cost-effective discharge standards (Khoramzadeh, Nasernejad, & Halladj, 2013; Nasrollahzadeh, Sajjadi, Dasmeh, & Sajadi, 2018; Yargıç, Şahin, Özbay, & Önal, 2015).

Beyond the stoichiometric use of reagents, catalysis is one of the most important foundation of "green chemistry" with novel processing systems and deployment of assorted novel catalysts with many benefits in terms of product selectivity, process utilization, energy reduction as well as the utilization of safer materials and alternative reaction media/conditions. Novel wastewater treatment approaches such as UV photolysis/ photocatalysis, activated carbon adsorption, ozonation, and perovskite adsorption, among others can be utilized for the degradation of pharmaceutically active compounds, metal ions, and toxic dyes (Cai et al., 2018; Garba, Xiao et al., 2019; Garba, Zhou, Zhang, & Yuan, 2020; Karnib, Kabbani, Holail, & Olama, 2014; Xu, Nasrollahzadeh, Sajjadi et al., 2019). Interestingly, the expensive energy-intensive commercially-activated carbons applied for this goal can be effectively replaced by renewable alternatives and low-cost biosorbents that are based on natural biopolymers (Crini, 2006; Xu, Nasrollahzadeh, Sajjadi et al., 2019). In general, the development of 'greener' and eco-friendly treatment technologies must be perceived as a key element for the industries dealing with toxic, hazardous and chemically laden wastewater (Atarod, Nasrollahzadeh, & Sajadi, 2015; Hatamifard, Nasrollahzadeh, & Lipkowski, 2015; Hatamifard, Nasrollahzadeh, & Sajadi, 2016; Iravani & Varma, 2020a; Khodadadi, Bordbar, & Nasrollahzadeh, 2017; Khodadadi, Bordbar, & Nasrollahzadeh, 2017; Maryami, Nasrollahzadeh, Mehdipour, & Sajadi, 2016; Nasrollahzadeh, Bagherzadeh, & Karimi, 2016; Nasrollahzadeh, Sajadi, & Maham, 2016; Omidvar, Jaleh, & Nasrollahzadeh, 2017; Sharma, Zboril, & Varma, 2015; Sivan et al., 2019; Varma, 2014; Zhang, Yu et al., 2018; Zhang, Hou et al., 2018).

Among the greener technologies, the synthesis of natural (nano) catalysts with lower costs, and enhanced efficiency has been a focus area for the treatment of wastewater pollutants as exemplified by nanoscale filtration procedures and the adsorption of pollutants by metal/metal oxide based nanoparticles (NPs) (Ai, Yue, & Jiang, 2012; Crini, 2006; Meng, Zhu, Choi, Park, & Oh, 2011; Nasrollahzadeh, Baran et al., 2020; Nasrollahzadeh, Sajjadi, Dasmeh et al., 2018; Xu, Nasrollahzadeh, Sajjadi et al., 2019; Zhang, Sèbe, Rentsch, Zimmermann, & Tingaut, 2014). The utilization of nanostructures with unique features namely large surface area, significant chemical reactivity, cost-effectiveness, and lower power consumption, can meaningfully exploit multifunctional nanosystems that enable particle retention and removal/elimination of pollutants.

Over the decades, the accessibility of synthetic polymers derived from gas, petroleum, and nonrenewable carbon sources is diminishing as researchers are exploring more readily available and sustainable alternatives, namely, natural biopolymer-derived materials from renewable resources. Natural biopolymers are polymeric organic molecules acquired from renewable resources (alga, plants, microbial biomass and animals) comprising monomeric parts that are bonded covalently to form larger molecules (Baran & Nasrollahzadeh, 2020; Den, Sharma, Lee, Nadadur, & Varma, 2018; Hebbalalu, Lalley, Nadagouda, & Varma, 2013; Iravani & Varma, 2020b; Mohazzab et al., 2020; Motahharifar, Nasrollahzadeh, Taheri-Kafrani, Varma, & Shokouhimehr, 2020; Nasrollahzadeh, Shafiei, Nezafat, & Bidgoli, 2020; Nasrollahzadeh, Issaabadi, & Varma, 2019). They represent a highly promising option for the generation of sustainable materials owing to their extraordinary structural and physical features, safety, availability, and economics; biocompatibility and the biodegradability of these natural resources can enhance their utilization as nanocatalysts and nanosorbents. Low-cost biopolymers such as polysaccharides are diverse in size, structure, and molecular chains, making them attractive candidates for stabilization and immobilization and the reduction of NPs; biopolymer-based (nano) catalysts can be immobilized on their uniquely featured reactive groups to enhance (nano)catalytic efficiency and stability (Crini, 2005; Kumar, 2000; Oladoja, Adelagun, Ahmad, Unuabonah, & Bello, 2014; Xu, Nasrollahzadeh, Sajjadi et al., 2019; Xu, Nasrollahzadeh, Selva, Issaabadi, & Luque, 2019). The salient advantageous features for the utilization of polysaccharide supports include the release of nanostructures during operations, the prevention of aggregation, the ease of recovery of catalytic materials, and importantly, improving the photocatalytic efficiency compared to the conventional slurry systems.

Pollution generated by dyes, heavy metals, nitroarenes, and pesticides in water/wastewater is a global major problem; in particular, the dye effluents are identified as largest class of industrial colorants and significant threat to aquatic environments as the discarded dyes seriously affect humans and flora/fauna (Albukhari, Ismail, Akhtar, & Danish, 2019; Khan et al., 2016; Sajjadi et al., 2020). Toxic dyes/nitroarenes are hazardous, biologically and chemically stable, non-biodegradable and water soluble organic contaminants that are responsible for a diversity of human diseases *e.g.* kidney failure, skin irritation, nervous system damage, liver disease, *etc.* (Chamjangali, Bagherian, Javid, Boroumand, & Farzaneh, 2015; Dai et al., 2009; Mazaheri, Ghaedi, Azqhandi, & Asfaram, 2017; Nasrollahzadeh, Nezafat, Gorab, & Sajjadi, 2020). The main sources of contamination from dyes have their origin in diverse industries, namely coloration of textiles, inks, paints, paper, plastics, dye sensitized solar cells, energy transfer cascades, display devices, light emitting diodes, laser welding processes, as well as food and/or cosmetic dyes which are particularly derived from azo dyes (Sannino, Vaiano, Sacco, & Ciambelli, 2013; Singh & Arora, 2011). Textile dye effluents are generally present as a mixture of several dyes in diverse percentages depending on the factory schedule, and the extent of dye fixation on a fabric (Yaseen & Scholz, 2018). Consequently, the removal of such admixed dyes (in diverse concentration levels and mixing ratios) in wastewaters is extremely vital. The development/improvement of novel eco-friendly treatment approaches should be considered as a critical element for the industries generating toxic and hazardous chemical-laden wastewater.

Generally, polysaccharide derivatives showed high removal efficiency of both inorganic (*e.g.* heavy metal ions) and organic (*e.g.* dyes, nitroarenes, and pesticide formulations) pollutants *via* adsorption, reduction/degradation and coagulation/flocculation methods (Kanmani, Aravind, Kamaraj, Sureshbabu, & Karthikeyan, 2017; Sajjadi, Nasrollahzadeh, & Tahsili, 2019; Sivan et al., 2019). Among these, adsorption can be considered as a good option for the removal of the hazardous organic contaminants, since it can be simply deployed thus avoiding the formation of various toxic intermediates, which gets generated while treating novel organic contaminants in aqueous solutions (Ertas & Uyar, 2017; Ghaedi et al., 2012; Liu et al., 2020). The utilization of biopolymer-based adsorbents is not only restricted to the removal of heavy metals, dyes and nitro compounds, but extends to a range of toxic contaminants including pharmaceuticals (Amouzgar & Salamatinia, 2015), hydrocarbons (Xu, Yong, Lim, & Obbard, 2005), pesticides (Sahithya, Das, & Das, 2015), phosphates (An, Jung, Zhao, Lee, & Choi, 2014), nitrates (Rajeswari, Amalraj, & Pius, 2016), fluo-rides (Jagtap, Yenkie, Labhsetwar, & Rayalu, 2011), perchlorates (Sayed & Jardine, 2015), and radioactive ions (Lu et al., 2016), *etc*.

Polysaccharides are sustainable and environmental-friendly organic biopolymers naturally engineered by living organisms and comprise the repeat unit of monosaccharides ($C_n(H_2O)_n$). In this respect, chitin/chitosan, cellulose (Ahmad, Ahmed, Swami, & Ikram, 2015; Olivera et al., 2016; Xu, Nasrollahzadeh, Sajjadi et al., 2019), starch (Yusof & Kadir, 2016), pectin (Sharma, Naushad, Pathania, & Kumar, 2016), alginate (Swain, Patnaik, & Dey, 2013; Xu, Nasrollahzadeh, Sajjadi et al., 2019), guar gum (Kee, Mukherjee, & Pariatamby, 2015) and xanthan gum (Kee et al., 2015; Pi et al., 2016) are important examples of sustainable and environmental-friendly organic biopolymers (Fig. 1). Among the polysaccharides, after cellulose (most abundant biopolymer on earth), chitosan, the second most abundant biopolymers have been preferred for broad ranging environmental appliances (Ahmad et al., 2015; Olivera et al., 2016; Xu, Nasrollahzadeh, Sajjadi et al., 2019). Herein, this paper sums up the recent advances in the remediation and elimination of aqueous pollutants and noxious contaminants using some of the most abundant natural biopolymer resources, namely chitin/chitosan, starch, gum, alginate, pectin, and cellulosic (nano)materials.

2. Polysaccharide derived (nano)catalysts for water treatment

Recently, polysaccharide derived (nano)catalysts have been investigated as heterogeneous and novel catalysts with excellent catalytic prowess for the water treatment. Different applications of polysaccharide derived (nano)catalysts in water treatment are summarized in this section.

2.1. Cellulose-based nanomaterials

2.1.1. Chemistry and properties—Cellulose-based materials for example, cellulose nanofibrils (CNFs) and nanocrystals (CNCs) have found numerous applications in medicine, bioplastics, barrier films, biomedicine, pharmaceutics, electronics, nanocomposites, membranes, supercapacitors, and cosmetic products. These nanomaterials have garnered substantial interest for deployment as (nano)sorbents because of their unique properties (Fig. 2) (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Ray & Shipley, 2015; Trache, Hussin, Haafiz, & Thakur, 2017); cellulose-based adsorbents and their use in water and wastewater treatment have been reviewed (Table 1) (Mohammed, Grishkewich, & Tam, 2018).

While the materials have shown demonstrative effectiveness in separating and eliminating various contaminating materials, the environmental influences of modified cellulose nanomaterials should be assessed; their non-toxicity and biodegradability attributes, though suitable for wastewater treatment, need stability evaluation. Sizeable amounts of cellulose nanomaterials are needed for remedial applications, thus their cost, feasibility of access, and life cycle considerations for the large scale manufacturing of these materials must be considered (Shatkin, Wegner, & Neih, 2013) although cellulosic nanomaterials have environmental advantages over activated carbon derived from charcoal. Biochar (obtainable from plant biomass) with its similarity to activated carbon has less functionality than cellulose nanomaterial. Cellulosic nano- and microfibers with suitable dimensions and strength have been used to generate membranes for water management. Membranes have been prepared as pristine cellulose nanomaterial mats as well as from cellulose nanomaterials incorporated into assorted polymer matrices such as cellulose triacetate, polypyrrole, poly(vinylidene fluoride), poly (ethylene oxide), poly(ether sulfone), poly(vinyl alcohol), poly(acrylonitrile), and poly(3-hydroxybutyrate) (Carpenter, de Lannoy, & Wiesner, 2015); they can be applied in membrane distillation, nanofiltration, hemodialysis, microfiltration, and ultrafiltration. The presence of cellulose nanomaterials within polymer matrices can noticeably change the membrane characteristics. For instance, better membrane tensile strength, surface hydrophilicity, superior permeability, resistance to biofouling, and enhanced selectivity can be attained by adding cellulose nanomaterials which are highly biocompatible and eco-friendly and ideally suited for pharmaceutical, biomedical and environmental applications of these nanocomposite membranes (Carpenter et al., 2015; Yin & Deng, 2015); challenge being the application of polymer-cellulose nanocomposites realizing uniform and homogeneous dispersing within polymer matrices (Xie, Mai, & Zhou, 2005). Homo-aggregating cellulose nanomaterials destructively influence the amorphous and semi-crystalline polymers by upsetting the polymer solutions homogeneity (Varma, 2016).

2.1.2. Applications for water treatment

2.1.2.1. Removal of oil and organic solvents.: Cellulose is an ideal adsorbent due to its low-cost and abundance relative to commercial ion exchange sorbents. Although unmodified cellulose lacks certain properties to be applied as an effective adsorbent, namely variable physical stabilities and low heavy metal adsorption capacities (O'Connell, Birkinshaw, & O'Dwyer, 2008), among others; thus, surface engineering *via* chemical modification have been studied in recent years. Modified cellulose nanomaterials matrices can be applied for the sorption of organic contaminants; inherently hydrophilic cellulose nanomaterials are modifiable to enhance their affinity for hydrophobic materials. The surface modification of cellulosic nanomaterials can be attained by insertion of both, the organic and inorganic groups as has been exemplified *via* the atomic layer placement of titanium dioxide (TiO_2) NPs onto cellulose nanomaterial aerogels (Korhonen, Kettunen, Ras, & Ikkala, 2011); TiO_2 veneer formed a low-energy surface on the fibers to generate nanocellulose-based material which has both, the oleophilic and hydrophobic properties and they could absorb oil and diverse organic solvents from the water's surface with 20–40 g/g and 80–90 % vol/vol capacity. Jiang and Hseih achieved better sorption capabilities of model organic solvents ranging from 139–345 g/g by vapor phase deposition of triethoxyl(octyl)silane on CNFs aerogels (Jiang & Hsieh, 2014). The addition of hydrophobic silanes to cellulose nanomaterials transformed them into water-repellant and oleophilic materials which could eliminate oil from the top or below the surface of water; heterogeneous catalyst could be reused 6 times. Wang, Yadav et al. (2014) and Wang, Zhang et al. (2014) prepared hydrogels with graphene oxide embedded in the nanocellulose matrix. After the H_2 gas reduction, the graphene oxide-cellulose nanomaterials composites could sorb cyclohexane and dimethylformamide (DMF).

Other hazardous atmospheric volatile organic compounds (VOCs), namely, phenol, toluene and xylenes are of health concern owing to their low solubility and volatility that adversely effects the environment and human health (Al Momani, 2007); toluene, an ingredient utilized in adhesives, paints, detergents, and inks, is a typical VOC in water (Zeng et al., 2009). Rezaee, Pourtagi, Hossini, and Loloi (2016) reported that TiO_2 NPs impregnated on the microbial cellulose (MC) surface (MC/TiO_2) could degrade toluene in air at ambient temperature under UV-irradiation conditions with maximum photodegradation abilities towards toluene pollutants being 87.79 % and 76.87 % after 40 min irradiation with UVC and UVA, respectively.

2.1.2.2. Removal of pesticides.: Pesticides are major organic pollutants in water bodies that are generally treated using assorted techniques such as photocatalytic degradation, aerobic degradation, ozonation, ultrasound combined with (photo)Fenton treatment, advanced oxidation processes, electrodialysis, reverse osmosis, adsorption, *etc*. (Ahmad et al., 2010; Hladik, Roberts, & Bouwer, 2005; Salman, Njoku, & Hameed, 2011). Based on target organisms, the main classes of pesticides are herbicides, fungicides, and insecticides, with herbicides accounting for approximately 46 % of the total pesticide (4.1 million tons) use worldwide (Mojiri et al., 2020). 2,4-Dichlorophenoxyacetic acid (2,4-D), one of the oldest herbicides and a common type of pesticide utilized broadly in the agricultural industry, is an organochlorine compound commercially accessible since 1945 (Kanmani et al., 2017). Nevertheless, pesticides are widely used in agriculture, industry and households, and they pose a risk to ecosystems and human health. Salman et al. (2011) reported that the maximum allowable concentration of 2,4-D in affordable drinking water is 100 μg L^{-1}. Due to its endocrine disrupting and plant hormone activities, 2,4-D (well-known plant growth regulator) has been listed as one of the top 10 bestselling pesticides (Wang, Ge et al., 2013). The 2, 4-D accumulation in agricultural products and natural environment not only can cause serious contamination to the environment/ecosystem, but also jeopardizes public safety, human health, and economic advancement; indeed, it is associated with the occurrence of human cancer, endocrine disruption, *etc*. (Smith, Smith, La Merrill, Liaw, & Steinmaus, 2017). In yet another attempt, Zhang, Zhao et al. (2019) and Zhang, Ma et al. (2019) described a facile and novel method to prepare fluorescent microfluidic paper chips (paper@QDs@MIPs) by depositing fluorescence signal material, CdTe quantum dots (QDs) onto cellulose paper as a base material, and studied the ability of the resulting paper@QDs@MIPs in rapid detection of pesticide 2,4-D.

2,4-Bis(isopropyl amino)-6-(methylthio)-*s*-triazine or prometryn (Pr), a colorless crystal, nonionic and hydrophobic herbicides pose a serious threat to the environment as well as human/animal's health (Plakas & Karabelas, 2009). In this context, Garba, Zhou, Lawan, Zhang, and Yuan (2019) synthesized a copper modified microcrystalline cellulose (Cu@MCC) by a facile synthesis and deployed it as an effective composite adsorbent for Pr herbicide adsorption from synthetic waste-water; good adsorption capacity of 97.80 mg g^{-1} at ambient temperature was discerned with sufficient stability for 6 sequential adsorption-desorption runs. In another study, a facile and novel process was developed for embedding triolein into cellulose acetate sphere as a sustainable and efficient composite adsorbent for removing lipophilic pollutants (Liu, Dai, Qu, & Ru, 2005); adsorbent could be used for the effective removal of two organochlorinated pesticides (OCPs) of low concentrations from water. In addition, a novel class of recoverable CdS@x%SCNF (x = 5, 10, 15, 20, 50) bionanocomposites was attained by depositing cadmium sulfide NPs on a matrix of biomass-derived silanized cellulose nanofibers *via* a solvothermal methodological route (Gupta, Kumar, Tikoo, Kaushik, & Singhal, 2020), and used for the adsorptive detoxification of pesticide (organophosphate insecticide chlorpyrifos) and textile dye (MB and safranin O) contaminants from wastewater. The as-synthesized CdS@10 %SCNF bionanocomposite exhibited maximum adsorption capacities for all the contaminants and could be reused up to six adsorptive runs.

Cellulose composites and metal organic frameworks (MOFs) are promising adsorption candidates as they combine the high adsorption capacities of MOFs and the sustainability of cellulose-based (nano)materials. Abdelhameed, Abdel-Gawad, Elshahat, and Emam (2016) selected Cu-BTC MOFs for the adsorption of ^{14}C-ethion as an organo-phosphorus insecticide pollutant. Cu-BTC@cotton was fabricated *via* a facile method by an interaction of Cu in MOF and cellulose functional groups; indeed, the ethion molecule can bind with adsorbent by forming chemical bonds with Cu-BTC (copper-benzene-1,3,5-tricarboxylic acid) and cotton fabrics (chemisorption). As a result, the maximum sorption capacity of as-prepared composite reached 182 mg g^{-1} and the ethion removal percent exceeded 97 %. After recovering five times, the Cu-BTC@cotton adsorption efficiency was still retained and surpassed 85 %. Interestingly, Gan et al. (2019) extracted carbon nanofiber (CCNF) from abundant cellulosic source *via* electrospinning and pyrolysis treatment strategy and coated $CoFe_2O_4$ on it *via* a hydrothermal method to generate a novel catalyst for the activation of peroxymonosulfate (PMS). The appliance of $CoFe_2O_4$/CCNF nanocomposite activated PMS has been illustrated in the degradation of dimethyl phthalate (DMP), a classical organic pesticide pollutant, in wastewater. Besides, the catalyst could be easily reused in catalytic degradation reactions for 5 cycles with an insignificant loss in catalytic performance.

2.1.2.3. Removal of heavy metal ions.: As aforementioned, there has been a growing ecological and global public health concern associated with wastewater contamination by heavy metals. Heavy metals represent any naturally occurring element that has a high atomic weight or a high density (5 times higher than that of water) and are toxic/hazardous even at very low concentration (Huang, Liu, Zhang, Wu, & Tang, 2017; Sajjadi et al., 2019; Varghese, Paul, & Latha, 2019; Yadav & Xu, 2013); numerous heavy metals are summarized in Table S1. One of the common heavy metals is chromium [Cr(VI)] that finds diverse applications in leather tanning, pigment production, stainless steel manufacturing, and is detrimental to the human health. Simultaneous exposure to several heavy metals can generate a toxic effect, which is either additive/synergistic or antagonistic. Yu, Tong, Ge, Wu et al. (2013) and Yu, Tong, Ge, Zuo et al. (2013) reported that applying succinic acid groups onto CNCs considerably accelerated the binding efficiency to Pb^{2+} and Cd^{2+} in water; transformation of the carboxylic acid groups to sodiated carboxylates improved their ability to eliminate toxic metal ions from solutions. Researchers have established the capability of COO-amended CNFs to sorb Ni^{2+}, Cd^{2+}, Pb^{2+} and Cr^{3+}, with competences 3–10 % greater than original CNFs (Srivastava, Kardam, & Raj, 2012). Besides, the catalyst could be easily separated and reused for 5 times. On the other hand, cysteine usage offered appended thiol functionalities to effectively bind Cr(VI) and Pb(II) (Yang et al., 2014). The amine group mobilization on the surface of CNCs enabled more than 98 % elimination of anionic chromate comprising Cr^{6+} in the concentration range of 12.5 mg g^{-1} (Singh, Arora, Sinha, & Srivastava, 2014). Moreover, the catalyst could be recycled and reused at least five times without any noticeable decrease in catalytic activity.

Bacterial cellulose (BC) possesses numerous advantages such as high purity and crystallinity, favorable biocompatibility, low density, high porosity, durable mechanical properties, high absorption capacity, low-cost, and three dimensional interconnected structures with ultrafine nanofibers (Brandes, Carminatti, Mikowski, Al-Qureshi, & Recouvreux, 2017; Campano, Balea, Blanco, & Negro, 2016; Chawla, Bajaj, Survase, & Singhal, 2009; Qiu & Netravali, 2014; Shao, Liu, Liu, Wang, & Zhang, 2015). The high crystallinity of BC endows it with excellent physico-chemical stabilities (Fang, Zhou, Deng, Zheng, & Liu, 2016), and its hydrophilicity originating from its abundant hydroxyl groups makes it suitable catalyst support for deployment in water bodies (Costa, Gonçalves, Zaguete, Mazon, & Nogueira, 2013; Thiruvengadam & Vitta, 2013). Bacterial nanocellulose (BNC) is another family member of natural biopolymers and renewable raw materials, similar to nanoscale forms of cellulose, *i.e.* CNCs and CNFs that display tremendous potential for environmental and water treatment as highlighted recently (Mahfoudhi & Boufi, 2017; Voisin, Bergström, Liu, & Mathew, 2017; Wang, 2019). For the water purification application, Ma, Lou, Chen, Shi, and Xu (2019) reported a BC@zeolitic imidazolate framework-8 (ZIF-8) composite aerogel with low density below (<0.03 g cm^{-3}), large surface area, and hierarchical porosity, which displayed prominent heavy metal adsorption performance and recyclability superior to original ZIF-8 NPs (1.2 times).

Magnetite NPs have been simply incorporated into the cellulose nanomaterial structure for their controlled retrieval through magnetic separation (Zhou, Wu, Lei, & Negulescu, 2014; Zhou, Fu, Zhang, Zhan, & Levit, 2014). Zhu et al. (2011) prepared CNFs encompassing magnetite NPs trapped inside the fibers *via* the growth media of CNFs making bacteria during their generation; a low energy pathway for altering cellulose nanomaterials is a major advantage although extended time for growth and up-scaling challenges may hamper the commercialization process. Bacteria-originated CNFs has been applied for removing the heavy metals (*e.g.* Pb^{2+}, Mn^{2+}, and Cr^{3+}) and the fabricated catalyst could be recovered and reused for three cycles without noticeable drop in catalytic activity.

2.1.2.4. Removal of dyes.: Organic dyes are complex organic pollutants exemplified by cationic, anionic and/or nonionic properties that originate from several industrial sources *e.g.* textile, printing, pulp and paper, rubber leather tanning and cosmetic industries for coloring various products; toxic pigments and dyes are notable environmental afflictions in various parts of the world that need to be eliminated (Crini, 2006; Nasrollahzadeh, Sajjadi, Maham, Sajadi, & Barzinjy, 2018; Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). It has been estimated that ~1.6 million tons of toxic dyes are generated each year and ~10–15% of aforesaid volume is released as wastewater. Various cationic dyes are eliminated deploying CNCs and CNFs modified with anionic moieties as adsorbent materials or catalysts. Carboxylation of cellulose-based nanomaterials is one of the most investigated procedures for enhancing their sorption capacity. He et al. (2013) investigated the adsorption characteristics of carboxylated nanocelluloses fabricated *via* a single-extraction step hydrolysis process. Carboxylated or COO-modified CNCs are prepared through an ammonium persulfate (APS) hydrolysis of microcrystalline cellulose, in which carboxyl groups could be introduced on their surface during the cellulose hydrolysis. Adsorption studies conducted for a cationic dye *e.g.* methylene blue (MB) confirmed that the carboxylate groups bind to positively charged dyes; the adsorption capacity of MB onto CNCs approached a balance (0.32 mmol g^{-1}) at 22 °C after 10 min. The MB desorption from CNCs by ethanol was vastly efficient with more than 90 % dye removal up to seven desorption cycles. Similarly, Yu, Zhang, Lu, and Yao (2016) described a facile and single-step method to prepare carboxylated CNCs by deploying HCl/citric acid hydrolysis of the microcrystalline cellulose which has been utilized for the adsorption of MB; nearly complete UV degradation of methyl blue by the COO-modified CNCs, was observed after 4 h, and with an increased rate compared to other types of CNCs prepared using acids like sulfuric acid and formic acid. This result is attributed to the surface modification of carboxylated CNCs wherein additional carboxyl groups could effectively serve as a binding site for the dyes.

Zhou et al. prepared porous hydrolyzed polyacrylamide (HPAM)/CNC nanocomposite hydrogels *via* facile thermal treatment, and studied their activities for MB dye adsorption in aqueous solutions (Zhou, Wu et al., 2014); synergy between CNCs and HPAM can effectively increase the removal of toxic MB *via* the improvement in swelling properties wherein enhanced adsorption capacity for toxic dye can be attained by increasing CNCs content (~20 wt.%), raising HPAM and decreasing the pH of the prepared solution. Generally, porosity and the availability of the hydroxyl groups on surfaces of CNCs and/or CNFs can provide an outstanding mechanical template and support for nanocatalysts, thus ensuring good dispersion of NPs and stability of nanocatalysts (Mohammed et al., 2018; Xu, Nasrollahzadeh, Sajjadi et al., 2019; Zeng, Liu, Cai, & Zhang, 2010).

In another study, the fabrication of a novel CoPc@BC by covalent immobilization and decoration of amino cobalt phthalocyanine (CoPc) onto BC nanofibers has been described (Chen & Huang, 2015); ensuing nanocatalyst could be successfully deployed in the ≥90 % destruction of Rhodamine B (RhB) dye in water/wastewater using H_2O_2 as an oxidant within 3 h. An effective approach was disclosed by Yang et al. (2011) for growing cadmium sulfide NPs and stabilizing them through coordination effects with the bacterial CNFs *via* hydrothermal reaction; CdS/BCNFs hybrid composites were affirmed as robust recoverable photocatalysts for the 82 % MO degradation after 90 min exposure to visible light irradiation. The nanocomposite could be reused 5 times with no remarkable decrease of catalytic activity/efficiency. In another development, Zhang, Yu et al. (2018) and Zhang, Hou et al. (2018) prepared BC@TiO_2 nanocomposite by immersing well-preserved 3D interconnected porous BC blocks into a solution of titanium source that exhibited tremendous potential as MO adsorbent. Furthermore, a novel class of robust and highly scalable polydopamine (PDA)/BNC hybrid membrane has been prepared by Derami et al. (2019) which could be effectively used for the adsorptive removal of organic dyes (rhodamine 6 G, MB, and MO) from contaminated water.; the membrane catalyst was separated and reused 10 times with no detectable decrease of the catalytic performance.

After the capture of toxic pollutants, the ability to isolate and separate them from the nanosorbent or nanocatalyst and especially the reuse of such nanomaterials are some key issues in producing and designing sustainable treatment systems. The development of novel and recoverable CNCs is of paramount importance in numerous research areas such as remediation of toxic pollutants *via* adsorption and degradation process, however, the recovery of nanosorbents (or nanocatalysts) can limit their practical utilization on large-scale remediation processes. One of the straightforward procedures for the fabrication of reusable adsorbents is the incorporation of pristine nanocellulose (CNCs and/or CNFs) into various nanocomposite hydrogels or polymers that can be easily recycled using sieves, filtration, and magnets, *etc*. These materials could also be packed within columns and applied in wastewater remediation operations. In this context, a novel class of recoverable microgel comprising pristine CNCs and amphoteric poly(vinyl amine) (PVAm) has been reported by Jin and co-workers (Jin, Sun, Xu, & Xu, 2015), which can be utilized for the adsorptive removal of anionic dyes. The protonation of amine functionalities on the microgel particle’s surface organized positively charged microgels under an acidic pH medium wherein the electrostatic attraction among negatively charged sulfate groups and protonated amine promote the adsorption of anionic dyes into/onto microgels surface.

Besides, active NPs for photocatalytic destruction of pollutants has been introduced by placing TiO_2 particles on CNFs *via* controlled surface hydrolysis strategy (Sun, Yang, & Wang, 2010); significant ultra violet degradation of methyl orange (MO) could be detected within 20 min, that was 20 % faster compared to the rate attained with TiO_2 alone. Likewise, Snyder, Bo, Moon, Rochet, and Stanciu (2013) fabricated hybrid gold/TiO_2- and silver/TiO_2-cellulose CNF composites which eliminated MB ~75 % and 70 %, respectively, after one hour *via* photocatalytic degradation and adsorption. Notably, the mechanical strength of the CNF films can be augmented by addition of metallic NPs thus rendering them recyclable and imparting them additional durability.

A variety of cellulose-based nanosorbents deployed for the elimination of dyes and heavy metals are presented in Table 2.

2.1.2.5. Removal of other pollutants.: Non-biodegradable nitrophenols are extremely hazardous, and carcinogenic and are responsible for several ailments in humans; their removal from water/wastewater is of utmost importance. They have numerous applications in diverse industries *e.g.* synthesis of anilines as a crucial feedstock to produce pharmaceuticals, dyes, explosives, resins, agrochemicals and synthetic polymers, among others (Crini, 2006; Nasrollahzadeh, Sajjadi, Dasmeh et al., 2018; Rafatullah et al., 2010) and are on the list of regulated materials. Shi et al. synthesized CNCs-supported gold NPs with a quick swelling rate and superior catalytic prowess to catalyze the aqueous sodium borohydride ($NaBH_4$)-mediated reduction of pollutant, 4-nitrophenol (4-NP) (Scheme S1) with turnover frequency value and maximum rate constant of 641 h^{-1} and 0.0147 s^{-1}, respectively (Yan et al., 2016); synthesis was accomplished *via* electrospinning and thermal treatment of polyethylene glycol, CNCs and $HAuCl_4$ at 80 °C for 60 min wherein CNCs and polyethylene glycol act as support and reductant, respectively.

Additionally, cellulosic nanomaterials can be applied for the passive nanoremediation of reactive NPs where they act as scaffolds or particle-stabilizers. These NPs are often altered by using polymers to prevent aggregation; though, these surface-bound stabilizers cover the surface of reactive particle and may hinder the degradation and sorption of targeted materials (Yu, Tong, Ge, Zuo et al., 2013). Nata, Sureshkumar, and Lee (2011) reported one-pot simple solvothermal approach by incorporating the aminated iron oxide particles in bacterial cellulose nanofibers (BCNFs) for the remediation of arsenic; hardy CNF template prohibited the aggregation of particles and simplified the amine modification of magnetite particles. Therefore, ensuing materials demonstrated extremely superior arsenic elimination capacity (36.49 mg g^{-1}) than the bare iron oxide-based adsorbents and the nanocomposite could be reused 5 times with a minimal catalytic activity impairment. In one of the studies, Ma, Hsiao, and Chu (2012) demonstrated the capability of CNFs for eliminating radioactive uranyl ions (UO_2^{2+}) from solutions; UO_2^{2+} ions coordinated to the carboxylate groups of TEMPO-oxidized CNFs removed more than 167 mg/g, which was 2–3 times more than traditional adsorbents including hydrogels, montmorillonite, silica and polymer particles.

Polyethylene glycol (PEG) modified CNCs composites have been prepared for adsorbing pharmaceutical compounds, including sulfa-methoxazole, acetaminophen, and *N,N*-diethyl-meta-toluamide (DEET) in aqueous media. Such cellulose-based nanocomposite can be applied for eliminating the hydrophobic drugs from water; PEG-functionalized CNCs could facilitate the interaction between the cellulose nano-crystals and drugs. Such composite have been prepared *via* carboxylation of CNCs surface *via* 2,2,6,6-tetramethyl-1-piperidinyloxy oxidation, tailed by covalent appendage of hydrophilic polyether diamine of molecular weight of 600 g mol^{-1} using sodium salt of *N*-(3-dimethylaminopropyl)-*N*′-ethyl-carbodiimide/*N*-hydroxysulfosuccinimide (Herrera-Morales et al., 2017).

2.2. Chitin/chitosan-based nanomaterials

2.2.1. Chemistry and properties—After cellulose, chitin and chitosan are the next most abundant bio-polymers in nature. Chitosan is a renewable and biodegradable carbohydrate and is essentially, *N*-deacetylated chitin, the main constituent of insect cuticles and crustaceous shells, built up from linear aminopolysaccharide of glucosamine (Fig. 3). Bioconversion of chitin into chitosan *via* enzymatic *N*-deacetylation could be achieved with chitindeacetylase. The hydrophilic functional groups, including hydroxyl and amino groups, present in chitosan cannot change its hydrophobic nature enough to allow its use for adsorption and modification (Wang & Zhuang, 2017). In general, chitin/chitosan as a biogenic raw material is of specific significance because of its abundance, high adsorption capacity and ease of modification; chitosan has been deployed in biocatalysis, wastewater treatment, drug/gene delivery, agricultural/industrial use, and cell/enzyme immobilization (Bagheri, Roostaie, & Baktash, 2014; Dotto & Pinto, 2017; Rangel-Mendez, Monroy-Zepeda, Leyva-Ramos, Diaz-Flores, & Shirai, 2009; Xu, Nasrollahzadeh, Sajjadi et al., 2019).

Chitosan-based nanomaterials have garnered significant interest as they are utilized as nanosorbents and nanocatalysts because of their distinctive physicochemical properties (Fig. 4). The presence of *N*-acetamido functionality is responsible for the formation of various inter/intra-molecular hydrogen bond between linear structures of chitin. Indeed, the extended hydrogen bonded chitin chains does limit their solubility in solvents, and therefore, their processing and novel appliances have been under scrutiny for the preparation of sustainable nanomaterials. Their application as eco-friendly, low-cost, sustainable and renewable resources for the synthesis of chitin/chitosan-based nanocatalysts and for the assembly of potable and safe water systems are under rigorous investigation (Crini, Morin-Crini, Fatin-Rouge, Deon, & Fievet, 2017; Krajewska, 2001; Xu, Nasrollahzadeh, Sajjadi et al., 2019).

2.2.2. Applications for water treatment

2.2.2.1. Removal of heavy metal ions.: Coagulation and flocculation of ionic substances and charged particles in wastewater has efficiently been performed with the aid of natural polymers, while diminishing the dependability on synthetic polyelectrolytes (Zemmouri, Drouiche, Sayeh, Lounici, & Mameri, 2013). Chitin, chitosan and their derived molecules have been exploited as natural and eco-friendly coagulants/flocculants to eliminate various charged particles such as dyes and metal ions from wastewater (Kanmani et al., 2017; Sami, Khalid, Iqbal, Afzal, & Shakoori, 2017). Chitosan and its derivatives present a cationic character in acidic media that facilitates their dissolution and enable ion-exchange interactions or electrostatic attraction with various anionic characters, while, the non-protonated amino groups in neutral media expedite complexation of metal ions and organic molecules. Polyvinyl alcohol-chitosan and PEG-chitosan composites have been investigated by Rajeswari et al. (2016) to remove aqueous nitrate ions with a adsorption capacity of > 35.03 and 50.68 mg g^{-1}, respectively, while the preparation of carboxymethyl chitosan (Borsagli, Mansur, Chagas, Oliveira, & Mansur, 2015) and goethite/chitosan nano-composites (goethite NPs 10~60 nm) (Rahimi, Moattari, Rajabi, & Derakhshan, 2015) were selective towards the complexation of Cd^{2+}/Cr^{6+} and Pb^{2+}, respectively. Wang, Chen, Yuan, Sheng, and Yu (2009) reported a highly water-soluble chitosan-based flocculant by grafting it with (2-methacryloyloxyethyl) trimethyl ammonium chloride (grafting percentage >236.4 %) for the treatment of pulp mill waste-water; as-prepared flocculant revealed a more notable flocculation capacity and performance than that of polyacrylamide.

Considerable endeavors have been explored to ameliorate the experimental processes towards capacitive deionization (CDI) using a diversity of conducting polymers (*e.g.* polypyrrole) in view of their ion-exchange property and doped process (Abdi, Nasiri, Mesbahi, & Khani, 2017; Fang, Jiang, Luo, & Geng, 2018). Besides, the synergistic effect of polypyrrole and chitin/chitosan was described to improve the stability of polypyrrole material because of its −COOH and $–NH_2$ (Huang et al., 2013). For example, Zhang, Xue, Li, Dai, and Zhang (2019) reported a polypyrrole(PPy)/CS/CNT nanoelectrode (34.57 nm) with various mass ratios of PPy and CS *via in-situ* polymerization for the adsorption of copper ion from water/wastewater by CDI process (Fig. S1); high adsorption competence of 16.83 mg g^{-1} for the Cu^{2+} removal was attained by this nanocomposite. The result of 100 cycles CV test shows that the specific capacitance of PPy/CS/CNT composite electrode decreased 13.1 % after 100 cycles, but only 3.4 % after the last 50 cycles, which indicated that this composite electrode has a good stability after 50 cycles.

The stabilization of various NPs has been achieved *via* their impregnation on organic renewable supports by preparation of nano-composite as shown by Chen, Cao, Quinlan, Berry, and Tam (2015) where the amino functionalization on surface of organic supports under mild conditions greatly diminished the agglomeration of metal/metal oxide NPs. The adsorption capacity of chitin/chitosan-supported NPs as nanocatalysts or nanosorbents could be further improved by a fusion of NPs and natural polymers culminating in promising natural polymer-based nanocomposites (Qiu, Ma, & Hu, 2014). Low-cost natural polymers, such as chitin/chitosan, has largely been applied as highly effective catalytic support in the heterogeneous catalysis field owing to its inherent functional groups (Murugadoss & Chattopadhyay, 2007; Wang, Zhu et al., 2017); reactive amino group-bearing chitosan has become an ideal support compared to other biopolymers. Environmental applications of bio(nano)composites of chitin/chitosan formed by combining them with diverse nanostructures, namely iron oxide (Fe_3O_4), titanium dioxide (TiO_2), *etc.* have recently been reported (Anaya-Esparza et al., 2020; Li, Xiao, & Qin, 2010). For example, a novel nano-TiO_2-enabled CS beads crosslinked with copper were prepared that could achieve the (photo)oxidation of toxic arsenite (As(III)) to a less-toxic and more easily adsorbed arsenate (As(V)) in UV light as well as the selective adsorption of As(III) and As(V) in presence of phosphate (Pincus, Melnikov, Yamani, & Zimmerman, 2018), which serves as a strong adsorption competitor and inhibitor of As removal in such protocols.

2.2.2.2. Removal of dyes.: Chitosan-based nanomaterials have been examined to adsorb or remove dye molecules wherein hydroxyl groups are effectively exploited in the dye adsorption, while the amine groups profoundly remain as a most active group and influences other biopolymer activities. Gibbs, Tobin, and Guibal (2003) have shown that by diminishing the acetylation degree of chitosan increases the relative proportions of amine groups available for protonation, thus favoring the adsorption of dyes like Acid Green 25. However, the alteration in these adsorption features is not proportional to the deacetylation or acetylation degree, but it varies with the nature of dyes (Saha, Ichikawa, & Fukumori, 2006) and also the repartitioning of acetyl groups in the macromolecular chains (Rinaudo, 2006), depending largely on the preparative process. Gopi and co-workers have reported the efficient wastewater treatment by using multifunctional bio-hybrid aerogels based on CNFs decorated with chitin nanocrystal (CNC) (Fig. S2a) (Gopi et al., 2017). A rare semi-square CNCs (20–100 nm) and wire-like CNFs (60–120 nm) were initially extracted from shrimp shells and corn husks, respectively (Fig. S2b). Hybrid bio-aerogels (neat AR, AR1 or AR2) were prepared with varying percentages of CNCs (0, 1% or 2%) and decorated on the CNFs *via* an eco-friendly freeze-drying procedure. This mixture comprised CNFs aqueous solution with well-dispersed CNCs that was frozen at about −70 °C in the dry ice-isopropanol and finally freeze dried at −88 °C under vacuum for at least 4 days. The higher amount of CNCs can lead to better alignment, organization and morphology of nanofibers in AR2, and higher crystallinity, in addition, the nanofibers orientation of AR2 mimicked the multilayer maple seed structure (Fig. S2b). The AR2 aerogel showed considerable adsorption capability for the remediation of dyes (MB and rhodamine 6 G) from aqueous solutions (Fig. S2c); the electrostatic interactions among positively charged dyes and negatively charged CNCs decorated AR2 with acetamide-enriched groups favored the dye adsorption. Besides, the hybrid bio-aerogels could be reused 5 times with no noticeable loss in activity/efficiency.

Marrakchi, Khanday, Asif, and Hameed (2016) developed a reinforced chitosan with sepiolite as an additive and epichlorohydrin as a crosslinker to fabricate crosslinked chitosan/sepiolite composites for the removal of reactive orange 16 and MB from aqueous solutions; attained maximum adsorption capacity of modified chitosan for MB and reactive orange 16, being 40.99 mg g^{-1} and 190.97 mg g^{-1}, respectively, at initial dye concentration of 100 mg L^{-1} and adsorbent dosage of 1 g L^{-1} at 30 °C for 30 h. The adsorption processes were best explained using pseudo-second-order kinetics and Freundlich model that provided a finer explanation of the adsorption process for both the organic dyes. The functioning of this crosslinked chitosan composite was superior to what has been reported in earlier studies (37.04 mg g^{-1}) (Xie, Li, Chi, & Wu, 2013), (11.94 mg g^{-1}) (Yao et al., 2014) and (24.690 mg g^{-1}) (Zeng et al., 2015) for the removal of MB. In addition, the elimination of Acid Red-2 from textile wastewater by a glutaraldehyde crosslinked magnetic chitosan nanocomposite has been investigated (Kadam & Lee, 2015); it could effectively adsorb 91.6 % textile pollutant, while iron oxide could adsorb only 16.4 %. This improved performance of magnetic chitosan nanocomposite in view of the available free amino and hydroxyl groups and 96 % pollutant removal with 100 % recovery bodes well for its practical uses.

Moreover, the combination of Fe_3O_4 and chitin/chitosan can afford fascinating magnetic support towards hassle-free separation of nano-catalysts. Chang and Chen (2005) designed carboxymethylated chitosan-conjugated magnetic nanosorbents (~13.5 nm) for the elimination of anionic dyes from aqueous solutions; excellent adsorption efficiencies were attained (1471 and 1883 mg g^{-1}) for acid green 25 and crocein orange G, respectively.

2.2.2.3. Removal of other pollutants.: The adsorption of pesticides onto low-cost materials could help effectively remediate contaminated waters; particularly, nanomaterials, nanosorbents and polysaccharide-based adsorbents display high performance in eliminating pesticides from water bodies as exemplified by chitin and chitosan towards the biosorption of pesticides. Indeed, the presence of hydroxyl groups in chitin/chitosan determined its conformation and also the stereochemistry of chemical transformations and kinetics. In this respect, chitosan removed more than 90 % of oxadiazon (herbicide) from aqueous solutions (Arvand et al., 2009) wherein strong binding of oxadiazon to the chitosan was observed (chemisorption). Moreover, 76.2 % of atrazine (herbicide) could be removed (with a maximum adsorption capacity of 17.92 mg g^{-1}) from aqueous solutions by chitosan/modified sepiolite (Liu, Chen, Cui, & Liu, 2015).

Modified chitosan nanomaterial matrixes can be applied for the biosorption of organic/inorganic contaminants; sustainability of chitosan and its derivatives can be boosted by mixing with reinforcement and/or supporting matrixes like crosslinkers and polymers. This entails the presence of at least two reactive sites or functional groups in linkers to suitably transform the chitosan by producing bridges amongst their polymeric chains and/or neighboring molecules (Xing, Ju, Yang, Xu, & Qian, 2013). The used crosslinkers for buttressing chitosan namely glutaraldehyde, silicate, tripolyphosphate, starch, polyvinyl alcohol and cellulose must enable the flow of organic/inorganic contaminants towards the charged particles of the supported chitosan and concomitantly ensuring the physicochemical stability of chitosan (Xing et al., 2013). To ensure the adsorption competence close to the parent chitosan, the use of various additives like alginate (Nadavala, Swayampakula, Boddu, & Abburi, 2009), polyethylenimine, chloroacetic acid and Fe_3O_4 is deemed necessary. The adsorption efficiency depends on numerous factors such as the adsorbent characteristics, the degree of crosslinking, crystallinity and the stiffness of the chitosan linkages, and the chemistry of pollutant (Alaba et al., 2018). Mi, Shyu, Chen, and Lai (2002) reported a novel protocol for the synthesis of bundle-like porous chitosan beads *via* a phase inversion wet process; this chemically modified chitosan could absorb anti-inflammatory drug such as indomethacin.

Chitin/chitosan-supported metal/metal oxide NPs have displayed high performances for removing pollutants from water/wastewater; indeed, the synergistic effects of chitin/chitosan and nanostructures can improve (nano)materials in terms of antimicrobial, UV blocking, and magnetic properties. In this context, Mujeeb Rahman et al. (Mujeeb Rahman, Muraleedaran, & Mujeeb, 2015) studied the antimicrobial properties of ZnO NP reinforced chitosan nanocomposites which could be utilized as photocatalytic and/or natural antimicrobial agents; superior antimicrobial activities against gram-negative and gram-positive bacteria (*E. coli* and *S. aureus*) was observed compared to chitosan itself. Utilizing the well-developed preparative procedures for chitin/chitosan-based (nano)materials, multifunctional chitosan/TiO_2 (nano)composite photocatalysts could be easily attained owing to the miscibility between CS and hydrophilic TiO_2 NPs (Wiaącek, Gozdecka, & Jurak, 2018).

In one study, TiO_2 NPs (1% w/v) were embedded in two different matrixes, *viz.* chitosan and polyvinyl alcohol-chitosan blend (PVA-CS), through a precipitation procedure using an alkali/solvent medium (Neghi, Kumar, & Burkhalov, 2019) where the nanocomposites/blends exhibited high metronidazole (MNZ) removal efficiency (76.1 % and 63.7 % in PVA-CS-TiO_2 and CS-TiO_2 systems, respectively) from aqueous solutions under UV irradiation as compared to the TiO_2 NPs suspension alone. As a result, PVA-CS-TiO_2 showed enhanced stability than CS-TiO_2 in an aqueous solution at different pH values and could be reused under UV exposure up to 15 cycles as an effective photocatalyst without significant loss of catalytic performance. In a recent study, Shoueir et al. (Shoueir, Kandil, El-hosainy, & El-Kemary, 2019) reported an efficient visible-light photocatalyst by stacking a layer of nano-structured Au@TiO_2 on a chitosan fiber substrate; the as-prepared plasmonic fiber displayed catalytic activities in visible light for the degradation of various water pollutants (MB, MNZ, and carbofuran (CBN)) and for the Cr(VI) reduction (~98.9 %) in presence of citric acid (pH = 1) within 21 min. The plasmonic fiber photocatalyzed the degradation of MB within 12 min under visible irradiation using a low catalyst dosage of 1×10^{-3} g L^{-1}, with an efficiency of 98.8 %. In the case of MNZ and CBN, the degradation reaction times were longer, namely 260 min and 130 min, respectively, which could be improved by deploying H_2O_2 in these systems, when the photocatalytic degradation degree of MNZ reached 96 % and 98.3 % for CBN.

Additionally, by designing the core/shell structures, the surface functionalities of the natural polymers could be made easily available to metal/metal oxide NPs (Ghosh Chaudhuri & Paria, 2012). In this regard, Antony et al. (Antony, Marimuthu, & Murugavel, 2019) developed a facile and novel approach for anchoring bimetallic AgNi NPs (20~25 nm) on Fe_3O_4@chitosan core/shell support (Fe_3O_4@CS_AgNi) as a heterogeneous retrievable nanocatalyst (Fig. 5); magnetic nanocomposite has been applied for the rapid and nearly quantitative reduction of 4-nitrophenol (4-NP) using $NaBH_4$ within 10 min under ambient conditions. Furthermore, the heterogeneous nanocatalyst could be simply recovered/separated using an external magnet and reused seven times.

Applications of wide ranging chitin/chitosan-based nanomaterials for the removal of water contaminants and toxic pollutants such as various dyes, heavy metals and pharmaceutical materials are summarized in Table 3.

2.3. Starch-based (nano)materials

2.3.1. Chemistry and properties—Starch, a natural, abundant, renewable, biocompatible and biode gradable biopolymer is present in sundry plants as a reserve carbohydrate and is commonly found in many parts of plants such as stalks, roots, and crop seeds; main sources being cassava, wheat, rice, maize or corn, and potatoes, among others. Starch granules have a 3D architecture with crystallinity in the range of 15–45 % and comprise D-glucose units with bio-macromolecules including amylopectin, branched (1→6) α-D-glucan, amylose, and linear (1→4)-linked α-D-glucan (Visakh, Mathew, Oksman, & Thomas, 2012; Zobel, 1988). Microcrystalline starch, starch nanocrystal, starch crystallite, and hydrolyzed starch all embody the crystalline part of the starch generated *via* hydrolysis (Le Corre, Bras, & Dufresne, 2010); modes for preparing crystalline and amorphous starch nanostructures with varying morphologies and crystallinities are shown in Fig. S3.

The mixing of fibrous clays with natural polymers is an appealing alternative for removing pollutants from water. Biopolymers *e.g.* guar gum or starch can be combined with polyacrylic acid (PAA) and polyacrylamide (PAAm) to develop eco-friendly and biodegradability superabsorbents (Li, Liu, & Wang, 2005). Generally, the incorporation of clays has boosted water absorption rate and water absorbency of these catalytic systems as noted for the starch/g-PAAm and guar gum-g-PAA (Ruiz-Hitzky et al., 2013). For example, the effect of sepiolite modification with cationic starch on the physical properties such as increased Young's modulus of the composites obtained as a reinforced starch film was investigated (Chivrac, Pollet, Schmutz, & Avérous, 2010).

Among the naturally occurring polymers, starch polysaccharides; especially starch nanocrystals, have been increasingly utilized as ideal supports to afford environmentally benign and practical catalyst systems due to their high surface area, high abundance, non-toxicity, low cost, renewability, and biocompatibility (Ghaderi, Gholinejad, & Firouzabadi, 2016; Gholinejad, Saadati, Shaybanizadeh, & Pullithadathil, 2016; Herreros-López et al., 2016). Nanocrystalline starch is ideal for the reinforcement of a biopolymer compared to amorphous or amorphous starch (Angellier, Molina-Boisseau, & Dufresne, 2005; Jenkins, Cameron, & Donald, 1993). Functionalized natural starches can generally be attractive supports for various colloidal metal NP-based catalysts owing to their abundance, biocompatibility, and biodegradability.

2.3.2. Applications for water treatment

2.3.2.1. Removal of organic pollutants.: The modified starch had significantly greater water binding capacities than native starch and their amylase digestibility decreased as their degree of crosslinking increased (Jyothi, Moorthy, & Rajasekharan, 2006); for example, epichlorohydrin is the most familiar crosslinking agent that can be utilized for natural polysaccharides. Guo, Li, Liu, Meng, and Tang (2013) synthesized a crosslinked porous starch by crosslinking corn starch with epichlorohydrin and then hydrolyzing it with α-amylase, ensuing catalyst could be successfully utilized in MB adsorption from water with a maximum adsorption capacity from Langmuir isotherm model being 9.46 mg g^{-1} at 293 k.

(Photo)catalysts, often deployed for (photo)degradation of environmental contaminants, are commonly metal oxide/metal acid salts of *n*-type semiconductors, including TiO_2, Fe_2O_3, ZnO, *etc;* (Rostami--Vartooni, Nasrollahzadeh, Salavati-Niasari, & Atarod, 2016; Wang, Wang et al., 2018; Wang, Li et al., 2018) relatively inexpensive TiO_2 NPs have been extensively studied as environmentally friendly (photo) nanocatalysts owing to their nontoxicity, and stability (Al-Harbi, Kosa, Abd El Maksod, & Hegazy, 2015; Hassan, Chen, Liu, Zhu, & Cai, 2014; Rostami-Vartooni et al., 2016). Starch as a biodegradable and renewable raw material, offers additional sustainability/stability to the nano-particles similar to graphene (Doustkhah & Rostamnia, 2016; Ye, Hao, Liu, Li, & Xu, 2017) and carbon nanotubes (Ihsanullah, 2019). The modification of starch can be accomplished easily because of its hydroxyl groups which have strong bonding with diverse functional groups and are amenable to easy chemical transformation. Guo, Wang, Zheng, and Jiang (2019) investigated the photodegradation and adsorption of cationic golden yellow X-GL/cationic yellow 28 dye from water/wastewater by TiO_2 NPs (~10 nm) loaded onto the crosslinked carboxymethyl starch (CCMS) surface (TiO_2 NPs/CCMS) as a novel biosorbent by the sol-gel technique (Fig. S4); TiO_2 NPs/CCMS was reused for four successive cycles.

Negatively charged starch can efficiently adsorb various cationic dyes (Huang, Chang, Lin, & Dufresne, 2014; Pourjavadi, Abedin-Moghanaki, & Tavakoli, 2016). In a related study, Guo, Wang, Zheng, and Jiang (2019) prepared crosslinked cationic starch from corn starch and 3-chloro-2-hydroxypropyl trimethylammonium chloride and epichlorohydrin as cationic etherification and crosslinked agents, respectively. Crosslinked cationic starch was applied to eliminate reactive golden yellow SNE dye from aqueous solutions and its maximum adsorption capacity was found to be 208.77 mg g^{-1} at 308.15 K. Besides, Pourjavadi et al. (2016) functionalized magnetic crosslinked starch materials with PVA modified by chlorosulfonic acid based vinyl acetate copolymerization onto crude starch (sulfation of its hydroxyl groups) to generate MNPs@Starch-g-poly(vinyl sulfate) nanocomposite (Fig. 6). It can effectively eliminate cationic dyes such as MG and MB from water; excellent adsorption capacities of 567 and 621 mg g^{-1}, respectively, were demonstrated and up to 90 % of MB and MG dyes could be removed from the solution by the regenerated adsorbent even after five cycles of adsorption-desorption.

The utilization of metal/metal oxide NPs on surface of biopolymers for the development of easily recoverable magnetic nanocatalysts has led to a dramatic expansion of their potential applications; in this regard, a variety of surface modified magnetic NPs with biodegradable polymers have been utilized for environmental remediation. Generally, starch nanocrystals help conceive more sustainable solutions to current technological challenges. Very recently, Sharma, Bhardwaj, Kour, and Paul (2017) fabricated a series of versatile magnetic Pd NP catalysts functionalized with starch and amine (Pd NPs@Fe_3O_4-NH_2/Starch); they accomplished the reductive amination of nitroarenes in EtOH:H_2O at ambient temperature with reuse for five successive cycles. Nevertheless, the adsorption capacity of easily retrievable magnetic nano-composites/nanosorbents functionalized with crude biopolymers is low which could be ameliorated by chemical modification. For instance, magnetic CMS/poly(vinyl alcohol) hydrogel (mCMS/PVA) was fabricated for MB removal from wastewater (Gong, Zhang, Cheng, & Zhou, 2015) and the catalyst was reused for eight successive cycles.

2.3.2.2. Removal of inorganic pollutants.: Other researchers (Sekhavat Pour & Ghaemy, 2015) have studied the adsorption of Cu^{2+}, Pb^{2+}, and Cd^{2+} contaminants from drinking water by versatile magnetic nano-composite hydrogel bead (mCVP) based on PVA/CMS-g-poly(vinyl imidazole) as is illustrated in Fig. S5. The adsorption capacities of mCVP beads for Cu^{2+}, Pb^{2+}, and Cd^{2+} were found to be 83.6, 65, and 53.2 mg g^{-1}, respectively with reuse of nanocomposite for four successive cycles.

Several studies on the documented exploitation of starch-based (nano)materials for handling of organic/inorganic contaminants in wastewater has been summarized in Table 4.

2.4. Gum-based (nano)materials

2.4.1. Chemistry and properties—Gums are an outstanding representative of eco-friendly, green bio-polymers and these natural polysaccharides and their derivatives have been used to produce a large number of materials for varied applications. Guar gum (GG), a natural water soluble, biodegradable, mucoadhesive, polysaccharide, is obtained from the endosperm of guar beans, comprising linear chains of D-mannopyranosyl with D-galactopyranosyl units. Gum arabic (GA) or acacia gum is a branched heteropolysaccharide and a complex exudate of *Acacia seyal* and *Acacia senegal* trees composed of D-galactopyranosyl units and is one of the oldest amongst all known gums with broad applications in pharmaceutical and food industries (Padil, Senan, & Černík, 2019; Patel & Goyal, 2015; Yadav, Igartuburu, Yan, & Nothnagel, 2007).

GG and GA have been extensively used as a binder, ion exchange resin and dispersing agent, thickening agent due to their good capability to alter rheological properties (Iqbal & Hussain, 2013; Miao et al., 2018; Patel & Goyal, 2015; Soumya, Ghosh, & Abraham, 2010). They have also been applied for stabilization or the reduction of nanomaterials and ordained to effectively stabilize magnetic NPs (Kattumuri et al., 2007; Padil, Wacławek, Černík, & Varma, 2018; Williams, Gold, Holoman, Ehrman, & Wilson, 2006) besides being used as additive, emulsifying and reducing agent, and potential stabilizer in preparation of various nanocatalysts (Devi et al., 2011; Padil et al., 2018), and as biosorbent in various applications (Fig. 7) (Sharma et al., 2018).

One of the straightforward biological methods for the assembly of inorganic materials is the biomimetic synthesis of various metal NPs on the surfaces of branched natural polysaccharides which serve as reducing, supporting, additive, emulsifying, and stabilizing agents; metal NPs have been stabilized on gum acacia (Chasteen & Harrison, 1999; Devi et al., 2011; Xie, Lee, Wang, & Ting, 2007). Along this theme, Supriya, Srinivas, Chowdeswari, Naidu, and Sreedhar (2018) have reported a series of Pd-based nanomaterials supported on modified ZnO/TiO_2 NPs built by gum acacia (GA) support (GA-Pd/ZnO and GA-Pd/TiO_2), and evaluated their catalytic prowess in the selective hydrogenation of highly toxic nitroarenes under very mild conditions. The remarkable activity of as prepared nanocomposite ensued from inherently biocompatible and nontoxic properties of GA, which could be applied as a modifier of crystal growth, stabilizer, and reductant in the preparation of nanostructures. The nanocomposite was reused for five successive cycles.

2.4.2. Applications for water treatment

2.4.2.1. Removal of heavy metals.: Gum kondagogu (GK) is a natural, partially acetylated, harmless polymer and in view of its various functional groups, the native gum itself could be deployed as a potential biosorbent for elimination of toxic metal pollutants (Vinod, Sashidhar, & Sreedhar, 2010; Vinod, Sashidhar, & Sukumar, 2010; Vinod et al., 2009). In this context, Saravanan et al. (Saravanan, Vinod, Sreedhar, & Sashidhar, 2012) described a magnetic nanosorbent by surface modification of Fe_3O_4 NPs (8~15 nm) with gum kondagogu (GK) for the adsorption/removal of highly toxic metal cations from water. The removal efficiencies of the GK grafted magnetic NPs (GK-MNPs) as a magnetic nanosorbent was investigated for the removal of diverse toxic metals namely Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+} and Pb^{2+}; a lowest of 35.07 mg g^{-1} and a highest of 106.8 mg g^{-1} adsorption competences were reported for the Hg^{2+} and Cd^{2+} cations, respectively.

In another work, a novel class of easily retrievable magnetic Fe_3O_4 nanocomposite comprising poly(methyl methacrylate) and Tragacanth gum [P(MMA)-*g*-TG-MNs] were reported by Sadeghi, Rad, and Moghaddam (2014), for highly selective elimination of Cr^{6+} from waste-water in presence of Cr(III). Notably, the excellent selectivity of the nanosorbent for Cr^{6+} ions in presence of Cr^{3+} (at pH 5.5), lower adsorbent dosage (3 g L^{-1}), high percent removal (~95 %), and ease of separation from solution, make this nanosorbent more effective and valuable compared to others (Hu, Chen, & Lo, 2005; Singh, Kumari, Pandey, & Narayan, 2009).

2.4.2.2. Removal of dyes.: One of the most premier adsorbents, 3D hydrogels, are suitable for the treatment of complex wastewater owing to their excellent concentration or adsorption capacities and high (photo)catalytic degradation. The 3D biopolymer-based hydrogels could be prepared from natural GG through self-assembly or using a cross-linking agent. Recently, GG based hydrogel nanocomposites have displayed potential in drug delivery, biosorption and separation owing to their intrinsic superior properties *e.g.* biocompatibility, biodegrad-ability, high active-site availabilities, large surface areas, and low-mass transfer limitations (Dai, Liu, Hu, & Si, 2017; Sharma, Kalia et al., 2015). Duan et al. (2020) prepared a versatile 3D hybrid nanocomposite hydrogel based on MIL-100(Fe) and Ag NPs *via* simple blending and self-crosslinking, and studied the activities of the resulting Ag NPs@MIL-100(Fe)/GG hybrid hydrogels in adsorption/(photo)catalytic degradation of dye pollutants, antibacterial property, and oily waste-water purification (Fig. 8).

Other documented studies on the use of gum-derived (nano)materials for the removal of heavy metals/dyes are summarized in Table 5.

2.5. Alginate-based (nano)materials

Among the low cost biomaterials, alginates are useful linear block copolymers comprising two uronic acid residues, *e.g.* β-D-mannuronic and α-L-guluronic acid linked by β−1,4-glycosidic bonds. This biopolymer has been extensively utilized in wastewater remediation due to its stability, high water permeability, biodegradability, and nontoxic nature (Ahmed, Moustafa, El-Masry, & Hassan, 2014; Xu, Nasrollahzadeh, Sajjadi et al., 2019) for the adsorption of contaminants, particularly, heavy metal cations (An, Lee, Lee, Lee, & Choi, 2015; Idris, Ismail, Hassan, Misran, & Ngomsik, 2012; Kuang et al., 2015; Li et al., 2013).

Alginate-based adsorbents have recently garnered attention as they could form stable biohydrogel beads and can be applied as a catalytic support material with numerous benefits, *e.g.* high surface area, network structure, and their rich surface functionalities (Li, Mo et al., 2016; Wang, Vincent, Roux, Faur, & Guibal, 2017). For example, mesoporous calcium-alginate/titania hybrid beads were prepared as a biosorbent for treating aqueous solutions comprising Cr^{6+}, Co^{2+}, Cr^{3+}, Cd^{2+}, and Cu^{2+} ions (Wu, Wei, & Zhang, 2012); adsorption capacity of 8.4 mg g^{-1} for $Cr^{6+}$was reported with reusable capacity for six successive cycles. Besides, Gupta et al. (Gupta et al., 2014) fabricated bimetallic and core/shell Fe@Ag NPs (15~20 nm) involving modified aminothiophenol-calcium alginate (Fe@Ag-ATP-CA) beads for the reduction of 2-NP and 4-NP in wastewater using $NaBH_4$. A heterogeneous core/shell Fe_3O_4@alginate-Fe magnetic nanocomposite has been fabricated, *via* an oxidation-precipitation technique, for the degradation of bisphenol A from aqueous media in the catalytic ozonation (Ahmadi, Rahmani, Takdastan, Jaafarzadeh, & Mostoufi, 2016); degradation or mineralization of bisphenol A is influenced by concentration of pollutant (10 ppm)/H_2O_2 (30 mmol L^{-1})/nanocatalyst (0.7 g L^{-1}), and O_3 dosage (0.1 g h^{-1}).

In addition to alginate-derived biohydrogel beads, carbon beads can provide an outstanding catalytic support, ensuring good dispersion of NPs and stability of nanocatalysts, and thus attracted interest due to their elevated porosity, large surface area, excellent mechanical stability, and adjustable surface chemistry (Teng, Wu, Fan, Zhang, & Zhao, 2015). Zheng et al. (2016) presented the fabrication of a novel alginate-obtained carbon beads (Alg/CB) with an advanced nano-network *via* a facile combinational carbothermal reduction and acid treatment of Ca^{2+} gelled sodium alginate biohydrogel beads (Fig. S6); they were successfully used/reused in the decoloration and removal of Cr^{6+} from wastewater in six successive runs.

One interesting property of alginate-based biosorbents is their selective cationic interactions with multivalent ions such as Ca^{2+}, Fe^{3+}, Ba^{2+}, Ag^{+}, Al^{3+}, *etc*. to transform them into macromolecular hydrogels, creating a 3D network structure (Cheng, Luo, Payne, & Rubloff, 2012; Topuz, Henke, Richtering, & Groll, 2012; Yang et al., 2013). In this context, Yang et al. (2013) successfully used a variety of multivalent cations to prepare a crosslinked alginate/polyacrylamide hydrogel, thereby, improving the mechanical features of the biopolyanionic network. Furthermore, Ai et al. (2012) fabricated Ag NPs *in situ* grown on a magnetic alginate/magnetite hybrid (Ag@AMH) biohydrogel *via* an eco-friendly light-driven technique (Fig. S7). Ag^{+} ions could be simply fixed and uniformly dispersed onto the AMH biohydrogel, thereby ensuring the next *in situ* photochemical preparation of Ag NPs (~72 nm) with good distribution; ensuing bio-hydrogel efficiently accomplished the catalytic reduction of toxic 4-NP in aqueous solutions and the catalyst could be reused for successive three cycles.

As mentioned earlier in Section 3.3, the integration or surface modification of fibrous clay with starch, guar gum or alginate has boosted water absorbency or water absorption rate of the catalytic systems. Along this theme, Olad and Farshi Azhar (2014) reported a facile method to synthesize an effective alginate/montmorillonite/polyaniline (Alg/MMT/PANI) hybrid nanocomposite by a chemical oxidative polymerization for the removal of Cr^{6+}. Additionally, Ahmad and Mirza (2015) synthesized Meth-bent/Alg nano-composite by integrating methionine-modified bentonite onto sodium alginate that lead to the enhanced performance of the as prepared nanosorbent; biosorption capacities of 217.39 and 30.86 mg g^{-1} for Cd^{2+} and Pb^{2+}, respectively, was discerned. This nanocomposite could be reused for five successive cycles.

The related works on the application of alginate-based (nano)materials in the wastewater remediation are summarized in Table 6.

2.6. Pectin-based (nano)materials

Pectin, as biocompatible, flexible, nontoxic, high-molecular weight and anionic naturally occurring polysaccharide, is extractable from the higher plant cell walls. Pectin is a linear polysaccharide as most plants contain it in intercellular layer between primary cell walls of adjoining cells. In recent years, pectin as a class of complex polysaccharides has gained increasing importance with applications in pharmaceutical, biotechnology and a number of other industries. Similar to most other polysaccharides, pectin’s composition differs with source and conditions deployed during isolation (Mualikrishna & Tharanathan, 1994;

Ridley, O'Neill, & Mohnen, 2001). Pectin mainly consists of D-galacturonic acid molecules that are joined in chains by *α*-(1–4) glycosidic linkage in which a number of carboxyl/hydroxyl groups are distributed along backbone, in addition to a certain amount of neutral sugars present as side chains (Mukhiddinov, Khalikov, Abdusamiev, & Avloev, 2000; Sundar Raj, Rubila, Jayabalan, & Ranganathan, 2012). Some of the carboxyl groups are naturally occurring as methyl esters while others can be treated with ammonia to prepare carboxamide groups; these functional groups can form complexes with metal ions in solution and reduce them to metal NPs without using any toxic reducing/stabilizing agents.

One of the simplest greener methods for the preparation of naturally recoverable Pd nanocatalysts is the direct immobilization of Pd NPs on the surface of carbohydrate-based materials; in this regard, Pd NPs were stabilized on polysaccharides such as Pd/starch, Pd/gelatin and Pd/chitosan (Balanta, Godard, & Claver, 2011; Budarin, Clark, Luque, Macquarrie, & White, 2008; Primo, Liebel, & Quignard, 2009; Sun et al., 2005). Hybrid organic/inorganic nanocomposites are of tremendous interest owing to their multifunctionality *via* combined incorporation of diverse compounds. Fe-pectin (Rakhshaee & Panahandeh, 2011), Fe°-PO-CHA (pectin derived orange skin-carboxylic acid) and Fe°-PO-IPA (isopropylglutaricacid) (Rakhshaee, 2011), FeNPs/Fe_3O_4NPs-CPA (crosslinked pectin adipic acid) (Rakhshaee, 2014), Fe_3O_4-pectin and Fe_3O_4-humic acid nanocomposites (Liu, Zhao, & Jiang, 2008) have been used for the adsorptional elimination of heavy metals and/or dyes. The combination of unique properties of NPs and carbohydrate-based materials leads to a novel nanomaterial with high mechanical/thermal stability, large surface area and sorption properties. Baran (2018) prepared Pd NPs (34~54 nm) immobilized on the natural agar/pectin composite (PdNPs@APC) and evaluated their catalytic abilities in the reduction of *o*-nitroaniline reduction using aqueous $NaBH_4$ at room temperature. The agar/pectin composite with highly active surface, high thermal stability (up to 239 °C), and strong covalent bonds was designed as a stabilizer. Subsequently, Pd NPs were synthesized through *in situ* reduction Pd ions and immobilized on the surface of APC without any hazardous reducing agents under greener conditions. Catalytic activity in reduction reactions showed that biopolymer composites could be efficiently used as stabilizers for various noble metallic NPs. Recycling studies of the nanocomposite were also conducted for *o*-nitroaniline reduction to 1,2-benzenediamine, wherein the reaction yield decreased approximately from 100 % to 83 % after eight cycles.

Pectin-based bio(nano)sorbents have been utilized for the heavy metal selective elimination from aqueous media with affinity sequence of Pb^{2+}> Cu^{2+}> Co^{2+}> Ni^{2+}> Zn^{2+}> Cd^{2+} (Kartel, Kupchik, & Veisov, 1999). The cumbersome separation, lack of stability, or low recovery post desorption are the main constraints for the broad utilization of pectin-derived biosorbents. Mata, Blázquez, Ballester, González, and Muñoz (2009) reported the adsorption capacities of multimetals like Cu^{2+}, Cd^{2+}, Pb^{2+} using a sugar-beet pulp pectin biosorbent. In another study, Gong et al. (2012) studied the adsorption capability of magnetically recoverable pectin-Fe_3O_4 nanocomposite for the Cu^{2+} removal (48.99 mg g^{-1}) from wastewater in 5 successive cycles. Additionally, the pectin-CuS nanocomposite (~50 nm) was fabricated *via* a facile co-precipitation route (Gupta, Pathania, Agarwal, & Singh, 2012), which was successfully utilized to photodegrade and adsorb MB after 10 h under solar-light conditions at 30 °C and could be reused for successive 10 cycles. Bok-Badura, Jakóbik-

Koloń, Karon, and Mitko (2018) produced hybrid pectin/titanium oxide nanobeads as an efficient nanosorbent for the elimination of ionic heavy multimetals; adsorption capacities of hybrid nanobeads were 0.83, 1.37, 0.51, and 0.68, mmol g^{-1} for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, respectively.

Table 7 summarizes other known examples concerning the applications of pectin-based (nano)materials in water/wastewater remediation.

3. Summary and discussion

There are several reports in the literature on the water treatment using different (nano)catalysts including natural biopolymer-based nanomaterials. The polysaccharide-based (nano)materials utilized in the adsorption and reduction/degradation reactions are summarized in Table 8. Having reviewed these publications, it became clear that there are no special rules or general ways to theoretically predict the outcomes of a catalytic reduction/adsorption process. Mostly, the differences in the catalytic prowess of these (nano)materials depend on their amount and type, surface area, particle size, morphology and porosity, chemical composition, loading of metal/metal oxide on the catalyst surface, reaction temperature, solvent, reducing agents, *etc*. In other words, this comparison depends on the preparative method and/or reaction conditions and follows no predictive rules.

4. Conclusion and future perspectives

Natural biopolymer-based resources (particularly polysaccharides) derived from diverse derivatives are unquestionably the future wave of abundant resources that need to be exploited. Natural biopolymers are especially preferred because such they have unique structural, biological, physicochemical and biomechanical features and biodegradable properties; indeed, abundant availability, nontoxicity, renewalability, ease of modification, biocompatibility, and application potential have steered research in their direction. Importantly, aforementioned polysaccharides are considered alternative renewable (bio)resources and effective supports for the (nano)catalysts fabrication such as biopolymer supported Pd, Ag, Cu, TiO_2, ZnO, Fe_3O_4, Au NPs; it is one of the more effective strategies in nanotechnologies.

Additional explorations need to be conducted to optimize the production of natural/biopolymeric-based (nano)materials to render them viable and sustainable towards the industrial application *e.g.* the traditional adsorbents. Coagulation/flocculation of solid substances in wastewater has been accomplished with the assistance of natural/biopolymeric-based (nano)materials. Among polysaccharides, cellulose and chitosan are promising natural/biopolymers because of their sustainability, reactivity, chemical stability, excellent physicochemical attributes, and considerable selectivity towards toxic metals, dyes and aromatic compounds that makes them competitive to the conventional activated carbon.

Treatment of water/wastewater (especially industrial water) is very critical and essential for safeguarding the environmental quality and maintaining human health, and it has been a main trepidation for public health. As is clear from this review, emerging nanotechnologies have the potential to make industrial water remediation more effective where the pollutants could be removed using relatively greener nanotechnology, but this field still needs extensive explorations; major technical hurdle being their non-adaptability for industrial/ large-scale systems and competitiveness to the traditionally deployed existing treatment options. Nonetheless, recent efforts have identified great potential for many appliances of the biopolymer-based (nano)materials across diverse research domains; the preparation of polysaccharide-based (nano)materials *via* conventional approaches is quite convenient, facile and harmless to the environment. Thus, they have the potential to emerge as an effectual, cost-effective, and environment-friendly substitute for predominant treatment supplies, from the standpoints of both environmental remediation and resource conservation.

In spite of notable advances in the synthetic and catalytic utilizations of natural biopolymer-based (nano)materials, particular consideration should be paid to the following aspects in future investigations:

- Scalable fabrication of polysaccharide-based (nano)materials, at a relatively lower cost.
- Application of diverse biowaste (nano)materials as renewable alternative feedstocks for fabrication of biopolymers and their wastewater treatment application.
- Exploitation of natural supports *e.g.* clays, zeolites, and montmorillonite as cost-effective, nontoxic and abundantly available resources for the synthesis of (nano)catalysts and application in water/waste-water treatment.
- Manipulation of agricultural and animal residues *e.g.* bone, bristles, or eggshell for the synthesis of biopolymer-based (nano)materials and application in water remediation.
- Greener biological processes to reduce the cost of the biopolymer-based (nano)materials production under mild conditions and improve their (nano)catalytic prowess.
- Improvement of polysaccharide-based magnetic nanomaterials for water/ wastewater treatment.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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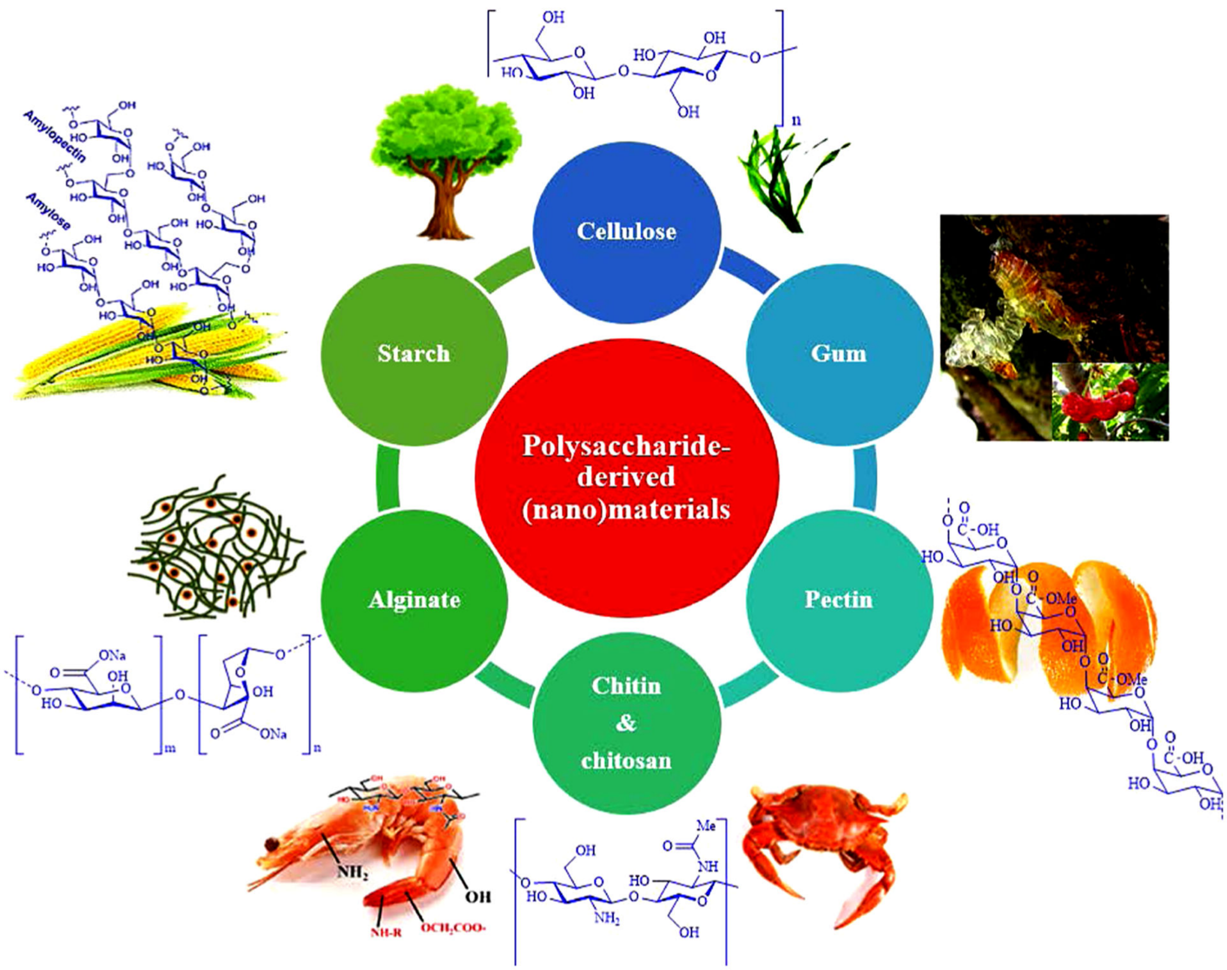

Fig. 1.
Sustainable and environmental-friendly organic polysaccharides.

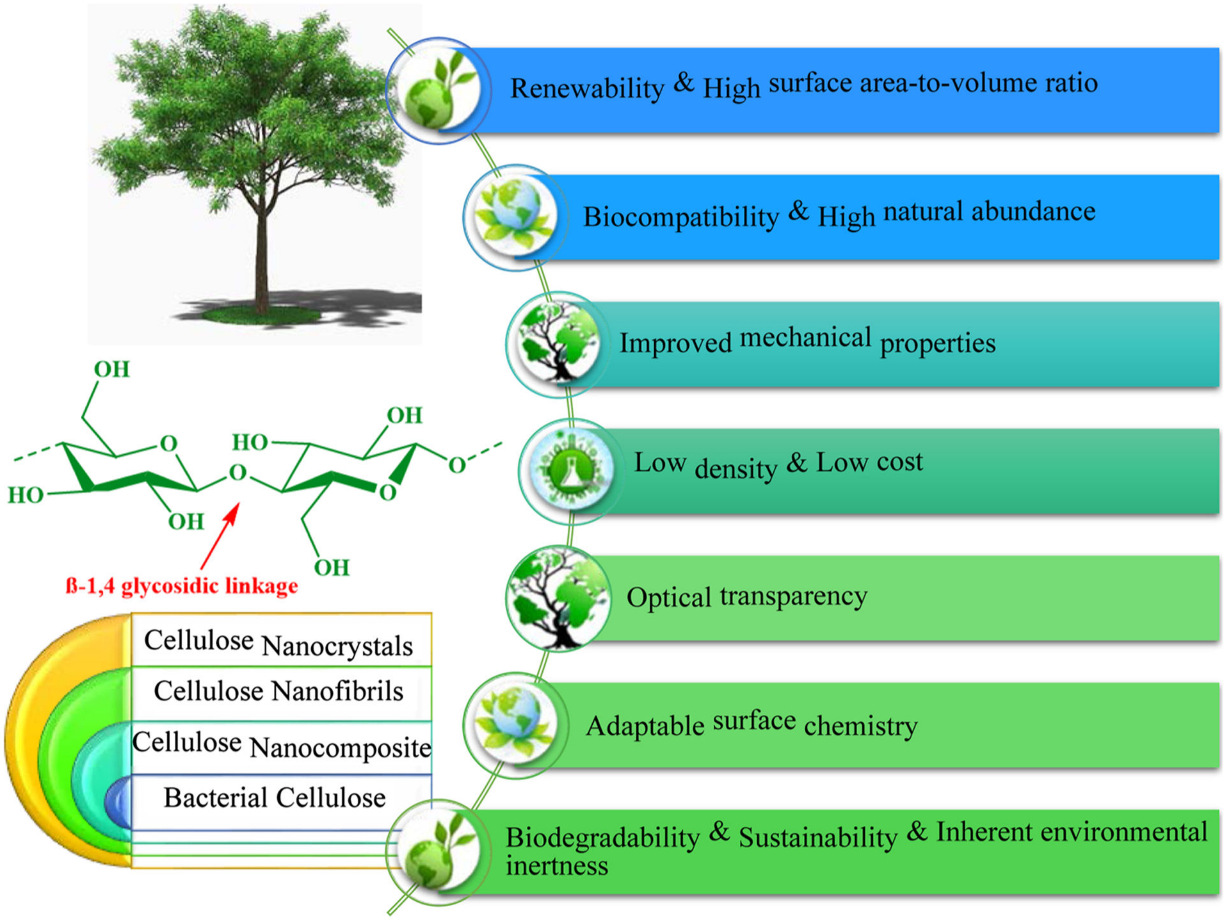

Fig. 2.
Significant properties and attributes of cellulosic nanomaterials.

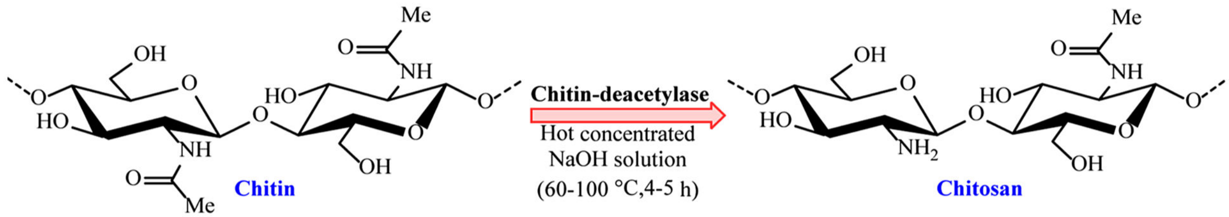

Fig. 3.

Deacetylation of chitin for the preparation of chitosan.

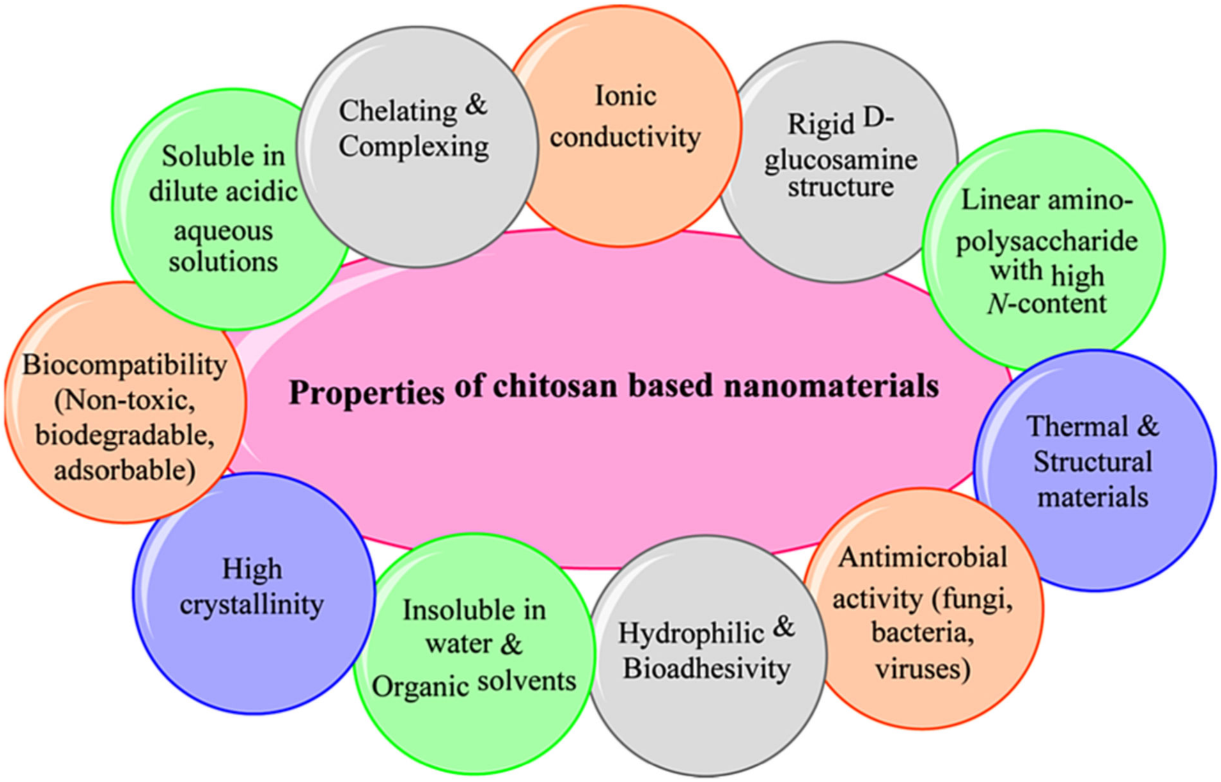

Fig. 4.
Essential physicochemical properties of chitosan.

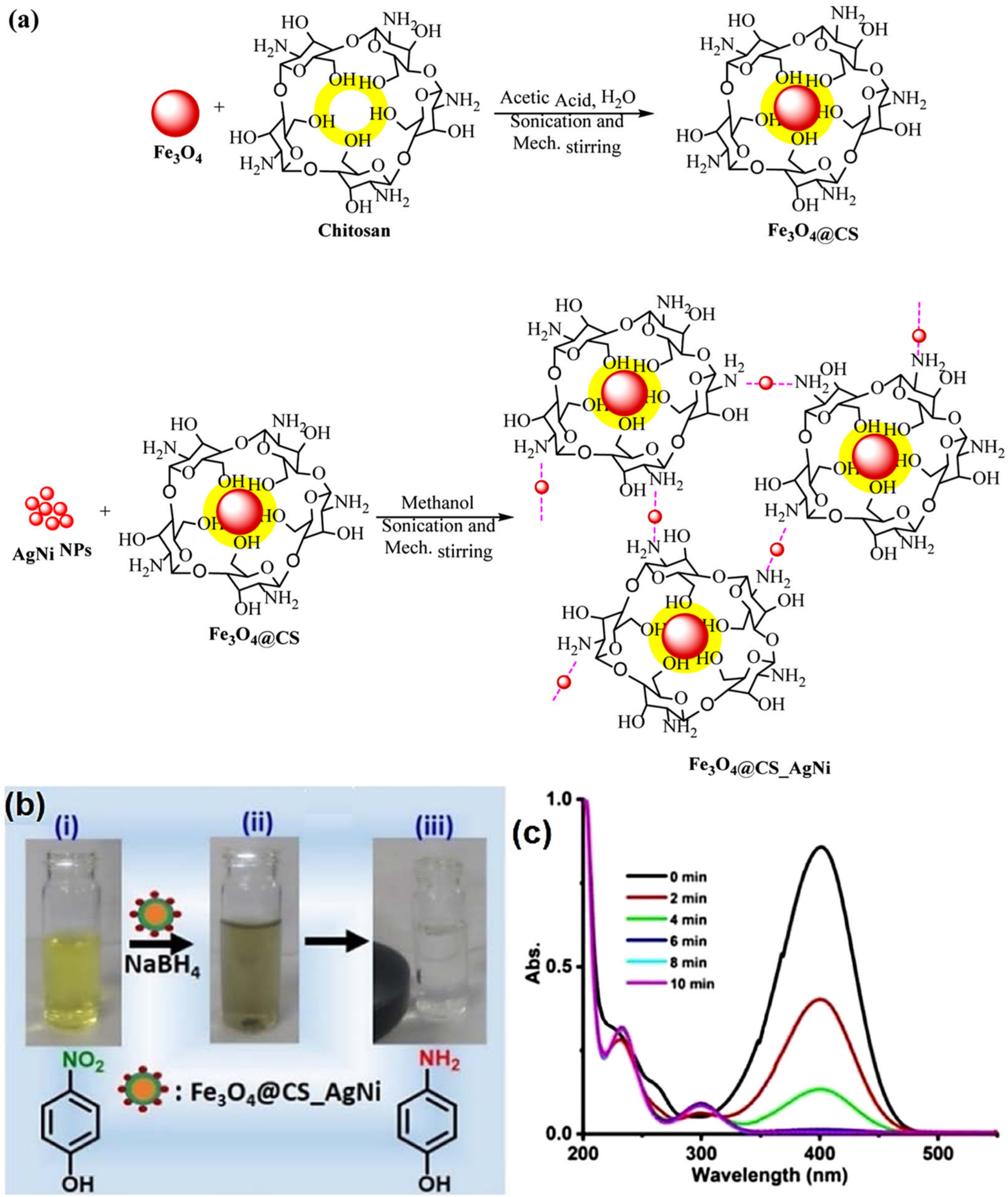

Fig. 5.

Preparation of Fe_3O_4@CS_AgNi nanocomposite, (b) Color changes observed during 4-NP reduction; (i) bare 4-NP, (ii) 4-NP + magnetic nanocomposite + $NaBH_4$, (iii) easy separation of magnetic nanocomposite *via* a magnet after the complete 4-NP reduction, (c) time dependent evolution illustrating the 4-NP reduction to 4-AP catalyzed by Fe_3O_4@CS_AgNi nanocomposite. Reproduced with permission from Ref. (Antony et al., 2019).

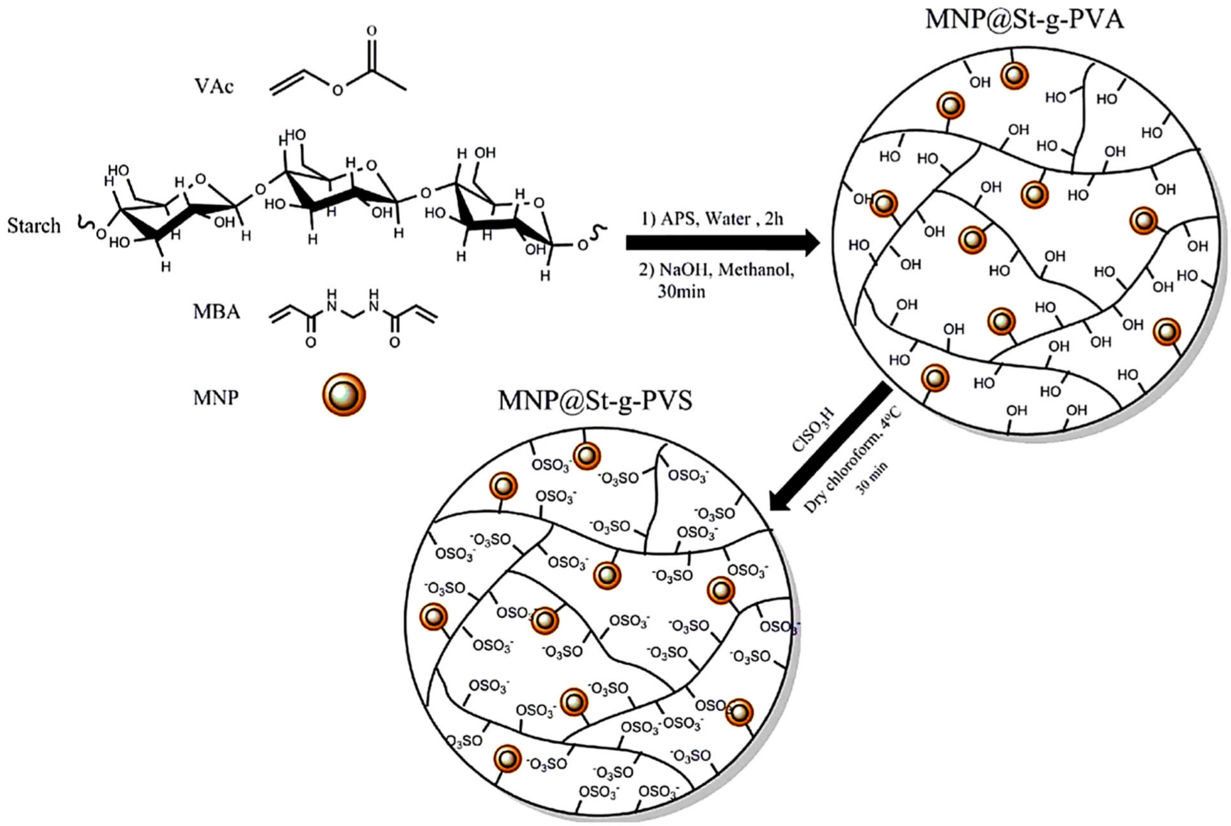

Fig. 6.
The MNP@St-g-PVS preparation. Reproduced with permission from Ref. (Pourjavadi et al., 2016).

Fig. 7.
Applications of guar gum. Reproduced with permission from Ref. (Sharma et al., 2018).

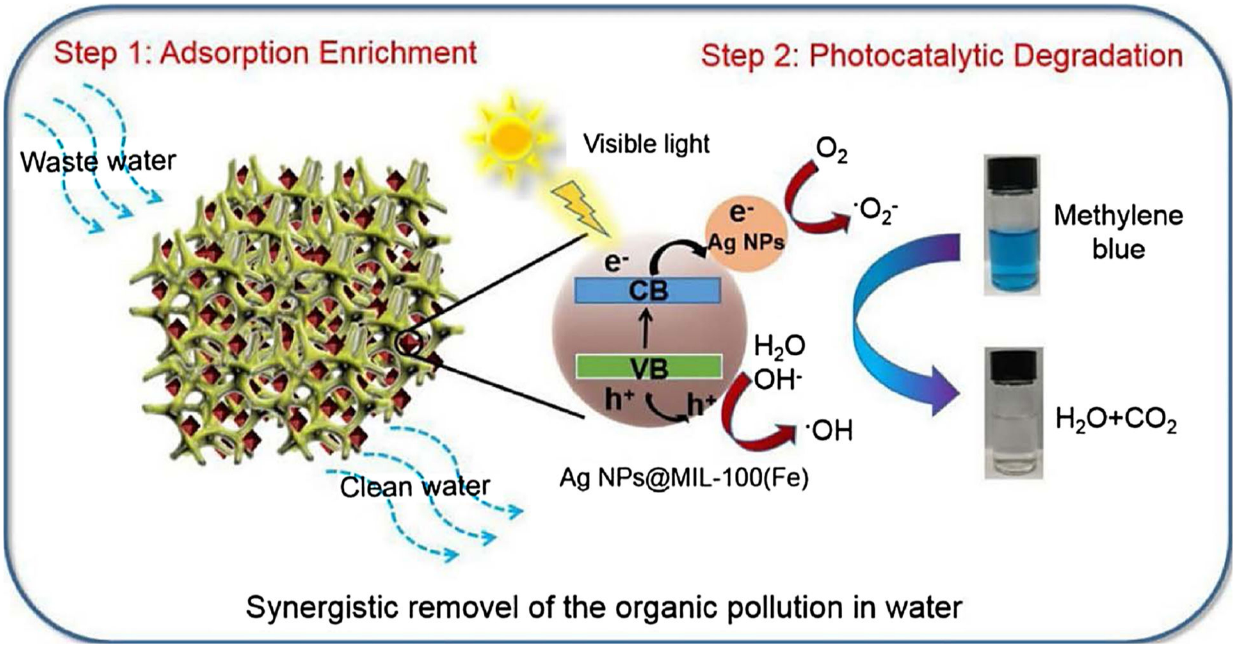

Fig. 8.

Adsorption and photodegradation mechanism of nanohybrid hydrogel. Reproduced with permission from Ref. (Duan et al., 2020).

Table 1

Cellulosic nanomaterial-based adsorbents for the removal of pollutants in water.

Cellulosic nanomaterial-based adsorbents	Contaminants	Ref.
β-Cyclodextrin modified CNCs@Fe_3O_4@SiO_2 superparamagnetic nanorods	Procaine, imipramine	(Chen, Berry, & Tam, 2014)
PEG modified CNCs	Acetaminophen, sulfamethoxazole, *N*, *N*-diethyl-meta-toluamide	(Herrera-Morales et al., 2017)
Pristine CNCs	Chlorpyrifos	(Moradeeya et al., 2017)
Dialdehyde functionalized CNCs	Creatinine	(Huang, Liu, Sun, & Fatehi, 2016)
Poly(acrylic acid) modified poly (glycidylmethacrylate) grafted CNCs	Trypsin	(Anirudhan & Rejeena, 2012)
Poly(methacrylic acid-co-vinyl sulfonic acid) grafted magnetic CNCs	Hemoglobin, immunoglobulin G	(Anirudhan & Rejeena, 2013)
Aminopropyltriethoxysilane modified, hydroxyl-carbonated apatite modified and Epoxy modified CNFs	Hydrogen sulphide	(Hokkanen, Repo, Bhatnagar, Tang, & Sillanpää, 2014)
Carbonated hydroxyapatite modified CNFs	Phosphate, nitrate	(Hokkanen, Repo, Westholm et al., 2014)
UiO-66/polydopamine/bacterial cellulose	Aspirin, tetracycline hydrochloride	(Cui et al., 2020)
Carboxy methyl cellulose/citric acid aerogel	Nitrate, nitrite, phosphate	(Darabitabar, Yavari, Hedayati, Zakeri, & Yousefi, 2020)

Table 2

Organic dyes and heavy metal ions adsorption onto assorted cellulose-related nanosorbents.

Cellulose-based nanosorbent	Contaminant	Max. adsorption capacity (mg g^{-1}) or removal percent	T. (K)/pH	Ref.
Pristine CNFs	Ag(I)	34.35 mg g^{-1}	298/5.45	(Liu et al., 2014)
Pristine CNCs	Ag(I)	15.45 mg g^{-1}	298/6.39	(Liu et al., 2014)
Pristine CNCs from sludge	Cu(II), Fe(III)	25.5, 1.85 mg g^{-1}	298/3.5–4.5	(Liu, Borrell et al., 2015)
Pristine CNCs from bioethanol	Cu(II), Fe(III)	30.15, 4.35 mg g^{-1}	298/3.5–4.5	(Liu, Borrell et al., 2015)
Pristine CNCs	MB	118 mg g^{-1}	298/9.0	(Batmaz et al., 2014)
TEMPO[a] oxidized carboxylated CNCs	MB	769 mg g^{-1}	298/9.0	(Batmaz et al., 2014)
Pristine CNCs	Crystal violet (CV)	185.19 mg g^{-1}	303/6.0	(Qiao et al., 2015)
Maleic anhydride grafted CNCs	Crystal violet (CV)	243.90 mg g^{-1}	303/6.0	(Qiao et al., 2015)
Pristine CNFs	MB	122.2 mg g^{-1}	293/9.0	(Chan, Chia, Zakaria, Sajab, & Chin, 2015)
Phosphorylated CNFs from sludge	Cu(II)	72.75 mg g^{-1}	298/3.5–4.5	(Liu, Borrell et al., 2015)
Phosphorylated CNCs from sludge	Cu(II)	72.8 mg g^{-1}	298/3.5–4.5	(Liu, Borrell et al., 2015)
Sodium substituted succinic anhydride-amended CNCs	Pb(II), Cd(II)	465.1, 344.8 mg g^{-1}	298/5.5, 6.5	(Yu, Tong, Ge, Wu et al., 2013)
Succinic anhydride-modified CNCs	Pb(II), Cd(II)	367.6, 259.7 mg g^{-1}	298/5.5, 6.5	(Yu, Tong, Ge, Wu et al., 2013)
Succinic anhydride modified CNCs	Cr(III)	2.88 mg g^{-1}	298/6.5	(Singh et al., 2014)
Acrylamide modified CNCs	Cr(VI)	2.77 mg g^{-1}	298/2.5	(Singh et al., 2014)
Carboxylated CNFs	Cu(II)	135 mg g^{-1}	298/6.2	(Sehaqui et al., 2014)
Carboxylated CNFs	UO_2^{2+}	167 mg g^{-1}	298/6.5	(Ma et al., 2012)
Fe-Cu@CNC	Pb(II)	93.98 %	–	(Chen, Yu, Deutschman, Yang, & Tam, 2020)
Sulfonated CNFs	Au(III)	57 and 60 mg g^{-1}	295/3.26	(Dwivedi, Dubey, Hokkanen, & Sillanpää, 2014)
Electrosterically stabilized CNCs	Cu(II)	185 mg g^{-1}	298/4.0	(Sheikhi, Safari, Yang, & Van De Ven, 2015)
CHA[b] modified CNFs	Ni(II), Cd(II)	99.33 %, 99.30 %	298/5.0	(Hokkanen, Repo, Westholm et al., 2014)
2-Mercaptobenzamide altered itaconic acid attached magnetite CNCs	Hg(II)	240.0 mg g^{-1}	303/8.0	(Anirudhan & Shainy, 2015)
Magnetic CNC@Zn-benzene-1,3,5-tricarboxylic acid	Pb(II)	558.66 mg g^{-1}	298.2/-	(Wang, Ouyang, Yang, & Omer, 2017)
TEMPO oxidized CNFs modified by PEI	Cu(II)	52.32 mg g^{-1}	303/5.0	(Zhang, Zang, Shi, Yu, & Sheng, 2016)

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Cellulose-based nanosorbent	Contaminant	Max. adsorption capacity (mg g^{-1}) or removal percent	T. (K)/pH	Ref.
Amino functionalized CNCs	Acid red GR	555.6 mg g^{-1}	298/4.7	(Jin, Li, Xu, & Sun, 2015)
Au@BSA NCs loaded CNC-ALG hydrogel beads	Hg(II)	26 mg g^{-1}	298/7.0	(Mohammed, Baidya et al., 2016)
Poly(itaconic acid/methacrylic acid) embedded CNCs/bentonite nanocomposite	Co(II)	350.8 mg g^{-1}	303/6.0	(Anirudhan, Deepa, & Christa, 2016)
FeNP modified CNFs	As(V)	241.8 mg g^{-1}	293/2.0	(Hokkanen, Repo, Lou, & Sillanpää, 2015)
Carboxylated CNFs/PVA hybrid aerogels	Hg(II), Pb(II), Cu(II), Ag(I),	157.5, 110.6, 151.3, 114.3 mg g^{-1}	–	(Zheng, Cai, & Gong, 2014)
Carboxylated CNFs/magnetic chitosan hydrogel beads	Pb(II)	171.0 mg g^{-1}	298/4.5	(Zhou, Fu et al., 2014)
CNCs/HPAM[c] nano-hydrogels (by casting)	MB	326.08 mg g^{-1}	298/5.0	(Zhou, Wu et al., 2014; Zhou, Fu et al., 2014)
CNCs/HPAM nano-hydrogels (by electrospinning)	MB	–	298/6.5	(Zhou, Lee, Dooley, & Wu, 2013)
MnO_2 coated CNFs	MB	99.8 %	298/9.6	(Wang, Yadav et al., 2014; Wang, Zhang et al., 2014)
D-CNCs/PVAm[d] microgels	Congo red 4BS, reactive light-yellow K-4G, acid red GR	869.1, 1250.9, 1469.7 mg g^{-1}	298/3.5	(Jin, Sun et al., 2015)
CNC@polydopamine	MB	2066.72 mg g^{-1}	298/10.0	(Wang, Zhang et al., 2020)
Cellulose nanocrystals	Victoria Blue 2B, methyl Violet 2B, rhodamine 6 G	98 %, 90 %, 78 %	r.t./5.01	(Karim, Mathew, Grahn, Mouzon, & Oksman, 2014)
CMC/GOCOOH[e] microbeads	MB	180.32 mg g^{-1}	298/10.0	(Eltaweil, Elgarhy, El-Subruiti, & Omer, 2020)
Ag, Au, Pt NPs- and Ag@Au, Ag@Pt NPs-CNF	4-nitrophenol (4-NP)	–	r.t./-	(Esquivel-Pena et al., 2020)
CTAB[f] modified CNC	CR	448.43 mg g^{-1}	298/7.5	(Ranjbar, Raeiszadeh, Lewis, MacLachlan, & Hatzikiriakos, 2020)
CNC-ALG hydrogel bead	MB	255.5 mg g^{-1}	–	(Mohammed, Grishkewich, Waeijen, Berry, & Tam, 2016)
CNF-GnP[g] aerogel	MB, CR	1178.5, 585.3 mg g^{-1}	–	(Yu, Hu, Dichiara, Jiang, & Gu, 2020)
CMC/g-C_3N_4/ZnO	Methyl violet	96.43 mg g^{-1}	298/8.0	(Sharma et al., 2020)
G-C_3N_4/CNCs-H hydrogel	MB	232.558 mg g^{-1}	r.t./7.0	(Wang, Li et al., 2020)
M3D-PAA-CCN[h]	MB	332 mg g^{-1}	–	(Samadder et al., 2020)
Carboxylated cellulose fabric filter	MB, Pb(II)	76.92, 81.30 mg g^{-1}	298/5.0	(Li, Ma, Venkateswaran, & Hsiao, 2020)
PAETMAC[i]-g-CNC	Neutral reactive blue 19 (RB 19)	>80 %	298/7.0	(Jiang, Lou, Hua, Deng, & Tian, 2020)
Cellulose-modified $La_{0.9}Sr_{0.1}FeO_3$	CR	38.46 mg g^{-1}	r.t./4.0	(Ali & Al-Oufi, 2020)
MBCNF/GOPA[j]	Malachite green (MG)	270.27 mg g^{-1}	298/7.0	(Arabkhani & Asfaram, 2020)

Cellulose-based nanosorbent	Contaminant	Max. adsorption capacity (mg g^{-1}) or removal percent	T. (K)/pH	Ref.
BC[k]@CdS nanocomposite	MB	10.92 mg g^{-1}	293/-	(Qian, Xu, Yue, Wang, & Liu, 2020)
CNF-Fe(0)@FeS	MB, CR	200.0, 111.1 mg g^{-1}	298/7.0, 5.0	(Sankararamakrishnan, Singh, & Srivastava, 2020)
CNF/PEI[l]/Ag NPs aerogel membrane	4-NP, MB, CR	96 %, 99.2 %, 96.4 %	–	(Zhang et al., 2020)
TOCN/CGG[m] hydrogel	Cu(II), MO, thioflavin T	498.5, 134.3, 430.2 mg g^{-1}	–	(Dai et al., 2020)
D-ZSM[n]/CNF, Cu- and Fe- ZSM/CNF	Rhodamine 6B, Reactive blue 4	34.36, 9.22 and 16.55 mg g^{-1}	r.t./≥ &≤7.0	(Lakhane, Mahabole, Bogle, Khairnar, & Kokol, 2019)
CA-PANI/β-CD[o] nanofiber	MB	49.51 mg g^{-1}	298/8.0	(Ali, El-Aassar, Hashem, & Moussa, 2019)
IDA@CMC-PBQ[p] microbeads	CV	107.52 mg g^{-1}	298/8.0	(Omer, Elgarhy, El-Subruiti, Khalifa, & Eltaweil, 2020)
PEI-Pt@BC[q] membrane	Acid black ATT	1157.9 mg g^{-1}	298/5.2	(Huang et al., 2020)
α-Fe_2O_3 nanodisk/bacterial cellulose membrane	Orange II (OII), MO, Rhodamine B (RhB), MB, CV, MG	–	–	(Zhu et al., 2018)
PMPC/BNC[r] nanocomposite	MB, MO	4.44 ± 0.32, 4.56 ± 0.43 mg g^{-1}	–	(Vilela, Moreirinha, Almeida, Silvestre, & Freire, 2019)
MoS_2-graphene-CFP[s]	MB	485.4 mg g^{-1}	298/7.0	(Gopalakrishnan, Singh, & Badhulika, 2020)
hPEI[t] modified cellulose-based bioadsorbent	Cationic bright yellow M-7 G, anionic reactive yellow X-RG, nonionic disperse brown S-3RL	571.43, 970.87, 581.40 mg g^{-1}	r.t./-	(Chen et al., 2018)
PANi/BC mat	Cr(VI)	–	298 ± 2/1–5	(Jahan, Kumar, & Verma, 2018)
CMC-Ni-BC	MB, 2-NP	>95 %, >90 %	–	(Kamal, Ahmad, Khan, & Asiri, 2019)
BC/PDA/TiO_2	RhB, MB, MO	100 %, 99.5 %, 95.1 %	–	(Yang et al., 2020)
BC/NiHCF[u] membrane	Cs(I)	175.44 mg g^{-1}	298/6.0	(Zhuang & Wang, 2019)
BC-AC[v]	MB	505.8 mg g^{-1}	–	(Khamkeaw, Jongsomjit, Robison, & Phisalaphong, 2019)
ZIF-67/BC/CH[w] aerogel	Cu(II), Cr(VI), active red X-3B	200.6, 152.1 mg g^{-1}, 100%	298/6.0	(Li, Tian et al., 2020)
Cellulose acetate-ceria/zirconia@Cu° NPs	Mixture of 4-NP-MB, 4-NP-RhB & 4-NP-MB-RhB	–	–	(Khan et al., 2020)
Cellulose/Ag_3PO_4	Mixture of industrial fertilizer effluent + RhB dye	52 % and 86 %	–	(Tavker, Gaur, & Sharma, 2020)

[a] 2,2,6,6-Tetramethyl-1-piperidinyloxy.

[b] Carbonated hydroxyapatite.

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[c]Hydrolyzed polyacrylamide.

[d]Polyvinylamine.

[e]Carboxymethyl cellulose/carboxylated graphene oxide.

[f]Cetyltrimethylammonium bromide.

[g]Cellulose nanofibrils-graphene nanoplates.

[h]Polyacrylic acid-magnetic 3D crosslinkers-carboxylated cellulose nanocrystal.

[i]Poly acryloyloxyethyltrimethyl ammonium chloride.

[j]Magnetic bacterial cellulose nanofiber/graphene oxide polymer aerogel.

[k]Bacterial cellulose/cadmium sulphide.

[l]Poly(ethylene imine).

[m]TEMPO-oxidized cellulose nanofibers/cationic guar gum.

[n]De-aluminated ZSM-5 zeolite.

[o]Cellulose acetate-polyaniline/β-cyclodextrin.

[p]Iminodiacetic acid@carboxymethyl cellulose-*p*-benzoquinone.

[q]Polyethylenimine caged platinum nanomaterials@bacterial cellulose.

[r]Poly(2-methacryloyloxyethyl phosphorylcholine)/bacterial nanocellulose.

[s]Cellulose filter paper.

[t]Hyperbranched polyethyleneimine.

[u]Nickel hexacyanoferrates loaded bacterial cellulose.

[v]Activated carbon.

[w]Zeolitic imidazolate framework-67/bacterial cellulose/chitosan.

Table 3

Various chitin and chitosan-based nanomaterials used for water/wastewater treatment.

Chitin and chitosan-based nanomaterials	Contaminants	Ref.
Chitosan films containing urea modified TiO_2	MG	(Pérez-Obando et al., 2019)
CS/MCM-41/nano-γ alumina	MB	(Teimouri, Ghased, Nasab, & Habibollahi, 2019)
Chitosan clay nanocomposites	Cu(II)	(Azzam et al., 2016)
Chitosan-polyethyleneimine-graphene oxide nanocomposite membrane coating	Cr(VI) and Cu(II)	(Bandara, Nadres, & Rodrigues, 2019)
Carboxymethyl chitosan coated nano zerovalent iron beads	Cr(VI)	(Xie et al., 2018)
Chitosan modified with polyhexamethylene biguanide	Cr(VI)	(Aslani, Kosari, Naseri, Nabizadeh, & Khazaei, 2018)
Chitosan/organic rectorite-Fe_3O_4 composite microspheres	Cu(II) and Cd(II)	(Xie et al., 2015)
Nano-ZnO/chitosan microspheres	MO	(Zhong, Zhong, Huo, Yang, & Li, 2020)
Attapulgite/$CoFe_2O_4$@SiO_2-chitosan/EDTA	Cd(II)	(Wang, Ran et al., 2020; Wang, Zhou et al., 2020)
Polymaleic acid-chitosan microspheres	Cd(II)	(Yu et al., 2017)
Cu@chitosan-silica nanoparticles	1,1-Dimethylhydrazine	(Wang et al., 2019)
Chitosan-coated fly ash	Cr(VI)	(Wen, Tang, Chen, & Gu, 2011)
Polyvinylidene fluoride/chitosan/dopamine	MB and orange G	(Zhang, Li et al., 2019)
Bilayer amino-functionalized cellulose nanocrystals/chitosan composite	Diclofenac sodium	(Hu et al., 2019)
Zinc ferrite-CS, Nickel ferrite-CS, Cobalt ferrite-CS	Fluoride	(Kumar, Dosanjh, & Singh, 2019)
Chitosan-magnetite nanocomposite	Cr(VI)	(Bavasso, Vuppala, & Cianfrini, 2019)
Chitosan-4-nitroacetophenone/CuO-CeO_2-Al_2O_3 and Chitosan-4-nitroacetophenon/ CuO-CeO_2-Fe_2O_3	Red 60	(Mohamed et al., 2019)
Fe_3O_4-chitosan micro- and nanoparticles	Bromothymol Blue	(Akın Sahbaz, Yakar, & Gündüz, 2019)
MIL-100(Fe) and nano-Fe_3O_4 onto the chitosan	Sb(III)	(Xiong et al., 2020)
Nano titanium oxide/chitosan/nano-bentonite	Levofloxacin and Ceftriaxone	(Mahmoud, El-Ghanam, Mohamed, & Saad, 2020)
Chitosan/cerium oxide/iron oxide nano-composite	Cr(VI) and Co(II)	(Farokhia, Parvareha, & Moravejia, 2019)
Chitosan supported ZnO and Ce-ZnO nano-flowers	Malachite green	(Saad et al., 2020)
Chitosan nano zerovalent iron activated carbon composite beads	Cu(II)	(Sikdera et al., 2019)
Salicylaldehyde functionalized chitosan NPs	Cu(II), Cd(II) and Pb(II)	(Hussain, Musharraf, Bhanger, & Malik, 2020)
2D Ag-TiO_2/γ-Al_2O_3/Chitosan nano-composite	Nitrate	(Zarei et al., 2020)
Chitosan/silver nanoparticle/copper nanoparticle/carbon nanotube multifunctional nano-composite	Cu(II), Cd(II) and Pb(II)	(Alsabagh, Fathy, & Morsi, 2015)
Zirconium chitosan composite	Cr(VI)	(Zhang, Xia, Teng, Liu, & Zhang, 2013)

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Chitin and chitosan-based nanomaterials	Contaminants	Ref.
Wet-spun nanoTiO_2/chitosan nanocomposite fibers	Free fatty acids	(Bao et al., 2019)
$MnFe_2O_4$ impregnated chitosan-microspheres	MB	(Jyothi et al., 2019)
Humic acid modified magnetic chitosan NPs	Uranium	(Basu, Saha, Pimple, & Singhal, 2019)
Pd NPs@Fe_3O_4/CS-AG microcapsules	4-NP	(Baran & Nasrollahzadeh, 2019)
Chitosan-zirconium phosphate nanostructures	Reactive blue-21, Reactive Red 141, Rhodamine-6 G	(Bhatt, Ageetha, Rathod, & Padmaja, 2019)
Chitosan grafted thin film nanohydrogel	Cr(VI)	(Sethy, Pradhan, & Sahoo, 2019)
Nanoscale zero-valent iron loaded chitosan	U(VI)	(Zhang, Zhao et al., 2019; Zhang, Ma et al., 2019)
Functionalized chitosan clinoptilolite nanocomposites	Nitrate	(Yazdi, Anbia, & Salehi, 2019)
Chitosan coated magnetic NPs	Cu(II)	(Zhou, Nie, Branford-White, He, & Zhu, 2009)
Nickel oxide/chitosan nano-composite	Zn(II)	(Abdolmohammad-Zadeh, Ayazi, & Naghdi, 2019)
Magnetic β-cyclodextrin-chitosan/graphene oxide	MB	(Fan, Luo, Sun, Qiu, & Li, 2013)
Magnetic graphene/chitosan	Acid Orange 7	(Sheshmani, Ashori, & Hasanzadeh, 2014)
Carboxymethyl chitosan coated Fe_3O_4 NPs	Direct Red 16	(Zinadini et al., 2014)
CS/β-CD/Nano-ZnO composite	CR	(Yan, Zhang, & Li, 2018)
Ag_2O/TiO_2 modified chitosan	MO	(Zhao, Tao, Xiao, & Su, 2017)
$NiFe_2O_4$ nanocomposite grafted chitosan	Cr(VI)	(Zhang, Wu, & Fan, 2019)
Thiocarbohydrazide chitosan gel	Cr(VI)	(Li et al., 2017)
3,5-Dinitrosalicylic acid/chitosan/$MnFe_2O_4$	MB	(Shoueir et al., 2018)
Chitosan zinc oxide nano-beads	MB and safranin	(Roshitha, Mithra, Saravanan, Sadasivam, & Gnanadesigan, 2019)
Chitin/chitosan nano hydroxyapatite composite	Cu(II)	(Gandhi, Kousalya, & Meenakshi, 2011)
Chitin powder	Ag(I)	(Songkroah, Nakbanpote, & Thiravetyan, 2004)
Chitosan gel beads	Ag(I)	(Zhang, Helleur, & Zhang, 2015)
Chitosan/triethanolamine composite	Ag(I)	(Zhang et al., 2012)
Thiol-functionalized chitin nanofibers	As	(Yang et al., 2015)
Chitosan-coated biosorbent	As	(Boddu, Abburi, Talbott, Smith, & Haasch, 2008)
Fly ash coated by chitosan	As	(Adamczuk & Kołodyńska, 2015)
Chitin	Au	(Côrtes, Tanabe, Bertuol, & Dotto, 2015)
Chemically modified chitosan	Au	(Donia, Atia, & Elwakeel, 2007)
Chitosan derivative	Au	(Wang et al., 2012)
Glycine crosslinked chitosan resin	Au	(Wang et al., 2012)

Chitin and chitosan-based nanomaterials	Contaminants	Ref.
Chitosan films	V	(Cadaval, Dotto, Seus, Mirlean, & de Almeida Pinto, 2016)
Ti-doped chitosan bead	V	(Liu & Zhang, 2015)
Protonated chitosan flakes	V	(Padilla-Rodríguez et al., 2015)
N-citryl chitosan	V	(Mujeeb, Alikutty, & Muraleedharan, 2014)
Chitin networks	U	(Schleuter et al., 2013)
Amidoximated chitosan polyacrylonitrile	U	(Xu et al., 2015)
Chitosan/bentonite composite	U	(Anirudhan & Rijith, 2012)
Magnetic chitosan resin	U	(Zhou, Shang, Liu, Huang, & Adesina, 2012)
Chitosan saturated montmorillonite	Pb(II)	(Hu, Zhu, Cai, Hu, & Fu, 2017)
Modified chitosan/$CoFe_2O_4$ particles	Pb(II)	(Fan et al., 2017)
Thiosemicarbazide-modified chitosan	Pb(II)	(Li, Zhang, Li, Wang, & Ali, 2016)
Magnetic chitosan/clinoptilolite/magnetite	Pb(II)	(Javanbakht, Ghoreishi, Habibi, & Javanbakht, 2016)
Magnetic chitosan	Hg(II)	(Kyzas & Deliyanni, 2013)
Coarse chitin	Hg(II)	(Barriada, Herrero, Prada-Rodríguez, & de Vicente, 2008)
Raw chitin and surface-modified chitin	Co(II)	(Dotto, Cunha, Calgaro, Tanabe, & Bertuol, 2015)
Chitosan polymethacrylate nanoparticles	Co(II)	(Shaker, 2015)
Modified chitosan resin	Co(II)	(Monier, Ayad, Wei, & Sarhan, 2010)
Cellulose acetate/chitosan/single walled carbon nanotubes/Fe_3O_4/TiO_2	As(V), Cr(VI), MB, CR	(ZabihiSahebi et al., 2019)
Titanium dioxide/chitosan/poly(lactide-co-caprolactone) composite membrane	Cu(II)	(He et al., 2019)
Molecularly imprinted polymer (MIP) chitosan-TiO_2 nanocomposite	Rose Bengal	(Ahmed, Abdelbar, & Mohamed, 2018)
TiO_2(KH-570)-g-(chitosan-glycidyl methacrylate)	Toluene, Pb(II)	(Chen, Song, Huang, & Wang, 2019)
TiO_2 doped chitosan microspheres supported on cellulose acetate	MO	(Shi, Zhang, Ma, Xiang, & Li, 2019)
Chitosan tripolyphosphate/TiO_2 nanocomposite	Reactive orange 16	(Abdulhameed, Mohammad, & Jawad, 2019)
Schiff's base cross linked chitosan-glutaraldehyde TiO_2 nanoparticles	Reactive red 120	(Jawad, Mubarak, & Abdulhameed, 2020)
Hybrid crosslinked chitosan-epichlorohydrin/TiO_2 nanocomposite	Reactive red 120	(Jawad, Mubarak, & Abdulhameed, 2020)
Chitosan ethylene glycol diglycidyl ether/TiO_2 nanoparticles	Reactive orange 16	(Abdulhameed, Jawad, & Mohammad, 2019)
TiO_2 supported 3D printed chitosan scaffolds	Amoxicillin	(Bergamonti et al., 2019)
Hybrid chitosan-TiO_2/ZnS	Aromatic amines, carboxylic acids	(Jbeli, Ferraria, do Rego, Boufi, & Bouattour, 2018)
Crosslinked magnetic EDTA/chitosan/TiO_2	Phenol, Cd(II)	(Alizadeh, Delnavaz, & Shakeri, 2018)
2D Ag-TiO_2/γ-Al_2O_3/chitosan	Nitrate	(Zarei et al., 2020)

Chitin and chitosan-based nanomaterials	Contaminants	Ref.
Chitosan-AgCl/Ag/TiO_2	Toluidine, salicylic acid, 4-aminomethyl benzoic acid	(Jbeli, Hamden et al., 2018)
Chitosan beads	Tartrazine, amido black, CR	(Mincea, Patrulea, Negrulescu, Szabo, & Ostafe, 2013)
Chitosan films	Mixture of Diclofenac and Ketoprofen	(Rizzi et al., 2019)

Table 4

Various starch-based nanomaterials used for water/wastewater treatment.

Chitin, chitosan and starch-based nanomaterials	Contaminants	Ref.
Starch stabilized Fe° NPs	Cr(VI)	(Alidokht, Khataee, Reyhanitabar, & Oustan, 2011)
Monodisperse functional magnetic dialdehyde starch nanocomposite	Hg(II)	(Wang et al., 2015)
Ag NPs base starch/PEG-polyacrylic acid hydrogel	Hg(II)	(Saberi, Sadeghi, & Alipour, 2020)
Fe_3O_4 based starch-poly (acrylic acid) nanocomposite hydrogel	Cu(II), Pb(II), Methylene Violet and Congo Red	(Saberi, Alipour, & Sadeghi, 2019)
Oxidized starch NPs	Urea	(Abidin et al., 2018)
Starch stabilized nanoscale zero-valent iron	Cr(VI)	(Chen, Xie et al., 2019)
Starch modified nano zero-valent iron	Cr(VI)	(Dong et al., 2016)
Starch, carboxymethyl cellulose CMC-stabilized nano zero-valent iron	Sulfamethazine	(Dong et al., 2020)
Starch modified nanoscale zero-valent iron	Acid Blue-25	(Elkady, Shokry, El-Sharkawy, El-Subruiti, & Hamad, 2019)
Starch stabilized nanoscale zero-valent iron	Nitrate	(Zhou, Sun, Chen, Wang, & Yang, 2017)
Na-montmorillonite NPs/P (acrylic acid-acrylamide)-g-starch	Safranin	(Zarei, Sadeghi, & Bardajee, 2018)
Starch-modified magnetic Fe° NPs	Naphthalene	(Malekzadeh, Nejaei, Baneshi, Kokhdan, & Bardania, 2018)
Starch- stabilized Fe° NPs	Nitrate	(Rajab Beigy, Rasekh, Yazdian, Aminzadeh, & Shekarriz, 2018)
Superparamagnetic starch functionalized maghemite NPs	Cr(VI)	(Singh, Tiwary, & Sinha, 2015)
Starch coated Fe_3O_4 magnetic NPs	Optilan Blue	(Stan et al., 2019)
Mungbean starch/PVA/ZnS bionanocomposite	Bisphenol A & MO	(Yun, Kim, Shim, & Yoon, 2018)
γ-Fe_2O_3@starch	Arsenic	(Siddiqui et al., 2020)
AgNPs-base starch/PEG-poly (acrylic acid) hydrogel	Hg(II)	(Saberi et al., 2020)

Table 5

Gum-based photocatalysts/catalysts in removal of organic/inorganic contaminants.

Gum-based photocatalysts/catalysts	Contaminants	Highlights	Ref.
L-Methionine montmorillonite encapsulated guar gum-g-polyacrylonitrile copolymer hybrid nanocomposite	Heavy metal ions	Adsorption capacities (mg g^{-1}): 125.00 for Pb(II) and 90.91 for Cu (II)	(Ahmad & Hasan, 2017)
Gum arabic modified magnetic nano	Copper ions	Adsorption capacity (mg g^{-1}): 38.5	(Banerjee & Chen, 2007)
Cellulose/carbon tubes hybrid adsorbent anchored with welan gum polysaccharide	MB	Adsorption capacity (mg g^{-1}): 302.1	(Deng et al., 2012)
Magnetic gel beads composed of Fe_3O_4 nanoparticles and gellan gum	Heavy metal ions	High adsorption capacities for Pb^{2+}, Mn^{2+} and Cr^{3+}	(Wang, Chen et al., 2009; Wang, Zhao et al., 2009)
Xanthan gum stabilized nano Pd/Fe	Polychlorinated biphenyls (PCBs)	Remediation of PCBs contaminated soils	(Fan, Cang et al., 2013)
Gum karaya-grafted poly(acrylamide-co-acrylic acid) incorporated Fe_3O_4 NPs hydrogel nanocomposite	Metal ions (Pb(II), Cr(VI) & Ni(II))	100 % removal in 5 min	(Fosso-Kankeu, Mittal, Waanders, Ntwampe, & Ray, 2016)
Xanthan gum-g-polyacrylamide/SiO_2	Pb(II)	Adsorption capacity (mg g^{-1}): 537.634	(Ghorai, Sinhamahpatra, Sarkar, Panda, & Pal, 2012)
Chitosan-guar gum blend silver nanoparticle bionanocomposite	Reactive blue-21 (RB-21), Reactive red-141, Rhodamine-6 G (RH-6 G) and 4-NP	High degradation and reduction	(Vanaamudan, Sadhu, & Pamidimukkala, 2018)
Titania/gum tragacanth nanohydrogel	MB	Efficiency of 88.86 %	(Rahimdokht, Pajootan, & Ranjbar-Mohammadi, 2019)
Gum Tragacanth-based carbon dots-nano zero-valent iron composite	Amoxicillin and ciprofloxacin	90 (amoxicillin) and 51 % (ciprofloxacin) removal	(Pirsaheb, Moradi, Shahlaei, Wang, & Farhadian, 2019)
Pt NPs stabilized by guar gum	4-NP	Efficiency of 97 %	(Pandey & Mishra, 2014)
Co-polymer-grafted gum karaya and silica hybrid organic-inorganic hydrogel nanocomposite	MB	96 % removal	(Mittal, Maity, & Ray, 2015)
Fe_3O_4 NPs incorporated gum ghatti based nanocomposite	MB	Adsorption capacity (mg g^{-1}): 671.14	(Mittal, Ballav, & Mishra, 2014)
Gum ghatti and Fe_3O_4 magnetic NPs based nanocomposites	RhB	Adsorption capacity (mg g^{-1}): 654.87	(Mittal & Mishra, 2014)
Composite hydrogels prepared by *in situ* incorporation of guar gum and nano sized bentonite clay in an acrylic network	Cr(VI)	97.8 % removal	(Maity & Ray, 2016)
ZnSe-WO_3 nano-hetero-assembly stacked on gum ghatti	Bisphenol A	99.5 % removal	(Kumar et al., 2017)
Guar gum-nano ZnO biocomposite	Cr(VI)	Adsorption capacity (mg g^{-1}): 55.56	(Khan, Nazir, Ali, & Kumar, 2017)
$CoFe_2O_4$@silica-shell@tragacanth gum-grafted-poly (methacrylic acid)	MO, methyl red	Adsorption capacities (mg g^{-1}): 336 and 387 for MO and methyl red	(Moghaddam, Jazi, Allahrasani, Ganjali, & Badiei, 2020)
Fe°@guar gum-crosslinked-soya lecithin nano hydrogel	Methyl violet	81 % removal	(Sharma et al., 2019)
PdNPs/guar gum	Mixture of MO, MB & CR	–	(Anjum, Gul, Khan, & Khan, 2019)

Table 6

Various alginate-based nanomaterials used for water/wastewater treatment.

Alginate-based nanomaterials	Contaminants	Ref.
Polyvinyl alcohol/alginate/zeolite nanohybrid	Ni(II) and Co(II) metal ions	(Tabatabaeefar, Keshtkar, Talebi, & Abolghasemi, 2020)
Nano zerovalent iron immobilized in alginate beads	Cr(VI)	(Ravikumar, Sudakaran, Pulimi, Natarajan, & Mukherjee, 2018)
Nano silver chloride and alginate incorporated composite copolymer	Brilliant cresyl blue	(Bhangi & Ray, 2020)
Glycine functionalized magnetic nanoparticle entrapped calcium alginate beads	Cu(II)	(Asthana, Verma, Singh, & Susan, 2016)
Activated carbon/nano zerovalent copper/hydroxyapatite-alginate	As(III)	(Iqbal et al., 2019)
Polyaniline nanofibers assembled on alginate microsphere	Cu(II) and Pb(II)	(Jiang, Xu, Dai, Luo, & Dai, 2012)
Three dimensional silver/polyethyleneimine/alginate hydrogel beads	4-NP	(Gao et al., 2018)
Sodium alginate dispersed nano zero-valent iron	Cr(VI)	(Iqbal et al., 2019)
Calcium alginate beads impregnated with nano zerovalent iron, magnetite NPs and powdered activated carbon	Nitrate	(Bahrami, Yu, Zou, Sun, & Sun, 2020)
PVA alginate maghemite and titania beads	Pb(II)	(Majidnia & Idris, 2016)
Maghemite and titania nanoparticles in PVA alginate beads	Iodine	(Majidnia & Idris, 2015)
Chitin/alginate magnetic nano gel beads	MO	(Li, Du et al., 2010)
CdS quantum dots immobilized on calcium alginate microbeads	Hg(II)	(Kumar & Dutta, 2015)
Fe@graphene oxide alginate beads	Cr(VI)	(Lv et al., 2017)
GOx/$MnFe_2O_4$/Calcium alginate nano-composite	MB	(Zolfaghari, Shojaat, Karimi, & Saadatjoo, 2018)
Bimetallic zerovalent iron silver nanoparticles immobilized in calcium alginate beads	4-Chlorophenol	(Barreto-Rodrigues, Silveira, García-Muñoz, & Rodriguez, 2017)
Oleic acid coated nanoscale palladium/zero-valent iron alginate beads	Trichlorophenol	(Chang et al., 2015)
TiO_2/ZnO calcium alginate beads	Cu(II)	(Kanakaraju, Ravichandar, & Lim, 2017)
Nanohydroxyapatite-alginate composite	Pb(II)	(Googerdchian, Moheb, & Emadi, 2012)
Nanozerovalent iron immobilized alginate beads	Cr(VI)	(Ravikumar et al., 2016)
Fe_3O_4@nano-hydroxyapatite alginate beads	Cr(VI)	(Periyasamy, Gopalakannan, & Viswanathan, 2018)
Poly(acrylic acid)-sodium alginate nanofibrous hydrogel	Cu(II)	(Wang, Wang et al., 2018; Wang, Li et al., 2018)
Nano zero-valent iron/carbon/alginate composite gel	Cr(VI)	(Wen et al., 2020)
Co(II)-doped Fe_3O_4 NPs immobilized in PVA alginate	Cu(II)	(Wong, Chan, & Idris, 2015)
Nanoporous hydrogel based on vinyl functionalized alginate	Pb(II)	(Wang, Zong, & Wang, 2013)
TiO_2/calcium alginate hydrogel	MO	(Zhao et al., 2014)
Acrylic acid grafted sodium alginate-based TiO_2 hydrogel nanocomposite	Methyl violet	(Thakur & Arotiba, 2018)

Alginate-based nanomaterials	Contaminants	Ref.
Polyvinyl alcohol alginate entrapped nanoscale zero-valent iron	Cu(II), Cr(VI), Zn(II), and As(V)	(Sun et al., 2018)
Cellulose nanocrystal alginate hydrogel beads	MB	(Mohammed, Grishkewich, Berry, & Tam, 2015)
Nano iron oxide loaded alginate microspheres	Malachite green	(Soni, Tiwari, & Bajpai, 2014)
Magnetic sodium alginate beads	Reactive Blue 222	(Shokoohi et al., 2019)
$MnFe_2O_4$/calcium alginate nano-composites coupled with GOx and laccase	MB, indigo and acid red 14	(Shojaat, Saadatjoo, Karimi, & Aber, 2016)
Nanocomposite bead based on biopolymer alginate caged magnetic graphene oxide	Pb(II) and Cu(II)	(Sharif, Khorasani, & Shemirani, 2018)
Fe_3O_4@nano hydroxyapatite/alginate	Fluoride	(Pandi & Viswanathan, 2015)
Nano hydroxyapatite/alginate composite beads	Ni(II) and rhodamine B	(Oladipo & Gazi, 2016)
Alginate/Fe@Fe_3O_4 core/shell structured nanoparticles	Norfloxacin	(Niu, Meng, & Cai, 2012)
Nano Zn-Al-Fe_3O_4 blended alginate/Ca beads	Rhodamin B	(Kumar, Vijayakumar, & Tamilarasan, 2019)
Nano-sized carbon immobilized alginate beads	Co(II) and Ni(II)	(Jung et al., 2015)
Nano-sized montmorillonite (MMT)/calcium alginate	Basic red 46	(Hassani, Soltani, Karaca, & Khataee, 2015)
Fe_3O_4/activated charcoal/β-cyclodextrin/sodium alginate	MB	(Yadav et al., 2020)
Pd nanocatalyst supported on cationic nanocellulose-alginate hydrogel	MB	(Wang, Ran et al., 2020; Wang, Zhou et al., 2020)
Alginate/CMC/ZnO Nanocomposite	CR	(Ramadhani & Helmiyati, 2020)
Calcium alginate activated carbon fiber beads	Tetrahydrofuran (THF)	(Chen et al., 2013)
Calcium alginate beads	Cu(II) removal from the tetra metallic [Cu(II), Cd(II), Ni(II) and Zn(II)] mixture	(Yang et al., 2019)

Table 7

Pectin-based photocatalysts/catalysts in removal of organic/inorganic contaminants.

Pectin-based photocatalysts/catalysts	Contaminants	Highlights	Ref.
Ethylenediamine modified pectins	Pb(II)	High adsorption capacity	(Liang et al., 2020)
$(PPA_3)^a$-Cu and (PPA_3/Fe_3O_4)-Cu nanocomposite hydrogels	2-Nitrophenol	High reduction	(El Fadl, Mahmoud, & Mohamed, 2019) (El Fadl et al., 2019)
Modified Fe_3O_4 NPs with the extracted pectin of *Azolla filicoloides*	Methyl orange	Maximum uptake capacity at 5 °C: 0.533	(Rakhshaee, Giahi, & Pourahmad, 2011)
Magnetite/silica/pectin NPs	Fluoroquinolones (Ciprofloxacin & Moxifloxacin)	Removal percent: 89	(Attallah, Al-Ghobashy, Nebsen, & Salem, 2017)
Pectin stabilized nanoscale zerovalent iron	Cr(VI)	Removal from water	(Chen, Yang, Wang, Zhou, & Zhang, 2015)
Pectin stabilized magnetic graphene oxide Prussian blue nanocomposites	Cesium	Adsorption capacity (mg g^{-1}): 1.230	(Kadam, Jang, & Lee, 2016)

[a]PPA: Crosslinked pectin-(polyvinyl alcohol-co-acrylamide) hydrogel.

Table 8

Summary of different kinds of natural polysaccharide-based nanomaterials used for the removal of MB in water.

Biopolymer-based nanomaterials	Preparation method	Reaction conditions	Ref.
Pristine CNFs	Acidified chlorite bleaching method	Adsorbent (0.1 g), MB (100 mL, 100 mg/L), pH 9, 20 °C, maximum adsorption capacity (122.2 mg g^{-1})	(Chan et al., 2015)
CNCs/hydrolyzed polyacrylamide nano-hydrogels (by casting)	Thermal method	Adsorbent (2 mg), MB (20 mL, 5 mg/L), r.t., adsorption efficiency >90 %, maximum adsorption capacity (326.08 mg g^{-1})	(Zhou, Wu et al., 2014; Zhou, Fu et al., 2014)
CNCs/hydrolyzed polyacrylamide nano-hydrogels (by electrospinning)	Electrospinning and thermal treatment	Adsorbent (2 mg), MB (20 mL, 5 mg/L), pH 6.5, 25 °C	(Zhou et al., 2013)
MnO_2 coated CNFs hybrid	A one-step *in situ* method using bamboo CNFs under alkaline conditions	Hybrid (25 mg), MB (25 mL, 80 mg/L), pH 9.6, r. t., 2 min, decolorization efficiency (99.8 %)	(Wang, Yadav et al., 2014; Wang, Zhang et al., 2014)
CMC/GOCOOH microbeads	Reaction of GOCOOH and CMC mixture with $AlCl_3$ solution	Adsorbent (0.1 g), MB (50 mL, 250 mg/L), pH 10, 25 °C, 2 h, maximum adsorption capacity (180.32 mg g^{-1})	(Eltaweil et al., 2020)
CNC-ALG hydrogel bead	Mixing the CNCs with alginate solution and then dispensing small droplets into a gelation bath containing $CaCl_2$	Adsorbent, MB (4.4 mL, 50 mg/L), 25 °C, 90 min, maximum adsorption capacity (255.5 mg g^{-1})	(Mohammed, Grishkewich et al., 2016)
CNF-graphene nanoplates aerogel	Incorporation of GnPs into CNFs	Adsorbent (5 mg), MB (20 mL, 100 mg/L), 25 °C, 16 h, maximum adsorption capacity (1178.5 mg g^{-1})	(Yu et al., 2020)
G-C_3N_4/CNCs-H hydrogel	Chemical method	Adsorbent (10 mg), MB (50 mL, 10 mg/L), pH 7, r.t., maximum adsorption capacity (> 198.6 mg g^{-1})	(Wang, Li et al., 2020)
Polyacrylic acid-magnetic 3D crosslinkers-carboxylated cellulose nanocrystal	*In situ* polymerization in water	Adsorbent (8 mg), MB (50 mL, 20 mg/L), pH 7.2, r.t., maximum adsorption capacity (332 mg g^{-1})	(Samadder et al., 2020)
Carboxylated cellulose fabric filter	2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation	Adsorbent (0.01 g), MB (10 mL, 50 mg/L), r.t., maximum adsorption capacity (76.92 mg g^{-1})	(Li, Ma et al., 2020)
BC@CdS nanocomposite	A "anchoring-reacting-forming" pathway	Adsorbent (1.1 g), MB (20 mL, 20 mg/L), r.t., visible light irradiation, 180 min, 77.39 % removal, maximum adsorption capacity (12.68 mg g^{-1})	(Qian et al., 2020)
CNF-Fe(0)@FeS	Chemical method	Adsorbent (0.5 g/L), MB (20 mL, 50 mg/L), r.t., pH 7, 15 min, maximum adsorption capacity (200 mg g^{-1})	(Sankararamakrishnan et al., 2020)
CNF/poly(ethylene imine)/Ag NPs aerogel membrane	A green method	Catalyst (diameter: 24 mm; height: 18 mm), MB (40 mL, 10 mg/L), $NaBH_4$ (10 mL, 50 mM), r.t., 4 min	(Zhang et al., 2020)
MoS_2-graphene-cellulose filter paper	Simple hydrothermal method	Adsorbent (30 mg), MB (30 mL, 100 mg/L), r.t., pH 7, 2 min, maximum adsorption capacity (485.4 mg g^{-1})	(Gopalakrishnan et al., 2020)
Bacterial cellulose activated carbon	Phosphoric acid activation at a carbonization temperature of 500 °C	Adsorbent (0.02 g), MB (40 mL, 50–100 mg/L), 30 °C, pH 7, 10 min, maximum adsorption capacity (505.8 mg g^{-1})	(Khamkeaw et al., 2019)

Biopolymer-based nanomaterials	**Preparation method**	**Reaction conditions**	**Ref.**
BC/polydopamine/TiO_2	Using BC nanofibers, coated with the polydopamine and a protective agent for immobilization of TiO_2 NPs	Photocatalyst (30 mg), MB (50 mL, 20 mg/L), 25 °C, 20 min, dark conditions, ultraviolet light, 99.5 % removal, maximum adsorption capacity (38.7 mg g^{-1})	(Yang et al., 2020)
CS/MCM-41/nano-γ alumina	Chemical method	Adsorbent (0.088 mg), MB (15 mg/L), pH 7.5, 45 min, maximum removal efficiency (90.23%)	(Teimouri et al., 2019)
Polyvinylidene fluoride/chitosan/dopamine	A facile one-step codeposition strategy	Adsorbent (100 mg), MB (500 mL, 5 mg/L), high adsorption efficiency (96.8 %)	(Zhang, Li et al., 2019)
Magnetic β-cyclodextrin-chitosan/graphene oxide	Chemical method	Adsorbent (0.01 g), MB (25 mL), pH 11, 25 °C, maximum adsorption capacity (84.32 mg g^{-1})	(Fan, Luo et al., 2013)
Chitosan zinc oxide nanobeads	A green method using the *Musa X paradisiaca*	Photocatalyst, MB (10 mL, 10 ppm), sunlight, 10 h, efficiency of the photocatalytic degradation (97.47 %)	(Roshitha et al., 2019)
Polymer coated ZnO with chitosan	Microwave hydrothermal method	Photocatalyst (0.75 g), MB (500 mL, 50 ppm), visible-light, pH 6, 90 min, decolorization adsorption efficiency (98.01 %)	(Sani, Aliyu, & Tukur, 2015)
Chitosan-Fe	Chemical method	CS-Fe (10000 mg L^{-1}), H_2O_2 (1200 mg L^{-1}), MB (100 mL, 120 mg L^{-1}), 30 °C, pH 6–7, 30 min, >99% removal	(Gao et al., 2016)
Chitosan/polyaniline hybrid	*In situ* polymerization of aniline in the presence of chitosan	Adsorbent (50 mg), MB (100 mL, 0.003 M), r.t., pH 11, 60 min, maximum adsorption capacity (81.3 mg g^{-1})	(Minisy, Salahuddin, & Ayad, 2019)
Iron oxide/chitosan magnetic nanocomposite immobilized manganese peroxidase	A green method	Nanocomposite (10 mg), MB (50 mL, 50 mg L^{-1}), 27 °C, pH 7, 50 min, 96% ± 2% removal	(Siddeeg, Tahoon, Mnif, & Ben Rebah, 2020)
Chitosan/zeolite composite	Chemical method	Adsorbent (2.5 g L^{-1}), MB (100 mL, 43.75 mg L^{-1}), r.t., pH 9, 138.65 min, 84.85% removal, adsorption capacity (24.5 mg g^{-1})	(Dehghani et al., 2017)
Co-polymer-grafted gum karaya and silica hybrid organic-inorganic hydrogel nanocomposite	Base-catalyzed hydrolysis and water condensation reactions of tetraethylorthosilicate in an alcohol medium containing a dispersion of GK-cl-P(AA-*co*-AAM)	Adsorbent (0.2 g L^{-1}), MB (50 mL, 200 mg/L), 25 °C, pH 7, 96% removal, maximum adsorption capacity (1408.67 mg g^{-1})	(Mittal et al., 2015)
Fe_3O_4 NPs incorporated gum ghatti based nanocomposite	Graft co-polymerization of acrylic acid onto gum ghatti and incorporation of Fe_3O_4 MNPs within the crosslinked network	Adsorbent (0.6 g L^{-1}), MB (50 mL, 100 mg/L), 25 °C, pH 7, maximum adsorption capacity (671.14 mg g^{-1})	(Mittal et al., 2014)
GOx/$MnFe_2O_4$/Calcium alginate nano-composite	Mixing the GOx-immobilized $MnFe_2O_4$ NPs with sodium alginate solution and then $CaCl_2$	Adsorbent (16 g), MB (200 mL), 30 °C, pH 10.68, 2 h, 73.68 % removal	(Zolfaghari et al., 2018)
$MnFe_2O_4$/calcium alginate nano-composites coupled with GOx and laccase	Chemical method	Adsorbent, MB (50 mL), 30 °C, pH 9, 3 h, 93.46 % removal	(Shojaat et al., 2016)
Fe_3O_4/activated charcoal/β-cyclodextrin/sodium alginate	Direct mixing of the polymer matrix with the nanofillers	Adsorbent (0.2 g), MB (10 mL, 5 ppm), r.t., pH 6, 90 min, maximum adsorption capacity (2.079 mg g^{-1})	(Yadav et al., 2020)

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Biopolymer-based nanomaterials	Preparation method	Reaction conditions	Ref.
Pd nano-catalyst supported on cationic nanocellulose-alginate hydrogel	Drop-by-drop addition of the CNCC and sodium alginate mixture solution into $CaCl_2$ solution	Catalyst (0.1 g), MB (2 mL, 30 mg/L), $NaBH_4$ (1 mL, 60 mg/L), 30 °C, 5 min	(Wang, Zhou et al., 2020)
Pectin-thorium(IV) tungstomolybdate nanocomposite	Sol-gel method	Photocatalyst (0.5 mg/mL,100 mg), MB (1.5×10^{-5} M), solar light, 5 h, 76% removal	(Gupta, Agarwal, Pathania, Kothiyal, & Sharma, 2013)
Starch-derived activated carbon	Carbonization of starch at 500 °C	Adsorbent (0.1 g, 5 g/L), MB (20 mL, 200 mg/L), 30 °C, pH 10.5, 90 min, 99.86 % removal	(Benhachem, Attar, & Bouabdallah, 2019)