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Chapter

Nanoengineered Polysaccharide-Based Adsorbents as Green Alternatives for Dye Removal from Wastewater

Hugues Kamdem Paumo, Lebogang Katata-Seru, Tshepiso Moremedi, Mpitloane Joseph Hato, Soumen Sardar and Abhijit Bandyopadhyay

Abstract

Water represents one of the essential resources on earth, and all living organisms rely on it for survival. However, freshwater systems are directly under serious threat by human activities. A recent World Health Organization report has estimated that 2 billion people use contaminated water sources. The major organic contaminants in water bodies include organic dyes. These are directly related to the spread of diseases owing to their allergenic, mutagenic, and carcinogenic characteristics. Dyes occur in the environment through untreated industrial effluents. Also, the advancement in human civilisation cannot be considered without the development of modern industries. However, an attempt to limit the resulting impacts of coloured effluents on global freshwater quality has become the focus of recent research. For this reason, the use of efficient, simple, and low-cost methods for the treatment of dyes-containing industrial wastewater could serve as a useful tool. An effort to meet the demand for “green chemistry” and sustainable development has led to several investigations on polysaccharide-based adsorbents. This chapter exposes a critical discussion on the literature concerning the biopolymeric xanthan gum and *kappa*-carrageenan polysaccharides as adsorbents for dye removal in an aqueous medium. Functionalisation of these biopolymers through graft copolymerisation and inclusion of inorganic nanoparticles for improved adsorption performance is systematically elaborated.

Keywords: xanthan gum, *kappa*-carrageenan, grafted polysaccharides, nanocomposite, dyes, adsorption

1. Introduction

Water is a precious resource indispensable for the sustainability of life on earth. It is vital to human well-being and economic development. However, safe water remains a significant issue around the world [1]. According to a recent report by the World Health Organization (WHO 2019), approximately 785 million people lack clean water for their basic needs. Supplying water to an increasing global population

necessitates concurrent consideration of several societal sectors that compete for limited resources [2]. For that reason, a vast majority are dependent on surface water and groundwater for drinking purpose. The WHO report also highlights the fact that more than two million people die every year from the use of unsafe drinking water. This is well-reported to spread sickness and waterborne diseases such as typhoid and cholera. This situation emerges from the occurrence of pollutants as a result of the environmental disposal of untreated effluent released by human activities [3]. Indeed, it is inconceivable to achieve progress in human civilisation without industrialisation. However, its exponential development in a competitive era and an increasing global population has seriously impaired the quality of freshwater systems.

Among an assortment of environmental pollution, waterbody contamination owing to the discharge of untreated water-containing organic species has attracted significant consideration in recent years [4, 5]. Organic dye-containing wastewater from industries such as textiles, petrochemical, cosmetics, papers and plastics, for example, has been described for their carcinogenic and mutagenic nature [6]. Also, the organic dyes are oxygen-sequestering agents capable of reducing light penetration in the water systems and thereby restraining the photosynthesis of aquatic vegetation [7, 8]. **Figure 1** illustrates the fate of organic dyes in the natural environment. Though the textile industry had played an enormous role in the development of the South African economy [9], this has also significantly impacted the water resources. The dye-containing effluents disposed to the environment without proper treatment can be highly toxic even at a concentration lower than one ppm [10]. Therefore, the removal of toxic organic dyes from contaminated effluents before being discharged into the environment has evoked considerable attention.

From the commercial and environmental viewpoint, the focus of this chapter is to provide a comprehensive discussion on the ability of natural polymers to perform as adsorbents for industrial wastewater remediation. The hybridisation of these

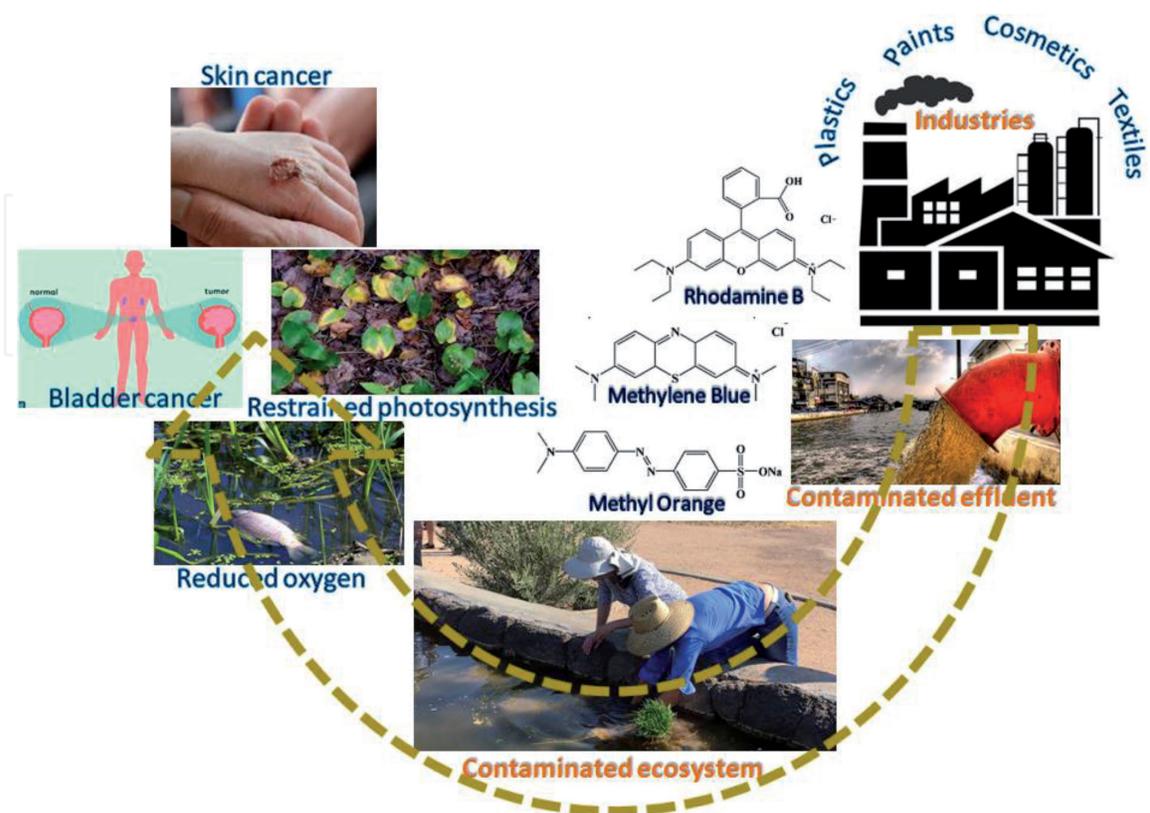


Figure 1.
The fate of the dye-contaminated effluent in the aquatic environment.

biomaterials by grafting of segments and combination with inorganic nanoparticles is presented as an ideal strategy to improve their inherent characteristics and sorption capacity.

2. Treatment of dye-contaminated water in adsorption procedure

Several techniques have been reported to be able of alleviating the occurrence of organic dye in contaminated industrial effluents, and these include flocculation, membrane filtration, biodegradation, chemical degradation, and photochemical treatment [11]. Although these treatment procedures have been applied successfully, they have also displayed shortcomings like high operational costs, low selectivity and toxic sludge production. Adsorption procedure, on the other hand, has frequently been described as a promising approach for wastewater treatment because of the reasons like simplicity in design, low operational cost and comparatively high efficiency [12, 13]. Furthermore, this treatment procedure can be applied on a large scale, as it can handle large flow rates and yields a high quality of water without producing sludge and residuals [14].

Numerous adsorbents are reported in the literature for the removal of contaminants in wastewater, and these include activated carbon, clay minerals, zeolites, industrial wastes, metal oxides, and polymeric materials [15–20]. Among these adsorbents activated carbon is the most widely employed material for the removal of dye in aqueous solution due to its high surface area [21]. However, activation of carbon sources is energy-intensive and requires the use of expensive chemicals and equipments. The low regeneration of spent activated carbon also restricts its practical application. A large majority of the reported adsorbents are also associated with drawbacks like non-biodegradability and low efficiency. These limitations can be overcome using naturally occurring “green” polysaccharide adsorbents owing to their cost-effectiveness, ease availability, and biodegradability.

3. Polysaccharide adsorbents for the removal of organic dye in aqueous solution

Polysaccharides are hydrophilic, non-toxic, and relatively cheap polymers consisting of repeating subunits of sugar linked with glycosidic bonds. The composition and sources of polysaccharides that are generally investigated for their potential to act as adsorbents in aqueous media are presented in **Table 1** [22–25]. The adsorption ability of these biomaterials is due to the occurrence of functionalities such as hydroxyl (-OH), sulphonic acid (-SO₃H), the carboxylic acid (-COOH), amino (-NH₂) and amide (-CONH₂) groups which can serve as binding sites [26]. This feature, complemented with the porous nature, make polysaccharides good candidates for water treatment applications. Some of the commercially available polysaccharides include cellulose, starch, guar gum, chitosan, xanthan gum and carrageenan. Among these, eco-friendly xanthan gum and carrageenan (**Figure 2**) with the ability to form gel have been gaining considerable attractions recently [27, 28]. So far, these have been described to be among the most effective adsorbents for the removal of toxic dyes in aqueous solution due to their tunable surface chemistry and feasible regeneration [29, 30].

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Name	Composition	Sources
Cellulose	Anhydroglucose units linked by the β -(1 \rightarrow 4) glycosidic bonds	Fruit, nuts, grains, and vegetables
Chitin	Glycosidically β -(1 \rightarrow 4)-linked 2-acetamido-2-deoxy-D-glucose	Shrimp shell
Chitosan	Copolymer of <i>N</i> -glucosamine and <i>N</i> -acetylglucosamine units	Deacetylation of chitin
Alginate	β -(1 \rightarrow 4)-Linked D-mannuronic acid and α -(1 \rightarrow 4)-linked L-guluronic acid	Algae, Bacteria
Starch	(1 \rightarrow 4)-Attached α -D-glucopyranosyl units with α -(1 \rightarrow 6) branch linkages	Cereal grains, tuber crops
Guar gum	Glycosidically β -(1 \rightarrow 4)-linked D-mannose subunits and glycosidically (1 \rightarrow 6)-linked D-galactose subunits	Guar seed
Xanthan gum	(1 \rightarrow 4)-Attached D-glucose D-mannosyl, D-glucuronyl acid, O-acetyl and pyruvyl residues	<i>Xanthomonas</i> bacteria
Carrageenan	D-galactose and 3,6-anhydrogalactose connected by α -(1 \rightarrow 3)- and β -(1 \rightarrow 4)-glycosidic linkages	Marine algae

Table 1.
Polysaccharides used as adsorbents for wastewater treatment.

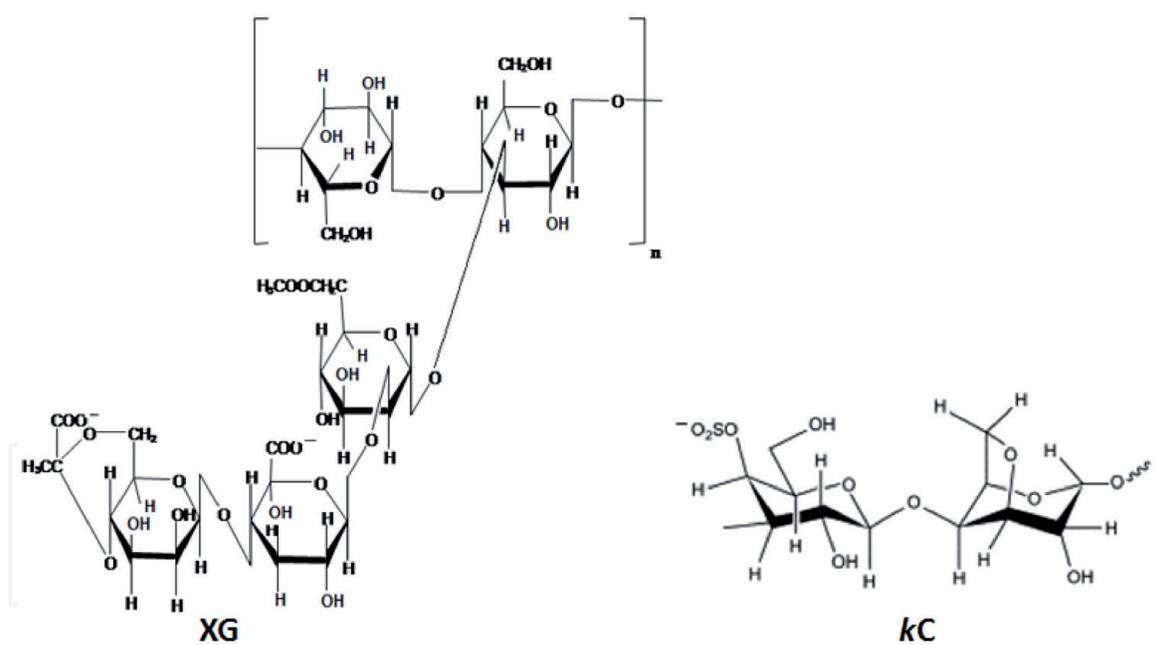


Figure 2.
The molecular structure of xanthan gum (XG) and kappa-carrageenan (kC) polysaccharides.

Xanthan gum (XG) is an anionic polymer obtained by *Xanthomonas campestris* bacterial fermentation of carbohydrate source. This biopolymer is recovered through precipitation in ethanol, isopropyl alcohol or *tert*-butanol [31]. It is a high molecular weight polysaccharide, which provides suspension, thickness, and stabilisation of the combined material. The negative charge of XG biopolymer is mainly ascribed to the presence of carboxylic acid group within its backbone, thereby indicating its affinity for cationic species. XG main chain is made of repeating cellulosic units with side chains involving an α -D-mannose with an acetyl group, a β -D-glucuronic residues and a terminal β -D mannose bearing the pyruvate substituent [32]. The physicochemical characteristics of XG include higher stability

in solution under a wide range of pH (2–12), higher viscosity at low concentration (1% or less), and higher shelf life. The presence of hydroxyl and carboxylic groups that are pH tunable also confers a polyionic character to XG. Thus this adsorbent can be used for binding various ions through electrostatic interaction. Moreover, the –OH groups are also capable of interacting with the electron clouds of the aromatic rings of organic dye molecules through hydrogen-bonding. Thus, adsorption of toxic dye onto the biodegradable polymeric adsorbent can be examined using Fourier transformed infrared spectroscopy (FTIR). For example, the as-described mechanism was reported by Lozano-Álvarez et al. during adsorption of disperse yellow 54 dye in aqueous solution onto XG [33].

Carrageenans are sulfated polysaccharides obtained through alkaline extraction from some red marine algae. Depending on the extraction method and the algae species from which this anionic polysaccharide is obtained, there are several types of carrageenans with different solubility. The polymer chains of carrageenans consist of alternate units of D-galactose and 3,6-anhydrogalactose joined by α -1,3- and β -1,4-glycosidic linkages. The main types are lambda (λ), kappa (k), and iota (i). k -Carrageenan is less soluble than the others owing to the hydrophobic 3,6-anhydro-D-galactose group, which form part of its repeating unit and the relatively lesser number of sulphate groups (one sulfate functional group for each disaccharide unit).

Although these renewable materials show unique properties for water treatment in the adsorption process, they exhibit poor specific surface area and mechanical properties which limits their applicability as lasting adsorbents [34, 35]. In general, the effectiveness of an adsorbent strongly depends on its chemical and mechanical stability, which determines the suitability for application under harsh conditions.

4. Functionalised polysaccharide adsorbents for the efficient removal of organic dye in aqueous solution

The polysaccharide surface modification can improve their physicochemical properties and mechanical characteristics [26]. This strategy has also been reported to avoid leaching of organic substances and improve the adsorption potential of the nanoengineered adsorbent. The polysaccharide surface modification can be accomplished through graft copolymerisation and/or incorporation of specific nanoscale inorganic particles. Deposition of inorganic nanoparticles such as SiO₂, Fe₃O₄, TiO₂, and carbon nanotube onto polymeric supports has been reported to enhance their chemical, mechanical and thermal stabilities [36, 37].

4.1 Polysaccharide functionalised by graft copolymerisation

Graft copolymerisation of vinyl monomers onto polysaccharides is a well-reported and versatile technique that allows for the increased potential applicability of biopolymers. This procedure usually involves the attachment of a vinyl monomer to the polysaccharide backbone. In general, the vinyl monomer will undergo polymerisation in the presence of polysaccharide chains to generate a copolymeric network. The vinyl monomers that are frequently reported for the modification of gum-based polysaccharides involve the acrylamide (AAm), methyl methacrylate (MAA), acrylic acid (AA), *N*-vinyl imidazole (VI), and acrylonitrile (AN). The synthesis of polysaccharide graft copolymers is achieved by amending the biopolymer molecules *via* formation of branches of synthetic polymers. This can be accomplished through “grafting onto” or “grafting from” methodology [38]. The “grafting from” process entails the development of polymer chains from initiating sites

onto the polysaccharide framework. In the “grafting onto” method, on the other hand, the pre-formed polymer bearing a reactive end-functionality interacts with the functional groups that are located on the polysaccharide backbone. However, the latter presents inherent shortcomings, including the crowding of chains at the polysaccharide surface and a limited number of attachments [39].

Many techniques have been employed for the attachment of monomers onto polysaccharide surface, and these involve free radical graft copolymerisation, living radical polymerisation, and ionic polymerisation. Grafting using free radical approach requires an initiator (chemicals, photoirradiation, plasma ions or gamma rays exposure) to generate a free radical on the polysaccharide backbone. In ionic polymerisation technique, on the other hand, the chemical initiator generates cationic or anionic active centers which participate in the grafting process. Nevertheless, more than 60% of all the reported polymers are still synthesised by free radical polymerisation method. It is worth noting that the solubility, wettability, glass transition temperature, and elasticity of polysaccharides are tailored through grafting with synthetic monomer. For example, grafting of chitosan with vinyl monomer *N*-acryloylglycine in the presence of 2,2-dimethoxy-2-phenyl acetophenone initiator was reported to yield a material with relatively decreased solubility and wettability profiles [40]. The polysaccharide affinity to water limits its adsorption property owing to competitive phenomenon between the water molecules and pollutants in the aquatic milieu. Characterisation of the graft copolymerised polysaccharides can be ascertained using FTIR spectra analysis. Data obtained from this technique indicate the formation of covalent bonds. Considering the involvement of hydroxyl groups during graft copolymerisation, a shift and change in intensity of the band corresponding to O–H vibration can be evidenced.

In a recent study by our research team, the surface-modified XG polysaccharide obtained through grafting with acrylamide and acrylic acid monomers to afford XG grafted poly(AAm/AA) [XG-g-P(AAm/AA)], was used as an adsorbent for the removal of rhodamine B and methylene blue (MB) in aqueous solution. The UV irradiation method in the presence of benzophenone as initiator was employed to effect the attachment of monomers. UV irradiation approach is of interest because of its mild reaction conditions and less adverse effect to change bulk properties [41]. Moreover, lower radiation energy may be applied for the modification to proceed. The structural change from XG to XG-g-P(AAm/AA) was elucidated using FTIR spectroscopy (**Figure 3**).

The spectra of pristine XG showed absorption bands at 3263, 2915, 1712, 1653, 1416 and 1019 cm^{-1} attributed to O–H stretching vibration, C–H stretching vibration, C–O stretching, O–H bending, the symmetrical stretching of –CCO– group of glucuronic acid and C–O–C of the ether group, respectively [42, 43]. The formation of XG-g-P(AAm/AA) was evidenced with the change in intensity of the band around 3263 cm^{-1} , the strong vibrational bands at 1593, and the shift of band at 1416 cm^{-1} . After dye adsorption, the FTIR spectrum of loaded XG-g-P(AAm/AA) was characterised by a shift in absorption bands, indicating a dye–adsorbent interaction. However, the peak of 2895 cm^{-1} attributed to C–H stretching did not experience a significant shift, suggesting that the dye adsorption took place through electrostatic and hydrogen-bonding interactions with the XG-g-P(AAm/AA) polysaccharide (**Figure 4**). Electrostatic interactions presumably occur between the nucleophilic functional groups (–COO[–]) and the positively charged centres of the organic dye molecules (S and N). Also, hydrogen-bonding interactions are expected to take place between the hydroxyl groups of XG and aromatic π -electrons and/or nitrogen lone pair of electrons of the dye molecules.

The adsorption kinetics investigation for the removal of rhodamine B and methylene blue dyes in synthetic solutions using our prepared XG-g-P(AAm/AA)

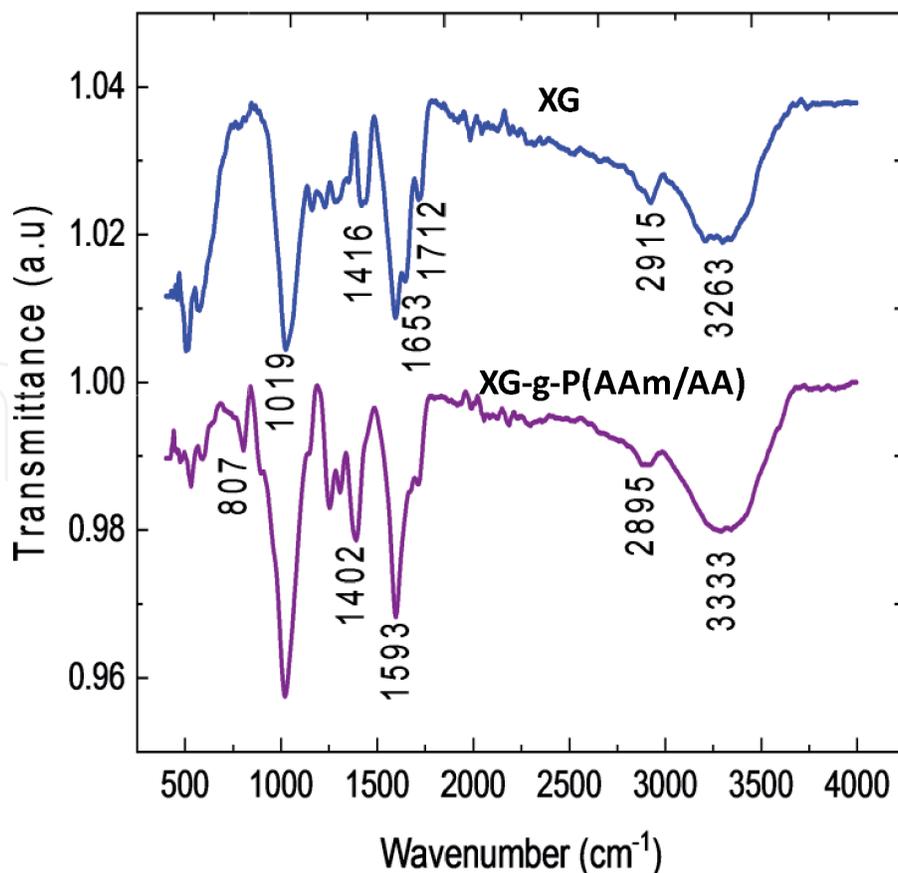


Figure 3.
FTIR spectra of XG and XG-g-P(AAm/AA).

material demonstrated that the procedure followed a pseudo-second-order model. On the other hand, the isothermal study indicated multilayer adsorption behaviour. In a different study, Elella et al. reported the synthesis of XG-g-poly(*N*-vinyl imidazole) copolymers using *N,N'*-methylene bisacrylamide as cross-linker [44]. This modified XG polysaccharide was obtained by a free radical technique using potassium persulfate initiator and then evaluated as an adsorbent for the removal of crystal violet dye from synthetic water samples. The maximum dye uptake onto this cross-linked grafted XG (0.04 g) was determined to be 625 mg/g in 50 ml crystal violet dye solution (500 mg/l, pH 7).

Interestingly, the analogous XG-g-poly(*N*-vinyl imidazole) derivatives without linker have also been found to exhibit antibacterial activity against *Staphylococcus aureus* and *Escherichiacoli* [45].

4.2 Polysaccharide functionalised by incorporation of inorganic nanoparticles

Incorporation of inorganic NPs with the higher surface area has also been described as a fascinating strategy for improved adsorption procedure. This results from a strong synergistic outcome between the organic polysaccharide matrixes and embedded inorganic NPs. This methodology also affects the modification in mechanical properties of the hybrid adsorbent. Moreover, the polysaccharide moiety is anticipated to stabilise the nanoparticles and prevent aggregation. Metal oxide nanoparticles having desirable attributes as adsorbents often suffer tendency to agglomerate in aqueous solution due to their higher surface energy, leading to lowered efficiency [46].

XG grafted polyacrylamide XG-g-PAAm incorporated with nanosilica (SiO₂ NPs), for example, was obtained *in situ* through hydrolysis and condensation of

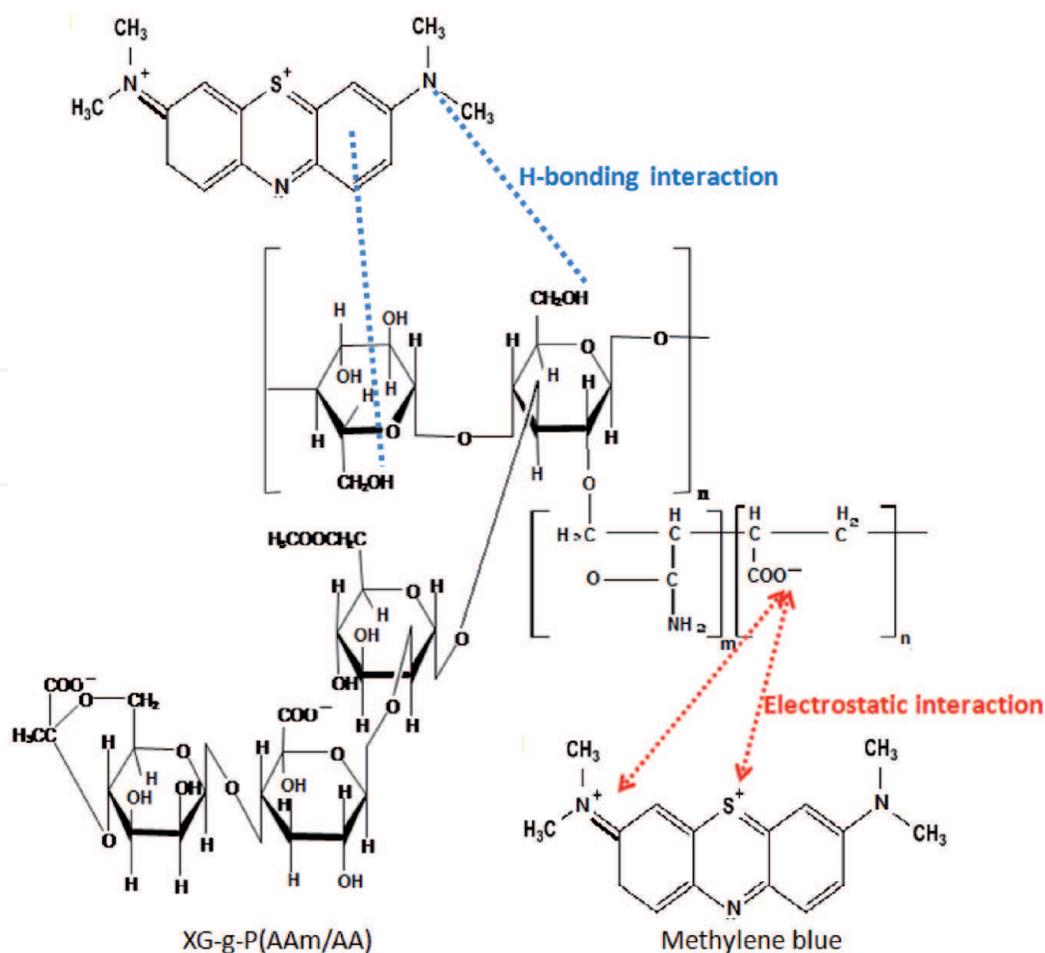


Figure 4.
The mechanism for dye adsorption onto XG-g-P(AAm/AA).

tetraethylorthosilicate [$\text{Si}(\text{OC}_2\text{H}_5)_4$] in the presence of ammonia at the copolymer surface [10]. This synthetic approach exploits the occurrence of hydrophilic groups on the polysaccharide backbone to control the hydrolysis, condensation and nucleation growth of metal oxide nanoparticles [47]. The functionalised SiO_2 NPs@XG-g-PAAm composite was described as a highly improved adsorbent for the removal of anionic Congo red dye in aqueous solution. Grafting of polyacrylamide chain on XG was accomplished *via* free radical polymerisation technique in the presence of potassium persulphate initiator. The branched XG gum matrix acted as a template for the formation, growth, and stabilisation of SiO_2 NPs through hydrogen bonding interaction between the $-\text{OH}$ bonded surface group of SiO_2 NPs with oxygen atom of the polysaccharide $-\text{COOH}$ surface group [48].

Decoration of XG-g-P(AAm/AA) with SiO_2 NPs (diameters range 2–7 nm) was also reported by Ghorai and coworkers [34]. These authors subjected the XG-g-PAAm material to hydrolysis in the presence of NaOH to generate the graft copolymer of XG [XG-g-P(AAm/AA)] (**Figure 5**). Subsequently, functionalisation of the later with SiO_2 NPs was achieved *in situ* through hydrolysis and condensation of silica sol-gel $\text{Si}(\text{OC}_2\text{H}_5)_4$ precursor (**Figure 6**). The resultant nanocomposite was employed as an adsorbent for the removal of cationic dyes in the aqueous milieu. The adsorbent exhibited good adsorption efficiency of 497.5 mg/g and 378.8 mg/g towards MB at pH 8 (adsorbent dose: 0.03 g/25 mL solution, contact time: 20 min, and temperature: 50°C) and methyl violet at pH 9 (adsorbent dose: 0.04 g/25 mL solution, contact time: 15 min, and temperature: 40°C), respectively.

kC modified with carbon nanotubes (10–20 nm diameter), and Fe_3O_4 (10–25 nm) was also synthesised following polymer grafting on the surface of multiwall carbon

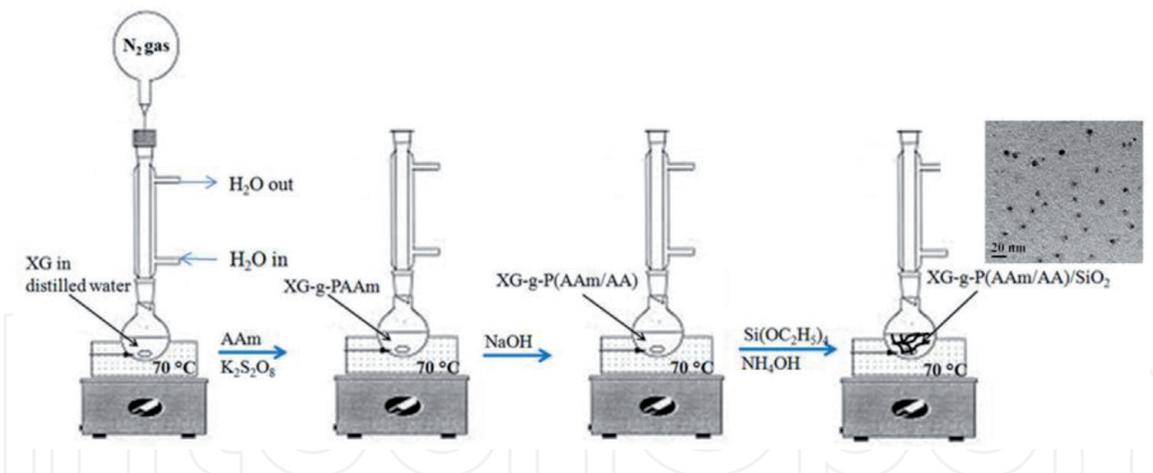


Figure 5.
 Fabrication of SiO_2 NPs@XG-g-P(AAm/AA) composite and TEM image.

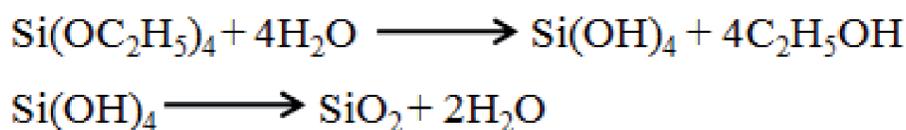


Figure 6.
 Hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and condensation of the silicic acid intermediate.

nanotubes and suspension in a solution of iron precursors Fe(III)/Fe(II) under nitrogen atmosphere [49]. The Brunauer–Emmett–Teller (BET) technique indicated an increase in specific surface area after attachment of carbon nanotubes (S_{BET} : $238 \text{ m}^2/\text{g}$) and deposition of magnetic Fe_3O_4 nanoparticles (S_{BET} : $55 \text{ m}^2/\text{g}$). The occurrence of this metal oxide was evidenced by transmission electron microscopy (TEM) pictures analysis. Magnetism is an exclusive physical property that has been demonstrated to ease the water treatment procedure in adsorption technique. This property allows for the removal of spent adsorbent from the aqueous solution by a simple application of a magnet. The prepared magnetic *k*C-carbon nanotubes- Fe_3O_4 composite exhibited high adsorption toward MB dye in aqueous solution. The maximum dye uptake onto 0.4 g/L of this biofunctional nanocomposite was determined to be $1.24 \times 10^{-4} \text{ mol/g}^{-1}$ at pH 6.5. In aqueous solution, the adsorption potential of metal oxide (MOH) is regulated by the pH-dependent formation of complex ions MOH_2^+ and MO^- [12, 50, 51]. Therefore, dye adsorption onto metal oxide surfaces arise from the Coulombic interaction between MOH_2^+ and MO^- , and the negatively charged (e.g. methyl orange R-SO_3^-) and positively charged (e.g. methylene blue $\text{R} = \text{N}(\text{CH}_3)^+$) centers, respectively. In a cognate investigation, Mahdavinia et al. described the modification of *k*C with polyvinyl alcohol (PVA) and Fe_3O_4 nanoparticles [52]. This nanocomposite was engineered using the *in-situ* chemical co-precipitation of Fe(II) and Fe(III) salts in the presence of PVA and ionic *k*C biopolymer under basic condition (**Figure 7**). Cross-linking of the occurring Fe_3O_4 nanoparticles and polymer matrixes was achieved by the freezing–thawing technique and $\text{K}^+/\text{k-carrageenan-SO}_3^-$ interaction. Freezing–thawing plays a crucial role in dispersing nanoparticles into gelatin environment and limiting their agglomeration. This technique has been reported to afford bio-related materials with better thermal stability and mechanical properties [53]. The magnetic behaviour of this cationic dye adsorbent was assessed with the vibrating sample magnetometer (VSM) standard method. The hysteresis loop revealed an S-shape with an estimated value of saturation magnetisation 3.4 emu/g , suggesting that the spent adsorbent can be removed easily with an external magnet.

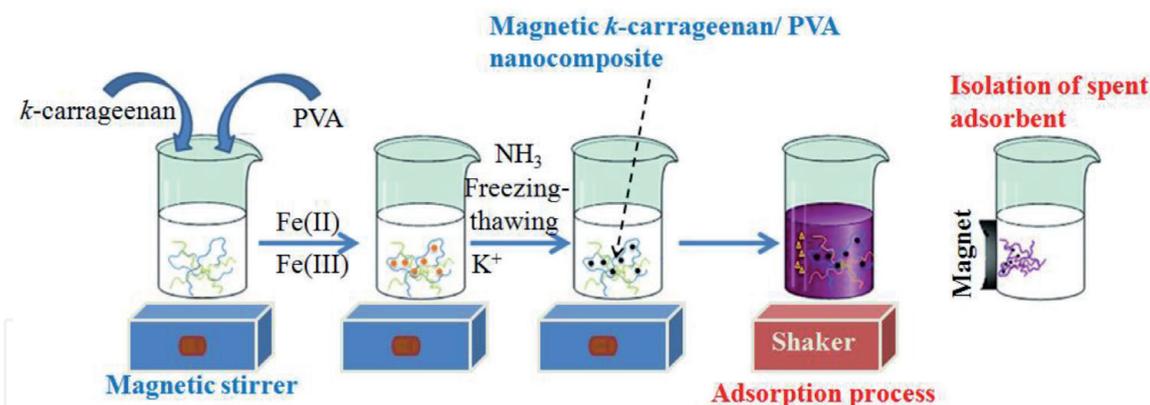


Figure 7. Fabrication of magnetic *k*C/PVA nanocomposite as an adsorbent for cationic dye removal in aqueous solution.

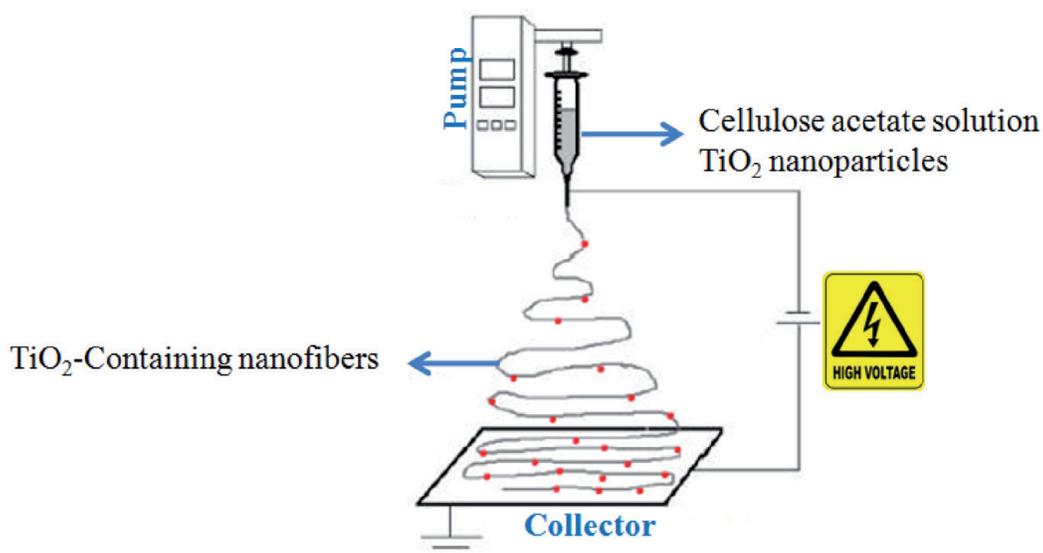


Figure 8. Experimental setup for electrospinning of TiO₂ nanoparticles in polysaccharide solution.

FTIR, X-ray photoelectron spectroscopy (XPS) spectra analysis and assessment of the pH at the point of zero charge (pH_{pzc}) can be used to clarify the adsorption mechanism at the surface of metal oxide in aqueous milieu. Thus, this additional interaction is anticipated to improve the adsorption capacity of polysaccharide adsorbents functionalised with metal oxides. The $-\text{OH}$ groups of polysaccharides are highly reactive in encouraging polycondensation, or in interacting with cations or hydroxylated cations, capable of undergoing nucleation and growth processes. Polysaccharide matrix also provides a cavity that is capable of immobilising the developing inorganic entities and controlling their growth. Furthermore, carbon nanotubes ability to abstract organic dyes from wastewater has been reported to take place through π - π stacking, hydrogen bonding, hydrophobic, Coulombic, and/or van der Waals interactions [54–56]. The occurrence of defects and active centers, and the morphology of the carbon nanotubes play a key role in their dye adsorption capability. The carbon nanotubes are rolled-up graphene or graphitic sheets of single-layer carbon atoms. These are π -conjugative structures possessing a hydrophobic surface. The dynamic mechanical investigation of polymer adsorbents and their inorganic particle-functionalised derivatives has uncovered relatively better properties of the latter through restriction of the mobility of polymer macromolecular chains [57].

Cai and coworkers also described the cellulose nanofibers (average diameter 237–443 nm) modified with TiO₂ nanoparticles as a precursor for the synthesis of

composite hydrogels [58]. Graft copolymerisation of these nanofibers using AAm, AA, and N,N'-methylene bisacrylamide in the presence of ammonium persulfate afforded the polysaccharide-based hydrogels with good MB dye adsorption capacity. The nanofibers material was fabricated through electrospinning of cellulose acetate solution containing TiO₂ nanoparticles of average diameter 25 nm, followed by deacetylation under basic condition. The voltage power and flow rate applied in this investigation were 20 kV and 1 mL/h, respectively. Electrospinning is a versatile and efficient method for the fabrication of nanofibers. This technique utilises high voltage to charge the surface of a polymer solution and initiates the ejection of fluid jets through a small hole (**Figure 8**). Solidification of these thin jets yields nanofibers. The size of nanofibers obtained using this procedure depends on parameters like solution physical properties, voltage, hydrostatic pressure, size of a hole, and distance hole-collector [59]. The light-driven catalytic activity of TiO₂ has also been described to improve the MB removal performance of TiO₂-containing cellulose nanofibers. TiO₂, also known as titania, is a low-cost and environmentally benign oxide that has gained commercial success in beauty, cosmetic, and personal care applications. Moreover, interest in TiO₂ nanoparticles for the degradation of organic pollutants in wastewater has been tremendous since the early report by Frank and Bard [60]. This is attributed to their unique electronic structure, impressive UV-light absorption properties, prolonged excited-state lifetimes and enhanced charge transport features. The high-energy photons emitted by UV-light initiates the excitation of TiO₂ valence band electrons and formation of $\cdot\text{OH}/\text{O}_2^{\cdot-}$ radicals. These species are responsible for the degradation of organic pollutants in aqueous solution.

Composite hydrogel of NH₂-silica functionalised TiO₂ NPs@kC-g-PAA was developed by Pourjavadi et al. for the removal of malachite green (MG) in synthetic water samples [61]. The functionalised TiO₂ NPs were synthesised by the hydrolysis of TiCl₄ at 90°C in the presence of HNO₃ followed by the treatment of hydrated TiO₂ NPs with 3-aminopropyltriethoxysilane. Graft copolymerisation of kC with AA monomer in the presence of ammonium persulfate initiator, methylenebisacrylamide as a crosslinking agent, and the pre-synthesised NH₂-silica functionalised TiO₂ NPs yielded an adsorbent with impressive potential for the removal of cationic dye. MG adsorption onto NH₂-silica functionalised TiO₂ NPs@kC-g-PAA hydrogel followed the pseudo-second-order rate model, and best fitted the Langmuir isotherm, with the maximum capacity of 666 mg/g.

5. Conclusion

Herein, we present a well-elaborated discussion on the developed polysaccharide-based materials for the removal of highly toxic organic dyes from contaminated water using adsorption procedure. Naturally occurring, non-toxic, and biodegradable xanthan gum and kappa-carrageenan matrixes were used as representatives for effective dye remediation owing to their surface charged functionalities that serve as active binding sites. The polysaccharide surface modification through graft copolymerisation with monomers and/or incorporation of nano-sized inorganic particles having high surface areas like metal oxides and carbon nanotubes has been found to yield composites with improved mechanical stability and impressive adsorption capacities.

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