Cross-Linked Polymer-Based Adsorbents and Membranes for Dye Removal

Marlene A. Velazco-Medel, Luis A. Camacho-Cruz, José C. Lugo-González, and Emilio Bucio

Abstract Contamination of water is a problem that severely affects the equilibrium of ecosystems and human health. Through the years, various techniques have been implemented for the elimination of colorants from the water discarded by the textile industry; nevertheless, some of the wastes obtained are hard to treat and toxic. Polymers can be used as an adsorbent membrane, a coagulant, or a flocculant, and the inclusion of them has been a promising strategy used for the versatility, effectivity, and low toxicity of some polymers. Organic polymers have demonstrated good ability for the elimination of colorants by the adsorption mechanism, and they have been useful for the preparation of membranes for nanofiltration. Synthetic and natural polymers mixed with other materials have improved the performance of membranes without altering the permeation and flux. The cross-linking has allowed the formation of polymeric networks with pores, which aid to the dye retention assisted by the functional groups in the polymer chains; additionally, this cross-linking is useful for the incorporation of other compounds such as nanomaterials of magnetic nanoparticles to improve the cleaning of wastewater. The control of the charge density in the polymer, the physical properties of the dispersed medium, the chemical structure of the dye, and cross-linked polymers for adsorption and coagulation are some of the aspects to review in this chapter.

Keywords Cross-linked · Polymers · Dye · Nanofiltration · Adsorption · Coagulation · Membrane · Wastewater

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1 Introduction

Contamination of water is a problem that generates several conflicts in human life. The excess of dyes and heavy metals in water from textile industries has attracted the attention of scientists in previous years, mainly for the cities with high production of textiles. Several of these dyes are highly toxic to animals and humans, and they render the residual water useless. The removal of dyes from wastewater is important to ensure human health; however, the elimination of them is hindered due to some limitations, e.g., the concentration of the dye, the chemical auxiliaries, and other aspects [1, 2].

For dye removal, several factors affect the colored wastewater, first, factors that only depend on the rest of pollutants from the dye industry and the physicochemical properties of the water, and second, the factors that depend on the dye. Generally, for any removal process, some of these factors are pH, ionic strength, temperature, among others. This is due to the destabilization process involved in the elimination of the dye, which is closely related to a complexation reaction or to other chemical interactions [3, 4]. Additionally, as it was mentioned, the chemical structure of the dye plays an important role in the process because the functionalities allow the interaction between the coagulant, flocculant, or adsorbent membrane. It is important to mention additionally that colorants present two main parts on their structures, the chromophore, and the auxochrome; which are responsible for the absorption–emission of light, and directly, the color.

On the one hand, the chromophore in a molecule is the conjugated double bond moiety (π bonds), which present adsorption in the visible region on the electromagnetic spectrum, that is the reason why almost all colorants present aromatic rings in their structure, connected to an auxochrome. On the other hand, an auxochrome is a functional group attached to the chromophore, which modifies the ability of the chromophore to absorb light. For this portion, acidic and basic groups are commonly used, the protonation or deprotonation of a group can extend the conjugation of a molecule and change the wavelength or intensity of the absorption. In this way, dyes are classified as cationic, anionic, or non-ionic, and this charge density is important for eliminate them from water.

One of the most employed strategies for wastewater treatment is the coagulation/flocculation (C/F) method. C/F is a two-stage technique that consists of the destabilization of dispersed solid particles in water. For the effect of the coagulants, the charged particles get to gather and for bigger particles. Coagulation is the first step in the process and is always accompanied by rapid mixing of the coagulant and the water to be treated. In this step, the coagulant is added, and the mixing favors the accumulation of molecules and the formation of flocs. In the flocculation stage, the speed of mixing is decreased, and the flocs aggregate to form bigger flocs. The use of metals and polymers is common for the destabilization of dye molecules to subsequently eliminate them by precipitation or filtration [5].

The use of inorganic coagulants is a strategy usually used; however, the waste is toxic to human health and the environment [6, 7] such as the residues of aluminum salts. Another disadvantage of using metal salts for water treatment is that the precipitate and the sludge produced are difficult to treat after the dye removal. For that reason, other alternatives have been employed, including, organic materials (e.g., polymers). An advantage of these materials is that they can be mixed with metals or other compounds to get a dual coagulant/flocculant or adsorbents, obtaining greener, cleaner, and more effective materials [8, 9].

Water-soluble polymers are the most used for C/F method; some natural and synthetic polymers have been explored [9–11]. As it was mentioned above, the chemical structure of the dye affects the way it is removed, the destabilization of the colloids dispersed in the medium influences the polymer used and the technique desired. In the case of C/F, the dyes are trapped by the effect of the charged groups in their structure-forming bigger structures, or by the anchoring of other functional groups similar to a host–guest chemistry.

Natural polymers have attracted attention in recent years because they are easy to get from plants or animals, and they are non-toxic to humans or animals. Biopolymers such as gums, chitosan, or cellulose are vastly used as adsorbents or coagulants; nevertheless, the disadvantage is that the molecular weights of these polymers cannot be controlled. Although synthetic polymers can be more toxic than natural polymers, the process of synthesis offers control in the chemical structure of chains, the functional groups, charge density, molecular weight, and microstructure. Moreover, ionic groups can be added to the polymer, i.e., polyelectrolytes, and this is important for the type of dye to remove from water. Hence cationic, anionic, and non-ionic polymers are used for dye removal. Amine- and carboxylic-functionalized polymers are extensively used. Additionally, acrylates, imines, acrylamide, polyguanidines, and other acid or basic groups are added to polymer chains.

Polymeric materials have been explored as alternatives to conventional inorganic alum or toxic metal coagulants. Depending on the chemical structure of the dye and polymer, polymers can act as both coagulant and flocculant, they trigger the destabilization of the dye molecules dispersed in the medium, which forms aggregates and flocs, with subsequent precipitation or sedimentation. To reach the formation of the flocs or micelle-type structures, the dosage, charge, and the size of the polymer are important factors to control; as well as agitation of the system since it can break the formed aggregates, very fast agitation is important to reduce the repulsive forces between the colloids before charge neutralization, and thus the formation of aggregates is favored [12, 13].

The pre-treatment of wastewater with coagulant/flocculant process followed by nanofiltration has allowed the water reusability, and the polymeric materials are easier to treat after the first stage. Otherwise, some studies have shown that the use of metallic coagulants, e.g., aluminum salts, as coagulant induces the formation of foulants hard to treat and that are highly toxic, such as aluminum hydroxide or aluminum derivatives [14, 15]. In contrast, iron and polymeric coagulants are easier to remove by other cleaning techniques, they are biodegradable or can be reused for various cycles of filtration.

The mechanism of dye removal involving polymers can be divided into four types: (1) electrical double-layer compression; (2) charge neutralization; (3) sweeping; and (4) adsorption [11, 16]. Table 1 summarizes these four mechanisms.

Furthermore, another way to remove dyes is by the retention in the polymeric matrix, the binding and attachment of dyes to the polymer depend on the chemical interactions between them. All the processes depend on electrostatic and non-covalent interactions such as hydrophobic interaction, hydrogen bonding, or the formation of complexes. For this reason, synthetic polyelectrolytes and natural polysaccharides are suitably used for water treatment, since they possess hydroxyl groups and can be manipulated to get charged groups [17, 18]. The selected polymer is dependent on the dye and they can either be cationic (e.g., quaternary amines), anionic (e.g., anionic polyacrylamide), or non-ionic (e.g., cellulose).

Adsorption has also been used as a wastewater cleaning method, nanomaterials made of organic ligands or dye receptors (based on the chemical structure of the desired dye) [19]. The adsorption mechanism is common for polymers as coagulants

Table 1 Mechanisms of dye removal from wastewater

	Mechanism	Description
Coagulation/Flocculation	Electrical double-layer compression	For this mechanism, highly charged ionic coagulants are used. They disturb the stability of colloids by changing the ionic strength in the media, thus the double layer around the particle collapses, which conduct to the formation of aggregates by electrostatic interactions
	Charge neutralization	In the case of neutralization, coagulants with different charges are added to de dispersion. The surface of colloids binds to the coagulant by the opposite electrostatic force and it drives to the neutralization of charges
	Sweeping	The sweeping is when the dispersed particles are captured into the matrix of the insoluble metal hydroxide (e.g., aluminum or ferric hydroxides) formed from the hydrolysis of the metal coagulant. These hydroxides are formed when alum or ferric coagulants are added to water
Filtration	Adsorption	This mechanism is the most common for polymeric coagulants. The polymer captures the dye assisted by the functional groups and forms a bridge between the molecules. In consequence, bigger aggregates and settleable flocs are obtained

and flocculants; polyaniline and other cationic polymers are useful for the elimination of colorants from water [20]. The adsorption process is used for the development of membranes for micro- and nanofiltration, for that, the polymer can be disposed of in bulk or packed in a column to carry out the absorption process. The physicochemical properties of the medium such as pH, ionic strength, and the nature of dye are important to select the method.

Several natural and synthetic polymers are used as adsorbents for the removal of different dyes; natural carbohydrate-based polymers such as cellulose, chitosan, and starch work with this mechanism. For example, membranes based on polysaccharides such as chitosan or cellulose have been prepared. The chemical structure of these biopolymers allows the retention of dyes in a large scale of pH since they have acid or basic groups [21–24]. The chitosan has been used for the adsorption and coagulation of several dyes, even sulfonic dyes [25], and it has been grafted with other polymers to obtain good adsorbents [26, 27].

Conveniently, some low molecular weight polypeptides from animals, plants, and seeds have demonstrated good ability to remove colorants by adsorption, due to their amphiphilic behavior. Moreover, this type of biomaterials is non-toxic, easy to treat after the cleaning process, and eco-friendly adsorbents. There are several reviews and summaries about the use of biopolymers for wastewater treatment [18, 28]. For example, the aqueous extract of the seed of *Moringa oleifera* has been tested as coagulant and adsorbent for the removal of dyes [29] such as azo-dyes [30, 31], indigoid dyes [32], and anthraquinonic dyes [33]. Even, this extract has shown better results for dye removal than metallic coagulants, e.g., polyaluminum chloride [34]. Other polymers are obtained from *Cassia angustifolia* seed, *Cassia javahikai* seed gum, mesquite bean, *Cactus latifaria*, chestnut, and acorn [29, 35–37].

It is worthy of note of not only the chemical interactions the dye keeps anchored to the matrix but also this retention in the polymeric matrix can also be enhanced by a porous system, working similar to size exclusion chromatography. Polymeric membranes in a 3D arrangement are achieved by the addition of cross-linking agents, to form a network with a reduced free volume between the polymer chains and pores. Those pores avoid the release of big molecules, thus they are trapped in the sludge or the waste from polymer, this approach is used for nanofiltration.

The cross-linking of polymers for this purpose has allowed the incorporation of other useful species to the polymer network, and it can be by supramolecular or covalent cross-linking. This approach, like the grafting technique, has been used to combine or add properties of two different polymers to a final material; for example, natural polymers have been mixed with synthetic ones, ionic liquids with polymers, organic–inorganic polymers [20], and magnetic nanoparticles with polymers [38, 39]. These types of 3D polymers, hydrogels, and membranes are vastly used for filtration and nanofiltration as well as for fractionation of salts and dyes.

Nanofiltration (NF) is defined as a pressure-driven method that allows the separation of solutes from liquid matrixes by size exclusion and charges repulsion (Donnan exclusion) throughout a semipermeable membrane. The term NF arises from the scale of separations (0.5–2 nm) that depends on the membrane pore dimensions.

Commonly, there have been two approaches for NF design, those based on polymeric matrixes (e.g., cross-linked polymers or polymeric hollow fiber membranes) and those based on ceramic membranes. For our purposes, we are going to deal with the former one, those based on cross-linked polymers, their design, and performance concerning the removal of dyes from wastewater processing.

Technologies based on polymeric nanofiltration membranes were developed at the end of the 1980´s decade with a broad spectrum of applications, e.g., water processing [40], plasma pool clarification virus, biomolecules removal [41], or petrochemical industries. Recently, it has been documented a growing number of publications concerning water processing using NF, almost 18% of nanofiltrations concerns with wastewater processing, replacing reverse osmosis, which has the advantage of operating at lower pressures [40]. NF employs membranes with a smaller pore dimension than micro- or ultrafiltration but bigger than in reverse osmosis (RO) with pore dimension about 0.1 nm. Additionally, NF requires higher pressures (4–10 bar) than RO and it is effective for solutes with molecular weights of about 100–5000 Da.

Among more important factors to get low-operating costs are the pre-treating processes to prevent membrane fouling as well as the need of housing them into appropriate modules that provide porous support for large-scale applications [42]. Membrane performance is characterized by quantifying the key aspects of their separation mechanisms such as solute rejection, pore dimensions, and permeate flux, which is related to applied pressure. These factors interplay a compromise between selectivity and efficiency.

It is worthy of note that in the literature, solute rejection is also taken by the rejection of total dissolved solids (TDS) or salt rejection, depending on the application or solute that is being removed. NF is useful for the removal of divalent or polyvalent ions (e.g., $CaSO_4$) while monovalent ions such as Na^+ and Cl^- commonly pass through.

Concerning wastewater from the textile industry, removal of azoic and basic dyes is an important application in the research to get membranes with high dye rejection that enables recycling the wastewater effluents. In aqueous media, azoic dyes (coming mainly from textile industries where they are applied to fibers) are generally anionic because of the strong acidity of the sulfonic group (pK_a values <0), so they are completely ionized and belong to the acid-dyes class. On the other hand, basic dyes (coming from cosmetic, food, and paper industries) are cationic species in aqueous media, e.g., methyl blue, crystal violet, safranin, etc. The differential chemistry of the solutes pointed out the importance of selectivity properties in NF membrane design.

Although it is possible to calculate performance parameters theoretically like dye rejection and permeate flux (the flux that passes through the membrane as a measure of the rate of the process) with a known membrane morphology, it is still more common to test membrane performance at the lab scale using relative ease accessible membranes based on cross-linked polymers.

Polyetherimide (PEI) is a thermoplastic with strong absorption properties has been the base of several cross-linked membranes for NF in water media. Their cross-linked structure with *m*-phenylenediamine (MPD) has been obtained for which the studied parameters were doped solution composition and cross-linking time as well as dye concentration upon membrane performance, resulting in increased dye rejection when the acetone concentration in dope solution was maximized. The best performance was reached with cross-linked membrane composition PEI: 15, acetone: 20 wt%, and 10 min of cross-linking time. This membrane showed 98% of dye rejection of Reactive Red 120 at 1500 ppm with an operating pressure of 4 bar. The increasing membrane performance with acetone content in the dope solution was related to a tighter membrane [43]. Figure 1 shows a typical procedure for testing membrane dye removal by NF.

Interestingly, PEI also has been used to make composite membranes by interfacial cross-linking with nylon for selective removal of anionic dyes. As an example, an inspired membrane inspired on thin-film composite (TFC) for RO and NF has been reported by amidation of PEI with trimesoyl chloride over nylon support. This composite membrane works selectively at pH = 3 by electrostatic interactions between positively charged PEI chains and anionic dye Sunset Yellow. The membrane can be regenerated at alkaline pH values and works at very low pressures compared with NF (only 0.01 bar) affording to permeate flux of about 10 L/m^2 h bar [44].

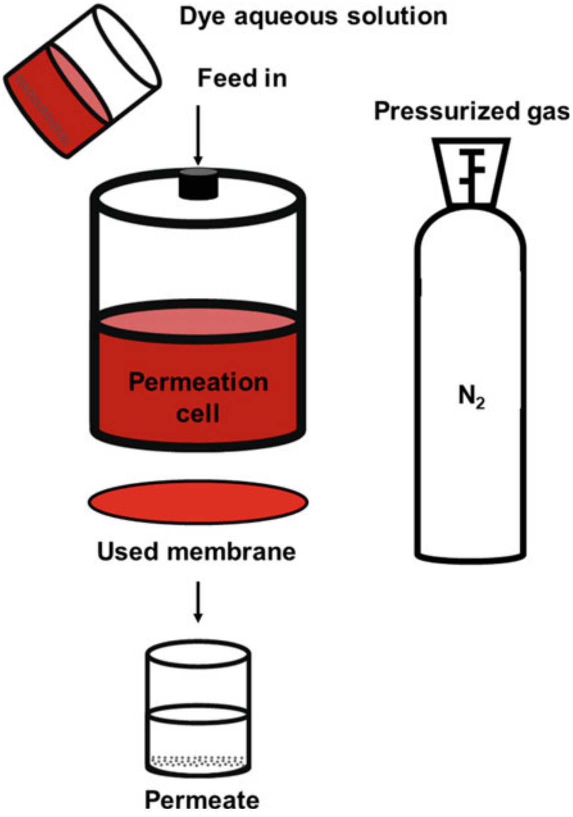


Fig. 1 Schematic setup for nanofiltration of dye aqueous solution

As shown above, the mechanism for dye rejection can be driven not only by size exclusion but also by electrostatic partitioning also known as Donnan exclusion. Thus, the design of positively charged membranes has played emergent attention given cationic charged solutes. In this regard, composite NF membranes have been obtained using PEI for cross-linking polyimide (PI). The resulting NF membranes have ortho-diamide groups with free amine groups available for protonation even at neutral pH values [45, 46]. However, cross-linking conditions are difficult to optimize in view that mechanical properties of the membranes can be damaged, which has driven to the cross-linking only at the surfaces of flat-sheet membranes efforts.

In this concern, substituting PI with Torlon® polyamide-imide (PAI) has shown advantages due to its superior mechanical properties as well as its pH stability. This NF membrane showed good dye rejection performance (>95%) toward basic dyes (Methylene Blue, Janus green B, methyl green, Alcian Blue 8GX) with a molecular weight ranging from 319 to 1300 Da [47]. Regarding synthetic details, it was found that stirring speed (500 rpm) at 70 °C for 80 min in cross-linker solution played a key role in successful surface functionalization. The cross-linked membrane showed a marked decrease in molecular weight cut-off (MWCO, defined as the lowest molecular weight retained at 90% by the membrane) from 17,520 Da in the parent non-cross-linked PAI to 458 Da in the cross-linked membrane, as well as a change from anionic to the cationic character.

More recently, ethylenediamine (ED) has been used as a cross-linking agent in PEI-based membranes. The resulting cross-linked membrane was obtained as a flat-sheet membrane by phase immersion method from dope solutions with 20% of acetone. Afterward, the membranes were submerged in ED 2.5% (v/v) methanolic solution by 30 min. The best performance was obtained when using PEI at 16% in dope solution (if raised to 17% the water permeation results too low to be practical). At 2.8 bar pressure and using the model azoic dye Reactive Red 120 (RR120), 98% of rejection was achieved compared with 84% for the pristine membrane. This work has underlined the sensitivity of the performance to polymer content in dope solutions, being significant variations even at 1% [48].

Li et al. prepared another loose nanofiltration membrane by coating onto a conventional ultrafiltration membrane made of polyethersulfone (PES); the mixture solution for coating was obtained by aqueous cross-linking between tannic acid (TA) and PEI. The resulting modified membrane (PEI-TA/PES) demonstrated good efficiency for the fractionation of inorganic salts and Congo Red. Moreover, it showed high permeability (40.6 LMH·bar^{-1} for 0.1 g/L Congo Red), high rejection to dye (99.8%) as well as low rejection toward NaCl and Na_2SO_4 (below 10%). The salts passed through the membrane and it allowed the good separation of those inorganic salts and the dye [49].

Another approach to get composite membranes has been developed by grafting cross-linked polymers on porous supports of polysulfones (PSf). In this approach, interfacial polymerization using piperazine (PIP) and trimesoyl chloride (TMC) has been the monomers to get the polyamides (PA). Interestingly, PSf supports have a MWCO of about 30,000 Da, this was reduced to 500 Da after coating it with cross-linked PA, which produces good NF performance in dye rejection toward Direct Red

81, Direct Yellow 8, and Direct Yellow 27. However, this method based on coating of porous PSf showed a disadvantage of membrane fouling, thus, pre-treatment with coagulant agents like ferric chloride of the dye solutions is necessary [50].

Regarding NF, polyvinyl chloride (PVC)-based membranes have received less attention compared with PEI, PI, or PAI-based membranes due to their flexible chains and their putative low resistance to high pressures used in NF. However, it has been reported the synthesis of the copolymer with of PVC and poly(*N,N*-dimethylaminoethyl methacrylate (PDMA, 31.1 wt%), resulting in a PVC-*graft*-PDMA in which ulterior cross-linking with XDC/*n*-heptane (2 wt%) yielded a positively charged membrane with a quaternization degree of 27.8%. Despite the lack of tests of dye rejection tests in this study, this membrane showed excellent salt rejection of $MgCl_2$ by Donnan exclusion mechanisms, which make cross-linked PVC-based membranes promissory for NF [51].

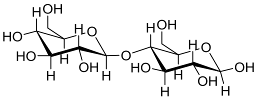
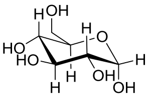
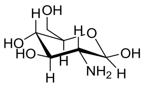
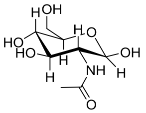
2 Cross-Linked Polymers Based on Natural and Synthetic Polysaccharides: Starch, Chitosan, Cellulose, and Cyclodextrins

The utilization of synthetic polymers and other systems such as composites including carbon nanomaterials and solid-state materials for the absorption of dyes is often very effective and represents many advantages in favor of other purification methods for the elimination of dye and related pollutants from the pigment and printing industries. Nevertheless, these systems have a series of disadvantages, which include a high cost of production and implementation, synthetic procedures that are also polluting, and the difficulty of disposal of the purification systems once they have been used (since they may not degrade easily and cause secondary contamination). For the aforementioned, systems for dye substrates removal based on natural resources have been developed which can be effective dye removal substrates, but also come from natural sources. One of the most popular choices for such substrates is the system based on polysaccharides [52–55].

Starch, chitosan, and cellulose are the three most abundant polysaccharides derived from natural sources, their abundance due to their presence in many biological systems such as plants and animals. The structures of these three natural polysaccharides are shown in Table 2. As a reference to the reader, the key characteristics and differences in the structures of these polysaccharides are presented in this table [52, 53, 56].

Even when these polymers are very abundant, the derivatization of these systems is not a trivial task, mainly due to synthetic limitations such as solubility. These polysaccharides are not readily soluble in most solvents used in polymer synthesis because of their rigid structures with high crystallinities (due to hydrogen bonds); therefore modification and cross-linking reactions often need to be carried out on unconventional solvents or solvent mixtures that may interact with these hydrogen

Table 2 Characteristics of the three most common natural polysaccharides used as cross-linked dye removal systems

Polysaccharide	Cellulose	Starch	Chitosan
Chemical composition	Composed of two repeating units of β-D-glucose bonded between carbons 1 and 4 through an alpha glycosidic bond	Composed of two different polymeric substructures: -Amylose: repeating units of α-D-glucose bonded between carbons 1 and 4 through an alpha glycosidic bond -Amylopectin: repeating units of α-D-glucose bonded between carbons 1 and 4 with branched with α-D-glucose units between carbons 1 and 6 through alpha glycosidic bonds	Composed of randomly organized repeating units of β-D-glucosamine and *N*-acetyl-D-glucosamine. Chitosan comes from the partial deacetylation of chitin, another natural polysaccharide that is composed of repeating units of β-D-glucosamine bonded between carbons 1 and 4 through a beta glycosidic bond
Repeating unit			 
Natural source	Present on the cell wall of all green plants and some algae. Cellulose is the most abundant natural polymer on earth. Cellulose may also be used on derivatized forms such as carboxymethylcellulose (CMC) or hydroxypropyl methylcellulose (HPMC)	Present as an energy storage source for plants and algae. Starch is therefore extensively present on food products	Chitosan comes from the partial deacetylation of chitin. Chitin is the main component of cell walls on fungi, and it is also present in the shells of many crustaceans and insects

bonds such as NaOH/urea and ionic liquids [56, 57]. As such, many of the synthetic procedures for cellulose, starch, or chitosan have strong similarities between them. Mainly, the cross-linking and modification of these polysaccharides are performed by one of the following methods:

- Physical cross-linking through weak interactions (supramolecular forces)
- Chemical cross-linking through chemical reactions with cross-linkers
- Chemical cross-linking and grafting of functional molecules
- Formation of interpenetrated polymeric networks (IPNs) or semi-interpenetrated networks (semi-IPNs).

Despite the great similarity of these polymeric systems these polymeric systems, from the fact that the three are composed of glucose-derived building blocks, to the fact they might be modified with similar synthetic procedures; the key differences between these systems are very crucial in the development of systems for dye absorption. Therefore, in the following subsections, examples of cross-linked systems derived from, consisting of, or containing these polysaccharides will be presented highlighting their key advantages and characteristics.

On the other hand, polymeric cross-linked systems based on cyclodextrins (CDs) also will be discussed. CDs are synthetic cyclic glucose oligomers obtained from starch degradation by hydrolases [58]. They have been used in membrane science as well as in chromatography due to their enzyme-like properties, chirality recognition, their capability to form inclusion complexes as well as the possibility to get modified and cross-linked CDs for membrane design [59].

2.1 Cross-Linked Systems Based on Cellulose

Cellulose is arguably the most important natural polymer for the production of systems for dye removal, probably because cellulose and its derivatives are the most abundant polymers in nature. Research on cross-linked cellulose systems for dye removal started in 1970 where the uptake of dyes cross-linked celluloses was studied as a means of improving the staining of these cross-linked cellulosic materials [60, 61]. However, the utilization of cross-linked cellulose materials for the removal of dyes started being an important topic around 2009, where research on hydrogels of carboxymethyl cellulose (CMC) and hydroxypropyl cellulose (HPC) was performed. One of these examples is presented as a testament to the remarkable advances in this field. In 2009, CMC was cross-linked and functionalized with poly(vinyl alcohol) using ionizing radiation, obtaining a material that was tailored for the absorption of anionic dyes such as Acid Green B, Ismative Violet 2R, and Direct Pink 3B with absorption capacities of around 30 mg/g [60]. After these developments, rapid advances on dye uptake by cross-linked cellulosic materials were performed; therefore, in this subsection, some of these developments are presented.

As a first example in which a cellulose-modified substrate was evaluated against cationic MB is the research performed by Zhou and collaborators in 2011 in which they investigated the possibility of modifying cellulose with grafts of polyacrylic acid (PAAc) using phosphoric acid as a solvent for cellulose. PAAc was used as a modifier for cellulose as a way of obtaining a superabsorbent hydrogel system based on cellulose. The synthetic procedure involved the dissolution of cellulose on phosphoric acid followed by cross-linking polymerization reaction with *N,N'*-methylenebisacrylamide, and APS as initiator, followed by a grafting polymerization reaction of acrylic acid (AAc). These hydrogels demonstrated the ability. This study demonstrated that the dye-absorption capability of the materials is dependent on the amount of poly(acrylic acid) graft present on the samples, which is probably related to the amount free of carboxylic acid groups on the sample. This was corroborated with adsorption testing in different pH conditions, having poor absorption at low pH as expected (carboxylic acid groups are on their protonated below their pKa value of approximately 4) [62].

Another recent example that is worthy of mentioning is the production of nanocrystalline nanogels formed of cross-linked cellulose for the removal of cationic dyes by Liang and collaborators. In this work, the research group developed a methodology for producing chemically cross-linked aerogels composed of poly(methyl vinyl ether-co-maleic acid), poly(ethylene glycol), and nanocrystals of cellulose through freeze-drying with liquid nitrogen and curing at 90 °C. In this series of studies, the authors evaluated the ability of this system in retaining Methylene Blue (MB) dye determining that these systems can adsorb up to 116.2 mg/g of MB. Additionally, the authors determined that these systems may be reusable up to five cycles of dye removal without losing efficiency [63, 64].

Another example, a system that also profits from the properties of nanocrystalline cellulose while also combining it with the benefits of chitosan (refer to the chitosan subsection) was produced in 2016. To modify nanocrystalline cellulose (NCC), an oxidation reaction with periodate and chlorite ions was performed to yield NCC with carboxylic acid and aldehyde moieties. A representation of this system is shown in Fig. 2. This procedure was followed by a cross-linking reaction via imine formation with carboxymethylated chitosan. In this study, the materials were characterized with a great variety of techniques such as conductimetric titrations, solid-state ^{13}C-NMR, AFM, SEM, porosity measurements, and adsorption isotherms. This system demonstrated excellent capabilities for dye adsorption (785 mg/g of MB) while also maintaining good behavior after several cycles of use [65].

A final recent example was the modification of CMC with a similar methodology in which the cellulosic material was oxidated to form dialdehyde moieties, which could later be cross-linked with gelatin for the removal of dyes such as Rhodamine B and Methyl violet. This system was crafted as an alternative dye-removal substrate, which was only composed of biopolymers and could also be mechanically stable and biodegradable [66].

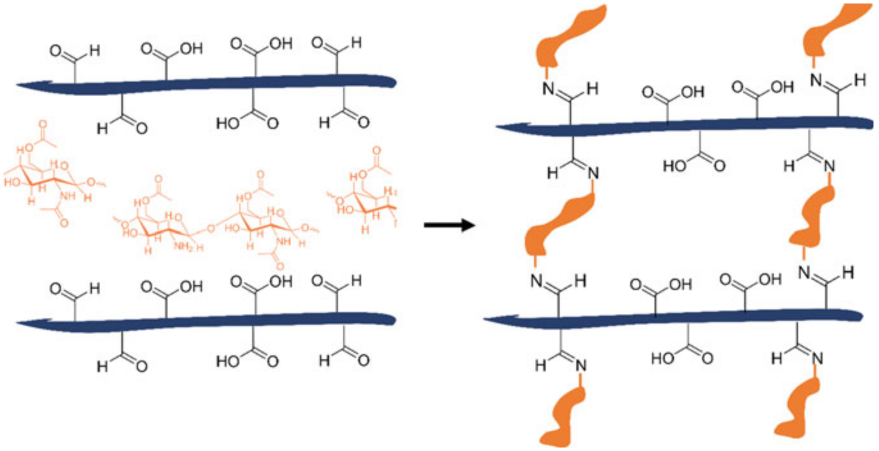


Fig. 2 Cross-linking via Schiff base formation of nanocrystalline cellulose using carboxymethylated cellulose [65]

3 Cross-Linked Systems Based on Starch

Similarly, to cellulose, starch is a natural polymer derived from glucose, which is mostly present in plants. However, the difference between cellulose and starch is that the latter is a combination of a linear polysaccharide (amylose) and a branched polysaccharide (amylopectin) while the former is a linear polysaccharide; therefore, the characteristics and behaviors of both polymers in the macroscale differ considerably. Due to the branched structure of starch, its capabilities of adsorbing and retaining chemical compounds are higher than that of cellulose: therefore, the use of cross-linked starches for the removal of dyes predates the use of cellulose [53, 67]. One of the first examples of starch systems for dye removal was developed in 2002, where Delval and collaborators produced a cross-linked starch substrate using epichlorohydrin (Fig. 3) in the presence of ammonium hydroxide as a cross-linker. In this early study, the absorption capabilities of the produced systems were evaluated, and it was verified that dye adsorption is dependent on the number of ammonium groups present on the polymer [68]. It is important to mention that epichlorohydrin is a very important cross-linker for the production of starch and even chitosan systems,

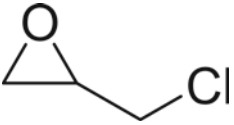


Fig. 3 Chemical structure of epichlorohydrin, a very important cross-linker for starch and chitosan-based systems

and as such, the original protocol described by Simkovic et al. is presented here as a reference to the reader [69].

A more recent example of starch-based materials for the removal of dyes, a 2006 study reported the behavior of a specially crafted cross-linked starch-containing both carboxylate groups and quaternary ammonium ions in its structure for the adsorption of both cationic and anionic dyes (Acid Red G, acid Light Yellow 2G, methyl green, and methyl violet). In this study, the effect of pH, times, concentration of dyes were evaluated allowing to obtain adsorption isotherms and kinetic parameters [70].

In 2019, Zhang Hao and collaborators developed a cross-linked starch system that was cross-linked using epichlorohydrin and containing γ-cyclodextrin by immobilization by esterification. This system was evaluated as an alternative for adsorption of MB, methyl purple (MP), and congo red (CR) as model anionic and cationic dyes in complicated matrices intended to emulate real conditions of adsorption (referred by the authors by dyestuff). The materials showed improved absorption of these three dyes compared with both cross-linked starch, and other absorbents such as diatomite and zeolite. Additionally, cyclodextrin containing starch showed improved stability to biodegradation; therefore, improving the durability of the material while not compromising its biodegradability [71].

A final example in which starch was modified to improve its capabilities of removing dyes was the research by Janaki and collaborators. In this work, maize starch was modified with polyaniline produced in situ by the oxidative polymerization of aniline with ammonium peroxydisulfate forming a cross-linked material due to hydrogen bonds (Fig. 4). In this study, the removal of dyes such as Reactive Black 5 and Reactive Violet 4 was studied in different conditions, in particular, it was interesting that the uptake of these dyes was possible at low pH, this is because amine groups of aniline are charged at low pH in contrast to carboxylic acid-based

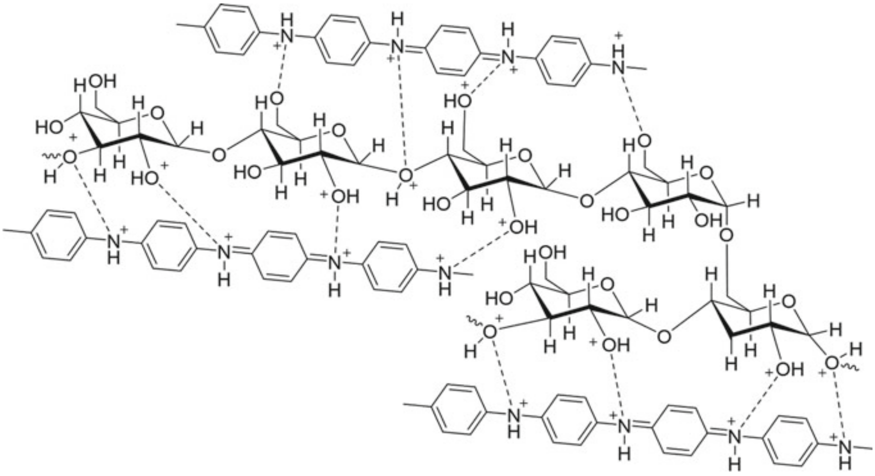


Fig. 4 Starch cross-linked with polyaniline via hydrogen–bond interactions

adsorption, which occurs at higher pH values with high effectiveness. Additional to this, the authors of this study verified that the adsorption of the dyes was due to ionic interactions [72].

It is important to mention that although these selected examples present an overview of the chemistry of cross-linked starch, there are many examples of functionalization and cross-linking of starch to obtain materials capable of dye absorption and other applications, as a reference to the reader, some of these works as well as some extensive reviews are presented as a conclusion to this subsection [53, 73–78].

4 Cross-Linked Systems Based on Chitosan

As it may be notable, chitosan is the only of these three polymeric systems (and cyclodextrins for that matter) that is not composed of repeating units of glucose; in contrast, the remarkable functional group present in chitosan is the amine group of glucosamine. The presence of this functional group in particular because, due to its acid–base properties, it has a positive charge at neutral pH (the amine group becomes an ammonium group below its pKa of around 9); therefore, in most conditions, chitosan is a positively charged polymer. With this in mind, chitosan systems are particularly effective with the adsorption of negatively charged species like anionic dyes [56, 79–82].

The first interesting example is a 2003 paper by M. S. Chiou and H. Y. Li in which they first produced chitosan beads that were then cross-linked using epichlorohydrin and NaOH or glutaraldehyde in aqueous conditions. The adsorption capabilities of this substrate were evaluated by batch adsorption assays against reactive red 189 and by evaluating the effect of pH and temperature on the absorption of this dye [83].

In another important example of chitosan modification, an interpenetrated network composed of chitosan chains and polymerized acrylamide. This material is interesting because it profits from the adsorption capabilities and abundance of chitosan as a polysaccharide, while also providing rigidity to the matrix by forming the interpenetrated network with poly(acrylamide). This interpenetrated network was formed by cross-linking acrylamide with *N,N'*-methylenebisacrylamide, and glutaraldehyde as cross-linkers (Fig. 5). This material arranged in cylinders was demonstrated to be an effective substrate for the absorption of EY-4GL Yellow and S-Blue in complicated matrixes [84].

In a recent example a combination system in which chitosan was integrated onto activated carbon and cross-linked with epichlorohydrin. This composite system was synthesized by dissolving chitosan into acetic acid and mixed with activated carbon and then cross-linking with epichlorohydrin and NaOH. In this work, the surface area of the materials was characterized by N_2 adsorption and desorption, the crystallinity was evaluated using X-ray diffraction. Additionally, SEM was used to visualize the materials before and after adsorption, FTIR to verify the presence of certain functional groups. As in other studies, the adsorption capabilities of this polymer against thionine were evaluated concerning pH, temperature, and contact time [85].

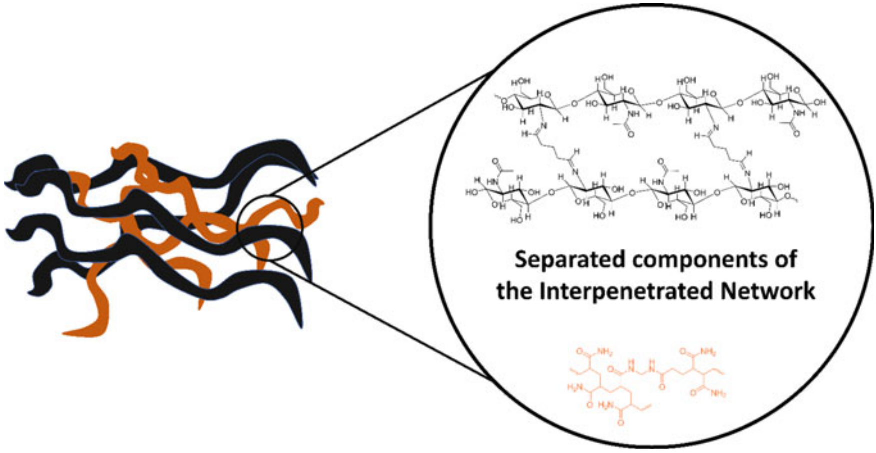


Fig. 5 Chitosan-polyacrylamide interpenetrated network

A final example of chitosan as a cross-linked matrix is a 2017 paper by Martina Salzano de Luna and collaborators. In this work, the authors wanted to investigate if the inherent absorption capabilities of chitosan could be enhanced by producing porous hyper cross-linked polymer particles that could entrap cationic and anionic dye molecules onto its pores. These substrates were produced by the hyper cross-linking reaction in which poly(VBC-DVB) is synthesized as a cross-linking precursor with the capability of cross-linking several times through Friedel Crafts reactions to form a hyper cross-linked resin, which was then mixed with chitosan to form a hydrogel. These materials were shown to be effective in dye adsorbing with different chemical structures such as Indigo Carmine, Rhodamine 6G, and Sunset Yellow even after several adsorption–desorption cycles while having improved mechanical performance when compared with chitosan and good and thermal stability [86].

5 Cross-Linked Systems Based on Cyclodextrins (CDs)

CDs have been known for more than 100 years but until the 1980s when the first applications in the food and pharmaceutical industry scale-up CDs research and production at industry levels. This led to the synthesis of pure native CDs, which are cyclic oligomers of glucose bonded by α-1,4 glycosidic bonds. They are called α-CD, β-CD, and γ-CD depending on the number of bonded glucose units (Fig. 6) and have characteristic toroidal shapes with hydrophobic central nanocavities capable to host small molecules due to their cage-type shape. CDs' surface shows hydrophilic properties surface due to the pointing outside OH groups.

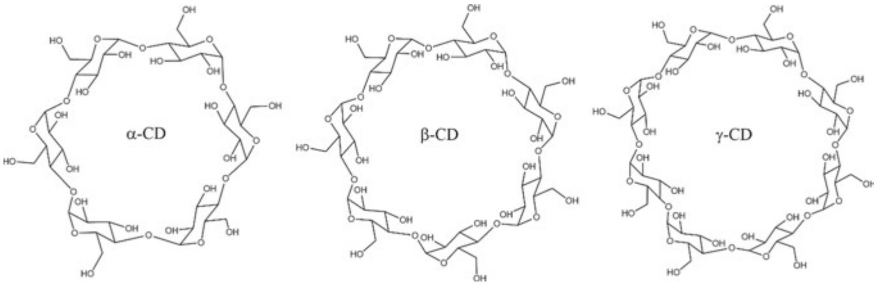


Fig. 6 Native CDs form starch degradation, α-CD (six glucose units), β-CD (seven glucose units), and γ-CD (nine glucose units)

Concerning materials with dye removal applications, cross-linked CDs have been implemented in membranes and adsorbents materials. The formers have the advantage of high dye removal properties when implemented in nanofiltration, as well as high regeneration capacities, but they are not always suitable from the cost operation point of view. On the other hand, adsorbent materials have arisen as an alternative due to their low cost of production and operation. However, typically adsorbent materials show either lower regeneration capabilities or lower dye removal capacity than membranes for nanofiltration (NF) [87]. Both will be discussed here with representative examples.

Among the most used methods to get flat sheet and hollow fiber membranes base on cross-linked CDs is phase inversion followed by cross-linking process and interfacial cross-linking [88]. For example, composite porous membrane based on β-CD and supported on a microfiltration nylon membrane (average pore size = 0.45 μm) has been reported to take advantage of mass transport in porous support without the need for high pressures. Nylon porous membrane was submerged in alkaline aqueous solution containing β-CD (0–0.14%) to get dip-coated membrane. After drying by evaporation, the cross-linking process was achieved by the addition of trimesoyl chloride (TMC, 0–2%) in hexane at 60 °C. The composite membrane showed rejection of bisphenol (BPA, a waste reagent in dye and plastic industry) with a feed solution of 10 mg L^{-1} and permeation flux of 80 L m^{-2} h^{-1}. The N element content on the pristine composite membrane was 11.3%, while a marked drop to 0.9% in N composition was confirmed by XPS surface analysis after cross-linking process [89].

The use of ceramic membranes (Al_2O_3) to support polymeric systems has also been reported concerning water purification from monocyclic aromatic hydrocarbons by sorption. For example, sylation of β-CD (60–70%) and subsequent sol–gel reaction yielded cross-linked triethoxysilylated cyclodextrins on the ceramic Al_2O_3 surface. Subsequent hydrolysis to silanols and thermic treatment yielded a siloxane network on the surface of the organic–inorganic filter. This membrane showed a higher affinity toward lipophilic pollutants than ceramic materials and high rejection of organic pollutants of low molecular weight, like those proceeding from textile finishing industries, i.e., dye color fixation process. [90].

Cyclodextrin solute complexation often improves the absorbency properties of the membranes. Poly(vinyl alcohol)/glutaraldehyde membranes have been modified by embedded β-CD to obtain membranes with high sorption of methyl orange, and Methylene Blue (MB) dyes. The β-CD is not covalently bonded to PVA but mixed into matrix polymer. With 8% β-CD, a maximum of adsorption capacity was obtained. Also, the swelling ratio increased from 58 in PVA/GA to 100% in PVA/GA/ β-CD, which indicates the more hydrophilic character of the modified membrane and their capability to promote interaction of non-polar MB with the nanocavity of β-CD. Additionally, the pH value controls the adsorption process since the surface charge of the polymer resulted in a pH function. In this case, the MB adsorption process is favored in an acid medium in which the PVA/GA/ β-CD membrane is stable and also shows regeneration capacities after one cycle of use [91].

Interestingly, the use of CDs in cross-linked polymers has also been applied to obtain insoluble nanofibrous membranes. β-CD functionalized with polyvinyl pyrrolidone (PVP) has been cross-linked using glutaraldehyde, an excellent cross-linking agent for CDs, by electrospinning preparation. The sorption experiments showed methyl orange adsorption (39.82 mg per gram of membrane) providing an alternative to traditional filtration technologies for dye removal from wastewater [92].

Recently, a gelatin/β-CD composite fiber has been reported. Gelatin is a type of protein produced by the hydrolysis of collagen, and its composites typically show excellent mechanical strength. The gelatin/β-CD composite was cross-linked with glutaraldehyde showed high removal capacity of MB, Basic Fuchsin, Brilliant Blue R, and Malachite Green dyes. After nine cycles of use, the fibers showed high adsorption efficiency. Figure 7 shows a schematic representation of the Gelatin/β-CD composite fiber in which is clear that the cross-linking agent can bind CDs units and gelatine polymer as well as gelatine chains [93].

Concerning the design and synthesis of polymers for sorption of anionic azo dyes, CDs and starch have been cross-linked with hexamethylene diisocyanate (HMDI), yielding insoluble resins. Host–guest interaction involving inclusion complex between β-CD and the azo dyes plays a key role in the mechanism of

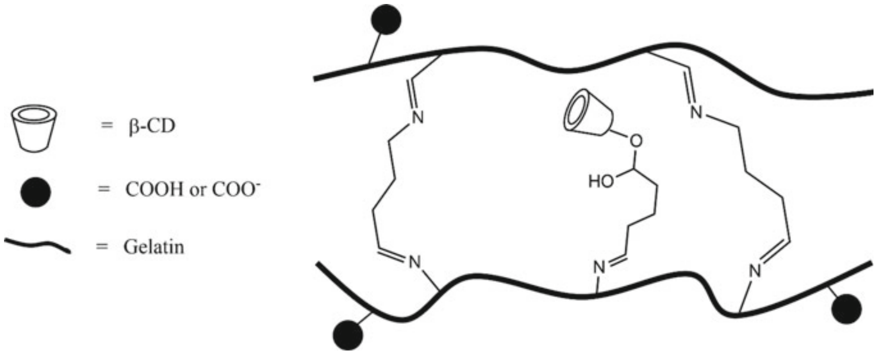


Fig. 7 Gelatin/β-CD composite fiber

dye removal from wastewater. These resins showed a high capacity for the removal of azo dyes, e.g., Direct Violet 51, Tropaeolin 000 (Orange II), and methyl orange [94].

More recently, a porous β-CD polymer containing carboxylic acid groups was obtained and tested as a sorbent of cationic MB, obtaining a dye removal of 672 mg per g of material. The results were interpreted in terms of triple effects in the mechanism of sorption; inclusion complex with β-CD, the porous network of the cross-linked polymers, and the electrostatic attraction between the cationic dye and the negative carboxylate groups of the polymer [95].

6 Polymeric Composites and Synthetic Polymers

On the other side, some blends, composites, and mixes are used as an alternative for the preparation of adsorbent membranes. Some of the most common are the polymer–metal coagulants, which have been demonstrated to be efficient as adsorbents in the cleaning water process, with a remotion of almost 90% of dyes in a solution [13]. Additionally, the combination or modification of these components allows the decreasing of the dosage of the metal coagulant reducing toxicity. Other hybrid materials and composites have been prepared for dye removal [39, 96], the combination of carbon nanomaterials, inorganic polymers [49], magnetic particles [39], and natural compounds has been tested. Carbon nanotubes and graphene oxide (GO) have demonstrated good performance for dye removal [97], and magnetic nanoparticles aid in the elimination of heavy metals and anionic dyes by coagulation [98].

In the case of carbon nanomaterials, GO has been mixed with natural or synthetic polymers to obtain adsorbents for dyes. Abdi et al. modified conventional PES membranes with magnetic graphene oxide sheets. They prepared a hybrid material based on magnetite (Fe_3O_4), metformin, and GO (metformin/GO/Fe_3O_4), and then it was introduced into the PES. The resulting material was able to remove copper ions by the interaction of Cu^{2+} with the primary and secondary amines in the metformin; and the azo dye, Direct Red 16, was retained by supramolecular interactions, π–π stacking with GO phenolic groups, and hydrogen bonding between carbonyl and amine groups. The membrane performance was not been affected, it maintains the water flux and the removal capacity with the addition of only 0.5 wt% of the hybrid material (metformin/GO/Fe_3O_4) [99].

Besides, polysaccharides have been mixed with GO for the removal of dyes; for example, Song et al. prepared a composite made of phosphorylated chitosan (PCS) PCS-GO by grafting deposited onto polyacrylonitrile (PAN) membranes (PSC-GO/PAN). By covalent immobilization of the chitosan derivative onto the GO surface, the separation performance for anionic dyes including Direct Black 38, Ponceau S, Xylenol Orange, NaCl, and Na_2SO_4, was successful. Additionally, the PSC-GO/PAN NF membrane showed a good technique for the treatment of salty anionic dye solutions with antifouling performance [100].

For crystal violet removal (cationic dye), a composite made of GO and polysaccharide hydrogels were tested for [101]. The GO was functionalized with a macroinitiator to obtain free vinyl groups on the surface of GO, subsequently, the hydrogel was cross-linked using the modified GO as a cross-linking agent. The final cross-linked hydrogel was synthesized by mixing (Acrylic Acid)-*co*-(2-acrylamido-2-methylpropane sulfonic acid) poly(AAc-*co*-AMPSA) and *xanthan gum* (anionic polysaccharide) with the previously modified GO. The cross-linked hydrogel was disposed of as a column for filtration with a successful separation of CV, by hydrogen bonding and π–π stacking with the hydrogel and the GO sheets. Additionally, the material demonstrated good performance by eliminating almost 99% of the dye at neutral pH, and good reusability (useful for 20 adsorption–desorption cycles) [101].

The grafting approach has allowed the incorporation of virtually any material onto a surface, the last examples used this technique to enhance the versatility and performance of membranes for filtration and separation of salts and dyes. AAc has been employed to remove cationic dyes by complexation with the carboxylate groups. Gamma radiation has been used to achieve cross-linked polymeric matrixes, and to modify surfaces; hence, it allowed the fabrication of hydrogels and membranes for dye removal. Dafader et al. made the modification of cotton (cellulose) with AAc (AAc-*g*-cotton) in aqueous media by grafting technique, the final material was tested for the adsorption of a cationic dye, MB. The authors suggested that the retention of the dye is due to electrostatic (ionic) interaction between the cationic group of MB and the anionic group (COO^-) of AAc-*g*-cotton. It is also found that dye adsorption increases with increased concentration of dye in aqueous solution, the material showed an adsorption capacity of 16.89 mg/g at room temperature [102].

Additionally, hydrogels have shown good adsorbent behavior through colorants and pollutants from textile water. PAAc has demonstrated ability to remove cationic dyes, since the carboxylate groups. Another hydrogel prepared by gamma radiation showed high adsorption of MB when the contact time with the colored water and the adsorbent dosage is increased. The poly(vinyl alcohol)/acrylic acid/poly-4-styrene sulphonic acid hydrogel (PVA/AAc/PSSa) exhibited a removal efficiency at neutral pH condition and it showed a reusability of four cycles [103].

As well as other polysaccharides, pectin has been combined with AAc to synthesize hydrogels for MB removal. Abdullah et al. used gamma and microwave (MW) radiation to obtain pectin-based hydrogels. The pectin was extracted from the dragon fruit peel waste (*Hylocereus polyrhizus*), and two different hydrogels were obtained, the first using MW polymerization and the second by gamma rays. Both hydrogels exhibited excellent performance in absorbing aqueous solution (tested by swelling) and MB in alkaline medium, although, the hydrogels prepared using gamma radiation showed better performance with about 45% of absorbency with 20 mg of the sample [104].

Also, azo dyes can be removed using hydrogels, it totally depends on de-chemical structure of the polymer and dye. Methacrylates, similar to acrylates, have been used to prepare adsorbent hydrogels. Hydrogels from 2-hydroxyethylmethacrylate (HEMA), methacrylate derivatives, and PVA were synthesized by Gupta and Sadegh group in 2015 as an adsorbent for the removal of Malachite green and Congo Red at pH 9 [105].

As a final example of synthetic polymers being used for this mean, a 2018 paper by Hernandez–Martinez and collaborators dealt with the synthesis of a cross-linked system using *N,N*-dimethylacrylamide and 2-hydroxyethyl methacrylate using AIBN as a polymerization initiator in an inert atmosphere. This work measured the swelling capabilities of these materials obtaining outstanding swelling in a couple of hours and uptakes of MB up to 30–40 mg/g at high concentration of dye on the initial solution [106].

7 Conclusion

The extensive use of dyes in a variety of industries and their incorrect disposal pose a serious threat to both the environment and human health due to concerns about the safety of the dyes once they entered water sources. The solution for this effect has, in recent years, developed from a handful of techniques, which, although effective, were costly, not as effective, or even generating secondary pollution. Nowadays, there exist the possibility of designing functional polymeric systems for removing dyes and related pollutants from water sources through cleaner and more effective methods profiting from the chemical composition of novel polymer systems, which are both derived from classical chemical synthesis and the derivatization of existing natural polymers. In the future, the utilization of more advanced systems that combine mechanisms like size exclusion, supramolecular interaction, and electrostatic forces will probably arise as means of effective wastewater purification for both dyes and many other pollutants.

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