



Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment

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Received 6 July 2004; revised 1 November 2004; accepted 22 November 2004

Abstract

The chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, aromatic molecules and dyes, is a serious environmental problem owing to their potential human toxicity. Therefore, there is a need to develop technologies that can remove toxic pollutants found in wastewaters. Among all the treatments proposed, adsorption is one of the more popular methods for the removal of pollutants from the wastewater. Adsorption is a procedure of choice for treating industrial effluents, and a useful tool for protecting the environment. In particular, adsorption on natural polymers and their derivatives are known to remove pollutants from water. The increasing number of publications on adsorption of toxic compounds by modified polysaccharides shows that there is a recent increasing interest in the synthesis of new low-cost adsorbents used in wastewater treatment. The present review shows the recent developments in the synthesis of adsorbents containing polysaccharides, in particular modified biopolymers derived from chitin, chitosan, starch and cyclodextrin. New polysaccharide based-materials are described and their advantages for the removal of pollutants from the wastewater discussed. The main objective of this review is to provide recent information about the most important features of these polymeric materials and to show the advantages gained from the use of adsorbents containing modified biopolymers in waste water treatment.

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Keywords: Polysaccharides; Biopolymers; Chitin; Chitosan; Starch; Cyclodextrin; Networks; Crosslinking; Grafting; Hybrid Materials; Adsorption; Adsorbents; Pollutants

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1. Introduction

Water pollution due to toxic metals and organic compounds remains a serious environmental and public problem. Moreover, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. They are common contaminants in wastewater and many of them are known to be toxic or carcinogenic. For example, chromium (VI) is found to be toxic to bacteria, plants, animals and people [1]. Mercury and cadmium are known as two of the most toxic metals that are very damaging to the environment [2]. In addition, heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, their presence in the environment, in particular in water,

should be controlled. Chlorinated phenols are also considered as priority pollutants since they are harmful to organisms even at low concentrations. They have been classified as hazardous pollutants because of their harmful potential to human health [3,4]. 2,4,6-trinitrotoluene (TNT) is a nitro-aromatic molecule that has been widely used by the weapon industry for the production of bombs and grenades. This compound is recalcitrant, toxic and mutagenic to various organisms [5,6]. Many synthetic dyes, which are extensively used for textile dyeing, paper printing and as additives in petroleum products are recalcitrant organic molecules that strongly color waste water.

Strict legislation on the discharge of these toxic products makes it then necessary to develop various efficient technologies for the removal of pollutants from wastewater. Different technologies and processes are currently used. Biological treatments [7–9], membrane processes [10–13], advanced oxidation processes [14–17], chemical and electrochemical techniques [18–20], and adsorption procedures

[21–49] are the most widely used for removing metals and organic compounds from industrial effluents. Amongst all the treatments proposed, adsorption using sorbents is one of the most popular methods since proper design of the adsorption process will produce high-quality treated effluents. Adsorption is a well-known equilibrium separation process. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation analytical purposes. The adsorbents may be of mineral, organic or biological origin: activated carbons [21–26], zeolites [27,28], clays [29–33], silica beads [34,35], low-cost adsorbents (industrial by-products [36–41], agricultural wastes [42,43], biomass [44,45]) and polymeric materials (organic polymeric resins [46,47], macroporous hypercrosslinked polymers [48,49]) are significant examples. Table 1 shows a non-exhaustive list of some selected examples of adsorbents used in wastewater treatment.

Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as chitin [50–52] and starch [53–55], and their derivatives (chitosan [56,57], cyclodextrin [58–60]) deserve particular attention. These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains. Moreover, it is well known that polysaccharides which are abundant, renewable and biodegradable resources, have a capacity to associate by physical and chemical interactions with a wide variety of molecules [61,62]. Hence adsorption on polysaccharide derivatives can be a low-cost procedure of choice in water decontamination for extraction and separation of compounds, and a useful tool for protecting the environment [63]. Besides, the increasing number of publications on adsorption of toxic compounds by these natural polymers shows that there is a recent interest in the synthesis of new adsorbent materials containing polysaccharides.

In this paper, the use of adsorbents containing polysaccharides has been investigated as

Table 1
Recent reports on various adsorbents used in wastewater treatment

Adsorbents	Pollutant	Reference
<i>Activated carbon</i>	Cr(VI)	[21]
	Benzoic acid	[22]
	Dyes	[23]
	Pb ²⁺ , Cd ²⁺	[24]
	Cresol	[25]
	Chlorophenols	[26]
<i>Zeolites</i>		
Scolecite	Pb ²⁺ , Cu ²⁺ , Cd ²⁺	[27]
Clinoptilolite	Pb ²⁺ , Cr ³⁺ , Cu ²⁺ , Fe ²⁺	[28]
<i>Clays</i>		
Montmorillonite	Mn ²⁺ , Zn ²⁺ , Ni ²⁺	[29]
Bentonite	Phenol	[30]
Organobentonite	Phenol	[31]
Sepiolite	Hg ²⁺ , Pb ²⁺	[32]
Kaolinite	Cu ²⁺ , Co ²⁺	[33]
<i>Silica beads</i>	Pb ²⁺ , Cd ²⁺	[34]
	Dyes	[35]
<i>Low cost-adsorbents</i>		
Rolling mill scale	Cu ²⁺	[36]
Saw-dust	Dyes	[37]
Metal hydroxide sludge	Dyes	[38]
Bagasse fly ash	Cd ²⁺	[39]
Sugar beet pulp	Cd ²⁺ , Pb ²⁺	[40]
Papermill sludges	Phenols	[41]
Corncob	Dyes	[42]
Wheat straw	Dyes	[43]
Baker's yeast	Cd ²⁺	[44]
Fungal biomass	As(V)	[45]
<i>Polymeric materials</i>		
Organic polymer resin	U(VI)	[46]
	Cu ²⁺ , Pb ²⁺	[47]
Hypercrosslinked polymer	Phenols	[48]
	Aniline, benzene	[49]

a replacement for current conventional methods of removing pollutants from solution. Since this review will only present data obtained using chitin, chitosan, starch and cyclodextrins, the discussion will be limited to these biopolymers and their properties. The main objectives are to provide useful information about the most important features of these polymeric materials and to give an overview of several studies. In particular, the review shows the recent developments in the synthesis and chemistry of polysaccharide-based materials, and presents a critical analysis of these materials; it examines various sorbents, which

are capable of removing pollutants from wastewater and describes their characteristics, advantages and limitations; it discusses the various mechanisms involved and reports on some regeneration methods; it discusses the optimal conditions and influencing factors on biosorption such as the chemical modification by grafting for improving the sorption capacity and selectivity, the influence of pH, etc. The paper also presents a brief review on the role of polysaccharide sorbents in the removal of unwanted substances from solution and compares their removal performance with other low-cost adsorbents. A number of recent references demonstrate the versatility of the material. Reported adsorption capacities are noted when possible to give some idea of sorbent effectiveness. These data will show that certain chemical substances such as dyes, heavy metals and phenolic compounds can be removed very effectively using the polysaccharide-based materials.

2. Polysaccharides

2.1. General considerations

Since its first introduction for heavy metals removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world [56]. Abundant information on the use of activated carbon for such purposes can be found in scientific literature. Because of their great capacity to adsorb pollutants, activated carbons are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture, which gives them a large surface area, and their chemical nature, which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages. It is non-selective, quite expensive, and the higher the quality, the greater the cost. The regeneration of saturated carbon by thermal and chemical procedure is also expensive, and results in loss of the adsorbent. This has led many workers to search for more economic and efficient adsorbents.

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in

recent years. Attention has focused on various adsorbents, in particular natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al. [52], a sorbent can be considered low-cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Starch and chitin may have potential as inexpensive, readily available materials and are classified as low-cost sorbents.

2.2. Polysaccharides and their properties

Native starch is one of the most abundant biopolymers on earth and is present in living plants as energy storage material. Starches are mixtures of two polyglucans, amylopectin and amylose, but they contain only a single type of carbohydrate, glucose. Chitin is a naturally abundant mucopolysaccharide extracted from crustacean shells, which are waste products of seafood processing industries. Chitin is the second biopolymer in nature, after cellulose, in terms of abundance, but it is the most abundant amino polysaccharide. The polymer contains 2-acetamido-2-deoxy- β -D-glucose through a β (1 \rightarrow 4) linkage. It may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group. Since such wastes (shrimp, lobster, crab shells) are abundantly available, chitosan may be produced now commercially at low cost. Starch and chitin are biologically inert, safe for humans and the natural environment. They possess several other advantages and characteristics that make them excellent materials for industrial use [64,65].

Polysaccharides, stereoregular polymers of monosaccharides (sugars), are unique raw materials in that they are: very abundant natural polymers (they are referred to as biopolymers); inexpensive (low-cost polymers); widely available in many countries; renewable resources; stable and hydrophilic biopolymers; and modifiable polymers. They also have biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, polyfunctionality, high chemical reactivity, chirality, chelation and adsorption capacities. The excellent adsorption behavior of polysaccharides is mainly attributed to: (1) high hydrophilicity of the polymer due to hydroxyl groups

of glucose units; (2) presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups); (3) high chemical reactivity of these groups; (4) flexible structure of the polymer chain.

In spite of these properties and advantages some problems can occur. For example, chitosan is soluble in acidic media and therefore cannot be used as an insoluble sorbent under these conditions, except after physical and chemical modifications. In sorption columns, chitin and chitosan are often used as powder or in flask forms. This technique usually causes a significant pressure drop in the column [57]. To avoid this problem, chitin and chitosan beads have been developed. Cyclodextrins, water-soluble in their native form, are often modified to prepare new insoluble derivatives. The hydrophilic nature of starch is also known to be a major constraint that seriously limits the development of starch-based materials. Chemical derivatisation has been proposed as a way to solve this problem and to produce water resistant materials. However, the strategy for modification depends on the final material's purpose. If a water soluble starch derivative is desired for application in waste water flocculation or as an additive in paper manufacturing, then a random conversion of hydroxyl groups to aminopropyl [72], hydroxyalkyl [73] or betaine [74] groups can be achieved. If the starch-based material is used as adsorbent resins, then a rigid macromolecular structure is necessary.

2.3. Polysaccharide derivatives

One of the most important and useful feature of chitin and starch is their good chemical reactivity. They possess a large number of reactive groups (hydroxyl and/or acetamido groups) present at the 2-, 3-, and 6-positions in the glucose unit. These groups allow direct substitution reactions (esterification or etherification reactions) or chemical modifications (hydrolysis, oxidation or grafting reactions, enzymatic degradation), usually referred to as chemical derivatisation, yielding different polysaccharide derivatives for specific domains of applications.

The starch and chitin derivatives can be classified in three main classes of polymers:

- (i) modified polymers such as cationic starches, carboxymethylchitin,...
- (ii) derivatized biopolymers, including chitosan, cyclodextrins and their derivatives
- (iii) polysaccharide-based materials such as resins, gels, membranes, composite materials...

From the polymer chemist's point of view, the chemical substitution of chitin and starch offers enormous challenges. These are provided by the presence of the numerous functional groups, which are available for chemical reactions. However, their reactivity depends on experimental conditions. This makes, in general, selective substitution relatively difficult, and different mono, di or tri-derivatives can then be obtained, yielding modified polysaccharides. The modification of the existing polysaccharides is one possible method of obtaining more polar sorbents. The possible chemical derivatization of starch and chitin is also an interesting property because it is well-known that the grafting of ligands can improve their adsorption properties. By incorporating some functional (hydrophobic) groups either into the backbone of the network structure or as pendant groups it is possible to prepare materials with strong adsorption properties. The chemical modification of the starch and chitin also allows preparation of two derivatized polysaccharides, cyclodextrin and chitosan, respectively.

An important class of starch derivatives are the cyclodextrins or cycloamyloses. Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The CD molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch. The three smallest CDs, alpha-cyclodextrin, beta-cyclodextrin and gamma-cyclodextrin which consists of six, seven and eight α -1,4 linked D(+)-glucopyranose units respectively are well known and are available commercially. The most characteristic feature of cyclodextrins is the ability to form inclusion compounds with various molecules, especially aromatics: the interior cavity of the molecule provides a relatively hydrophobic environment into which an apolar pollutant can be trapped. Several review articles were devoted to the detailed description of the applications of cyclodextrins [58–60,66–68].

More important than chitin is its deacetylated derivative, chitosan, although the *N*-deacetylation is almost never complete. Chitosan is a linear

polycationic polymer which contains 2-acetamido-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose residues. Chemically, it is a poly(*N*-glucosamine). This biopolymer has drawn particular attention as a complexing agent due to its low cost as compared to activated carbon and its high content of amino and hydroxy functional groups showing high potentials for a wide range of molecules, including phenolic compounds, dyes and metal ions. Chitosan has become the subject of considerable interest in different fields [50–52,56,57, 69–71] such as medicine, biology, pharmacy, food and biotechnology. Properties and applications of chitin and chitosan have been reviewed by Synowiecki and Al-Khateeb [50] and Ravi Kumar [51]. Metal complexation by chitosan and its derivatives has been recently reviewed by Varma et al. [57].

The modification of polysaccharides also offers enormous opportunities. Through chemical reactions, in particular crosslinking and grafting reactions, polysaccharides can give interesting macromolecular superstructures, e.g. gels and hydrogels networks, polymeric resins, beads, membranes, fibers or composite materials. These polysaccharide-based materials can then be used as adsorbents.

3. Polysaccharide-based materials

There are numerous studies in literature on the preparation of sorbents containing polysaccharides. There are several reported procedures to synthesize these materials and the methods can be generally classified in two main ways:

- (i) Crosslinking reactions. Polysaccharides can be crosslinked by a reaction between the hydroxyl or amino groups of the chains with a coupling agent to form water-insoluble crosslinked networks [57,59,75–138,119]. There are two main classes of gels and Berger et al. [77,78] suggest the following classification: a separation between physical [77] and chemical gels [78]. Chemical gels are formed by irreversible covalent links, while physical gels are formed by various reversible links. Formation of polysaccharide gels by polyelectrolyte complexation is an interesting alternative to covalently crosslinked

gels. Since this section will only present data obtained using insoluble chemical gels, the discussion will be limited to these materials and their characteristics.

- (ii) Immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials. This method relies on the bonding of polysaccharides to a pre-existing mineral or organic matrix via several spacer arms. Composite materials combine the physical and chemical properties of both inorganic and organic materials [59,119,139–170].

3.1. Insoluble crosslinked polysaccharides

Due to the unique structure of the macromolecule combined with their polyfunctionality, polysaccharides have the ability to form crosslinked networks, gels and macroreticular resins [59,119]. Crosslinking occurs when a reagent (namely a crosslinking agent) introduces intermolecular bridges and/or crosslinks between polysaccharide macromolecules. The crosslinking step is a well-known and well-documented reaction, and a relatively easy method to prepare polysaccharide-based materials. The crosslinking agent can react with macromolecules linear chains (crosslinking step) and/or itself (polymerization step) in an alkaline medium. Crosslinking drastically reduces segment mobility in the polymer and a number of chains are interconnected by the formation of new interchain linkages. A three dimensional network is then formed. If the degree of reticulation is sufficiently high, the matrix of the polymers becomes insoluble in water (but swellable in water) and in organic solvents. The two most important factors controlling the extent of adsorption properties of polysaccharide-based materials are the hydrophilicity of the polymer and the crosslink density [129]. When the crosslinking degree is high, the material is mostly amorphous [110].

Because they are covalently crosslinked networks, these gels are called permanent or chemical gels [127,77]. Like physical gels, chemical gels are not homogeneous. Crini et al. [59,116,126] investigated the structure of crosslinked epichlorohydrin–cyclodextrin polymers by solid state ^{13}C NMR techniques. They showed that, in these materials, two kinds of

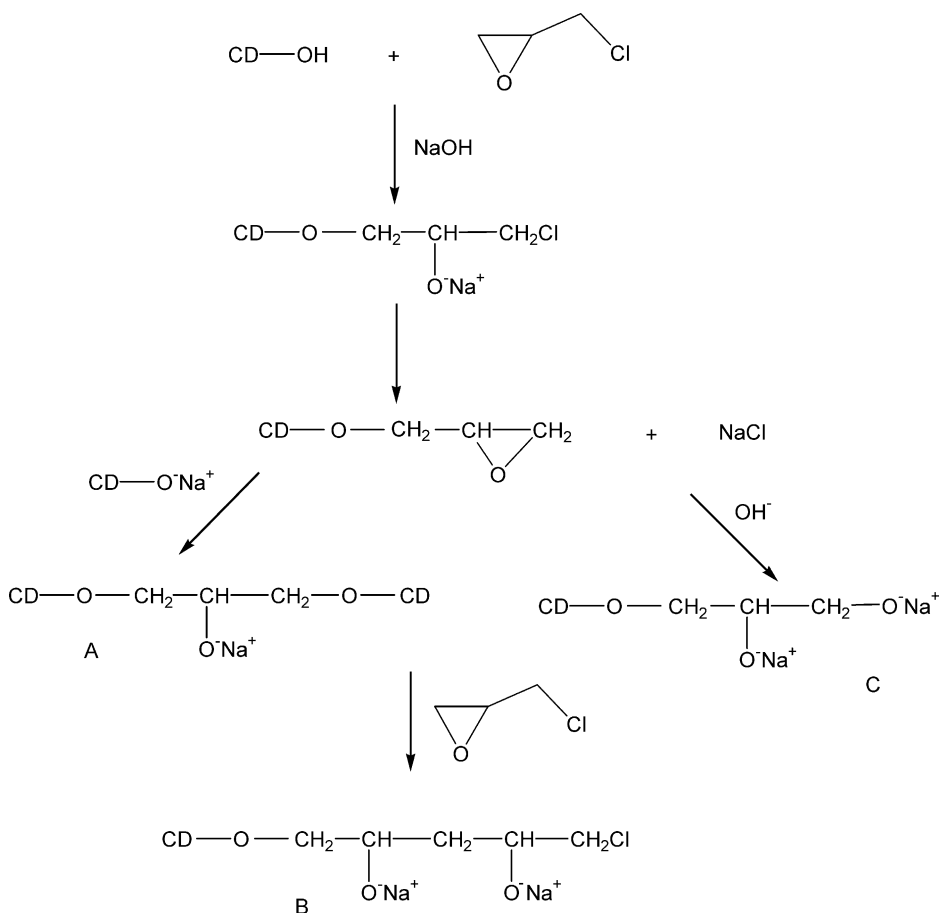


Fig. 1. Proposed mechanism for the reaction of EPI with cyclodextrin (A) crosslinking step, (B) crosslinked agent polymerization, (C) hydrolysis of the monografted EPI leading to a glycerol monoether.

structures can exist: a crosslinked network obtained when epichlorohydrin (EPI) reticules cyclodextrin and polymerized epichlorohydrin chains obtained when EPI reacts with itself. A classical reaction scheme is shown in Fig. 1. Although this scheme is generally accepted for the reaction of EPI with CD (or starch), some reports have suggested considerably more complex structures when EPI reacts with chitosan, because the crosslinking agent can also react with amino groups of chitosan chains. The possible structures of various crosslinked chitosan beads are represented in Fig. 2. Fig. 3 represents the possible structure of the crosslinked starch-polymer containing tertiary amine groups. Another recent NMR relaxation study showed that crosslinking was

not homogeneous and increasing the crosslinking degree increases the amorphous content [110].

The crosslinked polymers are obtained in homogeneous or heterogeneous conditions by using reticulation with bi- or polyfunctional crosslinking agents such as epichlorohydrin [76,84,88,105,109], ethylene glycol diglycidyl ether [81,85,88,102], glutaraldehyde [79–81,86–88,94,97,98], benzoquinone [91], phosphorus oxychloride [111], carboxylic acids [108], maleic anhydride [120] or isocyanates [118,119]. Among the crosslinking agents, the most popular is epichlorohydrin (abbreviated EPI). Although it is considered to hazardous environmental pollutant and potential carcinogen, EPI is widely used in chemical industries as intermediates for synthesis of many

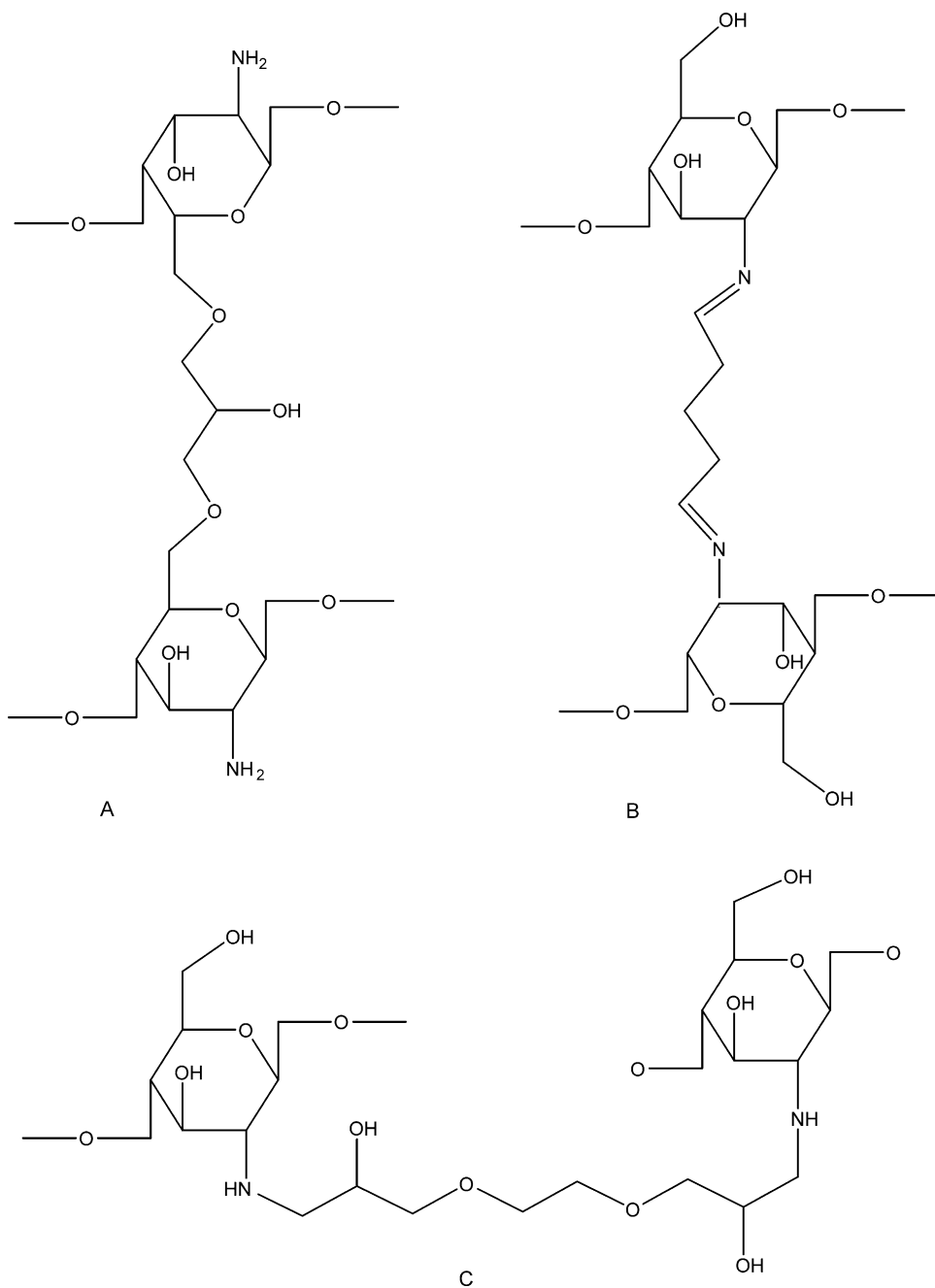


Fig. 2. Schematic representation of crosslinked chitosan beads: (A) chitosan-EPI, (B) chitosan-GLA, and (C) chitosan-EGDE.

products (epoxy-resins, glycerin, polyurethane foam, elastomers, surfactants, lubricants, drugs, etc). EPI, a bifunctional molecule, which contains two functional groups, is highly reactive with hydroxyl groups.

Another advantage of EPI is that it does not eliminate the cationic amine function of chitosan, which is the major adsorption site attracting the pollutant during adsorption. However, EPI is poorly soluble in water

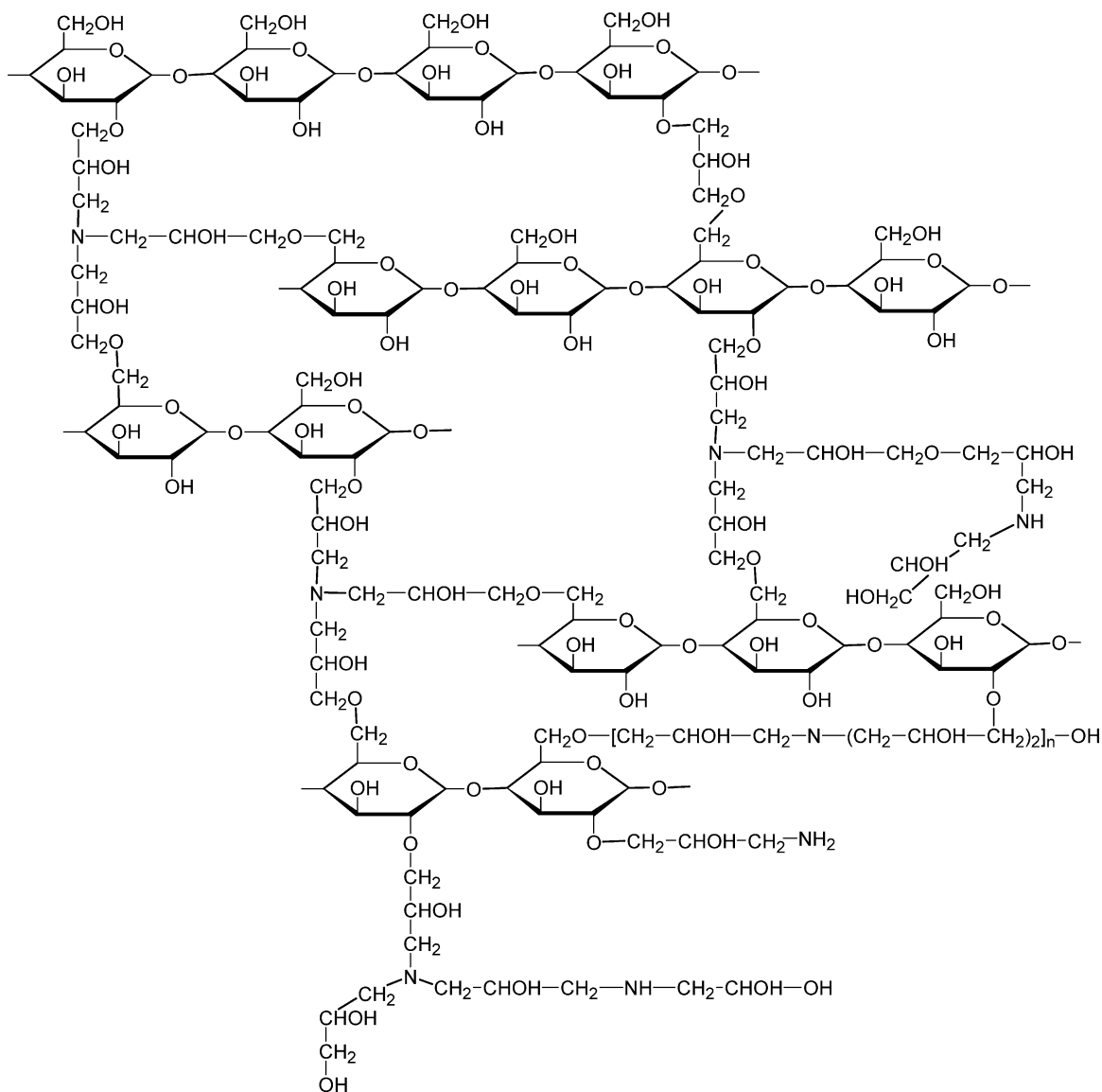


Fig. 3. A possible structure of a crosslinked starch-based ion exchanger.

and partly decomposes to glycerol [110]. Although the crosslinking reaction between EPI and polysaccharides has been known for eighty years [123,124], some basic questions concerning this reaction still continue to interest the scientific community [59,119,125,126]. Dialdehydes such as glutaraldehyde (abbreviated GLA) have also been frequently used to crosslink polysaccharides [93,122,136]. To date, the most common crosslinkers used with chitosan are

GLA [136], although it contains cytotoxic chemical species (GLA is known to be neurotoxic) [78,136]. The reaction occurs through a Schiff's base reaction between aldehyde groups of GLA and some amine groups of chitosan, but links with hydroxyl groups of chitosan cannot be excluded [78]. The precise mechanism of reaction and the structure of the chemical material (see Fig. 2) formed have not been studied in detail [101].

The crosslinking agents cited above are neither safe nor environmentally friendly. So, recently, other water-soluble crosslinking agents have been proposed, such as sodium trimetaphosphate [104], sodium tripolyphosphate [104,135], phosphorus oxychloride [111] or carboxylic acids [108]. For example, citric acid was selected taking into account its non-toxicity, its wide use in the food industry as a safe natural additive, and its high chemical reactivity. The carboxylic acids are interesting because they differ in the length of the spacer and in the kind and number of functional groups on the spacer. This has a significant influence on the sturdiness of the crosslinked gel [108]. Table 2 shows some selected examples of crosslinking polysaccharides used in wastewater treatment.

Crosslinked materials possess several characteristics, properties and advantages.

- Homogeneous crosslinked materials are easy to prepare with relatively inexpensive reagents and are available in a variety of structures with a variety of properties, and also in numerous configurations, e.g. gels, particles of irregular shape or regular beads, membranes, coatings, films, fibers, capsules and sponges.
- They are insoluble in acidic and alkaline mediums as well as organic solvents. Crosslinked gels are very stable hydrophilic polymers. They become more resistant to shear, high temperature and low pH compared to their parent polysaccharide.
- After crosslinking, they maintain their properties, original characteristics (except the crystallinity) and strength in acidic and basic solutions. These characteristics are important for an adsorbent so that it can be used in a lower pH environment. Furthermore, the swelling behavior of the beads in wastewater can be optimized.
- Crosslinking reduces the amount of the crystalline domains in the polysaccharide and can then change the crystalline nature of the raw polymer. This parameter significantly influences the sorption properties because it may control the accessibility to sorption sites.
- Crosslinked beads also have other advantages such as faster kinetics, increased ease of operation [52] and interesting diffusion properties. Due to the hydrophilic nature of their crosslinking units, materials possess a remarkably high swelling capacity in water, and consequently their networks are sufficiently expanded as to allow a fast diffusion process for the pollutants.

Table 2
Recent reports on various crosslinking polysaccharide materials capable of pollutant removal

Polysaccharide	Crosslinking agent	Material obtained	Pollutant	Reference
Chitosan	GLA ^a	Beads	Ni ²⁺ , Cu ²⁺ , Zn ²⁺	[86]
	GLA	Beads	Pd ²⁺	[97]
	EPI ^b	Beads	Dyes	[84]
	GLA	Membranes	Ni ²⁺ , Cu ²⁺	[92]
	Benzoquinone	Beads	Cu ²⁺ , Zn ²⁺	[91]
	GLA, EGDE ^c	Beads	Dyes	[81]
	EPI, GLA, EGDE	Beads	Cu ²⁺	[88]
Starch	EPI	Gels	phenols	[109]
	EPI	Gels	Dyes	[106]
	EPI	Beads	Dyes	[105]
	POCl ₃	Beads	Pb ²⁺ , Cu ²⁺ , Cd ²⁺	[111]
Cyclodextrin	EPI	Beads	Organics	[114]
	EPI	Beads	Bile Acids	[121]
	EPI	Gels	Organics	[59]
	EPI	Gels	Phenols	[138]
	EPI	Gels	Beta-naphtol	[116]
	EPI	Gels	Dyes	[112]

^a Glutaraldehyde.

^b Epichlorohydrin.

^c Ethylene glycol diglycidyl ether.

- Even though crosslinked polysaccharides have good sorption properties, their adsorption capacities can be improved by the grafting of various functional groups onto the polymer network or the polymer backbone [79,80]. This increases the density of sorption sites. The presence of new functional groups on the surface of the beads results in an increase of surface polarity and hydrophilicity and this enhances the sorption of polar sorbates and improves the sorption selectivity for the target pollutant. Chemical processes are also used for changing the pH range for optimum sorption, for controlling diffusion properties, and for decreasing the sensitivity of sorption to environmental conditions [79,96]. The grafting of carboxyl groups [75], amine functions [80,82] and sulfur compounds [79,87] has been regarded as an interesting method for these purposes. Other examples can also be found in the review by Kurita [122]. Fig. 4 shows some examples of chemical derivatization of chitosan.
- After adsorption, the crosslinked materials can also be easily regenerated by washes using a solvent or by solvent extraction.

Despite these numerous properties and characteristics, crosslinked materials have not been used at the industrial scale. There are several reasons for explaining this difficulty in transferring the process to industrial applications. They can be summarized as follows:

- The variability in the bead characteristics. The choice of the crosslinking agent has a significant influence on the adsorption properties because the chemical structure of the synthesized beads depends on the nature of the crosslinking agent and the degree of crosslinking [81,88,95]. Seidel et al. [108] showed that the crosslinking agent has a significant influence on the sturdiness of the material. Crosslinking alters both the physical properties and the thermal transition characteristics of the polymer [104]. Cyclodextrin or starch crosslinked gels exhibit poor mechanical properties, except for hypercrosslinked beads, and their use in sorption columns is limited. In this case, it is important to control the reticulation rate. The characteristics of the particles (shape, size and density) can also introduce hydrodynamic limitations and column fouling, which limits the use of these materials for large-scale columns.
- The conditions of the crosslinking reaction. It is important to control and characterize these conditions, since they determine the modulation of the crosslinking density, which is the main parameter influencing adsorption properties of the material [78]. The selectivity success also depends strictly on the crosslinking density, and in this case diffusion of pollutants into the polymer matrix becomes slower as the crosslinking density increases. It is well-known that, generally, the adsorption capacity decreases with increases in the extent of crosslinking. At higher levels of crosslinking the beads have lower swelling capacities. The accessibility decreases as a result of a more extensive three-dimensional network [110] and an increase in the hydrophobic character. This phenomenon can also be interpreted in terms of decreased hydrophilicity caused by the destruction of the crystalline structure.
- The stability, mobility and accessibility of the polysaccharide. Although crosslinking enhances the resistance of polysaccharide against acid, alkali and chemicals it involves a loss in the chain flexibility [110], a reduction of the mobility of chelating groups and their accessibility, and as a result causes a significant decrease in pollutant uptake efficiency and adsorption capacities of the adsorbent. However, this loss of capacity may be necessary to ensure the stability of material [52]. This restricting effect may be decreased using chitosan whose structure has been physically modified. The physical modification allows both the polymer network to be expanded (in order to enhance the diffusion of large size molecules) and the crystalline state of the polymer to be reduced [94].
- The variability in the sorption properties. It is well known that chitosan beads show higher adsorption capacity than crosslinked chitosan beads, however, the latter can be used in low pH solutions. When chitosan beads were crosslinked with glutaraldehyde, it was found that the saturation adsorption capacity of Cd^{2+} on crosslinked chitosan decreased exponentially from 250 to 100 mg/g as

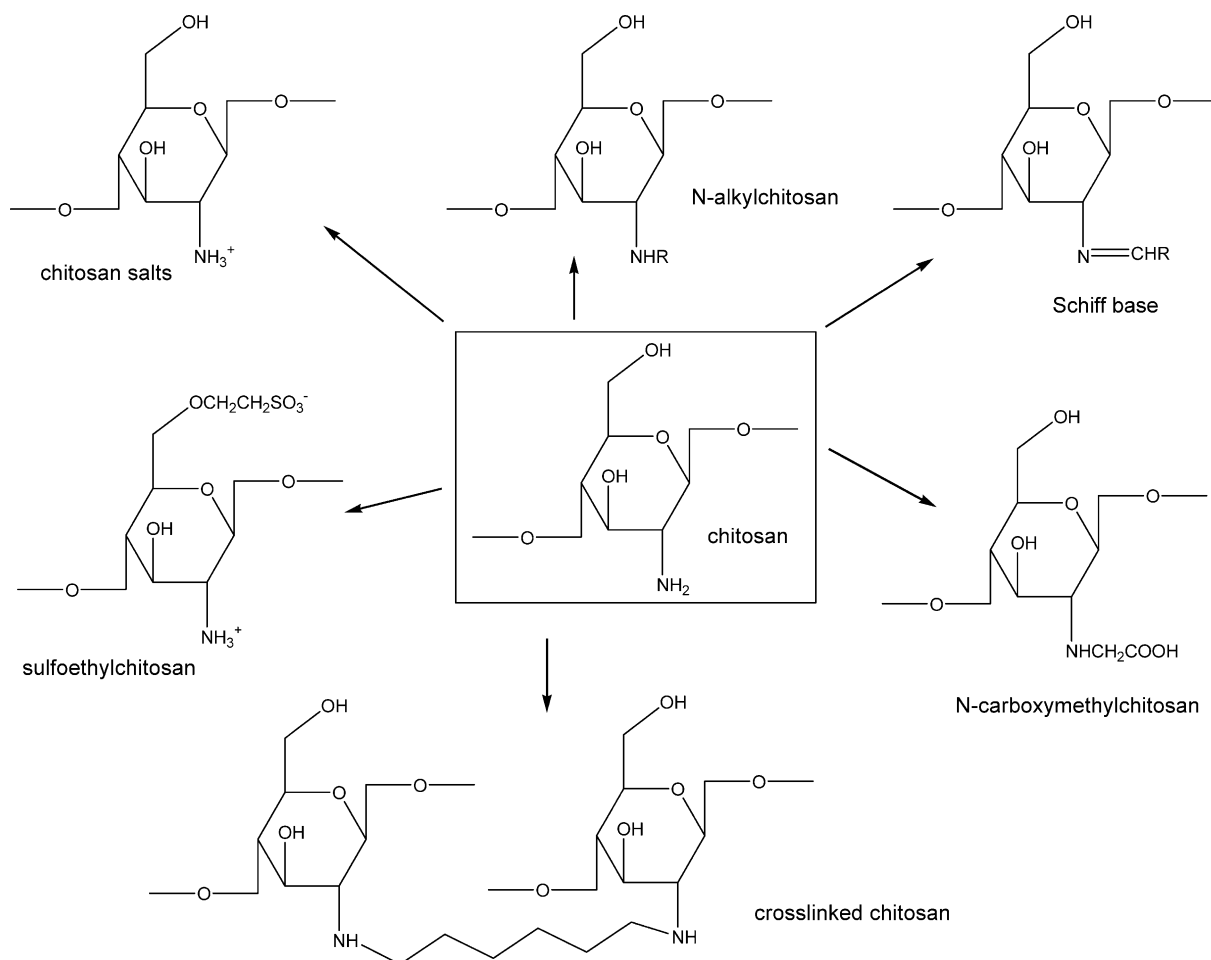


Fig. 4. Examples of chemical derivatization of chitosan.

the extent of crosslinking increased from 0 to 1.3 mol glutaraldehyde/mol of amine [57]. This is because of the restricted diffusion of pollutants through the polymer network and reduced polymer chain flexibility. Another explanation for this decrease is the loss of amino binding sites by reaction with crosslinking agents. The reaction of chitosan amine groups with GLA leads to a decrease in the number of free amine groups [94]. Consequently, these functional groups are no longer available for complex formation, and the adsorption capacity can decrease, especially in the case of metal ions sorbed through chelation mechanisms. In order to minimize this effect, an effort must be made to keep the degree of

crosslinking as low as possible. The amount of free amine groups that will be available for interactions with pollutants is thus a key parameter.

Recently, some novel crosslinked procedures [128–138] have been reported. Güven et al. [128,129] and Yoshii et al. [130–133] proposed to apply irradiation in order to induce crosslinking in polysaccharides. The preparation of gels by radiation treatment (ionizing radiation, gamma rays or electron beam) carries some advantages over the conventional methods. It does not require crosslinking agents (or initiators) and the reaction can be initiated at ambient temperature. The method is relatively simple and the process control is easy [128]. The degree of

crosslinking, which strongly determines the extent of properties in gels, can be easily controlled by varying the irradiation dose. In the synthesis of gels by chemical methods, crosslinking density is controlled by the concentration of the crosslinker, reaction time, temperature and others. While for the radiation method it is determined by the absorbed dose, which means by the irradiation time. Moreover, crosslinking by the chemical method can be performed only in liquid state. Since the ionizing radiation is highly penetrating, it is possible to initiate chemical reactions in liquid or in solid state. Recently, Zhao et al. [131] have applied for the first time, irradiation to prepare gels from chitin. They synthesized a series of novel gels of carboxymethylated chitin derivatives by electron beam and their characteristics are being studied in detail. Yamamoto and Tagawa [134] prepared a gel containing cyclodextrin by a radiation-induced gelation method.

Shyu et al. [135,136] reported the preparation of crosslinked chitosan microspheres using a coupled ionic and chemical co-crosslinking mechanism. Tripolyphosphate (TPP), a non-toxic polyanion and a naturally occurring crosslinking reagent, genipin, were employed, respectively as ionic and chemical crosslinkers to prepare chitosan gel beads. TPP can be used for the preparation of chitosan beads because of its quick gelling ability. The beads are significantly less cytotoxic than those crosslinked by GLA, thus, they can also be used for various biomedical applications. Cao et al. [137] proposed crosslinked chitosan resins prepared by microwave irradiation. Janus et al. [59,138] reported the synthesis of new monomers by grafting vinyl groups on polysaccharides. These new derivatives have the advantage of being a monomer ready to polymerize by reticulation, which allows the introduction of a polysaccharide into a material without the usual methods of chemical crosslinking of the polymer.

Despite the fact that crosslinked chitosan beads are a promising alternative to replace activated carbons or ion-exchange resins, more studies are needed to demonstrate the possible technology on an industrial scale. In addition, although a number of new useful crosslinked materials have been produced through crosslinking reactions and were used for wastewater applications, the crosslinked gels containing starch or cyclodextrin are not suitable for solid phase extraction

and their use as adsorbents in sorption columns is limited, since they present a poor mechanical strength, low surface area, non-porosity, and hydrodynamic limitations. Another drawback of crosslinked gels is their high water content, and as a result, a decrease in the density of sorption sites. For these reasons, as alternative, much attention has recently focused on the preparation of materials with polysaccharides chemically bonded to a support in order to yield materials with the required mechanical and diffusion properties, as shown in the next section of this review.

3.2. New hybrid adsorbents materials

Another typical approach to produce materials containing polysaccharides is to bind these macromolecules to a pre-existing insoluble matrix via several spacer arms using grafting reactions, in a way that allows the biopolymers to interact freely with the pollutants and to control the number of available sorption sites. These modified matrices are so-called immobilized polysaccharide resins, composite materials or hybrid adsorbents. Various composite materials have been manufactured and reported to exhibit unique properties. They have a variety of current and potential applications in chromatography fields, as chelating agents, in cleaning up pollution, etc.

In wastewater treatment, composite materials are of interest because they present several advantages:

- They combine the structure, strength and chemical properties of a support with the specific characteristics of polysaccharide. However, the major challenge is to select the most promising types of pre-matrix from a wide range of available supports. The matrix must present high mechanical strength and interesting physical and chemical properties such as an important surface area and a good porosity.
- If a proper and inexpensive support is used to immobilize biopolymers much lower quantities of polymer are needed to build the adsorbent materials.
- This synthetic approach provides two interesting properties. First, the molecular mobility of chelating groups of polysaccharides are not affected during grafting, while crosslinking reduces the mobility of ligand groups and as a result,

the pollutant chelating efficiency. The mobility of the chelating groups is a key parameter because it influences the sorption capacity, the diffusion properties and the uptake kinetics. Secondly, the presence of polysaccharides on the surface of beads results in an increased accessibility of the complexing groups. Since grafted chains of polymers have much more flexibility and are more accessible, the materials are expected to show rapid pollutant binding ability.

- This approach is also interesting because it permits to introduce others ligands (existing in the matrix) into the material, capable of, for example, coordination with a wide range of metal ions, by introduction of additional interactions so that the sorption capacity increases. Thus, hybrid materials containing polysaccharides display much better adsorption capacity than any of its components used alone (matrix or polysaccharide) [59].
- Biopolymers can also be easily modified if required by chemical processes such as grafting of functional groups. The chemical modification of composite materials may be justified by four objectives: (i) controlling and improving the affinity of the material for the pollutant; (ii) changing the selectivity series for sorption; (iii) enhancing sorption kinetics; (iv) improving the stability of the material. However, modifications of hybrid materials must be conducted under heterogeneous conditions and are usually accompanied by some difficulties arising from their insolubility and the polyfunctionality of the macromolecule. In order to prepare hybrid materials with unique properties and thereby to develop and manufacture advanced functional materials, it is also important to manipulate the polymer reactions in a well-controlled manner.
- The control of matrix conditioning may be helpful for designing the sorption process. The hybrid adsorbents can be used in batch methods, in fixed-bed systems or packed in sorption columns. The use of columns is perhaps the most effective device for the continuous removal of pollutant. One of the most interesting advantages of using sorption columns is the easy recycling of the sorbent after sorption and also desorption which can be carried out in the same column.

- Immobilization on a solid matrix has the advantages of high stability, recoverability and reutilization.

Recently, an important number of new hybrid materials [139–170] for the removal of pollutants from aqueous solutions have been successfully prepared and described, using both mineral and organic matrices such as glass beads [139,140], silica gel [59,119,138,141–143], polyamine beads [59,144,145], sand [146], alginate beads [147], polyethyleneterephthalate [148], polyurethane [149], polyvinylalcohol [150,151], polysiloxane [152], alumina [153], polyacrylic acid [154], polypropylene [155,156], polyester [157,158], etc.

In general, polysaccharides can be bonded to organic beads, membranes or films using chemical reactions or radiochemical techniques (e.g. graft polymerization, irradiation, electron beam activation). Amongst the numerous techniques of synthesis, the radiochemical method is one of the most promising techniques for modifying physical and chemical properties of polysaccharides. It is a potential alternative to conventional chemical methods. The method consists of activation of the support by irradiation, followed by graft polymerization of a reactive monomer is convenient and effective, because of its moderate initiation reaction conditions (ambient temperature, atmospheric pressure). Another advantage is the fact that grafting can be realized simultaneously or after radiation [154,155]. Most graft polymers are formed by radical polymerization. Graft polysaccharides containing reactive pendant groups are becoming increasingly important because of their large potential application in the industry.

Porous silica is one of the ideal rigid supports, which can be made with large and narrow pore size distribution. There are two main chemical methods reported to synthesize modified silica beads containing polysaccharides: the first one is to bind chemically these macromolecules to silica gel. The second method consists in coating the polymer onto the surface of silica beads. A comprehensive review of the chemistry and various approaches used in cyclodextrin-based silica materials preparation can be found in the recent compilation by Crini and Morcellet [59].

Another interesting idea is to combine the properties of two polysaccharides [159–166]. As already

mentioned, chitosan is a multifunctional polymer that has primary and secondary hydroxyl groups as well as highly reactive amino groups. It has been regarded as a useful starting support for various purposes. Numerous investigations on chemical activation of chitosan have been carried out to introduce novel functions into this biopolymer. In addition, the applications of chitosan are often common to those of cyclodextrin. Thereby, attempts were made to prepare adsorbents by coupling chitosan and cyclodextrin via several spacer arms without affecting the adsorption capacity and selectivity of the two polymers. CD can be bonded to chitosan via several spacer arms and these methods can be classified into three main types. First, a reactive group of a spacer arm coupled to a CD molecule is reacted upon with amino groups on the surface of chitosan. Secondly, part of a spacer arm is coupled to chitosan and another part to the CD, immobilization then consists in the reaction of these reactive groups of these parts. Thirdly, a spacer arm is grafted onto crosslinked chitosan beads and the CD is reacted with the reactive terminal group of the spacer arm. The novel resins containing both cyclodextrin and chitosan are in general more hydrophilic than synthetic resins made of such base polymers as polyethyleneimine, polystyrene or poly(styrene-divinylbenzene); therefore, the rate of chelate formation can be expected to be increased. Such resins can be applied to the simultaneous adsorption of heavy metals and aromatic compounds.

The first results concerning the preparation of chitosan beads with pendant cyclodextrins were reported by Tojima et al. [163]. The chitosan was crosslinked using hexamethylene diisocyanate as crosslinking agent. The beads containing amino groups were functionalized by CD using the 2-*O*-formylmethyl-cyclodextrin as the intermediate. The method presents two main disadvantages: it was necessary to crosslink chitosan before connecting the CD and to control the reaction. In other works, Sakairi et al. [164, 165] proposed two methods for the coupling reactions: condensation of carboxymethylated CD with chitosan oligomers, and reductive amination of (formylmethyl)-CD with chitosan. The later method was applicable to the synthesis of high molecular weight material. However, the methods introduced by Tojima and Sakairi also give an adsorbent with low CD

contents. For these reasons and in order to improve the methods, Aoki et al. [159] proposed chitosan bearing CD moieties prepared by a one-step procedure with *N*-succinylated chitosan and an amino-CD derivative in the presence of carbodiimide. The advantage of the method is that the reaction begins under homogeneous conditions allowing supports with a high CD content to be obtained. Another methodology was proposed by Martel et al. [162] They used a monochlorotriazinyl derivative of CD as the chemical reagent. This reactive derivative allowed the anchoring of the CD to chitosan through the nucleophilic substitution of the chloride atom by the amino groups.

4. Sorption mechanisms

The first major challenge for the adsorption field is to select the most promising types of sorbent from an extremely large pool of readily available materials. The next real challenge is to identify the sorption mechanisms. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle. Adsorption studies, in particular kinetics and isotherms, provide information on the mechanism of sorption: how is the pollutant bound within the sorbent. This knowledge is essential for understanding the sorption process and for selecting the desorption strategy.

Due to the complexity of materials used and their specific characteristics (such as the presence of complexing chemical groups, small surface area, poor porosity), the sorption mechanism of polysaccharide-based materials is different from those of other conventional adsorbents. These mechanisms are, in general, complicated because they implicate the presence of different interactions [51,136]. In addition, a wide range of chemical structures, pH, salt concentrations and the presence of ligands often add to the complication.

Some of the reported interactions include:

- Ion-exchange
- Complexation
- Coordination/Chelation
- Electrostatic interactions

- Acid–base interactions
- Hydrogen bonding
- Hydrophobic interactions
- Physical adsorption
- Precipitation.

An examination of the data in the literature indicates that it is quite possible that at least some of these mechanisms are to varying degrees acting simultaneously depending on the chemical composition of the sorbent, the nature of the pollutant and the solution environment.

The direct consequence of the interaction of chitosan with metal species (or dyes) is that the interaction, and thus the adsorption, is strongly dependent on pH [51,57,97]. Metal complexation by chitosan may thus involve two different mechanisms (chelation versus ion exchange) depending on the pH since this parameter may affect the protonation of the macromolecule [57]. Chitosan is characterized by its high percentage of nitrogen, present in the form of amine groups that are responsible for metal ion binding through chelation mechanisms. Amine sites are the main reactive groups for metal ions though hydroxyl groups, especially in the C-3 position, and they may contribute to adsorption [51,57]. However, chitosan is also a cationic polymer and its pKa ranges from 6.2 to 7 (depending on the deacetylation degree and the ionization extent of the polymer) [79]. Thereby, in acidic solutions it is protonated and possesses electrostatic properties. Thus, it is also possible to sorb metal ions through anion exchange mechanisms [97]. Although several contradictory mechanisms have been proposed, metal adsorption on chitin and chitosan derivatives is now assumed to occur through several single or mixed interactions including (i) chelation interaction (coordination) on amino groups in a pendant fashion or in combination with vicinal hydroxyl groups, (ii) complexation phenomena (electrostatic attraction) in acidic media, (iii) ion exchange with protonated amino groups through proton exchange or anion exchange, the counter ion being exchanged with the metal anion [51,97]. Physical adsorption plays little role in the interaction between crosslinked chitosan beads and pollutants because beads have a small surface area. The pH may also affect the speciation of metal ions, and changing the speciation of the metal may result in

turning the chelation mechanism into the electrostatic attraction mechanism. Another parameter can play an important role in the mechanism: the presence of ligands grafted on the chitosan chains.

For crosslinked starch materials, physical adsorption in the polymer structure and chemisorption of the pollutant via hydrogen bonding, acid–base interactions, complexation and/or ion exchange are both involved in the sorption process [105,106]. In most cases, though a combination of these interactions were proposed to explain adsorption mechanisms, the efficiency and the selectivity of these adsorbents are mainly attributed to their chemical network. When the materials contain cyclodextrin molecules, the mechanism is due to the formation of an inclusion complex between the CD molecule and the pollutant through host–guest interactions. It has also been reported that the presence of pollutant–pollutant hydrophobic interactions can explain the adsorption properties [105,112].

Despite the large number of papers dedicated to the removal of pollutants by hybrid materials, most of them focus on the evaluation of sorption performance and only a few of them aim at gaining a better understanding of sorption mechanisms. This can perhaps be explained by the fact that the mechanisms are even more complex, since not only does the polysaccharide play a role in the sorption but also the pre-matrix. So, it is important to observe that different kinds of interactions can act simultaneously. However, recent studies have indicated that, in general, a given pollutant-binding mechanism plays a dominant role in the sorption. For example, in the grafted or coated silica-based sorbents containing biopolymers, the formation of interactions between the polymer and the pollutant mainly explain the mechanism though the mineral matrix may contribute to sorption [142,143]. Morcellet and Crini [59,145] demonstrated that in the case of organic beads containing amine functions grafted by cyclodextrins used as sorbents, the sorption mechanism is due to the formation of an inclusion complex between the cyclodextrin molecules and the pollutant through host–guest interactions. However, even though the cyclodextrins play a dominant role, physical adsorption in the resin polymer network and chemical interactions via acid–base interactions, ion-exchange and hydrogen bonding due to the amino groups are also involved in the sorption process.

These interactions are significant. The authors also showed that the adsorption is strongly dependent on pH. The nature of the bonds between pollutants and these material surfaces depends on the extent of the acid–base interactions. For weak acid–base interactions, only hydrogen bonds may be formed. For strong acid–base interactions, the interactions may gradually change to a chemical complexation. The presence of co-existing interactions between the pollutants and the sorbent matrix must be taken into account for the regeneration of the loaded sorbent.

Although much has been accomplished in the use of polysaccharide-based materials as sorbents in terms of kinetics and sorption capacities, much work is still necessary to identify clearly the sorption mechanism.

5. Regeneration, stability and reproducibility

The regeneration of the sorbent may be crucially important for keeping the process costs down and to open the possibility of recovering the pollutant extracted from the solution. For this purpose, it is desirable to desorb the sorbed pollutants and to regenerate the material for another cycle of application. The desorption side of the process should yield the pollutants in a concentrated form and restore the material close to the original condition for effective reuse with undiminished pollutant uptake and no physical change or damage. In view of industrial developments of the various kinds of sorbents described in the literature, the stability of the materials and the reproducibility of the sorption properties is also of utmost importance. Unfortunately, in the area of recovery of pollutants from polysaccharide-based materials, the regeneration of spent sorbents, the stability and reproducibility of the sorbents, a literature survey produces very little information except in recent publications. Crini [112] demonstrated the reproducibility of the sorption properties of cyclodextrin polymers used as sorbents for the removal of various dyes and the regeneration of the sorbents after saturation. Since the interactions between the pollutant and cyclodextrin are driven mainly by hydrophobic interactions, organic solvents are good candidates for the regeneration of the material. As a result, the polymers were easily regenerated using ethanol as the washing solvent. The sorption capacity value

remained unchanged after this treatment. This showed the chemical stability of crosslinked gels and reproducibility of the values. Delval et al. [105] showed that crosslinked starches were easily regenerated using soxhlet extraction with ethanol rather than water, and the adsorption capacity of adsorbent in batch experiments remained constant. Kim and Lim [111] reported that crosslinked-starch derivatives can be easily regenerated by a weak acidic washing. Crosslinked chitosan beads can be easily regenerated using EDTA (a strong chelating agent) solutions, as demonstrated by Wan Ngah et al. [88]. The complexation of the pollutant by the ligand displaces the pollutant from the material. The free electron doublet of nitrogen on amine groups is known to be responsible for the sorption of metal cations on chitosan derivatives and the sorption usually occurs at a pH close to neutral. The desorption can then be carried out by contact with an acidic solution. This change in the pH of the solution reverses the sorption because the chelation mechanism is very sensible to pH.

Modified silica beads were reported to keep a constant capacity towards phenolic compounds after several cycles of sorption and regeneration with methanol [34,142,143]. However, the question of the long term stability of these sorbents is posed in different ways depending on whether they are prepared by grafting or coating. In the former case, the main factor is the stability of the covalent bond between the polysaccharide and the matrix. In spite of rather good results in terms of adsorption capacity, some stability problems were encountered with the grafted silicas [142]. When the coating method is used, the stability depends on the strength of the interactions between the polymer and the silica surface. In order to increase the stability and to avoid the desorption of the polymer, several researchers proposed a crosslinking reaction, after the coating of the polymer. Bacquet et al. [143] showed that for equal CD content, the coated supports are better than grafted supports.

6. A brief review of the adsorption of pollutants by polysaccharide-based materials

In this section, a brief and recent review of the adsorption of various pollutants by polysaccharide-based materials is described. This review, which is not

exhaustive, shows some selected examples of adsorbents used in wastewater treatment. Reported adsorption capacities are noted when possible to give an idea of the adsorbent effectiveness. In liquid-phase adsorption, it is commonly known that adsorption capacities of an adsorbent is attributed to many factors and the adsorbate–adsorbent interaction play an important role as well as that between adsorbate and water. The control of sorption performances of a sorbent depends on the following physicochemical factors: firstly, the nature of the adsorbent such as its physical structure (porosity, surface area, particle size), its chemical structure (ionic charge) and functional groups (variety, density); secondly, the chemistry and accessibility of the adsorbate (e.g. its pK_a , polarity, functionality, molecular weight and size); and finally, the solution conditions, referring to its pH, ionic strength, temperature and the adsorbate concentration. Consequently, the reader is encouraged to refer to the original papers for information on experimental conditions. Furthermore, the reported adsorption capacities may be taken as an example of values that can be achieved under specific conditions rather than as maximum capacities.

6.1. Removal of pollutants by chitosan beads

A large number of chitosan-based sorbents have been tested for their pollutant-binding capability under various conditions. The adsorption of dyes onto crosslinked chitosan beads has been investigated by Chiou and Li [81,84]. Chitosan-based materials were prepared using GLA, EPI and EGDE as crosslinking agent. The beads have a high adsorption capacity: 1642 g of reactive dye 189 can be treated by 1 kg of material. The dye uptake increased with a decrease in the particle size since the effective surface area is higher for the same mass of smaller particles. The adsorption is influenced by the temperature and the EPI/chitosan weight ratio. They showed that the chitosan–EPI beads presented a higher adsorption capacity than GLA and EGDE resins. Although the beads had a high adsorption capacity, they were soft beads and the mechanical properties needed to be improved for practical applications. In another recent work [76], they prepared new beads crosslinking using TPP in order to produce more rigid beads. The adsorption capacities had very large values of

1911–2498 g of dye per kg of bead. Wan Ngah et al. [88] used the same adsorbents for the removal of Cu^{2+} from aqueous solutions. The uptakes on chitosan–GLA, chitosan–EPI and chitosan–EGDE beads were respectively: 59.6, 62.4 and 45.9 mg Cu^{2+} /g beads. The metal adsorption was highly pH-dependent. The beads can be easily regenerated. Ruiz et al. [97] proposed the use of GLA–chitosan beads as effective chelating resins for removing palladium from dilute solutions. Sorption kinetics are controlled by particle size, crosslinking ratio, and palladium concentration. The adsorption of heavy metals onto crosslinked chitosan beads has been also investigated by Juang and Shao [86,90]. They showed that the adsorption capacity depends on the nature of the crosslinking agent. The adsorption increased with increasing pH of the solution, due to competitive adsorption of proton and metals.

An important work on chitosan derivatives was done by Guibal and co-workers [79,82,87,89,96,98–100,103]. They reported that crosslinked chitosan beads can be used for the removal and the recovery of toxic or valuable precious metals such as arsenic [89], molybdenum [99,103], vanadium [103], platinum [96,100], palladium [87], osmium [82], iridium [82] and gold [79]. For example, chitosan beads containing sulfur groups are very efficient at removing gold from dilute acidic solutions: maximum uptake capacity reaches 600 mg of Au per gram of beads [79]. Chitosan-based materials can be used not only for the decontamination of effluents but also for the recovery of valuable metals. They introduced a new procedure for the production of molybdate-impregnated chitosan sorbent. The impregnation was performed by direct coagulation in a molybdate bath [89]. These modified beads were tested for As(III) and As(V) removal from solutions with success.

Recently other modified chitosan beads were proposed. Krajewska [92] studied the diffusion of metal ions through chitosan membranes crosslinked by GLA. The results were compared with those obtained using a commercial cellulose membrane. The study showed that chitosan membranes offered a potential for protecting the environment against heavy metal ions. Lee et al. [136] proposed the use of spherical chitosan–tripolyphosphate chelating resins as sorbents for the removal of Cu(II). The excellent saturation sorption capacity at pH=5 was about

200 mg of Cu(II) per gram of beads at an initial concentration of 1000 ppm of Cu(II). The kinetics data revealed that the intraparticle diffusion is the rate-limiting step for the adsorption of Cu(II) onto beads. Cao et al. [137] studied the adsorption properties of crosslinked chitosan using Cu(II) as a template under microwave irradiation. The results showed that the resins have a better adsorption capacity and selectivity of Cu(II) than Ni(II) and Co(II).

6.2. Crosslinked starch and starch derivatives used in wastewater treatment

From the literature data, it is clear that for decontamination applications, the principal polysaccharide derivative of interest is chitosan. However, increasing recent attention is being given to the other carbohydrate polymers such as starch and cyclodextrins.

Zhang and Chen [107] proposed crosslinked-starch graft copolymers containing amine groups. The polymers, used as the sorbents for Pb(II) and Cu(II) ions, were prepared by grafting dimethylaminoethyl methacrylate onto commercial starch. It was found that 2 h of adsorption is sufficient for reaching the adsorption equilibrium and the adsorption capacity is important. However, due to the protonation and deprotonation of the amine groups on the surface of the sorbent, its adsorption behavior for metal ions is influenced by pH. Starch after crosslinking with POCl₃ and carboxymethylation has been proposed by Kim and Lim [111] as sorbents for the removal of heavy metal ions. Several hundred ppm of divalent metal ions (Cu, Pb, Cd and Hg) could be effectively removed from water by dispersing 1% of the modified starch within a few minutes. The kinetics are fast and the sorption capacities are significant. However, the removal efficiency of the metal ions depends on the carboxymethyl group and the starch content present in the solution.

Crosslinked starches with EPI have been proposed by Delval et al. [109] as adsorbents for the recovery of various organic pollutants from aqueous solutions. The particles can be packed in sorption columns, which are perhaps the most effective devices for the continuous removal of pollutants. In two other works [105,106], they prepared crosslinked starch

containing tertiary amine groups by reticulation of a starch-enriched flour in the presence of NH₄OH. These new beads exhibit high sorption capacities towards textile dyes. The kinetics of sorption are dependent on the presence of amino groups.

Several crosslinked cyclodextrins gels were prepared by Crini and Morcellet [59,112]. They proposed the use of these gels for the removal of various aromatic derivatives (chloro and nitro phenols, benzoic acid derivatives, dyes) from aqueous solutions. Results of adsorption experiments showed that these crosslinked polymers exhibited high sorption capacities. In another work, they proposed the synthesis of cyclodextrin-carboxymethylcellulose gels [116]. They modified the condensation process with EPI by working under different homogenous conditions. Results obtained with these gels showed that effective and efficient extraction of beta-naphthol is achieved. The presence of carboxyl groups in the polymer networks permit to increase significantly the sorption properties. Janus et al. [138] proposed the use of 2-hydroxy-3-methacryloyloxy-propyl-beta-cyclodextrin as monomer for the synthesis of cyclodextrin-based materials. New hydrophilic CD adsorbents were prepared by radical copolymerization in water using 2-hydroxyethyl methacrylate or vinylpyrrolidone as co-monomers. Several materials with various degrees of CD were synthesized and then used for waste water treatment. The results of sorption experiments showed that they exhibit high sorption capacities toward benzene derivatives. The control of the crosslinking reaction is the key parameter, which allows to improve the sorption properties of the material.

A novel solid phase extraction procedure for trace aromatic compounds in water has been developed by Yu et al. [114]. The method which is based on the use of cyclodextrin-EPI copolymer as adsorbent has high extraction efficiency with recoveries between 90 and 100% for aromatic compounds at 0.02–1.67 ppm. To improve the rigidity of the bead it is necessary to increase the amount of EPI. It is possible to selectively extract a species at a specific pH. Kitaoka and Hayashi [117] described the possibility of the removal of Bisphenol A (BPA) by using an highly crosslinked cyclodextrin-EPI copolymer. By stirring 5 mg/ml of copolymer in a 0.2 mmol BPA solution for 2 h, more than 98% of the BPA was removed.

6.3. Adsorption of pollutants on various composite materials

Liu et al. [139,140] prepared new hybrid materials that adsorb transition metal ions by immobilizing chitosan on the surface of non-porous glass beads. Column chromatography on the resulting glass beads revealed that they have strong affinities to Cu(II), Fe(III) and Cd(II). Fan et al. [141] proposed the use of a cyclodextrin bonded silica as sorbent for on-line solid-phase extraction coupled to a chromatographic system. The sorbent showed strong capacity in adsorbing *p*-nitrophenol. Bacquet et al. [142,143] studied different series of supports containing cyclodextrin for their ability to sorb aromatic pollutants. The sorbents are obtained by grafting or coating cyclodextrin derivatives (in particular, monochlorotriazinyl and methacryloyl derivatives) [142]. The sorption capacities of the two kinds of supports was very close for a given pollutant. The adsorption isotherms were correlated with the Langmuir and Freundlich models and permit to conclude that the sorption mechanisms depend mainly on the structure and the concentration of the pollutant [143]. The sorption capacities depend on the cyclodextrin content. However, the authors concluded that it is unnecessary to have a high CD content to improve the sorption.

Macroporous polyamines containing CD have been used by Crini et al. [59,145] for the recovery of various organic pollutants from aqueous solutions. The results of sorption experiments showed that these sorbents exhibit high sorption capacities toward substituted phenolic derivatives. The adsorption efficiency of the sorbent was confirmed. However, the selectivity was not obvious due to the co-existing interactions between the pollutants and the sorbent matrix.

Other mixed materials have been prepared and reported to exhibit novel adsorption properties. Wan et al. [146] proposed a new hybrid adsorbent based on chitosan immobilized on sand. The sorption results indicated the possibility of using chitosan-coated sand to build inexpensive large-scale barrier filters for metal removal from moving contaminated ground-water plumes. Alginate–chitosan hybrid gel beads were prepared by Gotoh et al. [147] for the first time and shown to very rapidly adsorb heavy metal ions.

Polyurethane membranes containing CD were prepared by Lue and Peng [149] using a two-stage synthesis procedure. The modified membranes demonstrated outstanding pervaporation properties on benzene/cyclohexane separation. The CD membrane is also excellent compared with other polymer membranes in terms of its permeability and selectivity properties. Polyvinylalcohol membranes filled with CD were prepared by Chen et al. [151]. Pervaporation experiments for separation of xylene mixtures were carried out. The results indicated that the new membranes effectively improved the pervaporation performance. Steenkamp et al. [153] investigated the capacity of Cu(II) adsorption on composite alumina/chitosan membranes. Capacity of adsorption was about 0.2 g Cu²⁺/g chitosan. These hybrid materials are preferred due to their chemical stability as a function of pH. Le Thuaut et al. [155,156] proposed a novel method for the preparation of immobilized CD on polypropylene non-woven fabrics. The new materials were prepared by graft-polymerization of glycidyl methacrylate onto filters using the electron-beam technique, following the coupling of CD with the epoxide group.

Aoki et al. [159] reported that the chitosan derivatives bearing CD are efficient as sorbents for the selective extraction of *p*-nonylphenol and bisphenol A. Martel et al. [162] proposed the coupling of a monochlorotriazinyl derivative of CD to chitosan in order to obtain a new kind of insoluble composite material. Decontamination of water containing textile dyes was carried out with these insoluble polymers. The results showed that the new derivatives exhibit excellent sorption properties toward dyes. Tojima et al. [163] covalently immobilized cyclodextrin to chitosan beads via a reductive amination strategy. The ability of these CD-linked chitosan sorbents to form inclusion complexes with *p*-nitrophenol was validated. Wang et al. [167–170] proposed the use of chitosan derivatives containing crown ether. The materials had high adsorption capacity for Pb(II), Cr(III), Cd(II) and Hg(II) and their selectivity properties were better than crosslinked chitosan without crown ether. The material can be regenerated. This is interesting because it is known that crown ethers are not recycled easily after being used and their applications are limited.

7. Advantages and possible drawbacks of using polysaccharide-based materials for adsorption

7.1. Advantages of using natural materials for adsorption

Generally, a suitable adsorbent for adsorption processes of pollutants should meet several requirements: (i) efficient for removal of a wide variety of target (hydrophobic) pollutants; (ii) high capacity and rate of adsorption; (iii) important selectivity for different concentrations; (iv) granular type with good surface area; (v) high physical strength; (vi) able to be regenerated if required; (vii) tolerant for a wide range of wastewater parameters; (viii) and low cost.

Compared with conventional sorbents for removing pollutants from solution, such as commercial activated carbons and synthetic ion-exchange resins, the sorption using polysaccharide-based materials as sorbents offers several advantages (Table 3):

- The sorbents are low-cost materials obtained from natural raw resources. The majority of commercial polymers and ion-exchange resins are derived from petroleum-based raw materials using processing chemistry that is not always safe and environmentally friendly. Today, there is a growing interest in developing natural low-cost alternatives to synthetic polymers. Polysaccharides can be used for this purpose.
- The use of biosorbents is extremely cost-effective. Crosslinked materials are easy to prepare with relatively inexpensive reagents (low operating cost). The volume of sorbent used is, in general, reduced as compared to conventional sorbents since they are more efficient. Much lower quantities of biopolymer are needed to build the hybrid materials. Activated carbon and synthetic ion-exchange resins are quite expensive, and the higher the quality, the greater the cost. Moreover, the volume of sorbent material required increases proportionately with the solute load, so that at higher solute concentrations, equipment size makes such conventional adsorption processes economically unfeasible, even on a small-scale.
- The materials are versatile. This versatility allows the sorbent to be used under different forms, from insoluble beads, to gels, sponges, capsules, films, membranes or fibers. Materials are available in a variety of structures with a variety of properties. The utilization of crosslinked beads or hybrid materials has many advantages in terms of applicability to a wide variety of process configurations and reusability for repeated runs [147]. The control of material conditioning may be helpful for designing the sorption process. Different analytical methods including the batch method, sorption columns, dynamic tests or reactors can be used. In general, conventional sorbents are commonly operated in fixed-bed processes.
- Sorbents containing polysaccharides are very efficient for the removal of pollutants at different concentrations. They possess a high capacity and high rate of adsorption, high efficiency and selectivity in detoxifying both very dilute or concentrated solutions. In general, activated carbon and synthetic resins suffer from a lack of selectivity and applications are typically limited to levels of contaminants in the ppm range. Biosorption on polysaccharide derivatives, in particular chitosan, is an emerging technology that attempts to overcome the selectivity disadvantage of adsorption processes. Chitosan beads are often more selective than traditional resins and can reduce pollutant concentrations to ppb levels.
- With repetitive functional groups, biopolymers provide excellent chelating and complexing materials for a wide variety of pollutants including dyes, heavy metals and aromatic compounds. Moreover, even though polysaccharides and their derivatives are highly sorptive in their natural state, their adsorption capacity can be improved selectively by the substitution of various functional groups onto the polymer backbone.
- Crosslinked materials, in particular cyclodextrin polymers, possess an amphiphilic character. It is precisely this character of these sorbents that makes them so appealing, since they are hydrophilic enough to considerably swell in water allowing fast diffusion processes for the adsorbates, while at the same time they possess highly hydrophobic sites, which efficiently trap non-polar pollutants. Synthetic resins have a poor contact with aqueous solutions and their modification

Table 3

Advantages and disadvantages of commercial activated carbons, synthetic ion-exchange resins and polysaccharide-based materials used as sorbents for the removal of pollutants from solutions

Adsorbent	Advantages	Disadvantages
Activated carbon	<p>The most effective adsorbent</p> <p>Very high surface areas</p> <p>Porous sorbent</p> <p>High capacity and high rate of adsorption</p> <p>Great capacity to adsorb a wide range of pollutants</p> <p>Fast kinetics</p> <p>A high-quality treated effluent is obtained</p>	<p>Expensive</p> <p>The higher the quality, the greater the cost</p> <p>Performance is dependent on the type of carbon used</p> <p>Requires complexing agents to improve its removal performance</p> <p>Non-selective</p> <p>Problems with hydrophilic substances</p> <p>Ineffective for disperse and vat dyes</p> <p>High reactivation costs</p> <p>Reactivation results in a loss of the carbon</p> <p>Expensive</p>
Ion-exchange resin	<p>Wide range of pore structure and physicochemical characteristics</p> <p>Good surface area</p> <p>Effective sorbent</p> <p>Excellent selectivity toward aromatic solutes</p> <p>Regeneration: no adsorbent loss</p>	<p>Derived from petroleum-based raw materials</p> <p>Sensitive to particle</p> <p>Performance is dependent on the type of resin used</p> <p>Not effective for all dyes</p> <p>pH-dependence</p> <p>Poor contact with aqueous pollution</p> <p>Requires a modification for enhanced the water wettability</p> <p>Nonporous sorbent</p>
Chitosan-based material	<p>Low-cost natural polymer</p> <p>Environmentally friendly</p> <p>Extremely cost-effective</p> <p>Outstanding metal and dye-binding capacities</p> <p>High efficiency and selectivity in detoxifying both very dilute or concentrated solutions excellent diffusion properties</p> <p>A high-quality treated effluent is obtained</p> <p>Versatile sorbent</p> <p>Easy regeneration if required</p>	<p>The sorption capacity depends of the origin of the polysaccharide and the degree of <i>N</i>-acetylation</p> <p>Variability in the bead characteristics</p> <p>pH-dependence</p> <p>Requires chemical modification to improve its performance</p> <p>Low affinity for basic dyes</p>
Starch-based material	<p>Very abundant natural biopolymer and widely available in many countries</p> <p>Renewable resource</p> <p>Economically attractive and feasible</p> <p>Easy to prepare with relatively inexpensive reagents</p> <p>A remarkably high swelling capacity in water</p> <p>Good removal of wide range of pollutants</p> <p>Important selectivity for different concentrations</p> <p>Fast kinetics</p> <p>Amphiphilic crosslinked adsorbent</p> <p>Applicable to a wide variety of process</p> <p>Easy regeneration if required</p>	<p>Low surface area</p> <p>Requires chemical derivatization to improve its sorption capacities</p> <p>Variability in the bead characteristics</p> <p>Its use in sorption columns is limited since the characteristics of the particles introduce hydrodynamic limitations and column fouling</p>

and/or pretreatment by activation solvents are necessary for enhanced water wettability. Activated carbons adsorb poorly some hydrophilic substances.

- The regeneration step is easy. The sorbents can be regenerated by desorption at low cost if required. They are easily regenerated by a washing solvent since the interaction between the pollutant and sorbent is driven mainly by electrostatic, hydrophobic and ion-exchange interactions. The desorption side of the process gives the pollutant in a concentrated form and restores the material close to the original condition for effective reuse with no physical–chemical changes or damage. The regeneration of saturated carbon by thermal and chemical procedure is known to be expensive, and results in loss of the adsorbent. The sorption properties are also reproducible. After saturation, the sorption capacity value remains unchanged.

7.2. Some limitations in adsorption by natural adsorbents

There are, of course, disadvantages in using polysaccharides in waste water treatment (see Table 3). They can be summarized as follows:

- The adsorption properties of an adsorbent depend on the different sources of raw materials. The sorption capacity of chitin and chitosan materials depends on the origin of the polysaccharide, the degree of *N*-acetylation, molecular weight and solution properties and varies with crystallinity, affinity for water, percent deacetylation and amino group content [122]. These parameters, determined by the conditions selected during the preparation [77], control the swelling and diffusion properties of the polysaccharide and influence its characteristics. These problems can explain why it is difficult to transfer the use of polysaccharide-based materials at an industrial-scale. It is also well-known that each cyclodextrin possesses a well-defined geometry, and the inclusion process is influenced not only by shape, size and polarity of pollutants, but also by the size of the CD cavity.
- The extreme variability of industrial wastewater must be taken into account in the design of any polysaccharide system. Each type of pollutant may need its own particular polysaccharide. Each polysaccharide has its specific application as well as inherent advantages and disadvantages in wastewater treatment. Chitosan-based materials have high affinities for heavy metal ions. Hence chitosan chelation is a procedure of choice for extraction and concentration techniques in the removal of heavy metals. However, chitosan has low affinity for basic dyes. Recently, Chao et al. [75] proposed enzymatic grafting of carboxyl groups onto chitosan as a means to confer the ability to adsorb basic (cationic) dyes on beads. The reactive groups grafted may serve as electron donors in an alkaline environment. Other examples: cyclodextrin sorbents have a remarkable capacity to form inclusion complexes with organic molecules, especially aromatics, but low affinity for metals. Therefore, the choice of the adsorbent depends on the nature of the pollutant.
- Performance is dependent on the type of material used. The adsorption properties depend on the extent of chemical activation and modifications. Depending on the nature of the substituents and the degree of substitution the properties of the materials can be varied extensively. For grafted polymer materials, pollutant sorption results were found to be a function of the degree of attachment of the polyfunctional groups. In the case of chitosan, the best method of achieving selective extraction is to use a metal specific ligand, but it has proved impossible to find specific ligands for each metal ion.
- The efficiency of adsorption depends on physico-chemical characteristics such as porosity, surface specific area and particle size of sorbents. Another problem with polysaccharide-based materials is their poor physicochemical characteristics, in particular porosity. Polysaccharides are, in general, non-porous and their derivatives possess a low surface area. Chitosan has a very low specific area ranging between 2 and 30 m²g⁻¹. Glutaraldehyde-crosslinked chitosan beads [91], EPI-cyclodextrin gels [141] and EPI-starch beads [105] have a specific surface area around 60, 213 and 350 m²g⁻¹ respectively. Most commercial activated carbons have a specific area of the order of 800–1500 m²/g. Recently, Mi et al. [85] proposed a new method for

the preparation of porous chitosan beads via a wet phase-inversion method. Delval et al. [105] prepared porous crosslinked starch by generating gas bubbles within the material during synthesis. The size of sorbent particles has also been shown to be a key parameter in the control of sorption performances [84,97,105]. In general, adsorption capacity varies randomly due to variation in the particle size [105]. The sorption increases with a decrease in the size of the particle since the effective surface area is higher for the same mass of smaller particles, and the time required to reach the equilibrium significantly increases with the size of sorbent particles. The influence of this parameter also depends on several other criteria: (i) the chemistry of the pollutant; (ii) the characteristics of the sorbent such as its crystallinity, the rigidity of the polymeric chains and the degree of crosslinking [97].

- Performance is dependent on the characteristics of the wastewater. In particular, uptake is strongly pH-dependent. The wastewater pH may be an important factor in the sorption of pollutants onto sorbents. In addition, most pollutants are weak electrolytes, for which the adsorption equilibrium depends on the solution pH. In acidic solutions, amine groups present in the chitosan beads easily form protonation, which induces an electrostatic repulsion of metal ions. This induces a competition between protons and metal ions for adsorption sites. Delval et al. [105,106] showed that starch-based materials containing tertiary amino groups have a low efficiency in dye uptake in the low pH range present in acidic waste waters because of the protonation of the amino groups. Others parameters must be taken into account in the sorption mechanism. For example, in typical dyeing systems, additives such as salts, surfactants, etc. strongly influence the sorption processes because the biopolymer may interact with these molecules. Therefore, the main challenge for researchers is taking into account the effects of the adsorbent surface chemistry, as well as the solution pH, simultaneously. It is important to discern the relative importance of the interactions in a given adsorbate–adsorbent system. Even though there have been extensive experimental studies in this area, the contribution of theoretical

studies is limited. This situation is due to the great variety of materials. The adsorption capacity also depends on the temperature. In general, an increase in temperature decreases the saturation adsorption capacity of chitosan.

- Pollutant molecules have many different and complicated structures. This is one of the most important factors influencing adsorption. There is yet little information in the literature on this topic. Further research is needed to establish the relationships between pollutant structure and adsorption in order to improve the sorption capacity. Although much has been accomplished in the use of polysaccharide-based materials as sorbents in terms of kinetics and sorption capacities, much work is necessary to clearly identify the sorption mechanism. This knowledge is essential for selecting the desorption strategy.
- The production of chitosan involves a chemical deacetylation process. Commercial production of chitosan by deacetylation of crustacean chitin with strong alkali appears to have limited potential for industrial acceptance because of difficulties in processing particularly with the large amount of waste of concentrated alkaline solution causing environmental pollution. However, several yeasts and filamentous fungi have been recently reported containing chitin and chitosan in their cell wall and septa. They can be readily cultured in simple nutrients and used as a source of chitosan. With advances in fermentation technology chitosan preparation from fungal cell walls could become an alternative route for the production of this biopolymer in an ecofriendly pathway.

7.3. Comparison of materials containing polysaccharides with other low-cost adsorbents

Which adsorbent is better? There is no direct answer to this question because, as already mentioned, the sorption capacity depends on the residual concentration of the pollutant in the solution. The uptake by two sorbents must be then compared only at the same equilibrium concentration. The comparison of sorption performance also depends on several other parameters related to the effluent (competition between pollutants) and the analytical method used for decontamination

tests (batch method, column, dynamics tests, reactors) [52,56,125,171]. Thus, a direct comparison of data obtained using different polysaccharide-based materials is not possible since experimental conditions are not systematically the same. In addition, due to scarcity of consistent cost information, cost comparisons are also difficult to make.

However, an examination of the sorption values given in the literature can provide basic information in order to evaluate the possibility of using polysaccharide-based materials for the removal of pollutants. Table 4 illustrates the adsorption capacity of some adsorbents mentioned in the above studies and reports the maximum sorption values cited for uptake of different pollutants. From our literature survey, it is evident that polysaccharide-based materials have demonstrated outstanding removal capabilities for pollutants and were competitive against conventional sorbents or other low-cost sorbents (see Table 4 and Fig. 5). Different toxic pollutants such as copper, cadmium, lead, arsenic ions, and dyes have been effectively removed from both concentrated and diluted solutions using materials containing polysaccharide. Chitosan sorbents, in particular crosslinked beads, are the most efficient adsorbents and the preferred materials for the removal of pollutants. Since they possess an ion-exchange character, chitosan derivatives have the highest chelating ability in comparison to other natural polymers. Results showed that chitosan possesses exceptional binding capacity, greater than 1 mmol metal/g for most metals (except for Cr). Chitosan-based materials also exhibit high sorption capacities toward dyes. In a series of works, Chiou and Li [76,81,84] demonstrated that chitosan–EPI beads have an outstanding adsorption capacity: 1 g of material permits to adsorb 2498 mg of dye. As a result, it is now accepted that chitosan materials offer many promising benefits for wastewater treatment applications today.

Despite the number of papers published on natural adsorbents for pollutant uptake from contaminated water, there is yet little literature containing a full study of comparisons between sorbents. In fact, the data obtained from the biopolymer derivatives have not been compared systematically with commercial activated carbons or synthetic ion-exchange resins, which showed high removal efficiencies, except in recent publications. The results reported by

Chiou et al. [76] demonstrated that the adsorption capacities of crosslinked chitosan derivatives toward anionic dyes are much higher (3–15 times) than commercial activated carbons at the same pH. The beads exhibit excellent performance and appear to be much more efficient and selective. Coughlin et al. [199] concluded that sorption on chitosan is competitive against precipitation techniques. Wan Ngah and Isa [200] found that sorption capacities were significantly greater for chitosan in the recovery of copper than commercial synthetic resin. Martel et al. [162] demonstrated that the chitosan beads containing cyclodextrin are characterized by both a rate of sorption and efficiency superior to that of the parent chitosan bead without CD and crosslinking cyclodextrin–epichlorohydrin gels.

8. Conclusions

Environmental requirements are becoming of great importance in today's society, since there is an increased interest in the industrial use of renewable resources such as starch and chitin. Considerable efforts are now being made in the research and development of polysaccharide derivatives as the basic materials for new applications. In particular, the increasing cost of conventional adsorbents undoubtedly make polysaccharide-based materials one of the most attractive biosorbents for wastewater treatment. Recent and continuing interest in these macromolecules is evident from the number of papers that appear each year in the literature on this topic (see for example two recent references [201,202]).

It is evident from our literature survey that polysaccharide-based materials have demonstrated outstanding removal capabilities for certain pollutants such as dyes and metal ions as compared to other low-cost sorbents and commercial activated carbons. Biopolymers adsorbents are efficient and can be used for the decontamination of effluents (removal of pollutants), for separation processes (recovery of valuable metals), and also for analytical purposes (such as solid phase extraction). They offer both a procedure of choice for complexation and extraction processes, and a lot of promising benefits for commercial purpose in the future. The literature data show that the sorption capacity, specificity and

Table 4

Reported maximum adsorption capacities (mg/g) in the literature for some pollutants obtained on polysaccharide-based materials and other low-cost adsorbents

Pollutant	Adsorbent	q_m	Reference	
Copper(II)	Alumina/chitosan composite	200	[153]	
	Crosslinked chitosan (TPP)	200	[137]	
	Crosslinked chitosan (GLU)	164	[136]	
	Crosslinked starch gel	135	[107]	
	Chitosan	80.71	[88]	
	Crosslinked chitosan (GLU)	59.67	[88]	
	Crosslinked chitosan (EPI)	62.47	[88]	
	Crosslinked chitosan (EGDE)	45.94	[88]	
	Synthetic resins	78.8	[47]	
	Steel-making by-product	40	[36]	
	Granular activated carbon	38	[172]	
	Activated carbon	21.5	[24]	
	Waste slurry	20.97	[173]	
	Peat	19.56	[175]	
	Sawdust	13.8	[176]	
	Clays	9.58	[29]	
	Zeolite	5.1	[174]	
	Scolecite	4.2	[27]	
	Fly ash	1.39	[177]	
	Fly ash–wollastonite	1.18	[178]	
Cadmium	Crosslinked chitosan (GLU)	150	[94]	
	Zeolite	84.3	[179]	
	Moss	46.5	[180]	
	Dead biomass	28	[181]	
	Bentonite	16.5	[182]	
	Peat	5.8	[183]	
	Clays	5.2	[29]	
	Activated carbon	5.1	[24]	
	Bagasse fly ash	1.2	[39]	
	Scolecite	0.18	[27]	
	Arsenic(III)	Chitosan gel beads	70	[89]
	Arsenic(V)	Chitosan gel beads	230	[89]
Fungal biomass		56.07	[45]	
Molybdate	Crosslinked chitosan (GLU)	700	[99]	
Lead(II)	Crosslinked starch gel	433	[107]	
	Synthetic resins	66.3	[47]	
Acid blue 25	Crosslinked starch (EPI)	249	[105]	
	Crosslinked cyclodextrin (EPI)	88	[112]	

Table 4 (continued)

Pollutant	Adsorbent	q_m	Reference
	Silica beads containing cyclodextrin	45.8	[143]
	Chitosan–cyclodextrin beads	77.4	[162]
	Bagasse pith	273–673	[184]
	Fuller's earth	220	[185]
	Chitin	190	[186]
	Peat	13	[187]
	Wood sawdust	5.99	[188]
Reactive dyes	Commercial resins	100–400	[189]
Acid blue 113	Fertilizer industries wastes	219	[190]
Acid yellow 36	Sawdust carbon	183.8	[191]
	Rice husk carbon	86.9	[191]
Basic violet 3	Biomass	113.6	[192]
Acid red 114	Activated carbon	101	[193]
Azo dyes	Metal hydroxyde sludge	48–66	[194]
	Metal hydroxyde sludge	56.2	[195]
Reactive red 141	Activated carbon	16.81	[196]
Congo red	Fungal biomass	14.16	[196]
	Coir pith	6.7	[197]
Reactive blue 2	Crosslinked chitosan (TPP)	2498	[76]
Reactive red 2	Crosslinked chitosan (TPP)	2422	[76]
	Non-crosslinked chitosan	1189	[84]
Reactive red 189	Crosslinked chitosan (EPI)	1642–1936	[84]
	Crosslinked chitosan (EPI)	1802–1840	[81]
Reactive red 189	Crosslinked chitosan (GLU)	1100–900	[81]
	Crosslinked chitosan (EDGE)	950–1000	[81]
<i>p</i> -nitrophenol	Activated carbon	225	[25]
	Silica beads containing cyclodextrin	116	[143]
	Macroporous cyclodextrin	167	[145]
Bisphenol A	Crosslinked cyclodextrin (EPI)	84	[117]
	Crosslinked cyclodextrin (EPI)	9	[116]
Beta-naphtol	Modified crosslinked cyclodextrin (EPI)	25.2	[116]
	Crosslinked cyclodextrin (EPI)	1	[198]
Phenol	Bentonite	1	[198]

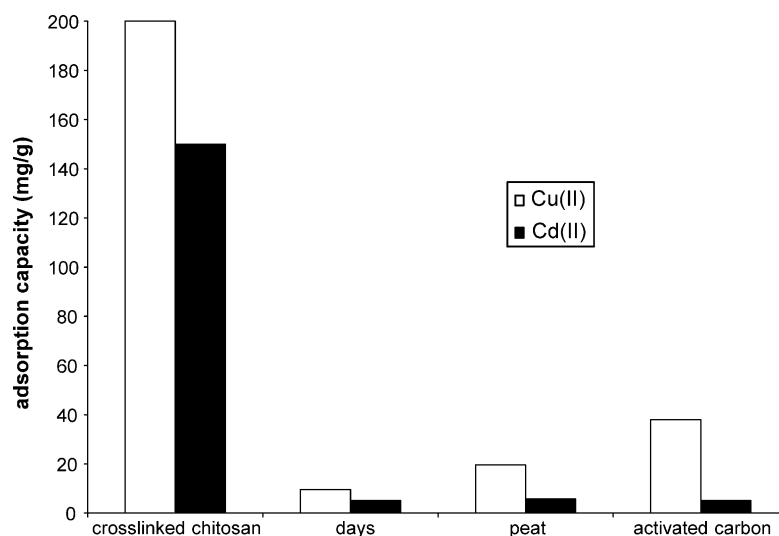


Fig. 5. Compared maximum adsorption capacities of Cu(II) and Cd(II) on crosslinked chitosan, clays, peat and commercial activated carbons.

adsorption kinetics are mainly influenced by chemical structure and composition of the polysaccharide-based material, and also by the accessibility of chelating or complexing groups.

Despite the number of papers published on natural adsorbents for pollutants uptake from contaminated water, there is yet little literature containing a full study comparing various sorbents. In addition, comparisons of different sorbents are difficult because of inconsistencies in the data presentation. Thus, much work is necessary to better understand adsorption phenomenon and to demonstrate the possible technology at the industrial scale.

Acknowledgements

I gratefully acknowledge the following colleagues for their critical reading of this review and the comments during the redaction: Pr. Michel Morcellet (University of Lille, France), Pr. Yahya Lekchiri (University of Oujda, Morocco), Pr. Joël Vebrel (University of Besançon, France), Dr James Dat (University of Besançon, France), Dr Nadia Morin (University of Besançon, France), and Dr Giangiacomo Torri (G. Ronzoni Institute, Milan, Italy).

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