

Recent Developments on the Application of Carbohydrate Polymers

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Abstract: The increased awareness of the effects of the use of harmful raw materials and their associated toxicity to the environment and humans have necessitated the current drive for the development of environmentally-friendly and cost-effective raw materials. The reported depletion of the fossil fuel reserves of nations and the impending economic impact has also shifted the focus of industrialised nations to the use of renewable raw materials. Carbohydrate polymers, like cellulose and starch, provide unique opportunity to explore raw material from renewable sources that pose no risk to the environment because they are products of natural processes such as plant metabolisms. These materials have shown unique properties and compared favourably with raw materials from other sources in even high technology applications. This review examined novel applications of carbohydrate polymers in industrial processes like adsorption, corrosion inhibition, catalysis, drug delivery systems and fuel cells.

Keywords: Renewable raw materials, Carbohydrate polymers, adsorption, catalysis, drug delivery systems, fuel cells.

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I. Introduction

Polymers belong to a class of long-chain, giant molecules made up by linking together discrete building units. The building units are monomers. The term repeating units are used when more complex building units are involved [1]. Biopolymers, natural polymers, are polymers formed during the life cycles of living organisms, which include green plants, fungi, bacteria and animals [2]. According to Ghanbarzadeh and Almasi [3], biopolymers can be classified according to their source into polymers obtained directly from biomasses and polymers obtained directly from natural or genetically modified organisms. Biopolymers obtained from biomasses were further classified as either polysaccharides, polypeptides or lipids.

Polysaccharides are complex carbohydrate polymers made up of monosaccharide monomers linked via glycosidic bonds to form linear or branched chain molecules of varying length. The property of a polysaccharide is determined by the type of monosaccharide component, the anomeric configuration of glycosidic linkages and the type of linkages. Carbohydrate polymers can be broadly grouped as reserve polysaccharides (starch), structural polysaccharides (cellulose) and protective polysaccharides (pectin and hemicelluloses) based on the function they perform in the living organism [4].

Gums, cellulose and starch are three main carbohydrate polymers obtained readily from biomass. Though, cellulose and starch are the prime polymers of interest in material applications. However, recent researchers in these carbohydrate polymers have examined complex polymers synthesised by fungi and bacteria such as curdlan, hyaluronic acid, xanthan and pullulan [3, 5-7]. Table 1 shows a brief overview of some carbohydrate polymers, their structure, repeating units, sources and industrial applications.

The current interest in the utilisation of carbohydrate polymers in various fields is driven by their cost-effectiveness as raw materials, ease of availability and the inherent simplicity of modification to produce superior materials [8]. The drive for the replacement of non-renewable raw materials with renewable alternatives to mitigate the rate of environmental degradation due to the use of fossil resources and synthetic raw materials has also played an essential role in the quest for the development of renewable materials from possible sources.

The potential application of carbohydrate polymers has been evaluated in a broad spectrum of fields such as drug delivery [8], adsorption [9], wastewater treatment [10, 11], corrosion resistance [12], catalysis [13]. This current review will focus on the novel applications of carbohydrate polymer.

II. Carbohydrate Polymers

2.1 Cellulose

With an estimated worldwide production of 1.5×10^{12} tons annually, cellulose is almost an unlimited raw material source and the most abundant carbohydrate polymer available at present [14]. It is the principal structural component of the cell wall of all plants and also obtained in living organisms like algae, bacteria and some animals referred to as tunicates. Its composition on the dry-weight basis in lignocellulosic plants is around 23-53%, while in straw plants it is around 35-45% [15, 16]. Cellulose can also be obtained from some bacterial species via fermentation, resulting in pure cellulose with unique properties such as large surface area and liquid absorption capacity [1]. Structurally, cellulose is a homopolymer, comprising chains of glucose unit ranging from 700-25,000 that are β -1,4 linked together as shown in Fig 1. The bonding in the polymer chain is responsible for the linear structure, high crystallinity and the indigestibility of cellulose by humans [17, 18]

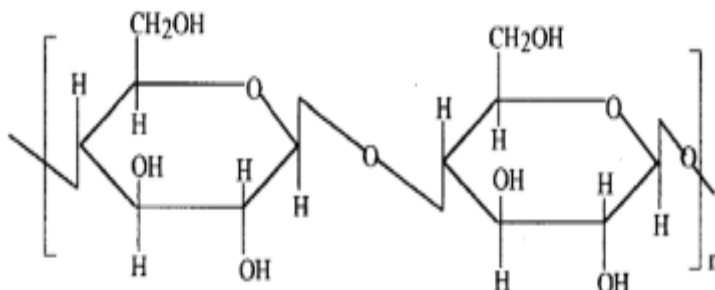


Fig 1: Structure of Cellulose repeating unit

Cellulose has found significant application in the paper, film, textile, wood product and fibre industry and most recently, it is being employed in the production of biofuel. To enhance its pertinence as adhesives and other unique applications, cellulose is often subjected to chemical modifications to impart some unique properties to it. These modification reactions include esterification (e.g. carboxymethyl cellulose, cellulose xanthate and cellulose acetate) [19, 20], etherification (e.g. methyl cellulose, hydroxypropyl ethyl cellulose and hydroxyl methyl cellulose) [21, 22] and acetylation [23].

2.2 Starch

Starch is a giant carbohydrate molecule made up of large amount of glucose units held together by glycosidic bonds. Starch is formed from a combination of two polysaccharides: amylose and amylopectin shown in Figure 2, with the weight percentage of the component polysaccharides (amylose and amylopectin) depending on the source of the starch [24, 25]. Amylopectin is a branched molecule, comprising of hundreds of short-chain α -D-glucopyranosyl monomers with α -(1-4) linkages in the linear portion of the molecule interrupted by α -(1-6) linkages at the branching point of the molecule. Amylopectin has a molecular weight range of 10^6 to 10^8 gmol^{-1} , and it is also highly branched. On the other hand, amylose is mainly a linear molecule of α -D-glucopyranosyl units linked by α -(1-4) bond with few branches due to α -(1-6) linkages. It has a molecular weight ranging from 10^5 to 10^6 gmol^{-1} .

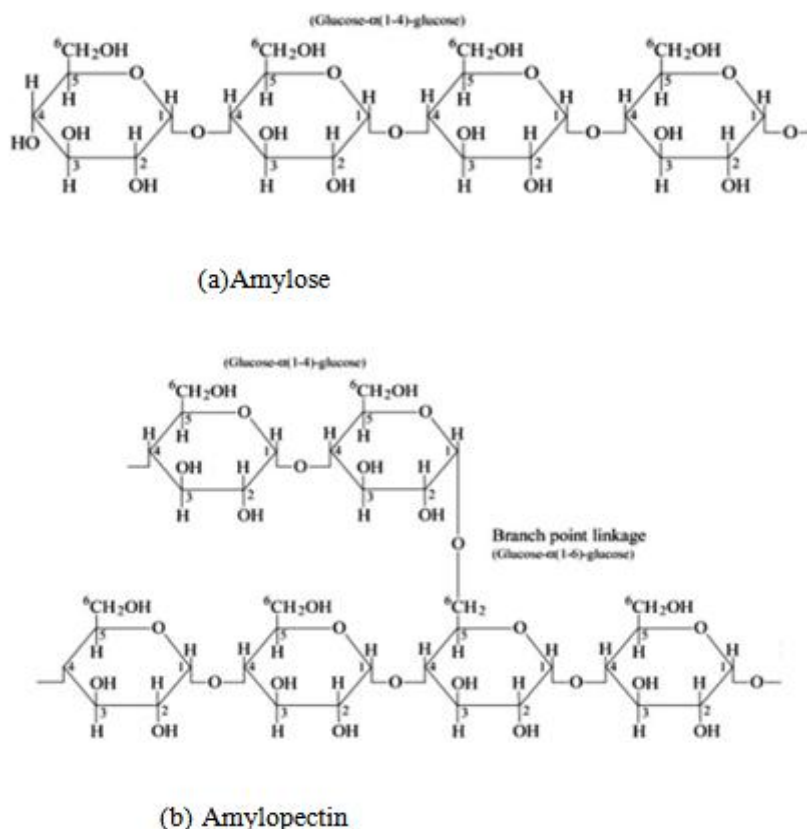


Fig 2: Structure of starch repeating units

With amylose concentration of 0, 28, 55, and 70%, industrial starches are classified as waxy cornstarch, regular cornstarch, high-amylose cornstarch type V, and high-amylose cornstarch type VII respectively[15]. Starch is employed as raw materials industrially, in film production, food package, loose fill products, disposables and composting bags[26]. It is also used as fillers and additive for various purposes in plastic production[27]. In the food industries, starch could be used as an additive or processed into simple sugars, glues and thickeners.

Modification of starch is usually carried out to improve its properties in some applications. This modification could be achieved either via physical or chemical methods. Modification of starch usually aims at its solubility, surface adhesion strength and to break open the tightly bound starch granules. Some modification treatments include heat treatment, alkali treatment, acid treatment and oxidation.

2.3 Dextrin and cyclodextrins

Dextrin is produced in nature by the hydrolysis of starch catalysed by the enzyme amylase produced in the human mouth. It can be synthesised from starch by dry-roasting in the presence of an acid catalyst. Structurally, it is a low weight polymer made up of glucose units held together by either α -(1 \rightarrow 4) or α -(1 \rightarrow 6) glycosidic bonds[24]. Dextrin can occur in different forms in nature which include α , β -dextrin, amylopectin, maltodextrin, cyclic and highly branched cyclic dextrin compounds. Based on the roasting time, amount of catalyst used and temperature, synthesised dextrin can be classified into three groups: white dextrins, canary or yellow dextrins and British gums.

2.4 Chitin and Chitosan

Chitin is a structural carbohydrate polymer that is made up of 2-acetamido-2-deoxy-D-glucose monomers that are connected via β -(1 \rightarrow 4) linkages. Chitin is found present in the exoskeleton of arthropods like shrimps, insects, lobsters, crabs and the cell walls of certain fungal[2, 28]. Chitosan-a crystalline, cationic and hydrophilic polymer with excellent gelation and film-forming property-is obtained by the N-deacetylation

of chitin[29]. Chitosan is a linear polysaccharide made up of D-glucosamine monomers with randomly located N-acetylglucosamine substituents that are β -(1 \rightarrow 4) linked. The level of substitution of the acetamido group with the amine groups is called the degree of deacetylation (DD) of the chitosan and ranges from 30% to 95% [30].

The repeating units of chitin and chitosan are shown in Figure 3. The physicochemical properties of chitosan like biodegradability, reactivity, solubility and cell response depend on the degree of deacetylation[8]. The conversion of chitin to chitosan leads to the production of a more soluble and tunable material. In an aqueous solution with a pH > 7.0, chitosan is insoluble despite its crystallinity; however, in dilute acids (pH < 6.0), its solubility is enhanced due to the presence of the positively charged amino group[31]. The presence of reactive functional groups (amino group, primary and secondary hydroxyl groups) makes the chitosan molecule accessible for chemical modification like ionic and covalent modifications to give materials with varying mechanical and physical properties.[28].

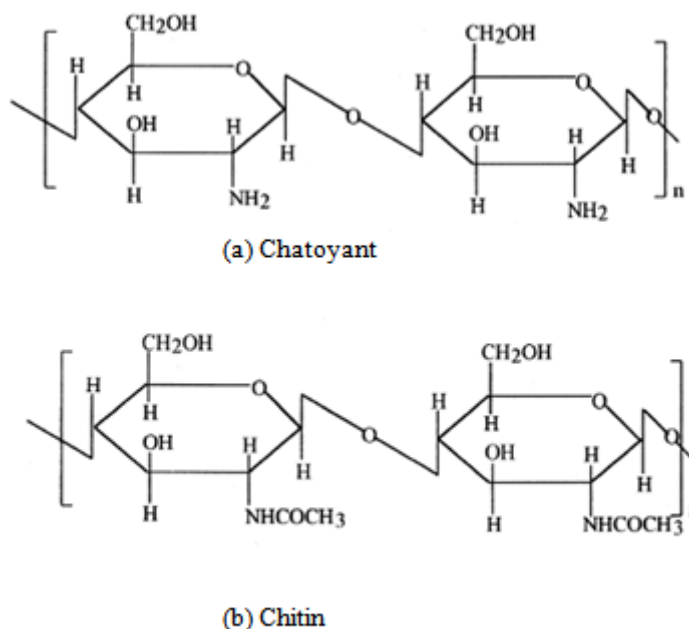


Fig 3: Structure of chitosan and chitin repeating units

Chitin and chitosan have been explored in a lot of industrial applications. They are used in treating skin infections due to their antibacterial and antifungal properties and as drug-delivery agents due to their biocompatibility. Chitosan in different forms like gels, films, fibres and powders have been explored in applications like membrane barriers, cell culture, contact lens materials, blood coagulation inhibitors and encapsulation[32]. Chitosan has also been explored in the food, paper and textile industries for numerous applications.

2.5 Gums

Carbohydrates that form gels when counter-ions are introduced into their solution are grouped into a class called gums. Examples include alginic acid obtained from within the cell wall of brown algae[33], guar gum from the seeds of *Cyamopsis tetragonolobus*[34], gellan gum from bacterium *Sphingomonas elodea*[35], xanthan gum produced by the bacterium *Xanthomonas campestris*[36], exudate gums produced by plants due to stress like physical injury or fungal attack [36] and mucilage gums extracted from seeds or stems of plants like *Hibiscus esculentus* and *Sinapis alba*. In the formation of gels, the degree of cross-linking is determined by factors like the type of counter-ion, the functional charge density of the polymer and the pH of the solution[37]. Alginic acid is a linear, anionic copolymer of β -(1 \rightarrow 4) linked D-mannuronic acid and α -(1 \rightarrow 4) linked L-guluronic acid. The percentage composition of L-guluronic acid determines the quality of the alginate polymer, and it depends on the source of the gum. The quantity of L-guluronic acid varies between 40% to 70%[28]. The properties and application of alginate polymers are determined by the amount D-mannuronic acid and L-guluronic acid content of the building block. Alginates with high L-guluronic acid content have been observed to be suitable for many biomedical applications due to their low immunogenicity in the body and ease of processing[38]. Table 1 shows the structure, sources and industrial uses of some carbohydrate polymers

Table 1: Some carbohydrate polymers

Carbohydrate polymer	Repeat Units	Structure	Source	Industrial applications	References
Pectins	(1→4)-linked α -D-galactosyluronic acid (1→2)-linked- α -L-rhamnosyl/(1→4)-linked α -D-galacturonic acid		Citrus peel, sugarbeet pulp	Gelling agents	[36]
Hemicellulose	(1→4)-linked- β -D-xylose (1→4)-linked- β -D-mannose D-xylopyranose(1→4)-linked- β -D-glucopyranose (1→3)-linked- β -D-galactose		Cell walls of higher plants	Thickening and stabilising agents; water binding and gelling agent	[36]
Pullulan	(1→4)- linked- α -D-glucopyranosyl and (1→6)-linked- α -D-glucopyranosyl		<i>Aureobasidium pullulans</i>	Adhesives; coating agents	[39]
Carrageenans	D-galactose/3,6-anhydro-D-galactose		Seaweeds (<i>Rhodophyceae</i>)	Thickening, gelling and protein-suspending agents	[40]
Algar	(1→3)-linked- β -D-galactose and (1→4)-linked 3,6-anhydro- α -L-galactose		<i>Rhodophyceae gracilaria</i> and <i>Rhodophyceae gelidium</i>	Production of less brittle gels	[36]
Hyaluronic acid	D-glucuronic acid and (1→3)-linked- β -N-acetyl-D-glucosamine		<i>Bacillus subtilis</i> ; <i>C. streptococcus</i>	Skin moisturisers, wound healing	[41]
Xanthan gum	(1→4)-linked- β -D-glucose/D-glucuronic acid/D-mannose		<i>Xanthomonas campestris</i>	Emulsion stabiliser; thickener; dispersant	[42]

III. Application of carbohydrate polymers

3.1 Drug Delivery

Carbohydrate polymers are thenew objects of interest in drug delivery due to their low toxicity, biodegradability, natural renewability and stability. These materials are also cost-effective, readily available and possess tunable properties. In drug delivery systems, modified forms of the polymers are employed or in

combination with other polymersto improve the targeting efficiency of the prepared drugs. Polymer modification can be achieved by chemical reactions, grafting of polymers or derivative formation[8]. In the development of polymers for controlled release, the end state of the polymer after the release of the drug is of paramount consideration. Naturally excreted polymers are suitable for controlled drug delivery; this may be achieved either by direct excretion by the kidney or biodegradation into smaller molecules that are excreted[43].

3.1.1 Hyaluronic Acid (HA)

The use of HA alone in drug delivery system is limited by its high water-solubility at room temperature and acidic pH and high *in vivo* turn-over rate[28]. However numerous cross-linking techniques have been employed to improve its stability. These include photo-cross-linking, divinyl sulfone (DVS) cross-linking, water-soluble carbodiimide cross-linking, disulfide cross-linking and polyvalent hydrazide cross-linking[44]. HA has been reportedly explored in ophthalmic drug delivery and liposomal dermal drug delivery systems. In ophthalmic drug delivery systems, HA ester systems of model drugs like tropicamide and locarpine prepared as gels, hydrogels and solutions were found to be effective. Covalent attachments of drugs also resulted in twice the retention time when compared to the free drug[28]. In liposomal dermal drug delivery, carbodiimide cross-linking technique was employed in the conjugation of HA to the surface of liposomes via the reaction between the carboxyl residue of HA and amine residues on the liposome. HA derivatives of sodium butyrate prepared by stepwise chemical treatment of HA was reported to enhance the *in vivo* half-life of the target drug and thus an increase in the antiproliferative response of breast cancer lines[45].

3.1.2 Chitosan

Chitosan is currently a polymer of great interest in the pharmaceutical industries. This is due to its many medicinal benefits even when directly consumed as a drug. It has also been explored in the synthesis of different drug types like gels, granules, micro-particles and liposome for oral and parenteral drug delivery. Interest in the application of chitosan in oral drug delivery systems has been fueled by its ability to improve residence time in the gastrointestinal tract via mucoadhesion and also improve absorption by enhancing permeability[46]. Other drug delivery properties of chitosan include anionic drug delivery, gelling and gene expressing properties[47]. To achieve the required stability expected of chitosan in most of its application, it is subjected to cross-linking either physically or chemically. The level of cross-linking and drug loading achieved are essential in chitosan drug delivery systems[48, 49].

Despite its excellent drug delivery properties, chitosan still suffers some limitations due to its insolubility at neutral pH and rapid rate of water absorption by the polymer. This limitation could be mitigated by chemically modifying the polymer via reactions at either its amine or hydroxyl groups. Some of the reactions include reductive amination, acylation, quaternization and polyelectrolyte complex formation[50-53]. Chitosan derivatives and its blends with other polymers have also been explored in different modes like nanoparticles, micro-particles and thin films. Chitosan-based drug delivery systems have been explored controlled delivery to the buccal, colon, dental system and gene[54].

3.2 Corrosion Inhibition

Metal corrosion is an electrochemical process with significant economic, environmental, technical and aesthetic impacts on the use of metals. The nature of the metal and that of the corroding environment are two broad factors that determine the rate and extent to which a metal corrodes. Nature of the metal could include a metal position in the activity series; overvoltage; metal purity; physical state of the metal; nature of the surface film; passivity of metal; corrosion product solubility and corrosion product's volatility. Some environmental factors include pH, temperature, moisture and electrolyte's nature[55]. Among other available corrosion prevention techniques like cathodic protection, anodic protection, coating and alloying, the use of chemical inhibitors is the main corrosion prevention technique as it is the most efficient and practical technique for corrosion inhibition[56].

Several reports on the use of inorganic and organic chemicals as corrosion inhibitors have been made, but these chemicals exhibit high toxicity and also require strenuous synthetic procedures that involve the use of costly materials[57-59]. To circumvent these problems, natural inhibitors, which are readily available and nontoxic to the environment are replacing organic and inorganic chemicals. Current trends are focused on the use of polymers in corrosion inhibition.

Application of carbohydrate polymers in corrosion inhibition provided a route to employ materials that are biodegradable, chemically stable, eco-friendly with the unique inhibiting property, low cost, and renewable[60, 61]. The molecular weights determine the strength of carbohydrate polymers as inhibitors, the presence of adsorption centres, availability of bond-forming groups and presence of cyclic rings in the class of the carbohydrate[62].

The corrosion inhibiting activities of these polymers are attributed to their ability to form complexes with metal ions on the surface of metals through their functional group. The complex formed blankets the surface of the metals due to their large surface area, thus protecting the metals from corrosive species present in their environment [63]. This inhibitive activity depends on the cyclic rings and heteroatoms (nitrogen and oxygen) present in the structure of the polymer.

3.3 Catalysis

There is an increase in research output on the application of carbohydrate polymer especially, chitosan in the area of heterogeneous catalysis. This awareness is due mainly to the shift in focus from homogeneous catalysis to heterogeneous catalysis due to its inherent advantages which include easy catalyst recovery, recycling and separation [64]. In heterogeneous catalysis, there is the need for the development of suitable materials as supports for the active catalytic species. These supports can also be employed to immobilise homogeneous catalysts to overcome the problem of catalyst separation.

Several inorganic materials like silica [65], activated carbon [66, 67], or alumina [68] have been employed as support materials for catalysts in heterogeneous catalysis. Recent trends, however, have focused on the use of polymer materials, particularly carbohydrate polymers. Advantages of these polymers include ease of tuning chemical and physical properties through modification; the presence of desirable functional groups; low cost, eco-friendly, biodegradable and non-toxicity and excellent thermal stability [69, 70]. Though there have been reported uses of some of these polymers with catalytic materials [71, 72], most studies on their use in catalysis have focused on their application as support materials. Already studied carbohydrate polymer based support include cyclodextrin [73, 74], cellulose [65, 75], gelatin [76], chitin and chitosan [77, 78], and alginic acid [79].

Chitosan-based supports have received much attention with several reviews already published on its application as a catalyst support [68, 80]. In his review, Guibal, (2005), showed that chitosan-based supports had been employed in oxidation reactions, hydrogenation reactions, allylic substitution reactions, Suzuki and Heck reactions, polymerisation reaction, cyclopropanation of olefins, asymmetric dihydroxylation of olefins, carbonylation reactions and monoglyceride synthesis. Eberhardt, et al. [81] studied the effect of the degree of deacetylation of chitosan support pretreated with methylaluminoxane on the catalytic activity of zirconocene catalyst in ethylene polymerisation. It was established that the degree of deacetylation greatly affects the activity of the prepared catalyst, with catalytic activity showing a direct proportionality with the degree of deacetylation. This was reported to be due to the availability of more NH-groups in the chitosan with a high degree of deacetylation to interact with the pretreating agent. In the same study, a comparative study of the effect of two other pretreated supports (cellulose and starch) on the activity of the catalyst was carried out. The yield of the catalysts were found to be in order chitosan > cellulose > starch.

Sadjadi, et al. [82] reported the synthesis of a novel ternary hybrid catalyst system comprising of halloysite nanotubes-cyclodextrin nanosponges-g-C₃N₄ supported palladium nanoparticle and studied its application in Sonogashira and Heck coupling reactions and the effects of each component on the activity of the prepared catalyst. It was observed that the incorporation of cyclodextrin into the support matrix led to an increase in the yield of the catalyst even at a shorter reaction time when compared to other prepared catalysts without cyclodextrin. The increased activity was believed to have resulted from the ability of cyclodextrin to form an inclusion complex with different guest molecules, thus leading to increase in the transfer of reactant molecules from solution to the active sites of the catalyst. In a similar study Sadjadi, et al. [82] reported the synthesis of carbon nanotube and cyclodextrin hybrid supported palladium catalyst and studied its catalytic activity for ligand and copper-free Sonogashira and Heck coupling reactions under aqueous media and mild reaction conditions. It was observed that there was a synergy in the activity of the carbon nanotube and the cyclodextrin as higher activity was observed when the hybrid support was used when compared to when used alone as supports.

Cirtiu et al., (2011), reported the synthesis of cellulose nanocrystalline supported palladium nanoparticles and evaluated its activity for catalytic hydrogenation and Heck coupling reaction under mild conditions. The result showed that the prepared catalyst showed good activity in the catalytic hydrogenation of phenol to cyclohexanone. To evaluate the importance of the support material, experiments were also carried out using a commercially available catalyst with carbon and alumina supports. The result showed the prepared cellulose supported catalyst compared favourably with the alumina-supported catalyst, while its activity far outshines that of carbon supported catalyst. Experimental runs without the palladium catalyst and the nanocrystalline cellulose support showed that both materials did not have catalytic activity for hydrogenation when used alone.

3.4 Fuel Cell

Electrochemical devices that convert the chemical energy of fuel into electrical energy are called fuel cells. They serve as alternative sources of energy to traditional energy sources like hydropower, coal and other fossil fuels. Despite the advantages of fuel cell technologies like its environmental sustainability and energy security[83], it still suffers from lack of durability, short cell life and the high cost of the cell components[84].

Carbohydrate polymers like chitosan, starch, cellulose and glycogen have found application in fuel cell development by providing an alternative route for the synthesis of cost-effective and eco-friendly polymer electrolytes. These electrolytes are an adequate replacement for the rather expensive and limited perfluorosulphonic acid membranes (e.g. Nafion and Flemion) currently being employed in polymer electrolyte membrane (PEM) fuel cells

Chitosan is presently receiving serious considerations for use as membrane materials for PEM. There are also reported uses of chitosan as electrode materials[85]. The advantage of chitosan as polymer electrolyte in PEM include low methanol permeability, hydrophobicity, availability for functional groups for property modification and its availability. Chitosan is often modified to tailor its properties for its application in fuel cells. This modification could be either physical or chemical. In fuel cell application, chitosan is subjected to several chemical modifications including sulfonation[86]; phosphorylation[87]; quaternization [70] and chemical cross-linking[88]. Chitosan based polymer electrolytes can be grouped as self-cross-linked or salt-complexed chitosan[89, 90]; chitosan-based polymer blend[91, 92] and chitosan-based composite membrane (which can be either chitosan/inorganic filler composite or chitosan/polymer composite)[93-96]. A cross-linked chitosan polymer electrolyte was prepared by Ma et al. (2012) using phosphate and triphosphate salt as the cross-linking agent. The triphosphate chitosan showed better parameters than the prepared phosphate chitosan. The prepared electrolyte with chitosan binder showed a higher peak density of 685 mWcm^{-2} at 60°C which is about 50% higher than that of Nafion.

Schmitt, et al. [97] synthesised a cellulose-based polymer electrolyte. Cellulose-p-toluenesulfonate was reacted with 1,4-diazabicyclo (2,2,2)-octane to give a quaternary ammonium moiety which was then crosslinked with diiodobutane to produce a crosslinked anion exchange membrane. The conductivity of the prepared material as a function of the quantity of the crosslinking agent was reported to range between 2.5×10^{-4} and $5.5 \times 10^{-3} \text{ S cm}^{-1}$.

3.5 Adsorption

Adsorption is an important physical process that involves the transfer of chemical species from solution onto a solid phase. It has become essential in water purification systems due to its cost-effectiveness, simplicity, high efficiency, easy of regeneration and it is environmentally benign[98]. Many adsorbent materials have been developed with excellent adsorbing properties like activated carbon, and silver-based nanoparticles, however, there were issues of high cost and toxicity associated with these materials. The focus is now on biopolymers, with excellent adsorbing properties, which are cheap and non-toxic. Lots of success has been achieved in this regard with the development of novel biopolymers based on carbohydrates such as chitosan, chitin, and starch. Table 2 shows the adsorption capacity of some carbohydrate polymer based adsorbents.

Carbohydrate polymer based adsorbent materials can be obtained via two routes:

1. Crosslinking of the polymer by reacting the hydroxyl or amino groups of the molecules with coupling reagents to obtain crosslinked network materials that are insoluble in water[99, 100]. If the gels obtained are held together by reversible bonds, then it is referred to as a physical gel. However, if irreversible covalent bonds hold the gels, then it is called a chemical gel[101].
2. Grafting or coupling of polysaccharides on insoluble supports leading to their immobilisation on the supports to give composite/hybrid materials. These materials exploit the physical and chemical properties of its component organic and inorganic materials[102-104].

According to Crini, (2005) and Guibal, (2004), the mode of action of these polymers includes complexation, electrostatic interaction, ion-exchange, precipitation, hydrogen bonding, acid-base interaction, physical adsorption, hydrophobic interaction and coordination/chelation.

The synthesis of polymeric adsorbents by crosslinking of cellulose, corn and maize derived starches (with variable amylose/ amylopectin content) with epichlorohydrin at an optimal temperature of 50°C was reported by Dehabadi & Wilson, (2014). The adsorptive properties of the adsorbents were tested towards nitrogen gas, solvents (water and ethanol) and p-nitrophenol in aqueous solutions at pH 6. The physicochemical properties of the adsorbents were found to depend on the amylose and amylopectin content of the copolymer adsorbents. The adsorptive uptake of water or dye was found not to depend on the level of crosslinking of the polymers but highly dependent on the structural properties like branching, amylopectin/amylose content and molecular weight of the polymer.

Unuabonah, et al. [11] reported the synthesis of several chitosan-hybrid clay composite by varying the ratio of chitosan to the hybrid clay using solvothermal and surface modification techniques. The composites

prepared were evaluated for their adsorptive uptake of three (3) enteric bacteria (*Escherichiacoli*, *Salmonella typhi*, and *Vibro cholera*). The best adsorptive uptake for the bacteria was obtained with adsorbent with chitosan/hybrid clay ratio of 1:5. The maximum percentage removal of the bacterial was 4.07×10^6 cfu/mL for *V. cholerae* after 20 min, 1.95×10^6 cfu/mL for *E. coli* after ~180 mins and 3.25×10^6 cfu/mL for *S. typhi*. The Brouers-Sotolongo model predicted a maximum adsorption capacity (q_{max}) of 103.07 mg/g and 154. 18 mg/g for the adsorption of *E. coli* and *V. cholerae* respectively, while the Sips model predicted a q_{max} of 83.68 mg/g for the adsorption of *S. typhi*.

Table 2: Carbohydrate polymer based adsorbents

Carbohydrate polymer	Form	Adsorbent composition	Pollutant	q_{max} (mg/g)	Reference
Chitosan	Magnetic chitosan composite	Chitosa/iron/activated carbon	Cu ²⁺	216.6 mg/g	[105]
	Reinforced chitosan composite	Chitosan/cellulose	Cd ²⁺	204.08 mg/g	[106]
	Protonated cross-linked chitosan	Chitosan/H ⁺	Methyl orange	180.2mg/g	[107]
	Crosslinked Chitosan-iron (III)	Chitosan/iron	Cr ⁶⁺	182.9 mg/g	[108]
	Magnetic chitosan composite	Crosslinked chitosan/nano-magnetite/heulandite	Methylene blue; Methyl orange	45.1 mg/g 149.2 mg/g	[109]
	Crosslinked chitosan	Chitosan/Diethylenetriaminepentaacety acid	Cr ⁶⁺	192.3 mg/g	[110]
	Chitosan composite	Chitosan/diatomite/poly vinyl alcohol	Hg ²⁺	195.7 mg/g	[111]
	Crosslinked chitosan	Chitosan/glutaraldehyde	Cr ⁶⁺	215 mg/g	[112]
Starch	Crosslinked starch	Starch microspheres	Methyl violet;	82.86%;	[113]
			Reactive brilliant red	24.22%	
	Porous starch xanthate;	Starch/carbon disulphide	Pb ²⁺	109.1 mg/g	[114]
	Porous starch citrate	Starch/citric acid		57.6 mg/g	
	Cationic cross-linked starch	Crosslinked starch/Cl ⁻	I ⁻	4.54 mmol/g	[115]
		Crosslinked starch/I		4.61 mmol/g	
	Crosslinked starch	Starch/4,4'-methylene-bis-phenyl-diisocyanate	o-nitrophenol; p-nitrophenol; 2,4-dinitrophenol;	-; 8.53; 11.5; 39.58	[116]
		Starch/hexamethylen diisocyanate	2-s-butyl-4,6-nitrophenol		
	Starch esters	Starch/maleic acid	Ni ²⁺ ; Zn ²⁺ ; Cd ²⁺ ; Pb ²⁺	8.29 mg/g; 8.44 mg/g; 8.03 mg/g; 25.16 mg/g	[116]
		Starch/itaconic acid		99.27 mg/g; 101.44 mg/g; 95.62 mg/g 506.44 mg/g	
	Crosslinked porous starch	Starch/N,N'-methylene-bis-acrylamide	Cr ⁶⁺ Cd ²⁺ Pb ²⁺	28.83 mg/g 17.37 mg/g 35.56 mg/g	[117]
Cellulose	Nanocrystalline cellulose	Cellulose	Methylene blue	101 mg/g	[118]
	Reinforced cellulose	Polyvinyl alcohol/carboxy methyl cellulose/graphite/bentonite	Methylene blue	172.14 mg/g	[119]

IV. Conclusion

Carbohydrate polymers are becoming materials of high importance in diverse fields of applications due to their non-toxicity, cost-effectiveness, ease of tuning physical and chemical properties and their renewability. We have highlighted in this review some novel use into which these materials and their many derivatives are currently being employed such as corrosion inhibition, catalysis, drug delivery, fuel cell and adsorption.

Conflict of interest

The authors declare there is no conflict of interest regarding the publication of this paper.

References

- [1]. G. M. Rao, P. Bharathi, and R. M. Akila, "A Comprehensive Review on Biopolymers," *Scientific Reviews & Chemical Communications*, vol. 4, no. 2, pp. 61-68, 2014.
- [2]. E. E. Tanase, M. Rapa, and O. Popa, "Biopolymers Based on Renewable Resources- A Review," *Scientific Bulletin. Series F. Biotechnologies.*, vol. XVIII, pp. 188-195, 2014.
- [3]. B. Ghanbarzadeh, and H. Almasi, "Biodegradable Polymers," *Biodegradation-Life of Science*, R. Chamy, ed., pp. 141-185, Croatia: InTech, 2013.
- [4]. A. V. Singh, "Biopolymers in Drug Delivery: A Review," *Pharmacologyonline*, vol. 1, pp. 666-674, 2011.
- [5]. W. W. Barker, and J. F. Banfield, "Biologically versus inorganically mediated weathering reactions: relationships between minerals and extracellular microbial polymers in lithobiotic communities," *Chemical Geology*, vol. 132, no. 1-4, pp. 55-69, 1996/10/30, 1996.
- [6]. T. Khan, J. K. Park, and J.-H. Kwon, "Functional biopolymers produced by biochemical technology considering applications in food engineering," *Korean Journal of Chemical Engineering*, vol. 24, no. 5, pp. 816-826, 2007.
- [7]. F. Donot, A. Fontana, J. C. Baccou et al., "Microbial exopolysaccharides: Main examples of synthesis, excretion, genetics and extraction," *Carbohydrate Polymers*, vol. 87, no. 2, pp. 951-962, 2012/01/15, 2012.
- [8]. R. K. Shukla, and A. Tiwari, "Carbohydrate polymers: Applications and recent advances in delivering drugs to the colon," *Carbohydrate polymers*, no. 88, pp. 399-416, 2012.
- [9]. H. Dai, Y. Huang, and H. Huang, "Eco-friendly polyvinyl alcohol/carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite for enhanced adsorption of methylene blue," *Carbohydr Polym*, vol. 185, pp. 1-11, Apr 1, 2018.
- [10]. J. Mu, H. Zhou, Y. Chen et al., "Revealing a novel bioflocculant resource from *Ruditapes phillippinarum*: Effective polysaccharides and synergistic flocculation," *Carbohydrate Polymers*, vol. 16, pp. 17-24, 2018.
- [11]. E. I. Unuabonah, A. Adewuyi, M. O. Kolawole et al., "Disinfection of water with new chitosan-modified hybrid clay composites adsorbents," *Heliyon*, vol. <https://doi.org/10.1016/j.heliyon.2017.e00379>, pp. 1-31, 2017.
- [12]. M. A. Fattah, A. M. A. Hasan, M. Keshawy et al., "Nanocrystalline cellulose as an eco-friendly reinforcing additive to polyurethane coating for augmented anticorrosive behavior," *Carbohydrate polymer*, vol. <http://doi.org/10.1016/j.carpol.2017.12.084>, pp. 1-32, 2017.
- [13]. S. Sadjadi, M. M. Heravi, and M. Malmir, "Pd@HNTs-CDNS-g-C3N4: A novel heterogeneous catalyst for promoting ligand and copper-free Sonogashira and Heck coupling reactions, benefits from halloysite and cyclodextrin chemistry and g-C3N4 contribution to suppress Pd leaching," *Carbohydrate Polymers*, vol. 186, pp. 25-34, 2018.
- [14]. Y. Cao, J. Wu, J. Zhan et al., "Room temperature ionic liquids (RTILs): a new and versatile platform for cellulose processing and derivatization," *Chemical Engineering Journal*, vol. 147, pp. 12-31, 2009.
- [15]. M. G. D. Baumann, and a. H. Conner, "Carbohydrate Polymers as Adhesives," *Handbook of adhesive technology*, A. Pizzi and K. L. Mittal, eds., pp. 299-313, New York: Marcel Dekker, Inc., 1994.
- [16]. M. Knauf, and M. Moniruzzaman, "Lignocellulosic biomass processing: a perspective," *International Sugar Journal*, vol. 106, pp. 147-150, 2004.
- [17]. M. M. Al-Taakha, "HPMC capsules: Current status and future prospects," *Journal of Pharmacy and Pharmaceutical Sciences*, vol. 13, pp. 428-442, 2010.
- [18]. L. Caraballo, "Factors affecting drug release from hydroxypropyl methylcellulose matrix systems in the light of classical and percolation theories," *Expert Opinion on Drug Delivery*, vol. 7, pp. 1291-1301, 2010.
- [19]. S. Spinella, A. Maiorana, Q. Qian et al., "Concurrent Cellulose Hydrolysis and Esterification to Prepare a Surface-Modified Cellulose Nanocrystal Decorated with Carboxylic Acid Moieties," *ACS Sustainable Chemistry & Engineering*, vol. 4, no. 3, pp. 1538-1550, 2016/03/07, 2016.
- [20]. D. Li, J. Henschen, and M. Ek, "Esterification and hydrolysis of cellulose using oxalic acid dihydrate in a solvent-free reaction suitable for preparation of surface-functionalised cellulose nanocrystals with high yield," *Green Chemistry*, vol. 19, no. 23, pp. 5564-5567, 2017.
- [21]. S. C. Fox, B. Li, D. Xu et al., "Regioselective esterification and etherification of cellulose: a review," *Biomacromolecules*, vol. 12, no. 6, pp. 1956-72, Jun 13, 2011.
- [22]. T. Heinze, O. A. El Seoud, and A. Koschella, "Etherification of Cellulose," *Cellulose Derivatives*, pp. 429-477: Springer, 2018.
- [23]. N. S. Cetin, P. Tingaut, N. Ozmen et al., "Acetylation of cellulose nanowhiskers with vinyl acetate under moderate conditions," *Macromol Biosci*, vol. 9, no. 10, pp. 997-1003, Oct 8, 2009.
- [24]. S. A. Umoren, and U. M. Eduok, "Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: A review," *Carbohydrate Polymers*, no. <http://dx.doi.org/doi:10.1016/j.carbpol.2015.12.038>, 2015.
- [25]. W. H. Brown, and T. Poon, *Introduction to Organic Chemistry*: Wiley, 2005.
- [26]. H. Xiong, S. H. Tang, and H. a. Z. Tang, "The structure and properties of a starch-based biodegradable film," *Carbohydrate Polymers*, no. 71, pp. 263-268, 2008.
- [27]. A. G. Pedroso, and D. S. Rosa, "Mechanical, thermal and morphological characterization of recycled LDPE/corn starch blends," *Carbohydrate Polymers*, no. 59, pp. 1-9, 2005.
- [28]. A. Aravamudhan, D. M. Ramos, A. A. Nada et al., "Natural Polymers: Polysaccharides and Their Derivatives for Biomedical Applications," *Natural and Synthetic Biomedical Polymers*, pp. 67-83: Elsevier Inc, 2014.
- [29]. I. Parios, N. Acosta, and A. Heras, "New drug delivery systems based on chitosan," *Current Drug Discovery Technologies*, no. 5, pp. 333-341, 2008.
- [30]. L. S. Nair, and C. T. Laurencin, "Biodegradable polymers as biomaterials," *Progress in Polymer Science*, no. 32, pp. 762-798, 2007.

- [31]. P. J. VandeVord, H. W. Matthew, S. P. DeSilva et al., "Evaluation of the biocompatibility of a chitosan scaffold in mice," *J Biomed Mater Res*, vol. 59, no. 3, pp. 585-90, Mar 5, 2002.
- [32]. J. M. Pachence, M. P. Bohrer, and J. Kohn, "Biodegradable Polymers," *Principles of Tissue Engineering*, p. 323: Elsevier, Inc, 2007.
- [33]. J. F. Mano, G. A. Silva, H. S. Azevedo et al., "Natural origin biodegradable systems in tissue engineering and regenerative medicine: Present status and some moving trends.," *Journal of the Royal Society Interface*, no. 4, pp. 999-1030, 2007.
- [34]. A. Tiwari, and M. Prabaharan, "An amphiphilic nanocarrier based on guar gum-graft-poly (epsilon-caprolactone) for potential drug-delivery applications.," *Journal of Biomaterials Science: Polymer Edition*, no. 21, pp. 937-949, 2010.
- [35]. D. F. Coutinho, S. V. Saint, H. Shin et al., "Modified Gelan Gm hydrogels with tunable physical and mechanical properties," *Biomaterials*, no. 31, pp. 7494-7502, 2010.
- [36]. M. Izdorezyk, S. W. Cui, and Q. Wang, *Polysaccharide Gums: Structures, Functional Properties, and Applications*: Taylor & Francis, 2005.
- [37]. R. Chandra, and H. Rustgi, "Biodegradable Polymers," *Progress in Polymer Science*, no. 23, pp. 1273-1335, 1998.
- [38]. B. E. Christensen, "Alginates as biomaterials in tissue engineering," *Carbohydrate Chemistry*, no. 37, pp. 227-258, 2011.
- [39]. R. K. Shukla, and A. Tiwari, "Carbohydrate polymers: Applications and recent advances in delivering drugs to the colon," *Carbohydrate Polymers*, vol. 88, no. 2, pp. 399-416, 2012.
- [40]. V. L. Campo, D. F. Kawano, D. B. d. Silva et al., "Carrageenans: Biological properties, chemical modifications and structural analysis – A review," *Carbohydrate Polymers*, vol. 77, no. 2, pp. 167-180, 2009/06/10, 2009.
- [41]. B. Widner, R. Behr, S. Von Dollen et al., "Hyaluronic acid production in *Bacillus subtilis*," *Appl Environ Microbiol*, vol. 71, no. 7, pp. 3747-52, Jul, 2005.
- [42]. F. Garcia-Ochoa, V. Santos Mazorra, J. Casas et al., *Xanthan gum: Production, recovery, and properties*, 2000.
- [43]. S. Kira, M. Rajedra, P. Yogesh et al., "Fundamentals of drug delivery systems," *Drug Delivery Systems- A Review*, A. V. Ghotoskar, ed., pp. 1-18: ceutics rocks, 2012.
- [44]. G. D. Prestwich, D. M. Marecak, J. F. Marecek et al., "Controlled chemical modification of hyaluronic acid: synthesis, applications, and biodegradation of hydrazide derivatives," *J Control Release*, vol. 53, no. 1-3, pp. 93-103, Apr 30, 1998.
- [45]. D. Coradini, C. Pellizzaro, G. Miglierini et al., "Hyaluronic acid as drug delivery for sodium butyrate: improvement of the anti-proliferative activity on a breast-cancer cell line," *International Journal of Cancer*, vol. 3, no. 81, pp. 411-46, 1999.
- [46]. M. Rinaudo, "Chitin and Chitosan: Properties and applications.," *Progress in Polymer Science*, no. 31, pp. 603-632, 2006.
- [47]. M. Elgadir, M. Uddin, S. Ferdous et al., "Impact of chitosan composites and chitosan nanoparticle composites on various drug delivery systems: A Review," *Journal of Food and Drug Analysis*, vol. XXX, pp. 1-11, 2014.
- [48]. O. Felt, P. Buri, and R. Gurny, "Chitosan: a unique polysaccharide for drug delivery," *Drug Dev Ind Pharm*, vol. 24, no. 11, pp. 979-93, Nov, 1998.
- [49]. M. P. Patel, R. R. Patel, and J. K. Patel, "Chitosan mediated targeted drug delivery system: a review," *J Pharm Pharm Sci*, vol. 13, no. 4, pp. 536-57, 2010.
- [50]. S. G. Kumbar, A. R. Kulkarni, and T. M. Aminabhavi, "Crosslinked chitosan microspheres for encapsulation of diclofenac sodium: effect of crosslinking agent.," *J. Microencapsul.*, vol. 2, no. 19, pp. 173-180, 2002.
- [51]. V. K. Mourya, and N. N. Inamdar, "Trimethyl chitosan and its applications in drug delivery," *J Mater Sci Mater Med*, vol. 20, no. 5, pp. 1057-79, May, 2009.
- [52]. M. Chen, H. Wong, K. Lin et al., "The characteristics, biodistribution and bioavailability of a chitosan-base nanoparticulate system for the oral delivery of heparin," *Biomaterials*, vol. 34, no. 30, pp. 6629-6637, 2009.
- [53]. Y. H. Lin, F. L. Mi, C. T. Chen et al., "Preparation and characterization of nanoparticles shelled with chitosan for oral insulin delivery," *Biomacromolecules*, vol. 8, no. 1, pp. 146-52, Jan, 2007.
- [54]. T. Sonia, and C. P. Sharma, "Chitosan and its derivatives for drug delivery perspective, anonymous chitosan for biomaterials," *J. Appl. Polym. Sci.*, no. 119, pp. 2909-2910, 2011.
- [55]. S. A. Umoren, and M. M. Solomon, "Recent Developments on the Use of Polymers as Corrosion Inhibitors- A Review," *The Open Materials Science Journal*, no. 8, pp. 39-54, 2014.
- [56]. A. A. Sabirneeza, R. Geethanjali, and S. Subhashini, "Polymeric corrosion Inhibitors for Iron and Its Alloys: A Review," *Chemical Engineering Communication*, no. 202, pp. 232-244, 2015.
- [57]. S. A. Abd-El-Maksoud, "Effect of organic compounds on the electrochemical behavior of steel in acidic media- A review," *Int. J. Electrochem. Sci.*, no. 3, pp. 528, 2008.
- [58]. R. T. Loto, C. A. Loto, and A. P. I. Popoola, "Corrosion inhibition of thiourea and thiazole derivatives: A review," *J. Mater. Environ. Sci.*, vol. 5, no. 3, pp. 885-894, 2012.
- [59]. D. Ozdemir, and V. Cicek, "Aqueous corrosion inhibition studies of mild steel alloy by oxyanion esters of A-hydroxy acids and their salts," *Int. J. Eng. Res. Appl.*, vol. 1, no. 3, pp. 969-985, 2013.
- [60]. A. A. Rahim, E. Rocca, E. J. Steinmetz et al., "Inhibitive action of mangrove tannins and phosphoric acid on pre-rusted steel via electrochemical methods," *Corrosion Science*, no. 50, pp. 1546-1550, 2008.
- [61]. P. B. Raja, M. Fadaeinasab, A. K. Quresi et al., "Evaluation of green corrosion inhibition by alkaloid extracts of *Ochrosia oppositifolia* and *Isoreserpine* against mild steel in 1 M HCl medium," *Industrial & Engineering Chemistry Research*, no. 52, pp. 10582-10593, 2013.
- [62]. S. Rajendran, S. P. A. Sridevi, N., and M. John A. A. Sundearavadevelu, "Corrosion behaviour of carbon steel in polyvinyl alcohol," *Anti-Corrosive Methods and Materials*, no. 52, pp. 102-107, 2005.
- [63]. S. Rajendran, S. P. Sridevi, N. Anthony et al., "Corrosion behaviour of carbon steel in polyvinyl alcohol," *Anti-corros. Method M*, vol. 2, no. 52, pp. 102-107, 2005.
- [64]. R. B. N. Baig, M. N. Nadagouda, and R. S. Varma, "Ruthenium on chitosan: A recyclable heterogeneous catalyst for aqueous hydration of nitriles to amide," *Green Chem.*, no. 16, pp. 2122, 2014.
- [65]. A. M. Eberhardt, M. L. Ferreira, and D. E. Damiani, "Heterogeneous Polymerization Catalysts on Natural substances," *Polymer Engineering and Science*, vol. 41, no. 6, pp. 946-954, 2001.
- [66]. S. B. Halligudi, and S. S. Khaire, "Kinetics of hydrogenation of 4-chloro-2-nitrophenol catalyzed by Pt/carbon catalyst.," *J Chem Tech Biotechnol*, no. 77, pp. 25-28, 2001.
- [67]. G. K. Yuan, M. A., "Liquid phase catalytic hydrodechlorination of 2, 4 dichlorophenol over carbon supported palladium: an evaluation of transport limitations.," *Chem Eng Sci*, no. 58, pp. 257-267, 2003.
- [68]. E. Guibal, "Heterogeneous catalysis on chitosan-based materials: a review," *Progress in Polymer Science*, no. 30, pp. 71-109, 2005.
- [69]. M. N. V. R. Kumar, "A review of chitin and chitosan applications," *React. Funct. Polym.*, no. 46, pp. 1-27, 2000.
- [70]. J. Ma, and Y. Sahai, "Chitosan biopolymer for fuel cell applications," *Carbohydr Polym.*, vol. 92, no. 2, pp. 955-75, Feb 15, 2013.

- [71]. R. Valentin, K. Molvinger, F. Quignard et al., "Supercritical CO₂ dried chitosan: an efficient intrinsic heterogeneous catalyst in fine chemistry," *New Journal of Chemistry*, no. 23, pp. 1690-1692, 2003.
- [72]. K. Molvinger, Quignard, F., D. Brunel, M. Boissiere et al., "Porous chitosan-silica hybrid microspheres as a potential catalyst," *Chem Mater*, no. 16, pp. 3367-3372, 2004.
- [73]. S. Sadjadi, M. M. Heravi, and M. Raja, "Combination of carbon nanotube and cyclodextrin nanosponge chemistry to develop a heterogeneous Pd-based catalyst for ligand and copper free C-C coupling reactions," *Carbohydrate Polymers*, no. <https://doi.org/10.1016/j.carbpol.2018.01.020>, 2018.
- [74]. S. Sadjadi, M. Heravi, and M. Malmir, "Pd@HNTs-CDNS-g-C₃N₄: A novel heterogeneous catalyst for promoting ligand and copper-free Sonogashira and Heck coupling reactions benefits from halloysite and cyclodextrin chemistry and g-C₃N₄ contribution to suppress Pd leaching," *Carbohydrate Polymers*, no. 186, pp. 25-34, 2018.
- [75]. H. W. Liu, f. Xin, L. M. Wu et al., "Catalytic behavior of silicalite-supported methylcellulose-oxalic acid-Pt complex in asymmetric hydrogenation of 2-butanone an itaconic acid.," *Polym Adv Technol*, no. 13, pp. 210-215, 2002.
- [76]. X. Zhang, Y. Geng, H. B. et al., "Asymmetric hydrogenation of ketones catalyzed by zeolite-supported gelating Fe-complex," *Polym Adv Technol*, no. 2001, pp. 642-646, 2001.
- [77]. M. Adlim, M. A. Bakar, K. Y. Liew et al., "Synthesis of chitosan-stabilized platinum and palladium nanoparticles and their hydrogenation activity," *J. Mol. Catal. A: Chem.*, no. 212, pp. 141-149, 2004.
- [78]. P. Khoza, and T. Nyokong, "Photocatalytic behaviour of zinc teteramino phthalocyanine-silver nanoparticles immobilized on chitosan beads," *J. Mole Catal. A: Chem.*, no. 399, pp. 25-32, 2015.
- [79]. W. L. Wei, H. Zhu, Y., C. L. Zhao et al., "Asymmetric hydrogenation of furfuryl alcohol catalyzed by a biopolymer-metal complex, silica-supported alginate acid-amino acid-Pt complex," *React Funct Polym*, no. 59, pp. 33-39, 2004.
- [80]. M. Lee, B.-Y. Chen, and W. Den, "Chitosan as a natural polymer for heterogeneous catalysts support: a short review on its applications," *Applied Sciences*, no. 5, pp. 1272-1283, 2015.
- [81]. A. M. Eberhardt, M. L. Ferreira, and D. E. Damiani, "Heterogenization of polymerization catalysts on natural substances," *Polymer Engineering & Science*, vol. 41, no. 6, pp. 946-954, 2001.
- [82]. S. Sadjadi, M. M. Heravi, and M. Raja, "Combination of carbon nanotube and cyclodextrin nanosponge chemistry to develop a heterogeneous Pd-based catalyst for ligand and copper free CC coupling reactions," *Carbohydrate Polymers*, vol. 185, pp. 48-55, 2018.
- [83]. H. Vaghari, H. Jafarizadeh-Malmiri, A. Berenijan et al., "Recent advances in application of chitosan in fuel cells," *Sustainable Chemical Processes*, vol. 1, no. 16, pp. 1-12, 2013.
- [84]. N. C. Mat, and A. Liong, "Chitosan-poly (vinyl alcohol) and calciu oxide composite membrane for direct methanol fuel cell applications," *Eng Letters*, no. 17, pp. 301-304, 2009.
- [85]. J. Ma, and Y. Sahai, "Chitosan biopolymer for fuel cell applications," *Carbohydrate Polymers*, no. 92, pp. 955-975, 2013.
- [86]. R. Jayakumar, N. Nwe, S. Tokura et al., "Sulfated chitin and chitosan as novel biomaterials," *International Journal of Biological Macromolecules*, no. 40, pp. 175-181, 2007.
- [87]. R. Jayakumar, N. Selvamurugan, S. V. Nair et al., "Preparative methods of phosphorylated chitin and chitosan--an overview," *Int J Biol Macromol*, vol. 43, no. 3, pp. 221-5, Oct 1, 2008.
- [88]. J. Berger, M. Reist, J. M. Mayer et al., "Structure and interactions in covalently and ionically cross-linked chitosan hydrogels for biomedical applications.," *European Journal of Pharmaceutics and Biopharmaceutics*, no. 57, pp. 19-34, 2004.
- [89]. K. Soontarapa, and U. Intra, "Chitosan-based fuel cell membranes," *Chemical Engineering Communications*, no. 193, pp. 855 - 868, 2006.
- [90]. J. Du, Y. Bai, W. Chu et al., "The structure and electric characters of proton conducting chitosan membranes with various ammonium salts as complexant," *Journal of Polymer Science. Part B: Polymer Physics*, no. 48, pp. 260-266, 2010.
- [91]. B. Smitha, D. D. Anjali, and S. Sridhar, "Proton-conducting composite membranes of chitosan and sulfonated polysulfone for fuel cell application," *International Journal of Hydrogen Energy*, no. 33, pp. 4138-4146, 2008.
- [92]. M. H. Buraidah, and A. K. Arof, "Characterization of chitosan/PVA blended electrolyte doped with NH₄I," *Journal of Non-Crystalline Solids*, no. 357, pp. 3621-3266, 2011.
- [93]. B. P. Tripathi, and V. K. Shahi, "Functionalized organic-inorganic nanostructured N-p-carboxy benzyl chitosan-silica-PVA hybrid polyelectrolyte complex as proton exchange membrane for DMFC applications.," *Journal of Physical Chemistry B*, no. 112, pp. 1567815690, 2008.
- [94]. J. Wang, Y. Zhao, W. Hou et al., "Simultaneously enhanced methanol barrier and proton conductive properties of phosphorylated titanate nanotubes embedded nanocomposite membranes," *Journal of Power Source*, no. 195, pp. 1015-1023, 2010.
- [95]. S. Zhong, X. Cui, T. Fu et al., "Modification of sulfonated poly(ether ether ketone) proton exchange membrane for reducing methanol crossover," *Journal of Power Sources*, no. 10, pp. 23-28, 2008.
- [96]. C. Zhao, H. Lin, Z. Cui et al., "Highly conductive, methanol resistant fuel cell membranes fabricated by layer-by-layer self-assembly of inorganic heteropolyacid," *Journal of Power Sources*, no. 194, pp. 168-174, 2009.
- [97]. F. Schmitt, R. Granet, C. Sarrazin et al., "Synthesis of anion exchange membranes from cellulose: Crosslinking with diiodobutane," *Carbohydrate polymers*, vol. 86, no. 1, pp. 362-366, 2011.
- [98]. R. Nassar, E. Browne, J. Chen et al., "Removing human immune deficiency virus (HIV) from human blood using immobilized heparin," *Biotechnol. Lett.*, no. 34, pp. 853-856, 2012.
- [99]. A. J. Varma, S. V. Deshpande, and J. F. Kennedy, "Metal complexation by chitosan and its derivatives: a review.," *Carbohydrate Polymer*, no. 55, pp. 77-93, 2004.
- [100]. G. Crini, and M. Morcellet, "Synthesis and applications of adsorbents containing cyclodextrins," *J. Sep. Sci.*, no. 20, pp. 341-359, 2002.
- [101]. J. Berger, M. Reist, J. M. Mayer et al., "Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications," *Eur J Pharm Biopharm*, vol. 57, no. 1, pp. 35-52, Jan, 2004.
- [102]. G. Mocanu, D. Vizitiu, and A. Carpov, "Cyclodextrin polymers.," *J. Bioactive Compatible Polym*, no. 16, pp. 315-342, 2001.
- [103]. X. D. Liu, S. Tokura, M. Haruki et al., "Surface modification of nonporous glass beads with chitosan and their adsorption property for transition metal ions," *Carbohydrate Polymer*, no. 49, pp. 103-108, 2002.
- [104]. X. D. Liu, S. Tokura, N. Nishi et al., "A novel method for immobilization of chitosan onto non-porous glass beads through a 1,3-thiazolidine linker," *Polymer*, no. 44, pp. 1021-1026, 2003.
- [105]. J. Li, B. Jiang, Y. Liu et al., "Preparation and adsorption properties of magnetic chitosan composite adsorbent for Cu²⁺ removal," *Journal of Cleaner Production*, no. doi: 10.1061/j.clepro.2017.04.156, pp. 1-28, 2017.

- [106]. Rahmi, Lelifarjri, Julinawati et al., "Preparation of chitosan compsite film reinforced with cellulose isolated from oil palm empty fruit bunch and application in cadmium ions removal from aqueous solutions," *Carbohydrate Polymers*, no. <http://dx.doi.org/10.1002/star.201500155>, pp. 1-20, 2017.
- [107]. R. Huang, L. Qian, J. Huo et al., "Adsorption of methyl orange onto protonated cross-linked chitosan," *Arabian Journal of Chemistry*, no. <http://dx.doi.org/10.1016/j.arabjc.2013.05.017>, pp. 1-9, 2013.
- [108]. C. A. Demarchi, and C. A. Rodrigues, "Adsorption of Cr(IV) by chitosan-iron (III) in an air-lift reactor," *Water Sciences and Technology*, vol. 4, no. 73, pp. 857-865, 2016.
- [109]. D.-W. Cho, B.-H. Jeon, C.-M. Chon et al., "Magnetic chitosan composite for adsorption of cationic and anionic dyes in aqueous solutions," *Journal of Industrial and Engineering Chemistry*, no. <http://dx.doi.org/10.1016/j.jiec.2015.01.023>, pp. 1-7, 2015.
- [110]. R. Bhatt, B. Sreddhar, and P. Padmaja, "Adsorption of chromium from aqueous solutions using crosslinked chitosan-diethylenetriaminepentaacetic acid," *Biological Macromolecules*, no. <http://dx.doi.org/doi:10.1016/j.ijbiomac.2014.12.041>, pp. 1-44, 2014.
- [111]. Y. Fu, X. Xu, Y. Huang et al., "Preparation of new diatomic-chitosan composite materials and their adsorption properties and mechanism of Hg(II)," *Royal Society Open Science*, no. <http://dx.doi.org/10.1098/rsos.170829>, pp. 1-10, 2017.
- [112]. G. Rojas, J. Silva, J. A. Flores et al., "Adsorption of chromium onto cross-linked chitosan," *Separation and Purification Technology*, vol. 44, no. 1, pp. 31-36, 2005.
- [113]. C. Li, Q. Lin, Q. Liu et al., "Synthesis and adsorption properties of crosslinked starch microspheres," *Advanced Materials Research*, no. 418-420, pp. 702-705, 2012.
- [114]. X. Ma, X. Liu, D. P. Anderson et al., "Modification of porous starch for the adsorption of heavy metal ions from aqueous solution," *Food Chemistry*, no. 181, pp. 133-139, 2015.
- [115]. R. Klimaviciute, R. Rutkaite, and P. P. Danilovas, "Adsorption of iodine on cationic cross-linked starches," *CHEMJA*, vol. 22, no. 4, pp. 188-196, 2011.
- [116]. D. Soto, J. Urdaneta, K. Pernía et al., "Removal of heavy metal ions in water by starch esters," *Starch - Stärke*, vol. 68, no. 1-2, pp. 37-46, 2016.
- [117]. J. Hu, T. Tian, and Z. Xiao, "Preparation of cross-linked porous starch and its adsorption for chromium (VI) in tannery wastewater," *Polymers for Advanced Technologies*, vol. 26, no. 10, pp. 1259-1266, 2015.
- [118]. X. He, K. B. Male, P. N. Nesterenko et al., "Adsorption and Desorption of methylene blue on porous monoliths and nanocrystalline cellulose," *Applied Materials & Interface*, no. 3, pp. 8796-8804, 2013.
- [119]. H. Dai, Y. Huang, and H. Huang, "Eco-friendly polyvinyl alcohol/carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite for enhanced adsorption of methylene blue," *Carbohydrate Polymer*, vol. <https://doi.org/10.1016/j.carbpol.2017.12.073>, pp. 1-32, 2017.

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