A Review of Chitosan-Based Materials for the Removal of Organic Pollution from Water and Bioaugmentation

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Abstract

Chitin is a natural polymer extracted mostly from shrimp or crab shells and is the Earth's second most abundant polysaccharide. After a simple deacetylation procedure, chitin is converted into chitosan that consists in a polysaccharide structure of deacetylated-β-glucosamine. Chitosan has been largely employed in wastewater treatment the removal of colloids through coagulation-flocculation processes. Different chitosan based materials have been produced and tested in the removal of inorganic pollutants such as toxic metals and metalloids, nutrients, dyes, micropollutants and hydrocarbons. Sorbents such as magnetic-activated carbon chitosan have been successfully tested in the removal of antibiotics (ciprofloxacin, erythromycin and amoxicillin) from water. Raw chitosan and ZnO nanoparticles entrapped in chitosan have demonstrated an excellent potential for the removal of the insecticide permethrin from aqueous effluents. Chitin and chitosan in flake and powder form have also demonstrated a promising effectiveness in the removal of oil spilled in seawater. Superhydrophobic and superoleophilic sponges modified by thioles have been also prepared from chitosan and used for the removal of oil spills. Chitosan hydrogels have been tested as well as entrapment matrices for the immobilization of hydrocarbon-degrading biomass for oil spills. Strains such as *R. corynebacteriorides* (QBTo), *Bacillus subtilis* LAMI008 and *B. pumilus* have been successfully immobilized and employed in hydrocarbon degradation processes. In this book chapter, the use of chitosan and chitosan-based materials in the removal of organic pollutants from water is reviewed.

Keywords: chitin, chitosan, adsorption, organic pollutants, sorbents, oil spill pollution, bioaugmentation, water treatment
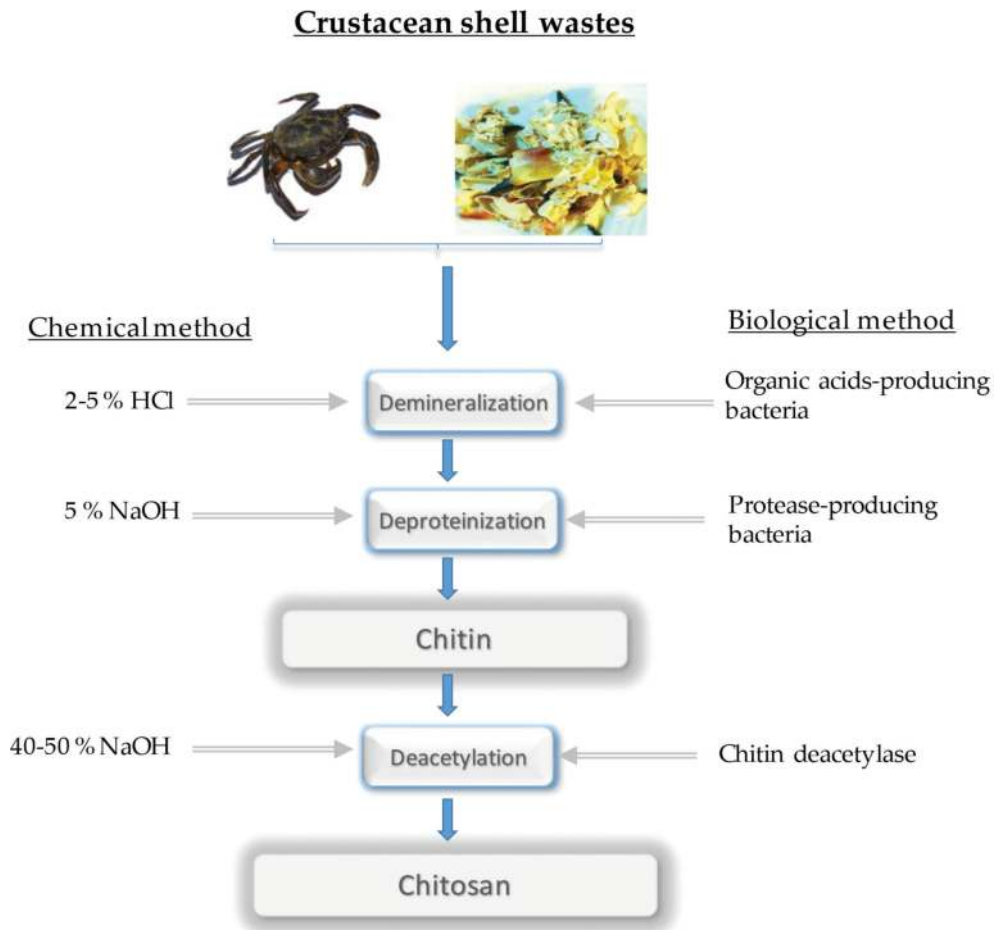
1. Introduction

Chitin is a natural polysaccharide and the second most abundant biopolymer on Earth after cellulose [1]. This biopolymer consists of units of β-(1–4)-N-acetyl-D-glucosamine and is the main component of the exoskeleton of arthropods and crustaceans but also can be found in relevant amount in the cell walls of fungi. Chitin is a structural biopolymer whose role is analogous to that of collagen in the higher animals and cellulose in terrestrial plants [2]. In a similar way, plants produce cellulose in their cell walls, and insects and crustaceans synthetize chitin and accumulate it in their shells. Chitin may be regarded as cellulose with hydroxyl at position C2 replaced by an acetamide group (-CONH$_2$). This similarity partly explains some analogies occurring in chitin and cellulose, such as low solubility and low chemical reactivity [3]. Chitin is found in three polymeric forms, α-, β- and γ-chitin, usually found in shrimp and crab shells, squid pen and stomach cuticles of cephalopod, respectively. From the three aforementioned forms of the biopolymer, α-chitin is the most abundant and stable form. α-, β- and γ-chitin correspond to antiparallel, parallel and alternated arrangements of polymer chains, respectively. A hydrogen bond between the acetamide group on the C2 carbons and the secondary alcoholic hydroxyl groups on the C3 carbon is linked through a water molecule with the primary alcoholic hydroxyl groups on a C6 carbon. As a result of this configuration, chitin possesses a strong crystalline structure, which explains the high chemical and solvent stability of the biopolymer. Due to its crystalline structure, chitin exhibits remarkable differences from cellulose in the solubility and reactivity despite of the relatively similar chemical structure [3].

The production of chitin uses basic raw materials of the cuticles of various crustaceans, principally crabs and shrimps. In regular fishery wastes, the biopolymer chitin is associated with proteins, minerals, lipids and pigments [4]. All these substances are considered impurities, and they all have to be quantitatively removed to achieve the required purity of the chitin. The chitin is normally extracted from the carapaces from crustaceans treating the crushed material with acid to achieve complete dissolution of the calcium carbonate structure. After this process, the material is submitted to an alkaline extraction to achieve the solubilization of the proteins. In a later purification step, the material obtained from the deproteinization process follows a decolorization step to remove residues of pigments to yield an almost colorless product [5]. Partial deacetylation of chitin leads to the formation of the polymer chitosan, consisting of units poly(D-glucosamine). A scheme of the production of chitosan from waste crustacean shells following chemical and biological approaches is presented in **Figure 1**.

When the degree of deacetylation of chitin reaches about 50%, the material obtained starts becoming soluble in aqueous acidic media and is called chitosan [5]. The degree of deacetylation is indicative of the amount of amino groups (-NH$_2$) along the chitosan chain and refers to the degree of removal of acetyl groups (-COCH$_3$) from the amido moieties. The degree of deacetylation and the degree of polymerization (DP), which in turn decides molecular weight of polymer, are two important parameters dictating the use of chitosans for various applications [1]. A scheme of the deacetylation reaction that converts raw chitin into chitosan is presented in **Figure 2**.

Figure 1. Production of chitin and chitosan using chemical and biological methods (adapted from Jo and co-authors [6]).

Chitosan is insoluble in water, alkali and organic solvents but soluble in most solutions of organic acids when the pH of the solution is lower than 6. Acetic and formic are two of the most widely used acids employed to solubilize chitosan. Some dilute inorganic acids such as nitric acid (HNO_3), hydrochloric acid (HCl), perchloric acid ($HClO_4$) and phosphoric acid (H_3PO_4) can also be used to prepare chitosan solutions but only after prolonged stirring and warming [7]. At low pH chitosan remains as a polycationic species, due to protonation of the amino group according to **Figure 3** [8].

Chitosan exhibits a unique set of properties that makes this polymer a great candidate for the development of water treatment processes. Among them, the most relevant are its high biodegradability, low toxicity, low price and natural availability. The weaknesses exhibited by
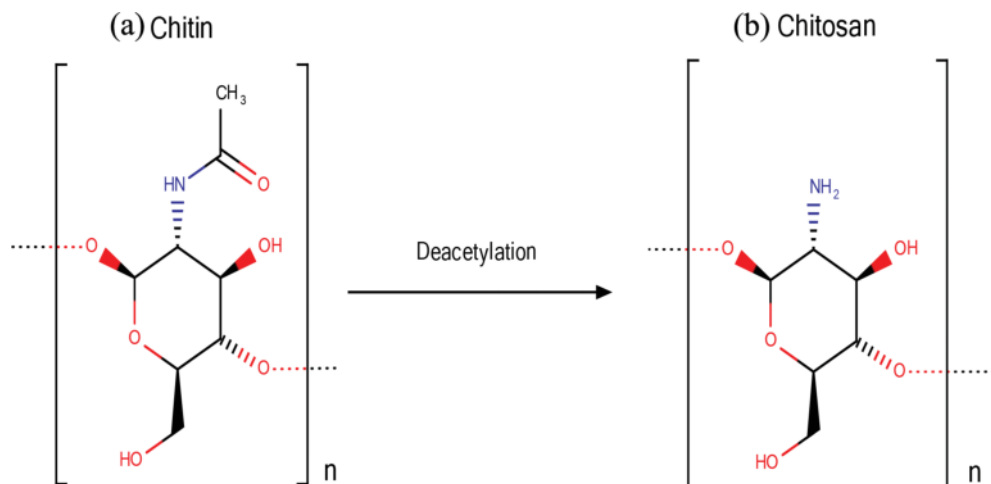
Figure 2. Chemical structure of (a) chitin and (b) chitosan.

this biopolymer however derive from its low acid stability, poor mechanical properties, low thermal stability, resistance to mass transfer, low porosity and surface areas [9, 10]. In order to overcome the drawbacks exhibited by chitosan, a large amount of effort has been devoted to the development of physicochemical modification methods to include different types of functionalization in the polymer. Chemical modifications such as oligomerization, alkylation, acylation, quaternization, hydroxyalkylation, carboxyalkylation, thiolation, sulfation, phosphorylation, enzymatic modifications and graft copolymerization have been carried out, allowing obtaining modified properties for specific end used applications in a large variety of fields [1]. Following physical and chemical methods, researchers have managed to produce a variety of forms of chitosan such as gel beads, membranes, film, fibers, porous frameworks, powders, sponges, hollow fibres and nanoparticles [11–20]. Some chemical modifications have been found capable of enhancing its flexibility and chemical stability and lower its susceptibility to acidic media. Among the most widely employed modifications that contribute modulation of
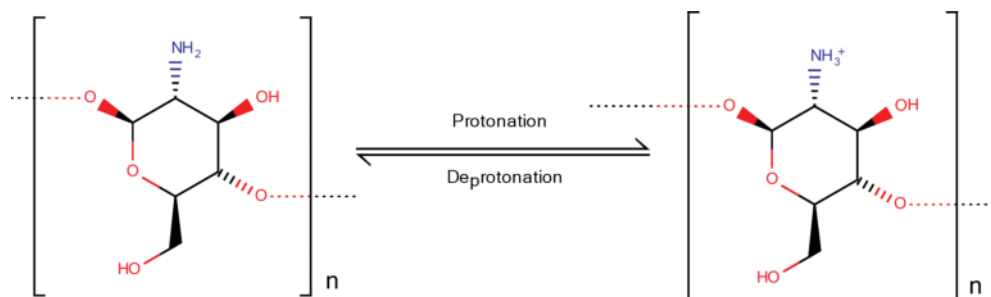

Figure 3. Protonation and deprotonation equilibrium of chitosan.

the functional properties of chitosan while improving the mechanical strength, cross-linking might be found. Several reagents such as glyoxal, glutaraldehyde and epichlorohydrin have been employed to reinforce the structure of chitosan by cross-linking [19, 21–23].

2. Chitosan-based systems for the removal of organic pollutants

Chitosan has revealed a large potential in the detoxification of polluted effluents. This biopolymer on itself and chitosan-based materials have not only shown a high capacity to remove a variety of toxic metals such as Cu(II) [24–27], Pb(II) [28, 29], Cr(VI) [30, 31], As(V) [32], Mo(VI) [33] and Hg(II) [34] but also have demonstrated a large potential to remove other concerning inorganic species from water such as nutrients (NO_3^-, NO_2^- and PO_4^{-3}) [35, 36]. In addition to the abatement of inorganic pollution from water, this biopolymer has been also explored as sorbent against organic pollution. In the next sections, we review the use of raw chitosan and chitosan-based materials in the removal of micropollutants and in the abatement of hydrocarbon pollution associated to oil spills.

2.1. Chitosan-based materials for the removal of organic pollutants

In recent years, chitosan-based composites using metals [37], metal oxides [38] and bimetals [39] have been receiving a large attention as alternative sorbents in water treatment processes. These kinds of materials have been chosen primarily due to their high adsorption capability [40]. Arayne and co-workers in 2011 studied the potential of raw chitosan beads and chitosan beads modified with ZnO nanoparticles (Cs/ZnO NPs) to remove permethrin, an insecticide largely employed in agriculture [41]. Through this study, the authors demonstrated that chitosan beads have an excellent adsorption performance and that the removal efficiency from a 0.1 ppm solution of permethrin increased from 49% when using chitosan beads to 99% when using Cs/ZnO NPs. Despite chitosan demonstrated a high capacity on itself to remove permethrin, including Cs/ZnO NPs in the matrix of the biopolymer, provided a large enhancement that leads to the almost total removal of this pollutant [42]. Saifuddin and co-authors, also in 2011, reported the use of a composite system based on cross-linked chitosan-silver nanoparticles (Cs-Ag NPs) to remove the pesticide atrazine (a very persistant herbicide of the triazine class) [43]. In their study, the kinetics of removal of the pesticide by the developed sorbent was evaluated. The authors reported an equilibrium time at about 65 min for 1, 5, 10, 20 and 25 ppm of atrazine. During their experiments, the authors detected a remarkable increase in the reduction of the pesticide content in water when increasing the sorbent dose. At the dosage of 2.0 g/L of Cs-AgNPs composite, 98% of the initial concentration of atrazine (from 1 ppm solution) was removed [43].

Danalıoğlu and co-authors, in a recent study, developed and tested a novel adsorbent based on a composite magnetic-activated carbon/chitosan system (MACC) for the removal of three widely employed antibiotics: ciprofloxacin, erythromycin and amoxicillin [44]. In their study, MACC nanocomposite demonstrated a good adsorption performance towards the targeted antibiotics [44]. Herein, the initial concentrations of antibiotics tested were 15, 60 and 60 ppm for ciprofloxacin, erythromycin and amoxicillin, respectively. To the initial antibiotic solution,

1 mg of MACC adsorbent was added. As a result, adsorption took place rapidly during the first 30 min, and then the adsorption rate slowed down to reach the equilibrium at about 120 min. The authors performed a set of equilibrium experiments and, by means of the Langmuir isotherm model, managed to calculate the maximum sorption capacity of the material for the different antibiotics (90.01 mg/g for ciprofloxacin, 178.57 mg/g for erythromycin and 526.31 mg/g for amoxicillin [44]). Danalıoğlu et al. also compared the adsorption capacity of MACC for ciprofloxacin to that reported for magnetic alginate-Fe_3O_4 hydrogel fiber and graphene oxide/calcium alginate [44]. Magnetic alginate-Fe_3O_4 hydrogel presented an adsorption capacity for ciprofloxacin ranging from 153 to 555 μg/g [45], and graphene oxide/calcium alginate varied from 18.45 to 39.06 mg/g [46].

In addition to the studies described above, other researchers have reported the removal of phenol and o-chlorophenol using chitosan beads modified with sodium alginate and calcium chloride [47]. These authors reported that such a modification improved the stability of the obtained material as well as the sorption capacity of the beads. The maximum sorption capacity for phenol reported by the authors in this study was 108.69 mg/g, while for o-chlorophenol was 97.08 mg/g. Lie and colleagues investigated the use of raw chitosan, chitosan chemically modified with salicylaldehyde (CS-SA), β-cyclodextrin (CS-CD) and a cross-linked β-cyclodextrin polymer (EPI-CD) in the removal of phenol, p-nitrophenol and p-chlorophenol from aqueous solution [48]. In their study, it was observed that the adsorption capacity of unmodified chitosan for phenol was remarkably lower than that observed for the modified biopolymer. While the chitosan modified by CS-CA was able to achieve a capacity of 8.50, 20.49 and 44.92 mg/g for phenol, p-chlorophenol and p-nitrophenol, respectively, the raw, unmodified chitosan was only able to barely remove about 2 mg/g of the substances. On the other hand, the sorption capacity of chitosan chemically modified by CS-CD was 34.93, 179.73 and 20.562 mg/g for phenol, p-chlorophenol and p-nitrophenol. The last modification by EPI-CD led to the sorption capacities of 131.50 mg/g (phenol), 74.25 mg/g (p-chlorophenol) and 41.11 mg/g (p-nitrophenol) [49].

The removal of phthalate esters (PAEs) [50] by molybdate-impregnated chitosan beads (MICB) in an aqueous solution has also been reported by Chen and co-workers in 2007. The experiments performed by the authors indicated that all PAEs studied were adsorbed by MICB; however, diheptyl phthalate (DHpP) was most efficiently removed, achieving capacity values of 3.01 mg/g and a removal value of 92.5% [51].

2.2. Chitosan-based materials for the removal of oil pollution from water

Among the different types of organic pollution affecting water bodies, a specially concerning type nowadays is the oil pollution. While catastrophic spills such as the Exxon Valdez oil spill in the coast of Alaska (1989) or the BP Deepwater Horizon oil spill in the Gulf of Mexico (2010) caused a very important harm and gathered a large amount of public attention, most of the oil spills are less extraordinary [52]. It is estimated that about 9 million barrels of oil are released globally into the oceans every year. Of this amount, however, more than half come from natural seepage from the ocean floor, and human consumption activities represent the second largest source of oil released into the oceans (about 35%) [52]. Eco-friendly and sustainable approaches to remove oil pollution from water are therefore required to avoid the environmental threat and hazards associated to it.

Different kinds of adsorbents have been explored for the removal of oil droplets from oil-in-water emulsions. For instance, activated carbon, biopolymers, organoclays, sawdust, vermiculite, walnut shell and resins have been tested for this purpose [53–58]. Biopolymer-supported materials have demonstrated being an efficient adsorbent for the removal of several contaminants from aquatic ecosystems. However, some of them have exhibited limitations when facing the scenario of oil removal. Chitosan has demonstrated being one of the most efficient biopolymers for the removal of oil droplets from water. The polymer, in addition to its oil sorption capacity, exhibits a unique structure that is very prone to chemical functionalization, allowing a large versatility in the production of novel sorptive materials with oil-enhanced selectivity and capacity. In addition to this, chitosan has a good biodegradability, biocompatibility, eco-friendliness and low cost [59, 60].

Barros and co-workers [61] investigated the adsorption capacity of chitin flakes, chitin and chitosan powder, chitosan flakes and chitosan solution towards crude oil spilled in seawater. In their study, 5 L of seawater were placed in a plastic container, and 7 g of petroleum were added to it. After 30 min, 50 mL of a 0.5% chitosan solution was sprayed over the oil spill. The results showed that, although chitosan flakes had a better adsorption capacity for oil (0.379 ± 0.030 g oil/g adsorbent) compared to the others, the biopolymer sank after adsorbing the oil. Such a characteristic offered a clear hinder in practical applications. On the other hand, chitosan solution, despite presenting lower adsorption capacity (0.013 ± 0.001 g oil/g adsorbent), did not present the low buoyancy drawback [61]. Elanchezhiyan and colleagues [62] investigated the recovery of oil from oil-in-water emulsion using chitosan/magnesium-aluminum layered double hydroxide hybrid composite (CS-LDHCs) obtained by a single co-precipitation method. CS-LDHC adsorbent was dispersed in 20 mL of deionized water solution containing 4% of oil and the effect of contact time in the oil removal by the CS-LDHCs and the layered double hydroxide hybrid (LDH) was investigated [62]. This was done by varying the contact time from 10 to 120 min at room temperature. Both adsorbents, CS-LDHCs and LDH, reached maximum oil removal saturation at 90 min, and, thus, the authors set 90 min as contact time for both adsorbents in further experiments. The researchers reported an oil removal capacity of 78% for CS-LDHCs, while for the LDH was found to be 30%. Since CS-LDHCs showed a much higher oil adsorption capacity, further studies were performed just targeting this material [62]. The effect of pH was also investigated in their study in the range from 3 to 11. This was done because normally the change in pH of oil-in-water emulsions cause emulsion breaking, which means that demulsification takes place [59, 63]. After their pH study, the authors demonstrated that the adsorption of oil was enhanced in acidic medium (pH 3.0) [62].

Elanchezhiyan and co-workers also studied the effect of contact time on the removal of oil from oil-in-water emulsion using zirconium-chitosan composites (Zr-CS-HC) in time-course experiments at room temperature [59]. The study of the effect of sorbent dosage of Zr-CS-HC indicated that a maximum oil removal percentage of 79% was achieved when exposing 400 mg of sorbent to 25 mL of polluted solution [59]. The authors determined that the maximum oil uptake on chitosan was reached after 4 h contact time. In their study, the authors demonstrated that Zr-CS-HC had a higher removal efficiency compared to chitosan and provided an explanation based on the higher number of vacant sites on the surface of Zr-CS-HC [59].

Grem and co-authors reported that chitosan microspheres produced by ionic gelation of chitosan with sodium tripolyphosphate (STP) were able to separate 90% of the oil from produced water containing 200 ppm oil suspension using packed columns [64].

In another very recent study, Doshi and colleagues [65] studied amphiphilic sodium salt of oleoyl carboxymethyl chitosan (NaO-CMCS) for the removal of oil from a simulated oil spill. Marine diesel was chosen as oil phase for the emulsion studies [65], and in their study, both deionized water and seawater were used to simulate oil-in-water (o/w) emulsions (1:1 v/v). The o/w creamy emulsions were prepared with different dosages of NaO-CMCS (0.5–5 g/L), and a calcium chloride dihydrate solution (0.1%) was also added to that mixture. From the results obtained, the authors concluded that about 75–85 and 19–49% of oil was recovered from the emulsified oil using deionized water and seawater, respectively [65]. The recovery of oil from the polluted aqueous phase was 76% in the case of deionized water containing a 0.5 g/L concentration of NaO-CMCS and 20% from seawater with a 2 g/L dose of NaO-CMCS. It was therefore concluded that this chitosan derivative was an effective material for the removal of oil from spills from polluted seawater [65].

Ummadisingu and co-workers [66] prepared chitosan from seafood industry waste and tested the purified material for the removal of oil from aqueous solutions. The authors explored the effect of contact time, pH, initial concentration and mass of adsorbent. They reported that the sorption equilibrium of oil on chitosan was reached after only 6 min of contact time, and the maximum capacity of chitosan to adsorb oil from oil–water solution was found to be 17.96 g/g of adsorbent [66].

Su and colleagues [67] have recently reported the preparation of a superhydrophobic and superoleophilic chitosan sponge using a freeze-drying method with the assistance of a cross-linking process employing tripolyphosphate/citral followed by octadecanethiol modification. In their paper, the authors describe a procedure that allowed getting a three-dimensional porous structure with large pore volume and good compressive properties. The obtained sponge was able to effectively absorb oil, reaching an absorptive capacity up to 60 times its own weight. The material was able to selectively absorb the emulsified oils in water and achieve continuous oil–water separation. The authors reported an oil–water separation efficiency up to 99% and claimed that the sponge still maintained a highly absorptive capacity after being reused for many cycles while having a good biodegradability.

Bibi and co-workers [68] investigated the adsorption capacity of carbon nanotubes (CNTs) mixed with chitosan (Cs)/poly(vinyl alcohol) (PVA) and cross-linked with silane. In their experimental setup, naphthalene was selected as polycyclic aromatic hydrocarbon (PAH) model, and its removal was studied with two membranes, CM10 and CW with and without CNTs, respectively [68]. A standard solution of 3 mg/L of naphthalene was prepared, and 30 mg of membranes were placed in 40 ml naphthalene-containing solution. The removal percentage of naphthalene with the CW membrane during the first 5 min reported by the authors was 10% and after 150 min 93%. For the CM10 membrane, more than 50% of naphthalene was removed during the first 5 min and 97% after 150 min. These results showed that CM10 membrane had good sorption capacity for naphthalene and that the sorption process took place fast [68]. The correlation between CNT content of the membrane and the removed amount of the naphthalene was 0.16 mg of naphthalene/1 mg CNTs. The authors reported that CW

membrane had equilibrium swelling of 217 g/g and CM10 of 162 g/g and concluded that the best membrane was CM10 due to its excellent sorption capacity and fast removal kinetics [68].

2.3. Chitosan-based materials containing immobilized bacteria for the removal of oil pollution

Among the different clean-up actions and materials employed as a first response against oil spills, the use of booms, skimmers, absorbent materials, controlled burning and vacuum and centrifuges might be found. These techniques cannot however achieve a complete clean-up of the polluted area, and their implementation should be done short after the oil spill occurs [69]. In the last years, the use of bioremediation-based techniques has largely attracted the attention of researchers and industrial stakeholders. The use of microorganisms for these decontamination purposes is considered as an effective and environmentally friendly treatment for, i.e., shorelines contaminated as a result of marine oil spills. Most of the compounds present in crude oil and refined products are prone to biodegradation and therefore might be removed from the environment through consumption by microbes [69]. There are mostly two complementary approaches: bioaugmentation and biostimulation. While the first approach involves addition of oil-degrading bacteria to the polluted system, the second approach intends to support the growth of the indigenous hydrocarbon degraders present in the system by the addition of nutrients and/or other growth-limiting substances [69, 70]. A scheme of a biodegradation is presented in **Figure 4**. The most rapid and complete degradation of the majority of organic pollutants is brought about under aerobic conditions. Such a process is normally initiated through an intracellular oxidative attack and the activation of the organic molecule through incorporation of oxygen in a reaction catalyzed by oxygenases and peroxidases [71]. A complete oxidation of the target hydrocarbon would lead to the production of CO_2 and water. The generation of different series of structures corresponding to different transformation products should however not be disregarded when this kind of bioremediation techniques is explored.

In order to improve the performance of the degradation of oil-related pollutants, some researchers have proposed strategies that involve the use of biomass in immobilized systems. One of the preferred entrapment systems for these purposes has been chitosan. In addition to the natural trend of chitosan to absorb oil, chitosan hydrogels have excellent water permeability and mass transfer properties (allowing the required access of the biomass to the nutrients they require). In addition to the aforementioned benefits, chitosan contributes to providing shelter to the valuable biomass while helping preserving the integrity of the culture. The use of microorganisms entrapped in chitosan gel matrices is therefore expected to have a very positive impact in both bioaugmentation- and biostimulation-based decontamination processes.

Dellagnezze and co-workers studied a bacterial consortium composed of four metagenomic clones and *Bacillus subtilis* strain CBMAI 707 (all derived from petroleum reservoirs) entrapped in chitosan beads towards hydrocarbon degradation capacity [72]. Experiments were carried out in mesocosm scale (3000 L) with seawater artificially polluted with crude oil. The compounds present in the oil that were the target of the biodegradation studies were benzo (a) pyrene ($C_{20}H_{12}$), benzo (a) anthracene ($C_{18}H_{12}$) and benzo (K) fluoranthene ($C_{20}H_{12}$) [73–75]. The degradation of hydrocarbons was evaluated in two different treatments: bioaugmentation and control. The authors performed time-course experiments, following the system at days 0, 5, 10, 20 and 30. The researchers demonstrated that degradation ratios increased abruptly from
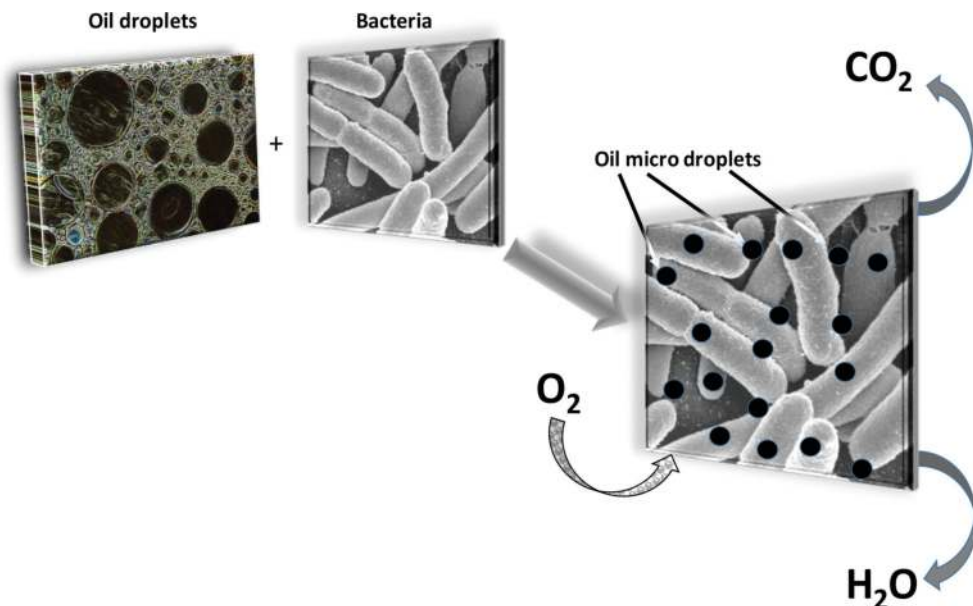
Figure 4. Oil biodegradation scheme under aerobic conditions.

the 5th to the 10th day and then just slightly increased until the end of the experiment. The system remained closed during the first 5 days to allow the acclimation of the bacteria to both treatments, and during this period, the authors did not observe significant biodegradation rates [72]. More than 90% of hydrocarbons' degradation was produced by the 10th day in both treatments. Similar to the 10th day, in day 20 most of the hydrocarbons were totally degraded. After 30 days from the beginning of the assays, the degradation percentages in the bioaugmentation treatment were higher than those observed in the control treatment. For instance, 35% of benzo (k) fluoranthene was degraded in the control treatment, 70% was degraded in the bioaugmentation treatment, and benzo (a) pyrene was almost completely degraded (99%). Likewise, benzo (a) anthracene showed higher degradation percentage, reaching 85% in the bioaugmented series compared to a 68% observed in the control [72].

Sar and Rosenberg [76] studied the biodegradation of n-hexadecane and its biosurfactant recovery. For this purpose, spores of *Bacillus subtilis* LAMI008 were entrapped in 3 mm chitosan beads and cross-linked with 0.3% glutaraldehyde [76]. The authors performed biodegradation assays in 50 mL of mineral medium containing 1% n-hexane (v/v) supplemented with 1% glucose (w/v) and inoculated with 10% of spore suspension (v/v) or with 10% of spore-entrapped chitosan beads (w/v). Both cultures were adjusted to 10^7 CFU/mL [76]. The biodegradation of n-hexadecane by *Bacillus subtilis* LAMI008 entrapped in chitosan beads was compared with that by free cells under similar conditions, and almost 100% of 1% n-hexadecane was degraded within 48 h in both assays.

In another study Gentili and co-authors [77] examined the potential of chitosan flakes as carrier material for the immobilization of *R. corynebacteriorides* (QBTo), a hydrocarbon-degrading

bacterial strain. The authors performed biodegradation tests in a crude oil-polluted seawater microcosms [77]. For this purpose, three different microcosm situations were tested. In the microcosms inoculated with QBTo immobilized onto chitosan, 60% of hydrocarbons in the hexane extracts were removed compared with the control microcosms sample and the seawater microcosms. In the control microcosms, QBTo could not produce a significant reduction in the hydrocarbon concentrations [77]. In the seawater microcosms, QBTo was inoculated without a carrier, and a decrease of 30% of hexane extract was obtained. The degradation of hydrocarbons in the microcosms with the strain QBTo immobilized onto chitosan was higher than that obtained in the microcosms without the carrier. The explanation to this improvement is due to the enhancement of the strain survival, since the carrier material and the biofilm structure that the cells developed on it exert a protective effect [77].

Costa and co-authors [78] investigated the potential of the bacterial strain *B. pumilus* entrapped in chitosan in the degradation of hexadecane. The biodegradation assays were performed with free-living and immobilized bacterial cells with 1% hexadecane (v/v). In addition to this, 5 mL of an adjusted culture with 10^9 CFU/mL were used in free-living cell assays [78]. For the immobilized assays with bacterial cells, 5 g of chitosan beads containing the selected strain were used, and the biodegradation was studied at 0, 48, 96 and 144 h. The biodegradation results indicated that after 48 h, the free-living cells removed 81.83% of the hydrocarbon, while the culture of immobilized cell was able to remove only 38.12%. The authors provided an explanation to this based on the fact that in the assays performed with free-living cells, there was approximately 10^4 times more biomass than in the experiments performed with immobilized cells. The authors pointed out that during the immobilization process there was an important loss of cells. Cell counting performed by the authors during the biodegradation experiments showed that the immobilized biomass grew progressively and removed 84.53% of hexadecane after 96 h. These results, obtained in a larger time span, where similar to the 86.28% removed in assays performed with non-immobilized, free-living cells. Moreover, the authors found that the biomass concentration inside the beads was similar to that observed in the free-living cultures at 144 h and also removed hexadecane efficiently [78].

3. Conclusions

Chitosan offers a large potential in the development of sorbent materials for abatement of organic pollution from water. The biopolymer can be used in many different applications on its raw form or included in the preparation of a large variety of materials such as hydrogel beads, nanoparticles, films, membranes and meshes. Among the different scenarios of severe organic pollution, the pollution caused by hydrocarbon spills into water bodies deserves a special mention. Chitosan and materials based on this polymer have demonstrated an enormous potential to efficiently remove hydrocarbons from contaminated water. In addition to the aforementioned, the potential offered by chitosan to develop biological remediation systems deserves a special mention. The excellent biocompatibility of this polymer makes possible development of oil remediation biosystems based on bacteria entrapped into chitosan.

Conflict of interest

The authors certify that they have no conflict of interest.

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