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Green Polymers and Their Uses in Petroleum Industry, Current State and Future Perspectives

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Abstract

The concept of green chemistry has been established to find safe methodologies and environmentally benign solutions for the present and the onset problems. In this regard, extensive work has been carried out worldwide to replace the currently used materials with green ones. The terminology green relies on all the non-pollutive or the degradable materials regardless of their source. Therefore, there are biobased green materials and non-biobased green materials. This review sheds light on several green polymers used in different petroleum industries. The polymers are reviewed according to the stage of oil processing in which they are applied. Furthermore, different modification methodologies of natural polymers are revised. Also, the role of green non-biopolymers in different petroleum industries is investigated. It is worth mentioning that we concentrate our efforts on the utilization of different natural polymers in petroleum applications. Thereafter, some natural polymers such as chitosan and cellulose and their derivatives were specifically reviewed.

Keywords: Green polymers, corrosion inhibitors, demulsifiers, oil spill dispersants

1. Introduction

The majority of raw materials used today derived from non-renewable sources such as coal and petroleum. This caused many drawbacks such as a severe depletion of non-renewable resources, continuous growth in petroleum prices, environmental impact with the rise in the emission of greenhouse gases, and accumulation of non-biodegradable waste on earth [1–3]. Currently, major global attention has shifted to other sources, for many reasons such as, need for enormous novel and sustainable material resources; supplement, reuse, and replace of petroleum-based polymeric materials; biodegradability of materials to prevent a buildup of waste; the toxicity associated with the preparation, usage, and environmental safety. Therefore, the utilization of natural resources as alternatives for petroleum-based products has been increased (**Figure 1**).

Consequently, some new terms have been developed, such as green, environmentally benign, biodegradable ... etc. Therefore, polymers are referred “green” if they exhibit one or more of the following properties: source renewability,

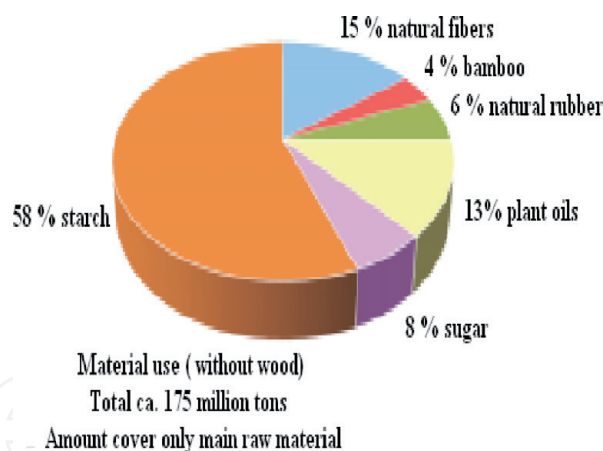


Figure 1.
Worldwide use of renewable resources for materials in 2008.

biodegradability, composability after end of the life and environmentally friendly processing [3, 4].

Many materials can be categorized under this term such as:

- Biopolymers: Biodegradable polymers (From biopolymers or petropolymers).
- Recyclable polymers: (From biopolymers or petropolymers).
- Polymers from renewable resources: The input materials for the production of these polymers may be either renewable (based on agricultural plant or animal products) or synthetic (derived from or based on petroleum crude oil).

Sustainable polymers from renewable resources can be prepared through chemical modification of natural polymers, such as cellulose, starch, chitin, etc. Bio-based polymers also synthesized through a two-step process from biomass (lignin, cellulose, starch, plant oils) [5–7]. Carbohydrates are the most prominent raw materials for industrial chemicals as they account for around 95% of annually produced biomass. The conversion methods including chemical and biological methods, direct extraction and selected technological advancements will be discussed. Furthermore, the application of green polymers in some petroleum processes also will be investigated.

2. Biopolymers versus green polymers

Macromolecules which are produced by living organisms and given the term biopolymers have numerous functions. Some of them, as DNA molecule, have so specific functions in information storing and convey. Others are formed in considerable level (scale) and offer protection in the form of hard shells or structural integrity [8–11]. These ‘structural’ biopolymers symbolize a various range of chemical functionality and compositions and can be largely categorized as polysaccharides, triglycerides, polypeptides (**Figure 2**). As general, all biopolymers are green but not all green polymers are derived from natural sources, there are green synthetic polymers such as polyesters and some green polymers are derived from crude oil such as polycaprolactam (PCL) (**Figure 3**).

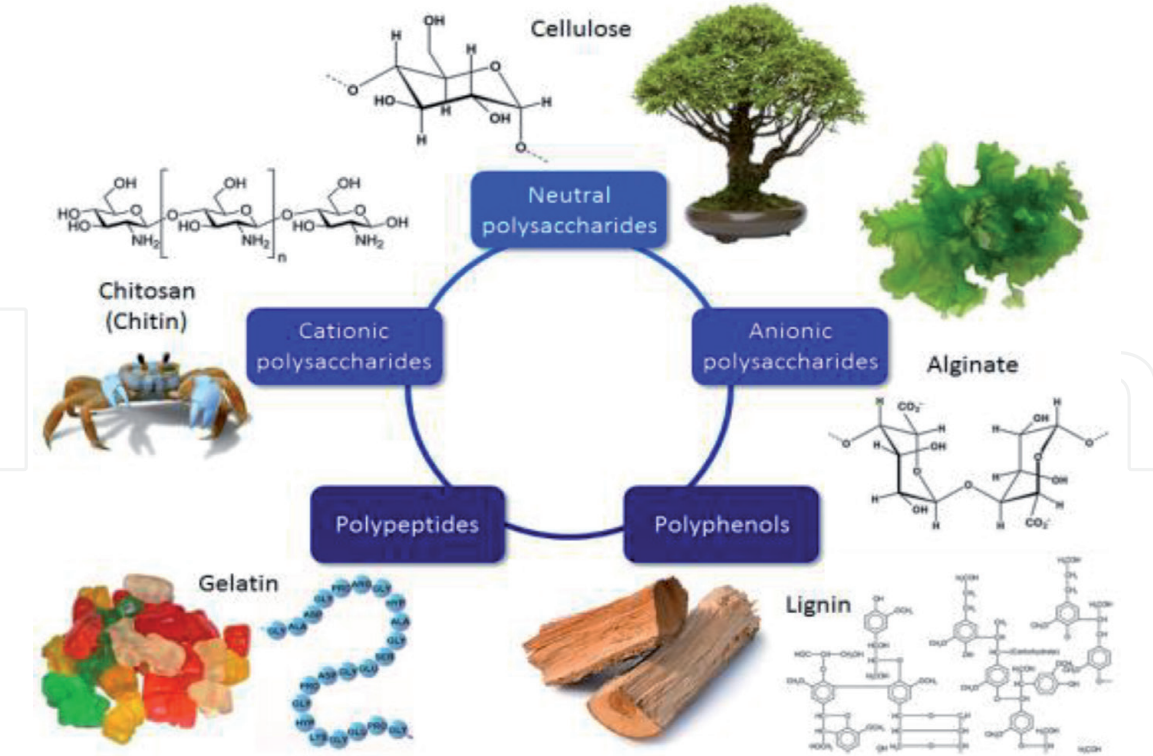


Figure 2.
Different types of biopolymers.

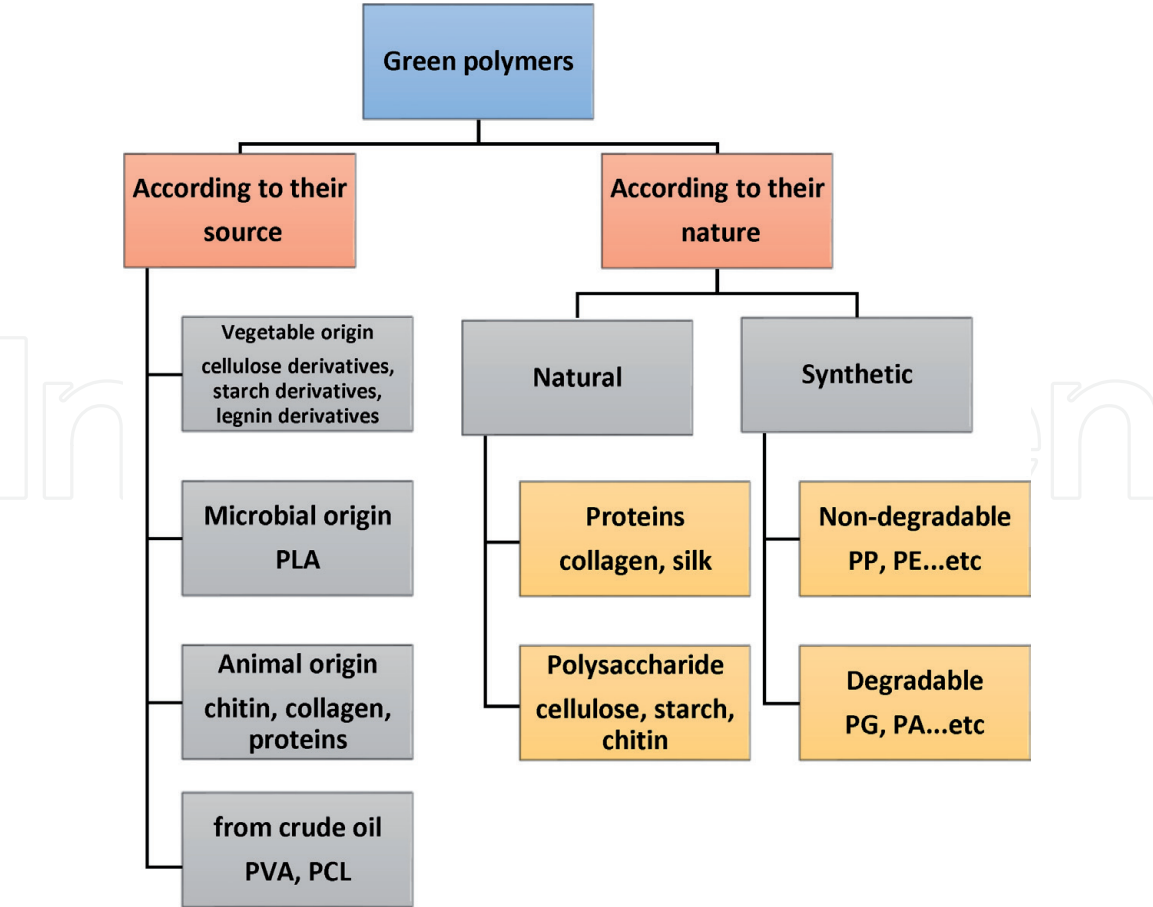


Figure 3.
Classification of green polymers.

2.1 Advantages of green polymers

The green polymers show superior and unique properties incomparable to other materials, these properties are [12–14]:

• Economically feasible	• High flexibility relative to properties and implementations
• Lighter weight	• Excellent anticorrosion property
• Easy processing with short period in injection molding, blow molding, fiber spinning, and extrusion	• Highly cost-, resource-, eco-, and energy-effective mass production
• Flexible base of raw materials (oil, coal, gas, and biomass)	• High energy content similar to that of oil and superior to wood
• Recycling as materials and sources of energy and chemical feedstocks	• Significant contributions to energy savings in applications

The green chemistry concept, which was initiated in the 1990, is linked to the term green economy. Both terms aim to minimize the claim for energy and resources, lessen wastes, avoid ecological pollution and hazards, reduce greenhouse gas release, optimize industrialization processes, and establish efficient recycling of wastes [15–17]. These elements are essential parts of sustainable chemistry.

2.2 Green principles of polymer production

Important green principles of polymer production handle the following issues [18, 19]:

- High resource usefulness and elevated atom economy, capitalizing the content of raw materials in the manufactured goods.
- Clean and lean production processes, preventing wastes and reducing greenhouse gas emissions
- High safety criteria.
- Secondary substances use like blocking groups, and organic solvents are not recommended.
- No healthiness and ecological hazards by eliminating toxicity.
- High-energy efficiency of materials’ manufacturing and applications.
- Utilization of renewable resources and renewable energy.
- Low carbon footprint.
- Controlled product lifecycles with useful and effective waste recycling.

However, the properties of biopolymers are strongly influenced by their source. Visibly, the structure and characteristics of a polysaccharide are totally different from a polypeptide. Even so, there can still be spectacular variation in properties of a single biopolymer, depending on the species that produce it. A typical model of

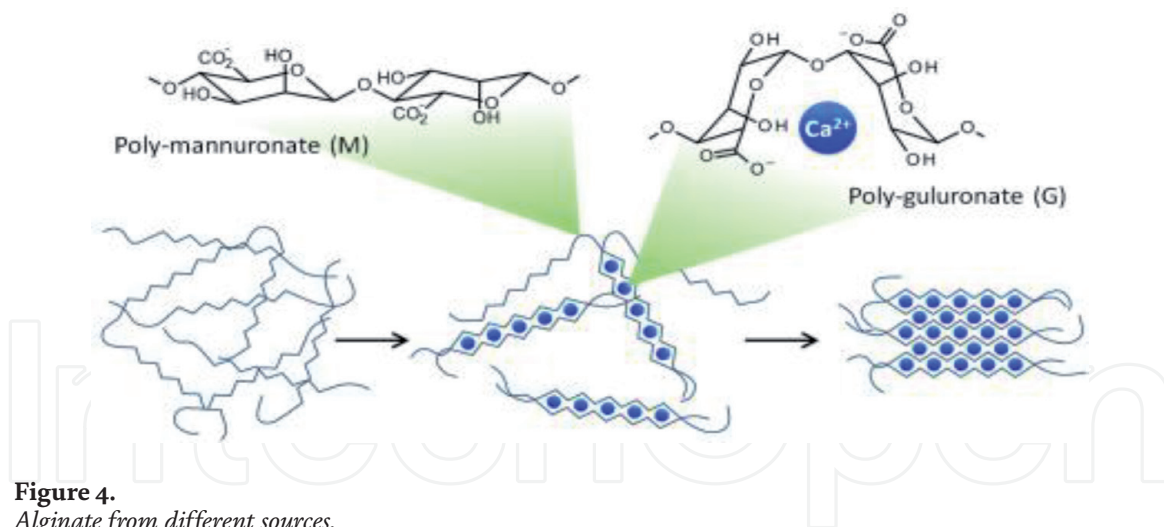


Figure 4.
 Alginates from different sources.

this natural variability is alginate, which is an extract from seaweed. Alginate is a linear copolymer of α -L-guluronate and β -D-mannuronate and the segments are not random copolymers but contain blocks of alternating or identical monomers. The strength of this biopolymer count on its composition, which varies significantly between different species and growth environment as well as within different parts of the original plant (**Figure 4**).

2.3 Physico-chemical properties of green polymers

Gel or viscous solutions formation is one of the most attractive features about green polymers; a lot of them form viscous solutions or gel in water due to intermolecular hydrogen bonding formation (**Figure 5**). This specific property used widely in different industries to control rheological properties and stability [20].

Another important feature that most green polymers possess is their high functionality, which allows versatile modification routes in order to produce endless products [12]. Extensive works are carried out to design and invent green alternative routes for effective biomass transformation to chemicals.

These modification methodologies depend on the nature of the functional group(s), distribution of these functionalities within the polymer chain, the nature, and the usability of the product. The most common modification procedures involve esterification, ethoxylation, depolymerization, amination, etherification ... etc. [21]. The next sections include thorough review for modification of green polymers for

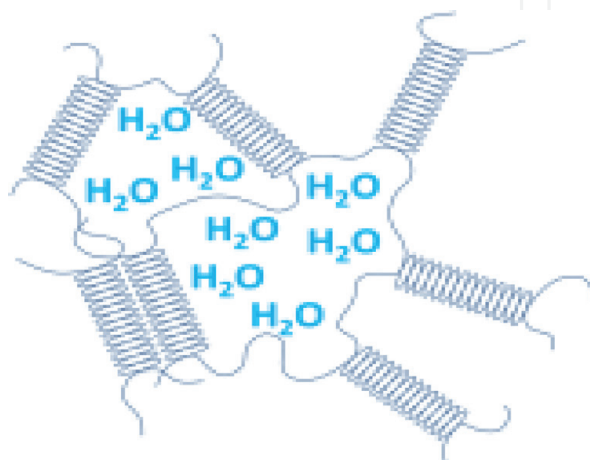


Figure 5.
 Intermolecular hydrogen bondings.

The stage	The chemical applied
Production	Drilling fluids
Transport	Demulsifiers – Corrosion inhibitors – Coating materials Oil sorbers – Oil spill dispersants
Refinery	Corrosion inhibitors Coating materials

Table 1.
Utilization of green polymers in the petroleum sector.

utilization in different petroleum sectors. They are categorized according to the stage they are applied in – as in **Table 1**.

3. Green polymers in petroleum industry

3.1 Drilling fluids

The expression drilling mud implies to fluids, which are used to save up well control and transport drill cuttings from the boreholes to the surface. In the drilling process, the fluid is pumped from the surface, down the drill string, through the bit, and back to the surface via the annulus. Drilling mud constitutes an essential part of the drilling process. The appropriate fluid selection is controlled by drilling performance, expected well condition, the safety of workers, cost, and mud cuttings discarding [22]. Drilling muds must be verbalized to eliminate problems associated with formation damage, well chemistry, and other well disturbances. Choosing suitable drilling fluids and control of their properties within desirable ranges are pivotal aspects of successful oil well drilling [23]. Drilling muds are mainly composed of liquid (i.e., water, oil, or brine) and solid materials (i.e., clay, polymer, barite, and additives). The main types of drilling muds are illustrated in **Figure 6**.

There are many green polymers used as thickening agents in drilling mud formulation as either single materials or a blend of components. These include Polyethylene glycol [24], Carboxymethyl cellulose [25, 26], combination of cellulose and clay [27], amide modified polysaccharide [28], cellulose nanofibril [29], chitosan [30]. Based on their superior thickening properties, Green gums were used are excellent candidates in drilling fluid designs. In this regard, Guar gum was used during drilling operations as a first-rate additive for mud systems because of its unique properties. These properties include, but are not exclusive to, loss control agent, viscosifiers and polymer [31, 32].

Xanthan gum has used as a highly beneficial drilling mud additive that reduces related well instabilities [33, 34]. Xanthan gum also, can be used in other applications such as an emulsifier, stabilizer (in some cases), a thickener for mud systems and suspending agent [34–37].

Moreover, other natural water-insoluble cellulosic materials; peanut hulls, bagasse, and sawdust were investigated as lost circulation control materials [38]. The chemical composition of these materials is given in **Table 2**; the data revealed that Peanut hulls have the best results relative to bagasse and sawdust as they have 60% crude fiber and the least content of cellulose.

Furthermore, some mixed green formulations were applied as thickening agents such as Sulfonate-containing polymer/polyanionic cellulose [39], sulphone cross-linked galactomannans [40].

Olatunde et al. [41] introduced a blended water-based drilling fluid based on guar gum, bentonite, polyanionic cellulose (PAC) and arabic gum. The rheological

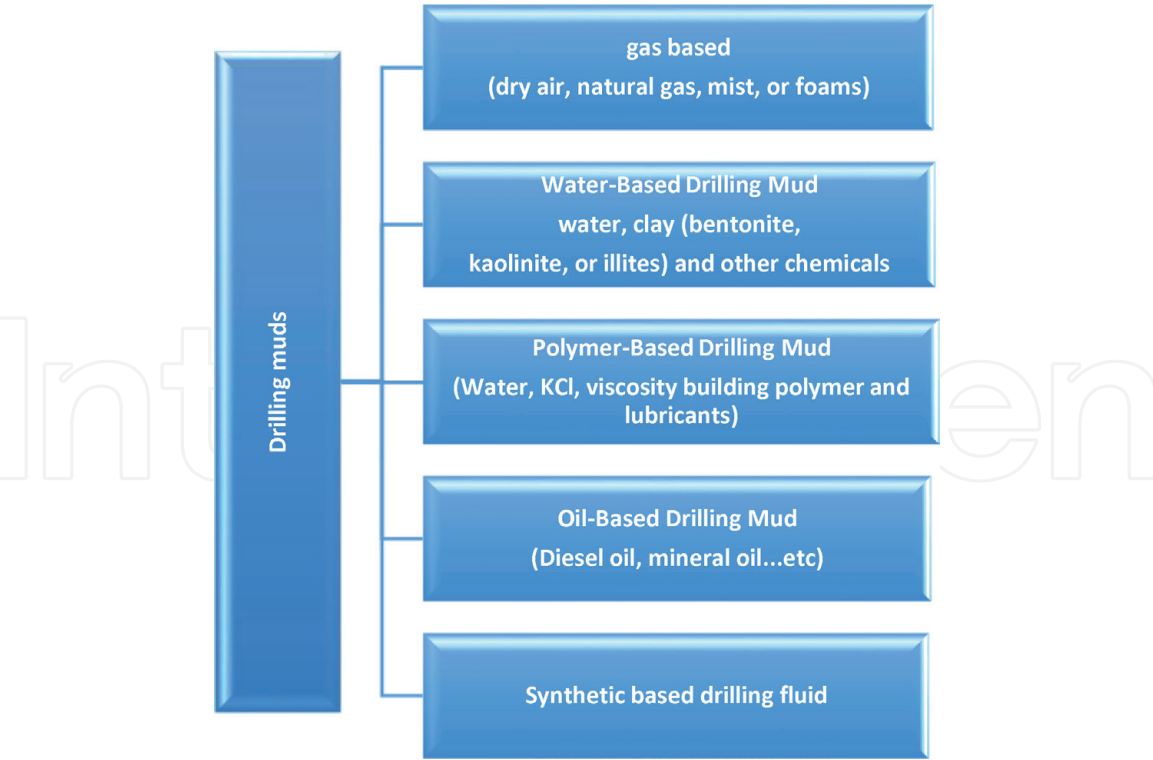


Figure 6.
Different types of drilling muds.

The material	Chemical composition
Peanut hulls	Cellulose (25%), Crude fiber (60%), Water (8%), Protein (6%), Ash (2%), and Fat (1%)
Bagasse	Cellulose (55%), Hemicellulose (25%), Lignin (24%), Ash (4%), and waxes (1%)
Saw dust	Cellulose (58.2%), Lignin (28.4%), Moisture (4.8), and Ash (0.21%).

Table 2.
Chemical composition of some cellulosic materials [38].

behavior and the filtration loss property of each drilling fluid developed were measured using API standard procedures. Guar gum showed the highest gel strength and the best stable rheological properties. The rheological properties of borate-guar gum crosslinked fluids were studied by Oscar [42] and he found that anionic galactomannans, which are derived from guar gum suitable as thickeners. They are capable of enhancing viscosities when used either alone or in combination with a cationic polymer and distributed in a solvent.

3.2 Demulsifiers

The process of crude oil formation is usually associated by incorporation of salty water within the crude. This formation water constitutes very drastic water-in-oil emulsions, which affect the production process and causes corrosion to the production facilities and equipment. Therefore, crude oil free of water is a significant demand for oil and gas treatment. The demuslification process is a stepwise process starts removing the natural stabilizing agents that present in the crude oil (asphaltenes), then replacing them with demulsifiers which allow water droplets to approach each other and coalesce into bigger and bigger droplets which finally leads to separation of the emulsion into two phases (Figure 7).

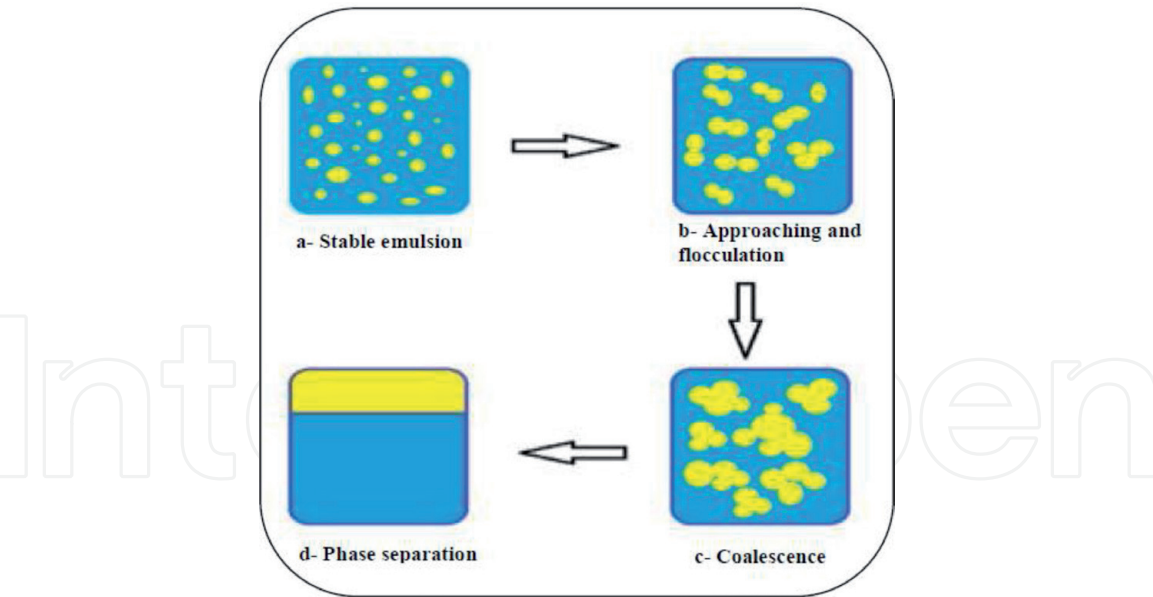


Figure 7.
Demulsification process.

Environmental restrictions limit the use of most traditional demulsifiers despite of its effectiveness in breaking (W/O) emulsions. Since most traditional demulsifiers are pollutive and have high environmental hazards, green demulsifiers have been applied to break down petroleum emulsions. In this regard, Abu-Bakar and Aliyu [43] investigated plant extracts of some vegetable oils such as the coconut, olive oils, and green tea as effective environmentally friendly W/O demulsifiers. The plant extract was obtained by Soxhlet extraction method while the vegetable oil (triglycerides) was obtained from coconut oil (100%), the compositions, and the purity of the extracts and the vegetable oils were determined by gas chromatography (GC) while the non-toxic effect of the tested demulsifiers was proved by potential toxicity tests. The demulsification efficiency of the investigated green demulsifiers was confirmed via bottle tests, the data revealed that the green tea extract and olive oil separated lesser amount of water than the coconut oil for all W/O emulsion samples. Moreover, Abdulraheim [44] developed chitosan-based nonionic surfactants by modification of chitosan (chemically) via esterification then etherification to produce ether amides surfactants (**Figure 8**). The synthesized surfactants were characterized by IR spectroscopy and their thermal properties were investigated. Furthermore, the surface properties of these surfactants were calculated through surface tension measurements at different temperatures and the

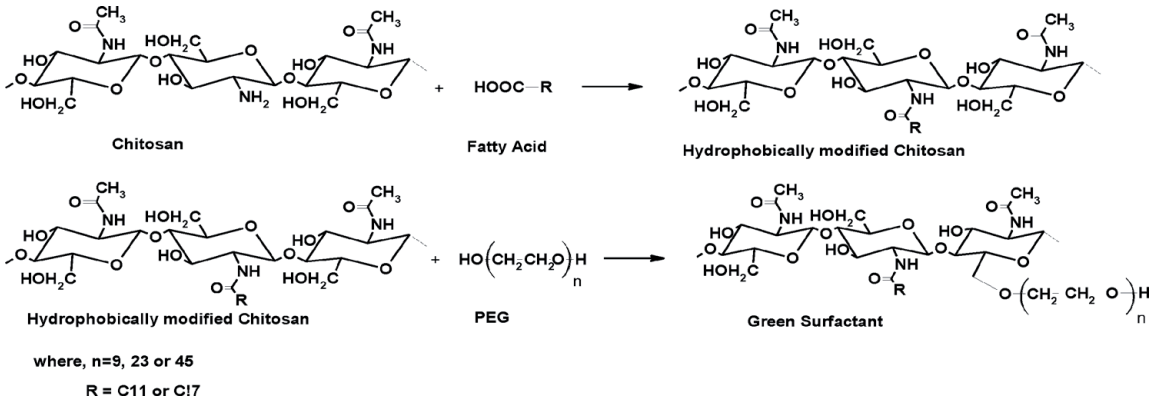


Figure 8.
Chemical modification of chitosan into nonionic surfactants.

demulsification efficiency of the prepared surfactants was verified under different conditions. Viscosity of the crude oil before and after demulsification was used as a parameter for demulsification process. Moreover, the demulsification process was monitored by using the optical microscope. Cellulosic materials were extensively used as bases for green demulsifiers for crude oil emulsion. Regarding this, cellulose was separated from saw dust and depolymerized into pure glucose, which is modified into nonionic surfactants via esterification then etherification, Abdel-Raouf et al. [45]. The surface properties of the synthesized surfactants were verified under different conditions. The demulsification efficiency of the prepared demulsifiers was verified for breaking two types of crude oil (light and heavy crudes) at different conditions of aqueous phase [46]. The data revealed that the light crude was more easily demulsified than the heavy crude, besides that, changes in pH or salinity of the aqueous phase of the emulsion enhance its stability and decrease the demulsification efficiency of the applied demulsifiers.

Furthermore, a number of glucose fatty ester ethoxylates were prepared and tested as demulsifiers for oil sludge (Figure 9). Results showed that the prepared demulsifiers achieved about 90% water separation from the sludge after 6 h of injection. The hydrocarbon composition of oil phase recovered from the treated sludge was determined.

The oil phase was rich in low molecular weight hydrocarbons this is also an indication of their efficiency as demulsifiers for petroleum sludge [47]. Zhang and Merchant [48] prepared nonionic saccharide surfactants with an amide group linking hydrophilic saccharide segment to hydrophobic alkyl segment and investigated their surface-active properties (Figure 10). The surface properties of these surfactants were studied versus the length of hydrophobic and hydrophilic and the obtained data was interrelated to structural variation in the saccharide surfactants. Roostaie et al. [49] used some cellulose, ethylcellulose, microcrystalline cellulose, at different viscosity grades, and the blend of ethylcellulose and ethoxylated coco amine to break the crude oil emulsion through bottle test. According to the obtained results, ethylcellulose was very efficient in breaking emulsion but with slow dehydration rate, which is the main weakness of that agent. Finally, the effect of temperature, agent composition, and demulsifier amount on the dehydration capacity and rate of selected agents were evaluated. Three unrefined fatty oils were used as sources for demulsifiers. The hydrolyzed form of each type of oil was adducted

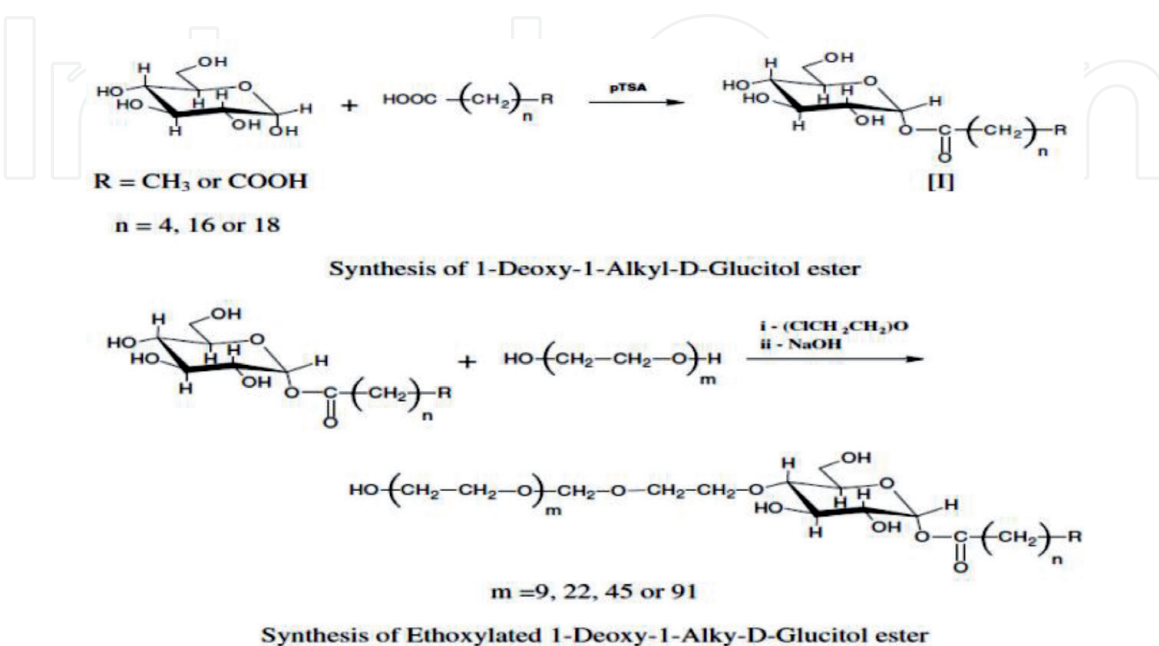
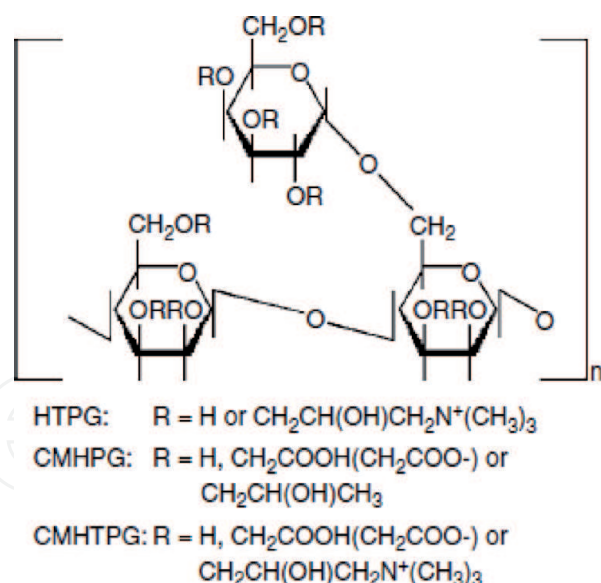


Figure 9.
 Synthesis of ethoxylated glucose fatty esters.

**Figure 10.**

The chemical structures of three water-soluble chemically modified guar derivatives with different functional lateral groups.

with maleic anhydride then modified by esterification with polyethylene glycols or ethyleneoxide-propyleneoxide block copolymers. The demulsification efficiency, coalescence rate, some surface active, thermodynamic properties, and partition coefficient of a selected demulsifier were investigated [50].

Atta and Elsaed [51] prepared some nonionic polymeric surfactants from rosin by esterification of it with different molecular weights of polyethylene glycol to produce rosin ester surfactants. The surfactants were tested as sludge dispersants via viscosity measurements of sludge crude oil mixtures at different times.

Demulsifiers from green non-bio polymers were also prepared. A series of propylene oxide (PO) ethylene oxide (EO) block copolymers with different EO/PO ratios and molecular weights have been synthesized and tested for their demulsification potency in breaking water-in-benzene emulsions stabilized by asphaltenes. The demulsification competence of the prepared surfactants was studied versus the change in molecular weight and HLB, the data revealed that the amounts of separated water are directly proportional to both of them., also the effects of temperature, NaCl concentration (salinity), pH value, and solvents on the demulsification effectiveness were thoroughly inspected [52, 53].

Dalmazzone and Noik [54] performed large screening of different chemicals that could be used as demulsifiers for oil production by classical bottle tests. Silicone derivatives were proved as effective demulsifiers in breaking two types of emulsions come from an asphaltenic and a paraffinic crude oil. According to this first round study, silicone demulsifiers appeared as good candidates for the further development of new green formulations for oil production and demulsification. Alsabagh et al. [55] studied the demulsification process of Water-in-oil emulsion at petroleum field using some demulsifiers derived from propylene and polyethylene oxides. The data revealed that the chemical structures, which containing propylene oxide, might play a vital role to ease and enhance the demulsification competence and that rising of the surfactant dosage (100–600 ppm) decreases the time taken for complete water separation.

3.3 Corrosion inhibitors

Corrosion is a severe engineering problem in this current era of industrial evolution, which causes economic losses and irreversible damage to metallic

structures [56]. **Figure 11** illustrates the electrochemical corrosion process. Several efforts have been made to control the destructive effects of corrosion using several preventive methodologies.

Corrosion inhibitors are essential petroleum additives during transport and refinery stages. In general, corrosion inhibition technology uses more than one of the following techniques:

- a. Adopting metals with materials that improve the surface corrosion-resistant during the corrosion course of action
- b. Addition of corrosion inhibitors that shield the surface of the metal and prevent reaction with oxidizing agents
- c. Deposition of reactive coatings

Many green inhibitors have been developed, which are safe, biodegradable, eco-friendly and have proven effectiveness in controlling the corrosion of different metallic equipments and facilities made from steel, mild steel, stainless steel, iron, copper, aluminum, 2024-T3 aluminum alloy, steel in concrete structures, carbon steel, AA5083 Al-Mg alloy, nickel and zinc [57]. The use of inhibitors for the control of corrosion of metals and alloys, which are in contact with an aggressive environment, is highly recommended [58, 59]. The general requirements for selection of a proper inhibitor are illustrated in **Figure 12**.

The inhibitors are absorbed on the metal surface and suppress the corrosion. They are classified as cathodic, anodic and mixed type inhibitors, depending upon whether the inhibitor affects the anodic metal dissolution reaction or the cathodic oxygen reduction in near-neutral solutions or hydrogen discharge reaction in acid solutions [60]. Great numbers of organic compounds have been studied to investigate their corrosion inhibition potential [61–64].

All these studies have revealed that organic compounds particularly those with N, S, and O show significant inhibition efficiency. Plant extracts and organic species have become important as an environmentally acceptable, readily obtainable and renewable source for wide range of inhibitors [65–67].

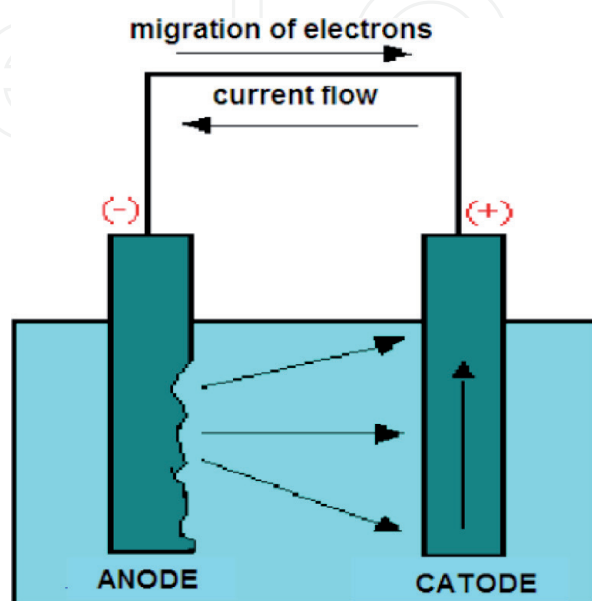


Figure 11.
Representation of electrochemical corrosion.

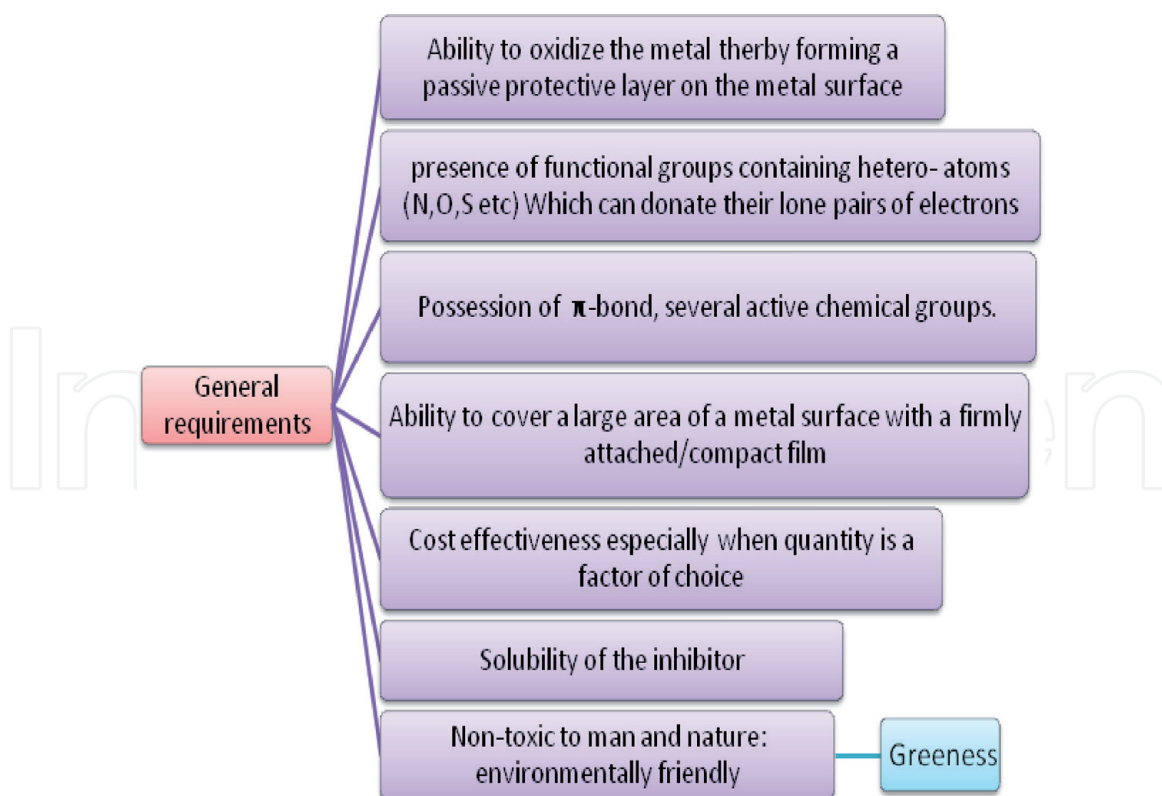


Figure 12.
General requirements for corrosion inhibitors selection.

The most common green polymers that can be made into corrosion inhibitor formulations are cellulose and cellulose derivatives, chitosan, fatty acids and alcohols, guar gum and starch. They can be used either in their original forms or chemically modified or blended in different formulations or as nanocomposites. This variability leads to countless designs of green inhibitors. Therefore, the most effective designs are summarized in **Table 3**.

The bigger size and the greater number of characteristic anchoring groups of polymeric corrosion inhibitors afforded superior performance. These functional groups facilitate the adsorption on the surface of metal and coat greatly more surface than the matching repeating units.

Therefore, efficient protection operation is influenced by the corrosion alleviation properties of polymers such as molecular weight, molecular size, composition, and nature of the anchoring groups. However, corrosion inhibitors from green non-biopolymers are well known. Organic inhibitors have been the most extensively used in petroleum refining processes because of their ability to form a shielding layer on the metal surface in media with high hydrocarbons content. Currently there are many of organic inhibitors belonging to diverse chemical families i.e. fatty amides [85, 86], pyridines [64, 87], imidazolines [68, 88–90] and other 1, 3-azoles [91–93] and polymers [94] have showed outstanding performance as CIs (**Table 4**).

Moreover, protonated polyanilines were identified as a pioneer corrosion inhibitor in acid for a number of metals of the last century. Also, polyanilines as anticorrosive coatings were reported by several authors [95].

Most aniline-based polymeric materials show efficient inhibition due to their good of adhesion on the surface of metals. The metal/polymer interactions are mostly of hydrogen-bridge type or secondary interaction due to dispersion, dipole interactions, or van der Waals forces. Polyethylene terephthalate waste was modified into powerful corrosion inhibitors for API XL65 carbon steel, in a solution of 2 M HCl [96].

Inhibitor system	Type of substrate/Corrosive medium	Ref.
Saturated waxy fatty acids and waxy fatty alcohols.	carbon steel/1 M HCl-hydrogen sulfide brine	[68]
Chitosan/Chitosan derivatives:		
Chitosan	Mild steel/0.1 M HCl	[69]
Chitosan	Copper/0.5 M HCl	[70]
Carboxymethyl chitosan Cu ²⁺	Mild steel/1 M HCl	[71]
Acetyl–thiourea–chitosan conjugate polymer	Mild steel/0.5 M H ₂ SO ₄	[72]
β-Cyclodextrin modified natural chitosan	Low carbon steel/0.5 M HCl	[73]
Modified chitosan surfactants	API 65 pipeline steel/1 M HCl	[74]
	Mild steel/1 M HCl	[75]
Starch and its derivatives:		
Activated and carboxymethylated starch cassava starch	XC35 carbon steel/Alkaline 200 mg/l NaCl	[76]
Tapioca starch	AA6061 alloy/seawater	[77]
Acryl amide grafted cassava starch	Cold rolled steel/1 M H ₂ SO ₄	[78]
Cassava starch	Mild steel in 1 M HCl	[76]
Exudates gums:		
Gum Arabic	Aluminum/mild steel/0.1 M H ₂ SO ₄	[79]
Guar gum	Carbon steel (L-52 grade) 1 M H ₂ SO ₄ containing NaCl	[80]
Cellulose and its derivatives:		
Ethoxylated oligoglucose surfactants	X-65 carbon steel in 1 M HCl	[81]
Hydroxyethyl cellulose	Mild steel in 1 M HCl	[82]
Sodium carboxymethyl cellulose	Mild steel in 1 M HCl	[83]
Sodium carboxymethyl cellulose in combination with potassium halides (KCl, KBr, KI)	Mild steel (AISI 1005 grade)/2 M H ₂ SO	[84]

Table 3.
The most effective inhibitor formulations based on biopolymers.

Amines polymer are superb corrosion inhibitors for iron in acid solutions. Jeyaprabha et al. [97, 98] investigated the corrosion inhibition act of poly(diphenylamine) and poly(aminoquinone) on iron in 0.5 M H₂SO₄. Other imine- and amide-based polymers have been employed as potent corrosion inhibitors for different metallic systems [99–101].

3.4 Coating materials

A coating material is an anticorrosion agent applied in the form of a thin layer covering the metallic surface. The selected coating materials shall be appropriate for the intended use and shall be chosen after verifying the following properties:

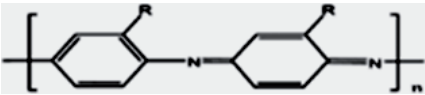
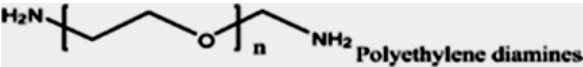

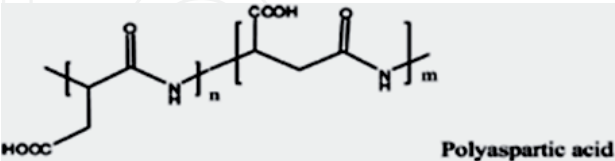
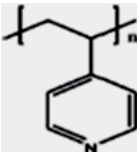
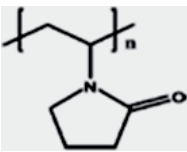
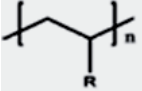
Common name	Structure
Polyanilines	
Polyamines	 Polyethylene diamines
Polyimines	 Polyethyleneimines
Polyamides	 Polyaspartic acid
Polyvinylpyridines	
Polyvinyl pyrrolidines	
Polyvinyl alcohols/acetates/benzenes	 R = OH, polyvinyl alcohol R = OCOCH ₃ , polyvinyl acetate R = C ₆ H ₅ , polyvinyl benzene

Table 4.
Structural groups of green non-biopolymer inhibitors.

- Corrosion protective properties
- Product impact on public health and the environment
- Properties related to application conditions, equipment, and people.
- Availability and economics

Based on the above-mentioned criteria, green polymers specially biopolymers are excellent candidates for coating formulations. In the last few years, cellulose-based materials (sp. Nano and micro cellulose) have recognized themselves among the most frequently used materials for superhydrophobic coatings.

In this regard, A number of polyurethane nanocrystalline cellulose composite (PNCCC) and polyurethane micro-powdered cellulose composite (PMPCC) coatings were prepared with various loading levels of NCC and MPC, these coatings were applied onto the pretreated mild steel substrate at room temperature. The results showed that the NCC and MPC affected positively on the properties of the polyurethane coating [102].

Cleide et al. [103] studied the effect of aminopropyl triethoxysilane (APS), cellulose and polyaniline emeraldine-salt (PAni ES) as an additives to epoxy coating on the corrosion protection of mild steel. Microcrystalline cellulose (MCC) and cellulose nanowhiskers (CNW) functionalized or not with PAni ES were used and compared. The coating properties were checked by electrochemical impedance

spectroscopy (EIS), salt spray test and scanning electron microscopy (SEM). The surface of the carbon steel, after 1000 h of exposure, did not present evidence of surface corrosion. Polymer coatings using CNW and PANi ES displayed amended corrosion protection properties even after 90 days of immersion in 3.5 wt% NaCl solution.

Another series of epoxy resin-based nanocomposites were prepared in the form of coatings with different amounts of NC loadings, and the coatings were applied onto mild steel at room temperature. The corrosion protection properties of the coated mild steel substrates immersed in a 3.5% NaCl solution were studied relatively by electrochemical impedance spectroscopy (EIS). The results showed that all of the nanocomposite coatings with NC clearly influenced the epoxy-diamine liquid pre-polymer, both physically and chemically [104].

Lignin occupies the second rank in most widespread organic polymer. It contains benzyl alcohol, carboxyl, hydroxyl, methoxyl, phenolic and aldehydic characteristic groups. Extracted alkali lignin has shown corrosion inhibition behavior on various metal alloys in HCl solutions [105].

Chitin and chitosan are nitrogen derivative of cellulose. Chitosan is polyelectrolyte (cationic type), which can gel with polyanions and form complexes with metal ions. In our work [106], Chitosan was mixed as natural organic filler with epoxy coating in various loading levels from 2–20% to get chitosan – epoxy coating composite. The corrosion resistance and the antimicrobial activity of coatings formed by chitosan and epoxy were investigated. The corrosion resistance was evaluated via a salt spray test and the antimicrobial activity of the prepared composites was investigated against different pathogens. The obtained results demonstrated that the chitosan – epoxy coating composite showed uniform and lower corrosion rates than that of absolute epoxy coating. The DMA proved that chitosan improved the viscoelastic characteristics of epoxy coating; the mechanical and chemical resistance were also enhanced with increasing chitosan. Other chitosan derivates such as acetyl thiourea, carboxymethyl, and hydroxyapatite composites were used as efficient corrosion inhibitors [107].

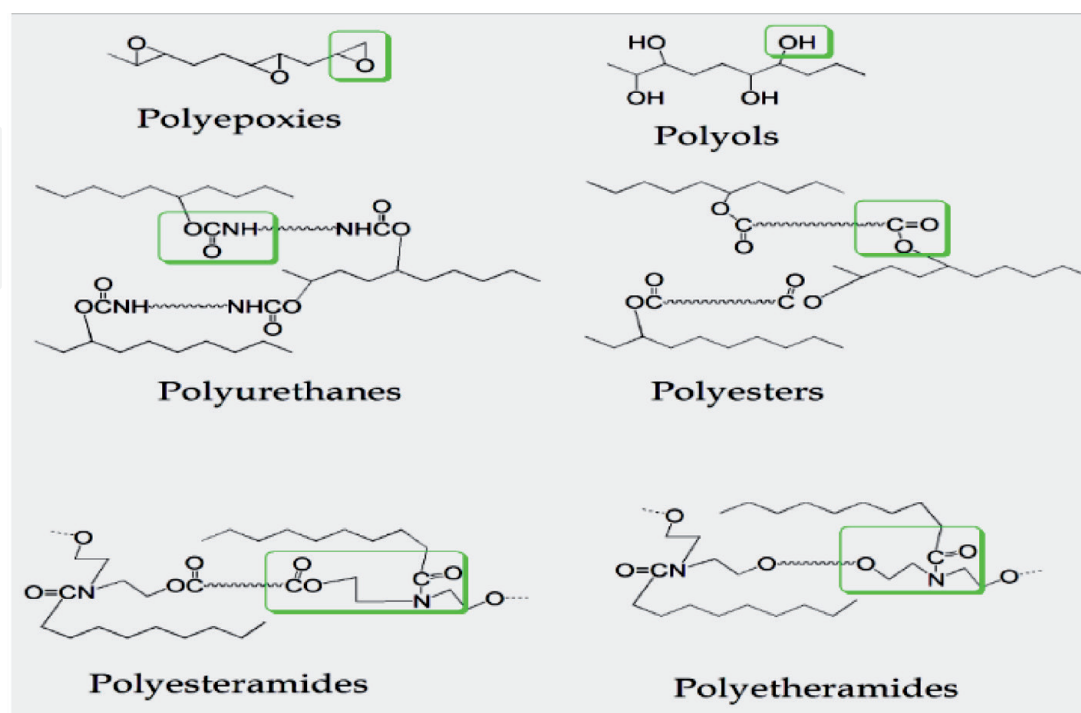


Figure 13.
Some green polymers used in coating formulations.

Rosin is another natural polymer that can be adopted into highly durable coatings. In our work [108], Ketone type derivative of rosin was synthesized by dehydrocarboxylation of isomerized abietic acid. Acid-catalyzed Diel-Alder reaction was carried out for coupling of dipimaryl ketone with maleic anhydride. The corresponding tetra glycidyl ester was obtained by epoxidation of the dipimaryl ketone. The thermal properties of the cured resins using a rosin-based crosslinker and p-phenylene diamine (a viable crosslinker) were investigated using dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and some preliminary universal coating tests. Results showed that the fully rosin-based epoxy coatings gave better performance than bisphenol-A based one. These findings and results were attributed to a liquid crystal behavior of the rosin-based crosslinker. Furthermore, a tetrafunctional rosin-based epoxy was prepared and cured with either rosin-based hardener or common phenylene diamine to study the viability of creating high performance thermosetting polymer from a renewable resource. The analytical results indicate that fully bio-based epoxy system holds high glass transition temperature (T_g), high modulus (G') and enhanced thermal stability [109].

Additional biopolymers such as vegetable oils [110] and Fatty acids [111] have been modified into successful coating formulations. However, other green polymers such as polyesters, polyester amides, polyether amides – (**Figure 13**) – have been used as coatings by many authors [112–114].

3.5 Oil sorbent materials

Over the past few decades, there have been many oil spill accidents. These accidents occurred during the extraction, transportation, and storage of oil, The spilled oil significantly affects the marine ecological system and the surrounding environment [115, 116]. Oil spill accidents have commended scientists all over the world to advance instant cleaning technology to treat oil spill disasters. Therefore, the removal of spilled oil from water resources is a very worthy matter.

The increased environmental awareness pushed the efforts towards inexpensive, non-toxic and biologically degradable compounds along with diverse biomasses to make multi-sized materials, sponges/aerogel, membranes, etc. for the remediation of oil spill [117]. Generally, there are two methodologies for oil spill remediation; Dispersion and/or recovery of the spilled oil (**Figure 14**).

The selection of the suitable method for oil spill control is dependent on the nature of the spilled oil, its location and the surrounding conditions [118]. When oil sorbents were chosen as a treatment method, environmental designs are required. However, the growing global inhabitant's rate has enlarged the rate of food consuming, producing immense amounts of biological waste. Therefore, the sensible solution is to consume such easily biodegradable waste or biomass to make cheap sorbent materials with higher oil uptake capability that is simple to scale up for the removal of an oil spill, rather than toxic chemicals. The most important natural polymer applied as oil sorbents or modified into gel structures are provided in **Table 5**.

Beside our previous works concerning the utilization of natural polymers as oil sorbents, we paid some attention for modifying some plastic wastes into effective oil sorbents for oil spill remediation. In this context, polymeric sorbents based on polystyrene waste were prepared and evaluated as sorbents for different oil phases under different application conditions. These sorbents are synthesized through radical polymerization of p-CMS with styrene in the presence of benzoyl peroxide as a free radical initiator. The oil uptake of organogel was determined through oil absorption tests; the highest oil absorbencies were 82.6, 74.4, 46.7, and 38.1 g/g in N,N-dimethyl formamide, CHCl_3 , toluene, and diesel, respectively [126].

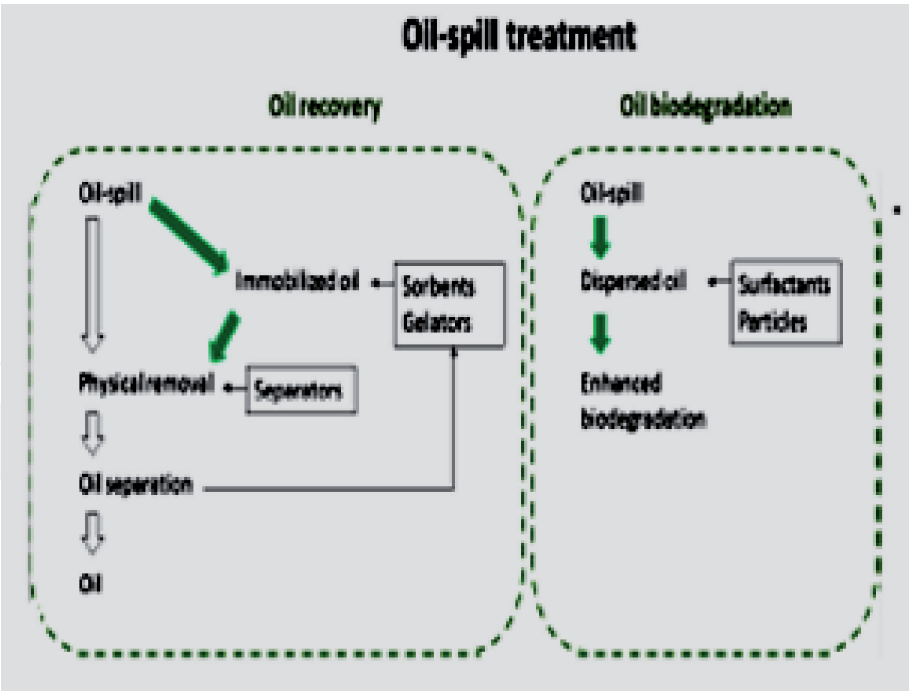


Figure 14.
Oil spill treatment processes based on oil dispersion or oil recovery.

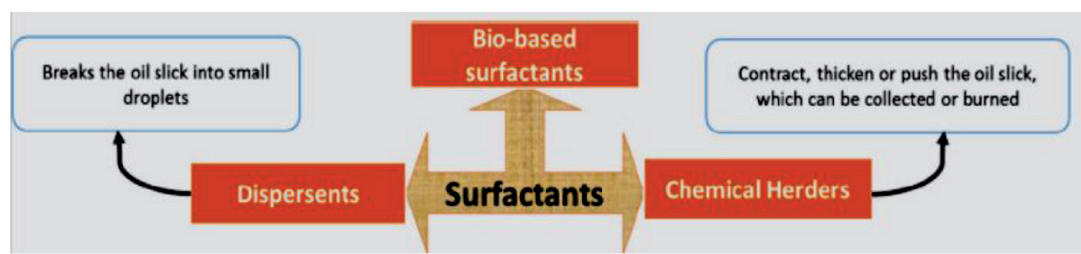
Raw material	Oil sorption (g/g)	Recovery cycling	Reference
Lignin	2–4	5 (Gasoline)	[119]
Cellulose foam	9–24	15(paraffin and motor oil)	[120]
Cotton	25–50	10 (n-Hexane and chloroform)	[121]
Chitosan	14–30	15 (different organic solvents)	[122]
Cellulose nanofibers	80–190	10 (Constant absorbency)	[123]
Cellulose acetate	15–30	10 (Constant absorbency)	[124]
Cellulose acrylate	15–30	Differ according to oil phases	[125]

Table 5.
The most common natural polymers used as oil sorbers.

3.6 Oil spill dispersants

Addition of some chemical agents to breakdown the spilled oil into tiny particles to facilitate the process of biodegradation is another treatment mean for spilled oil. The proposed mechanism of dispersants action is illustrated in **Figure 15**.

Therefore, utilization of natural polymers in dispersant formulation is highly required. Generally, all multifunctional biopolymers can be modified into dispersants due to their high functionality. Water-soluble surfactants based on rosin acids were prepared from condensed rosin acid-formaldehyde, which esterified with different poly (ethylene glycol) chains into rosin esters. The dispersion effectiveness of the prepared surfactants as oil spill dispersants was investigated and linked with the surface activity, concentrations of the surfactants and type of petroleum crude oil. Additionally, Xanthan gum formulation comprised of Polyoxyethylene Sorbitan Fatty Acid Esters (48%), bis (2-ethylhexyl)sulfosuccinate sodium salt (35%) and Xanthan

**Figure 15.**

Proposed mechanism of action of dispersants.

Gum was applied as a dispersant for crude oil with dispersion efficiency more than 50% [127]. Some Octyl carboxymethyl chitosan as a green polymer was applied as a dispersant for waxy crude and fresh asphaltic crude with more than 90% dispersion efficacy [128]. Our environmental awareness has been extended to oil spill treatment. In this context, our attention was paid for chemical recycling of plastic wastes such as poly ethylene terephthalate into effective dispersants [129]. Moreover, green some poly oxyethylenated pentaerythritol (PE) ester surfactants have been synthesized and investigated as oil spill dispersants. Furthermore, the biodegradability of the investigated esters was studied at various conditions in order to explore their usability as oil spill dispersants. The data revealed that the investigated esters were very efficient as dispersing agents and they were completely biodegraded after 8 days [130].

4. Future perspectives

The greatest challenge with the industrial development that is a rocket rising is to maintain the environment and develop environmentally benign multi-purpose materials especially those designed for the petroleum sector. The sustainability of these materials is guaranteed as they are constructed from natural polymers. The future concern is concentrated on the following points:

1. Increasing the effectiveness of the present formulations
2. Modifying the functionality such that a single product can achieve several functions simultaneously with the same efficiency.
3. Massive production of the most successful formulation in order to minimize the production cost.
4. Establishing green synthetic routes that produce minimal or no wastes and consumes the least energy

Our future concern is to explore more products derived from natural polymers, mainly cellulose and cellulose derivatives, as it is the most abundant biopolymer to be used as multi-purpose products in the petroleum sector and to overcome the disadvantages of the currently applied formulations such as improper mechanical properties, decreased efficiency at higher temperature or at elevated salt concentration. Our current research is the synthesis of cellulose nanocomposites as demulsifiers for petroleum sludge at ambient temperature. The breaking down of sludge requires sophisticated methodology, and the introduction of efficient demulsifiers to recover the oil from the sludge without heating will greatly reduce the sludge treatment costs. So, our future work will be extended on developing new

organic–inorganic nanocomposites to increase the effectiveness of the working agents so as to double its surface area and to include inorganic core material inside a polymer shell to build up nanoparticles of a proper size.

5. Conclusions

Petroleum is the first and most important energy source. Therefore, the petroleum industry is rapidly growing and necessitates great attention. At the same time, the green chemistry concept is linked to this industry such that most if not all the materials used in this sector become green material. The concept ‘green’ was demonstrated and the difference between biomaterial and green material is discussed. The advantages of the green materials were mentioned. Moreover, the materials utilized in the petroleum sector were categorized according to the stage of application. Some products such as corrosion inhibitors and coating materials can be used in more than one stage. Furthermore, corrosion inhibitors perform the same function but differ in application methodology. The difference between the oil sorbers and the oil spill dispersant was discussed and the need for each category was identified. The green polymers included in this work are tabulated in **Table 6**.

The additive	The biopolymers	The non-biopolymers	Blended formulation
Drilling fluids	Carboxymethyl cellulose, amide modified polysaccharide, cellulose nanofibril, chitosan, guar gum, xanthan gum, peanut hulls, bagasse, saw dust	Polyethylene glycol,	bentonite, guar gum, polyanionic cellulose PAC and gum arabic. borate-guar gum
Demulsifiers	Green tea and some vegetable oils, ether amide chitosan surfactants, glucose esters, micro crystalline cellulose, ethyl cellulose, fatty oils, rosin	Ethylene oxide-propylene oxide block copolymers Silicone derivatives	
Corrosion inhibitors	Cellulose derivatives, chitosan, fatty acids, guar gum, starch,	Pyridine, imidazolines, 1,3 azoles, polyanilines, Poly ethylene terephthalate,	Poly(minoquinone) and poly(diphenyl amine)
Coating materials	Nano and microcellulose, lignin, chitin and chitosan, rosin, vegetable oils, fatty acids	epoxy resin-based nanocomposite, polyesters, poly amides, polyether amides	Polyurethane nanocrystalline cellulose composite, aminopropyl triethoxy silane, polyaniline emeraldine salt, chitosan blended with epoxy coating
Oil sorbers	Lignin, cellulose foam, cotton, chitosan, cellulose derivatives	poly styrene-co-p-chloromethyl styrene	
Oil spill dispersants	Rosin esters, xanthan gum, octyl carboxymethyl chitosan	Polyethylene terephthalate, oxyethylenated pentaerthyritol quadric esters	Tween 80, bis (2-ethylhexyl) sulfosuccinate sodium salt and Xanthan Gum

Table 6.
The green polymer reviewed in this work.

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