**Industrially Useful Corrosion Inhibitors: Grafted Biopolymers as Ideal Substitutes**

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**Abstract**

Currently, the new research activities announced predominantly in the fields of corrosion and material engineering are subjected to the production, modeling, and usage of eco-friendly chemical breeds in substitution of previously used harmful chemicals. This all due to the increase in interest in environmental conservation is based on fixed ecological rules. Recently, several eco-friendly substitutes are regularly being derived from natural sources like plant extracts, biopolymers, etc. are extensively used to substitute harmful corrosion inhibitors. In addition, several biopolymers in their natural or altered forms, are rigorously applied as eco-friendly corrosion inhibitors. Those composites or molecules which are derived via ultrasound irradiations, and microwave or multicomponent reactions are also regarded as eco-friendly substitutes. Here polymers especially biopolymers such as ionic liquids, natural rubbers polyethylene glycols (PEGs), lignin, cutin and cutan etc. are also becoming a point of interest due to various derivatives they form. An exhaustive review analysis shows that these materials are mainly being used as corrosion inhibitors for several corrosive materials used in industries.

**Keywords:** Industries, Corrosion Inhibitors, Grafted Biopolymers, Metals.

1. **Introduction**

The decay of materials by the chemical reactions occurring between the materials/metals and their reactive atmosphere is termed as Corrosion. It is a dangerous incidence producing an overwhelming effect on technological and industrial applications, predominantly in the field of oil and gas manufacturing industries. [1] It is triggered mainly in an aqueous media and occurs due to reduction-oxidation (i.e. redox) reactions taking place in gas and oil production, pipeline structures, and management. [2] Redox reaction consists of both reduction-oxidation processes occurring simultaneously. Redox reaction mainly affects the outer surface of materials (mainly metals) that are in contact with their environment, influencing the discharge of electrons by dissolving metal and their sequential migration of electrons to other sites on the surface responsible for the hydrogen ions to be reduced, which results in deterioration of the metal surface. The process of corrosion involves three things- an anode, cathode, and electrolyte. At the anode, free electrons are generated as a consequence of the corrosion of metals, which passes through the electrolytic towards the cathode. At the cathode, hydrogen ions are reduced to form hydrogen gas. In many industrialized countries, corrosion has become a matter of vast concern. Crude oil and natural gas generally comprise numerous contaminated materials, that are naturally corrosive. Around the world, oil companies are spending a huge proportion of money on tackling corrosion [3]. Hence, monitoring the decomposition of metals in oil and gas refineries has become a very important issue to be taken care of concerning environmental, technical, and economic aspects to protect enormous expenses on materials and equipment. Inhibitors can either be obtained from natural resources or can be synthesized using the available synthetic methods or by modifying the available methods. Recently, the practical use of carbohydrates and their derivatives has been an emerging effort to be used as corrosion inhibitors that decreases environmental pollution [4,5]. Organic corrosion inhibitors having a hydrophobic nature show limited solubility due to aromatic rings and non-polar hydrocarbon chains, which unfavourably affect the shielding proficiency. Hence, a recent study on corrosion science is mainly focused on the production of different corrosion inhibitors which contain hydrophilic polar functional group in its molecular structure. Although the practice of using corrosion inhibitors is the only option for monitoring metallic deterioration in numerous corrosive environments. Organic corrosion inhibitors usage is the best and most profitable technique to avoid corrosion. However, numerous problems are associated with these organic inhibitors. The biggest challenge is its very less solubility in polar solvents. [6]. Consequently, present investigations in the field of corrosion science are focused on creating the corrosion inhibitors which comprise mainly hydrophilic polar functional groups in their structure. But several complications were provoked by the usage of small organic molecules and inorganic corrosion inhibitors, hence corrosion inhibitors containing polymeric chains came to the attention. Extracts of natural products which comprise alkaloids, polyphenols, quinine, nicotine, terpenes, and other functional groups such as carboxylic acids, and having atoms similar to C, N, O, S, etc., provoking adsorption by developing a thin film coating on the surface of the metal to protect it and hinder corrosion. This review deliberates recent research contributions related to organic corrosion inhibitors which are eco-friendly, particularly based on natural product materials, biopolymers, ionic liquid, and organic compounds. Polymers especially biopolymers such as polyethylene glycol (PEG), ionic liquids (ILs), natural rubbers, suberin, cutin, cutan, and melanin are also becoming a point of interest due to the various derivatives they form. Ionic liquids (ILs) and polyethylene glycol (PEG) have low vapor pressure and are considered eco-friendly substitutes. The chemicals synthesize using water, ILs, or supercritical CO2 (i.e. green solvents) are also regarded as eco-friendly chemicals. Many reviews report that these materials are extensively used as metallic corrosion inhibitors for a large number of corrosive electrolytes. This review deals with various types of green/sustainable corrosion inhibitors and their applications in numerous industries and environments. The growing requirement for the production of eco-friendly corrosion inhibitors forces us to work with corrosion chemistry to produce the utmost demanded sustainable corrosion inhibitors. Scientists are also searching for a possible alternative in ILs as a green option to use them as green corrosion inhibitors apart from inhibitors attained from plants.

1. **Different Corrosion Inhibitors used in Industries**

Different industrial techniques require exertion of extremely robust acid solutions [7-9]. It has been reported by the Verma et.al that acidic pickling is the utmost important and highly recognized acidic process which needs the elimination of corrosion products i.e. the rusts and superficial impurities of wires, pipelines, and metal equipment of multiple industrial zones having heat transfer, heat exchange, cooling system, and boiler industries. [10] Aggressive media such as H2SO4, HNO3, H3PO4, HF, HCl, citric acid, are generally applied for acid pickling as well as despoiling practices to extract the exteriority metal oxides dependant corrosions and scales [10-11]. Due to the exceptional acidity of the solutions which can affect the structures corrosion failures. Moreover, different gases especially hydrogen gas can be produced that may go to the pits formed in metallic arrangements that can promote hydrogen embrittlement. However, some additional external chemical species known as corrosion inhibitors are required under these kinds of industrial procedures. For this, mainly organic heterocyclic compounds can be of best used [11]. The organic compounds, such as urea, amines, quaternary ammonium salt, thiourea derivatives, alkaloids, rosin amine, acetylenic compounds, etc., are highly applied corrosion inhibitors used for pickling in sulphuric acid solution [12-14]. The pickling of different metallic alloys via acid mainly mild steel and carbon steel in HCl mostly contains nitrogen (N), oxygen (O), phosphorus (P), sulphur atom (S) along with heterocyclic organic compounds [15-19]. Thiourea and ammonia-dependent compounds are generally used as inhibitors of corrosion for the process of pickling in aggressive solutions. For the case of boiler and metal oxides which are generally solubilized in an acidic medium of nitric acid, as its solution is highly oxidizing in nature so very little number of inhibitors have been made for pickling. For example, a solution complex of hydrazine (C8H7N) and Na2S or NH4SCN in addition to the complex mixture of thiourea and Na2S is mainly applied as corrosion inhibitors for pickling in HNO3 [20]. The process of pickling in aggressive H3PO4 media finds the utilization of different heterocyclic compounds like urea and its derivative, triazole, sulfonated imidazoline, and polyvinylpyrrolidone (PVP), benzotriazole and polyethyleneimine (PEI), etc [21-24].

In addition, with these things, the inorganic and some of their mixed procreation can also be used for inhibition of corrosion. The adsorption sites become electronic-rich centers wherein the inhibitors best attach to the metallic surfaces. The concentration of acid plays a big role in differentiating between two processes such as descaling and pickling, if the concentration is less, it can be descaled otherwise at a high concentration the process pickled itself. Also, the oil-well acidification in petroleum industries needs highly concentrated aggressive/acidic media [25, 26]. Here super concentrated aggressive media of hydrochloric acid (HCl) with a percentage range of 15%-28% is allowed to add to the well via any metallic pipeline to increase its flow of oil. The plumbing of these kinds of super acidic solutions can cause huge corrosion of metallic surfaces while the acidification procedure.[10] So, small amount of additional additives called corrosion inhibitors must be added to the aggressive solution. The previous reports reveal that earlier applied corrosion inhibitors used in acidization operations are heterocyclic organic compounds having N and O heteroatoms. The mode of action of these compounds is that they become in action via absorbance on the exposed metallic surface via electron-rich centers, which are positively known as adsorption centers. These kinds of adsorbance result in the manufacture of resistive films that further declines the metallic surface from acidic media and mainly guard the metal against the damage of corrosion. Numerous industrial procedures include consumption of extremely concentrated acidic solutions [27, 28]. Acid pickling is of utmost importance and is an extensively used process that includes the elimination of corrosions, filths of metal surfaces, pipelines, wires, and several metallic apparatuses in numerous industrialized sectors containing heat transfer, heat exchange, and cooling systems, and boilers. Acids such as HCl, H2SO4, HNO3, H3PO4, HF citric acid sulphamic acid are typically applied for acid pickling and scraping procedures to eliminate oxide-based rusts present on the metallic surface [29]. Due to the tremendously destructive nature of these acids, they are responsible for the corrosion related damage of metals while these processes. Hydrogen gas produced during this process penetrates inside the metallic structure and stimulates hydrogen embrittlement. [30]. Hence, some external chemical substances must be added to prevent corrosion and this external chemical substance is known to be a corrosion inhibitor. Hence, it is significant to state that the best and most effective corrosion inhibitors are those which originate from the organic compounds and mainly contain the heteroatoms in their molecular structure [31]. The addition of corrosion inhibitors doesn’t only prevent metallic corrosion but also increases the life of apparatus used in oil and gas industries and it also reduces the use of acid. Organic compounds, particularly amines, urea, thiourea derivatives, quaternary ammonium salt, acetylenic substances, rosin amine, alkaloids, etc. are extensively used as corrosion inhibitors for pickling in sulphuric acid solution [32, 33].

In the back history of corrosion inhibition in industries, most of the applied inhibitors were non-environmentally friendly due to their noxious nature. So, due to their enhanced ecological awareness and strict environmental regulations. To overcome these issues inhibitors were derived from eco-friendly components such as amino acids. Some other organic complexes such as heterocyclic compounds are also well-known inhibitors for corrosion applied in industrial processes [34-38]

**3. Industrially Applied Corrosion Inhibitors**

*3.1 Ionic liquids (ILs):Green Corrosion Inhibitors*

Ionic liquids generally consist of ion-pair species having a very low melting point. Depending upon the requirement, the characteristics of these ILs can be changed by selecting the suitable cation and anion species as shown in **Figure 1**. Ionic liquids are characterized by numerous attractive properties such as their non-inflammability, negligible vapor pressure, high chemical and thermal stability, as well as their high capacity to dissolve most organic and inorganic compounds, and long-time stability. Furthermore, ionic liquids can also be dissolved in aqueous solutions at a high level [39].



**Figure 1.** Different combinations of ionic liquids can be synthesized by varying cations and anions.

Ionic liquids are categorized as green compounds due to their negligible impact on health and the environment [40]. All compounds of these characteristics make them potential candidates to substitute conventional organic solvents. This involves its utilization in many applications including solvent extraction, separation of petrochemical relevance, solvent for polymerization, chemical analysis, synthesis of nanomaterials, the catalyst of chemical and biochemical transformations, and many more have been shown in **Figure 2. [41, 42]**. Recently, the assessment of ionic liquids as sustainable corrosion inhibitors to substitute conventional inhibitors seems to be a hot topic about the “green corrosion inhibitors”. Several attractive properties of the ILs such as low volatility, high thermal stability, and pH, the competency to dissolve a large number of organic and inorganic substances, capacity to solubilize gases like CO2, H2, CO, etc., make ILs be suitable materials to be used in place of toxic corrosion inhibitors which affects the environments as well as human beings also. In the recent literature survey, several works report describing the ILs as the best and most used corrosion inhibitor in industries.[43]

ILs were stated as efficient corrosion inhibitors for iron and copper-based metallic materials immersed in different destructive media [43]. Among current ionic liquids, imidazole derivatives have been extensively employed [44]. Similar to convention inhibitors, the anti-corrosion effect of ionic liquids is predicted to be the creation of protecting layer upon the metallic surface through their direct or indirect adsorption. This process involves the isolation of metal from the corrosive’s species present in media.



**Figure 2.** Application of Ionic Liquids

*3.2 Biopolymers: Eco-friendly corrosion Inhibitors*

Biopolymers are known as natural polymers which are mainly formed by the cells of plants and animals. As they all are derived from natural origin, can be called eco-friendly alternatives that are positively applied for biological and industrial supplications. Likewise, polymers that are synthetically made, biopolymers are easily biodegradable and will not accumulate in the future. Few polysaccharides such as cellulose, chitosan and starch also act as biopolymers. Others are lignin, nucleic acids (RNA & DNA), natural rubber, etc.

To enhance the environmental knowledge and ecological rules, the application of green biopolymers must be motivated. In this context, different news has been reported that tells about the anticorrosive property of the biopolymers. Up to now, different corrosion inhibitors have been evaluated for their corrosion inhibitive properties. For example, carbohydrate-dependent polymers, mainly chitosan and cellulose, and their secondary parts mostly are in use as biopolymers. The linear polysaccharide of N-acetyl-D-glucosamine and D-glucosamine is mainly connected via β-1,4-glycosidic linkage. N-acetyl-D- glucosamine, and D-glucosamine are best known as acetylated and deacetylated units [4, 45-47]. Substantially the making of chitosan can best opt via deacetylation of chitin. Chitosan has various industrial and eco-friendly requisitions and is economically drafted in a limited way of deacetylation of chitin which is a basic constitutional component of the crustacean’s like that of shrimps and crabs which are the exoskeleton and cell walls of fungi [48, 49]. In the market, chitosan can form a degree of deacetylation of 60-100 and molecular weight of 3800-20000 Daltons [10, 50-51] Multiple substituents like as –CH2OH (hydroxymethyl), –NHCOCH3 (acetyl), –OH (hydroxyl), –NH2 (amine) and –O– (ether) are existing in the atomic structural organization of chitosan which can efficiently form bonds amidst metallic surface. The potential for the antagonistic corrosive effect of chitosan on materials made from metals and alloys is hugely reported [52-55]. Due to its intuitive origin, chitosan-established corrosion inhibitions can be best said as eco-friendly [56-58]. Mainly the chitosan altered with different organic compounds can show the enhanced inhibition efficiencies comparable to original chitosan molecules. Umoren and his team 2013, demonstrated that the inhibition efficiency of corrosion for mild steel in aggressive media of HCl best opted with the percentage of 96% and 93% achieved at a temperature of 60°C and 70°C with techniques such as electrochemical and surface analysis respectively [59]. The adsorption of inhibitors monitored the Langmuir adsorption isotherm model and acts as a mixed-type inhibitor for mild steel aggressive corrosion. The synergistic effect of potassium iodide (KI) with a concentration of 5ppm along with chitosan got a percentage of 90% corrosion inhibition efficiency. Here the chitosan acts as a mixed-type corrosion inhibitor. Its deposition over the mild steel was roughly studied by surface studies such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition, the outcome of corrosion inhibition gives perfect results with the presence of potassium iodide with chitosan. This process where the corrosion inhibition efficiency can be effectively increased by the addition of any other chemical compound or salts is called Synergisms [60-69]. Chitosan also acts as an inhibitor for metals other than metals such as copper in different media such as acid and salt solution of sodium chloride [70-72]. Other researchers also saw the effect of chitosan which was derived from the organics such as shrimps and mussel shells to inhibit corrosion of tin in aggressive media of 2% sodium chloride solution. [73]. At present time, a new technique of crosslinking organic compounds to improve their corrosion inhibition efficiency has also been introduced. Good examples include crosslinking of chitosan, which results from the amalgamating of two or more polymeric chains of chitosan via a different organic linker. This kind of chitosan cross-linking enhances the miscibility solubility in addition to corrosion inhibition efficiencies of the chitosan-derived molecules [74, 75]. Nearly in the year 2018 Chauhan along with his co-workers cross-linked the parent chitosan molecules with polyethylene glycol (PEG) molecules and checked their corrosion efficiency for mild steel metal in an aggressive solution of 1 Molar sulfamic acid and achieved elevated resistance of 93.9% at 200 mgL-1 concentration.[10] Langmuir adsorption isotherm model was followed and the electrochemical method approves it as a mixed type inhibitor [76]. And in the year 2020 Mouaden with his team tested the cross-linked chitosan incorporated with thiocarbohydrazide as a corrosion inhibitor in a 3.5% NaCl solution and found remarkable results achieving 94% efficiency at the concentration of 500 mg L-1. They confirmed the result by applying the Langmuir isotherm while electrochemical results reveal that the inhibitor behaved as cathodic-type [77]. Menaka et.al tested Chitosan- salicylaldehyde as a corrosion inhibitor on mild steel in 1 M HCl and found an efficiency of 70.08% at a concentration of 1500 ppm via weight loss measurements. The results were also cross-checked with Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic Polarization Technique (PDP), Energy Dispersive X-Ray Analysis (EDX), and Scanning Electron Microscopy (SEM) [78]. P.Kong with his team cross-linked Chitosan with polyaniline (PANI/CTS) and found the best result of inhibition of 79.02% at an inhibitor concentration of 200 ppm and in an acidic medium of 0.5 M HCl over Q235 steel.[10] The studies done were EIS, PDP, SEM, and DFT [79].

**3.3. Polyethylene glycol: An eco-friendly corrosion inhibitor**

Polyethylene glycol (PEG) is extensively used as a corrosion inhibitor in different electrolytes. Due to their large molecular weight, environment-friendly nature, excessive solubility in polar electrolytes, and biocompatibility, they are broadly used as corrosion inhibitors for metals and alloys. PEG is found to be a very extraordinary eco-friendly and biological useful material used as corrosion inhibitors in most of the industries working in the field of oil and gas refineries. Low vapour pressure, flammability, cost, environmental toxicity, and high chemical and thermal stability make PEG widely used in industries as a corrosion inhibitor at higher temperatures and over variable pH ranges.[80-83] PEG have a massive surface and protective area because of their polymeric nature and hence act as effective corrosion inhibitors. PEG interact with metallic surface to form a strong coordination bond with a metallic surface.[84-85] PEG is also extensively used as corrosion inhibitor in NaCl [86-87] and metal oxide solutions [88-89 ]. PEG can be recovered from the medium and can be reused again and again.[90-91] PEG is obtainable in different molecular weights ranging from 200 to 10000.[92-93] PEG having very low molecular weight i.e 200-600 D are found to exist in the liquid state at room temperature. PEG of 600-800 D molecular weight found to be water-soluble viscous materials. PEGs with a molecular weight greater than 800 D found to exist in solid-state. The solubility properties of PEG polymers drop with the growth in the molecular weight. PEGs with molecular weight 200-600 D are completely soluble in water, whereas PEG with molecular weight 2000 indicates solubility up to 60% only in water at room temperature. Recent studies show that PEG is an extensively used inhibitor for metals in the H2SO4 medium.[94-95]

**Conclusion**

The present review reports the collection of literature which reveals the effectiveness of biopolymers and bio-grafted polymers as corrosion inhibitors for industrial uses, as they are eco-friendly routes in place of basic toxic inhibitors of corrosion. The review investigates that different forms of natural or grafted biopolymers are in demand for the development of green chemistry ideologies. The usage of natural eco-friendly polymers along with plant extracts is best as they are originated from a biological origin and will not accumulate in the environment and hence declared biological safe. Due to their simple molecular structures, they sometimes give low corrosion inhibition efficiencies. To overcome this issue bio grafted polymers have been introduced so that their molecular structure can become bulky and hence acts as better corrosion inhibitors for the metals used for various applications mainly for industrial use. The perfection in industries causes the economy to rise for any country. The literature surveys show researchers may develop many more grafted products of biopolymers that have not been in use till now.

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