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Green Polymeric Corrosion Inhibitors: Design, Synthesis, and Characterization

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1.1 Introduction

Different industrial practices require the use of metals and metal-based structures [1, 2]. In these environments, the metals can directly contact the aggressive acidic, alkaline, saline, etc. media [3]. This can cause considerable damage to the underlying metallic surface that causes significant economic losses and is a potential hazard to the environment. The application of organic molecules as corrosion inhibitors is one of the most effective means to counter corrosion issues. Most effective corrosion inhibitors are based on inorganic and organic molecules, which are toxic and pose serious environmental concerns. Due to strict environmental regulations, there is growing research attention in the area of environment-friendly alternatives as corrosion inhibitors. This includes the categories of naturally occurring plant extracts, drugs, biopolymers, amino acids, proteins, and ionic liquids (ILs) [4–7].

This chapter presents a brief overview of corrosion, impact, and its background, emphasizing green corrosion inhibitors. The significance of biopolymers as corrosion inhibitors is described, and a comprehensive review of literature is presented on the application of biological polymeric corrosion inhibitors derived from polysaccharides and proteins. The importance of the chemical functionalization of corrosion inhibitor molecules and the application of chemically modified biopolymers as corrosion inhibitors are also outlined. This review article is expected to benefit the scientists and researchers working in this area and would act as a reference tool for the chemists/biochemists working in this field.

Polymeric Corrosion Inhibitors for Greening the Chemical and Petrochemical Industry, First Edition.
Edited by Mohammad A. Jafar Mazumder, Mumtaz A. Quraishi, and Amir Al-Ahmed.

1.2 Corrosion and Its Economic Significance

Corrosion is a major industrial nuisance, and its control is a considerably challenging issue in different industrial applications. The corrosion damage incurred upon the metals and alloys in the presence of aqueous corrosive environments is considered a major concern in several industries. The metals are generally purified from their respective ore forms by applying a considerable amount of energy. Therefore, these metallic surfaces have a significant tendency to revert to their original ore forms when exposed to the environment. This process of natural degradation and deterioration of the metals and alloys to their original forms is referred to as corrosion, which poses enormous economic losses and can even lead to potential structural failure and even loss of human life. According to a study by the National Association of Corrosion Engineers (NACE), the number of developed and developing nations estimated that the global annual loss is due to corrosion amounts to around US\$3.4 trillion [8]. A number of different methods are in practice to control and mitigate corrosion. This includes anticorrosion coatings, corrosion inhibitors, corrosion-resistant alloys, and cathodic protection. The use of corrosion inhibitors becomes a preferred choice to counter the aqueous corrosion of metals and alloys in various media. For this reason, many researchers working in chemical engineering, mechanical engineering, materials science, computational studies, and organic chemistry are devoted to developing efficient corrosion inhibitors.

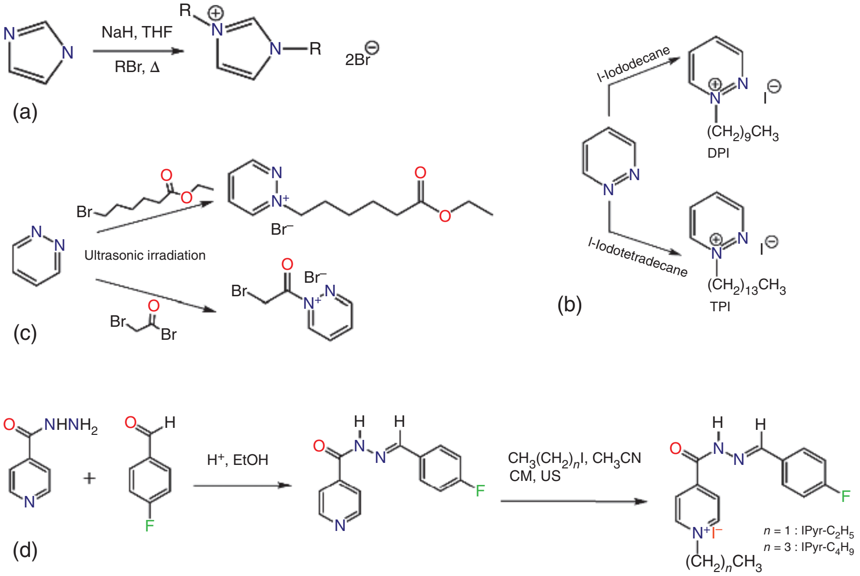
1.3 Corrosion Inhibitors

The corrosion inhibitors can be described as chemical additives, when introduced to a corrosive environment, and can minimize corrosion losses [3]. Conventionally, the inorganic chemical compounds from the classes of chromates, nitrites, nitrates, and phosphonates are the preferred choice as corrosion inhibitors [9]. In addition, the organic molecules from the categories of azoles, pyridines, and pyrimidines are also a preferred choice. This is due to the presence of an abundance of heteroatoms (N, S, O, etc.) on the inhibitor backbone and the existence of phenyl rings, π-bonds, etc. that can aid in the adsorption of the inhibitor molecules on the metallic surface. However, the use of conventional inorganic/organic corrosion inhibitors has caused severe environmental concerns forcing scientists and researchers worldwide to focus on using greener alternatives as corrosion inhibitors.

1.3.1 Green Corrosion Inhibitors

Several organic corrosion inhibitors come into the category of environmentally benign molecules. This includes synthetic heterocyclic molecules, amino acids, natural extracts, biological polymers, and ILs. The criteria of greenness include: (i) Toxicity in terms of EC_{50} and LC_{50} values $> 10\ \mathrm{mg\,l^{-1}}$ to North Sea species (algae, fish, crustacean, and seabed worms); (ii) Biodegradability: >60% in 28 days; (iii) Bioaccumulation: $\log (P_{\mathrm{o/w}}) < 3$ or Mol. Wt. $> 600\ \mathrm{g\,mol^{-1}}$. Literature shows the number of natural extracts derived from different plant parts, such as leaves, stems, fruits, flowers, peel, and pulp [7], has been explored as corrosion inhibitors for various media. The presence of different phytochemical constituents in these extracts is responsible for the adsorption and corrosion inhibition behavior.

Another example is the pharmaceutical products that contain a number of heterocycles, heteroatoms, and phenyl rings and can undergo adsorption on the metal surface [10, 11]. The ILs that are the room-temperature liquid molecules containing organic cations and ions are another category of green inhibitors. Their appreciable solubility in the corrosive media has led to the application of several ILs in corrosion inhibition [12]. Some of the examples of IL-based corrosion inhibitors are given in Scheme 1.1. Imidazolium and pyridinium-based ILs were studied for mild steel in 1 M H_2SO_4 [13]. High inhibition performance of 82–88% at 100 mg l^{-1} was noticed with chemical adsorption supported from the surface analytical measurements. A pyridazinium-based IL was prepared by El-Hajjaji et al. and evaluated for mild steel in 1 M HCl medium. High inhibition performance at high temperatures was observed [4]. The same group studied two pyridazinium-based ILs 1-decylpyridazin-1-ium iodide (DPI) and 1-tetradecylpyridazin-1-ium iodide (TPI) for mild steel in 1 M HCl using electrochemical and surface analysis [14]. Density functional theory (DFT)–based computational investigation of the inhibitors was in good agreement with the experimental results. Two pyridinium ILs were studied on mild steel in 1 M HCl by electrochemical methods. [15]. Tafel evaluation revealed anodic type of corrosion inhibitors. The experimental studies supported by the computational methods of analysis indicated that the inhibitor having longer alkyl chain length provided better performance. Other examples of green inhibitors are



Scheme 1.1 Synthesis of different ionic liquid-based corrosion inhibitors. Source: (a) Likhanova et al. [13]/Elsevier, (b–d) El-Hajjaji et al. [4, 14, 15]/Elsevier.

bio-derived polymers [16] and amino acids [17] that undergo effective adsorption on the metallic substrates.

1.3.2 Importance of Biopolymers as Corrosion Inhibitors

Polymeric corrosion inhibitors find significance due to the high surface coverage and the availability of plenty of adsorption sites to interact with the metallic surface. The biopolymers refer to the polymeric corrosion inhibitors derived from the classes of polysaccharides and proteins. Biopolymers gain their market share by their intrinsic biodegradable nature in combination with the exciting properties that have been applied for specific applications. The biopolymers can be extracted from natural resources, biosynthesized by living organisms, or chemically produced from biological materials [18]. Being of natural origin, biopolymers present a significant advantage over plastic-based materials. Additional advantages include biocompatibility, renewal origin, biocompatibility, barrier action against moisture/gases, low toxicity, and cost-effectiveness. A primary benefit associated with these molecules is the greenness and the environmentally benign nature. Several research articles are focused on the development of corrosion inhibitors based on biopolymers. To further improve the solubility and the corrosion inhibition performance, researchers have also investigated the chemical functionalization of these corrosion inhibitors. The global biopolymers market can be expected to attain around US$10 billion by 2021, at a growth rate of approximately 17% [19]. A detailed account of the corrosion inhibitors developed from polysaccharides, proteins, and chemically modified biopolymers is given in the following sections.

1.4 Polysaccharides as Corrosion Inhibitors

Carbohydrates are naturally abundant and are green in nature. Naturally occurring carbohydrate polymers have emerged as a potential class of corrosion inhibitors due to their appreciable biodegradability, biocompatibility, and solubility in aqueous media [16]. Some of these are given in Figure 1.1. A beneficial aspect of using these polymers as corrosion inhibitors is their natural origin, due to which they do not pose any environmental concerns. In addition, being of a polymeric nature, these molecules contain a number of heteroatoms, functional groups, and a large molecular weight that can afford a considerable coverage of the metallic surface. In the below section, a literature review on the application of some of the corrosion inhibitors developed from carbohydrate polymers is discussed. The biopolymer-based corrosion inhibitors are designed using DFT-based computational studies. From these studies, the computational parameters of frontier molecular orbital energies (E_{HOMO}, E_{LUMO}), molecular orbital energy gap (ΔE), electronegativity (χ), hardness (η), softness (σ), etc. are evaluated. On that basis, the reactivity and tendency to adsorb on a given metallic substrate can be determined [20]. The synthesis/chemical functionalization of the biopolymers can be accomplished using simple single-step chemical methods. The biopolymers are

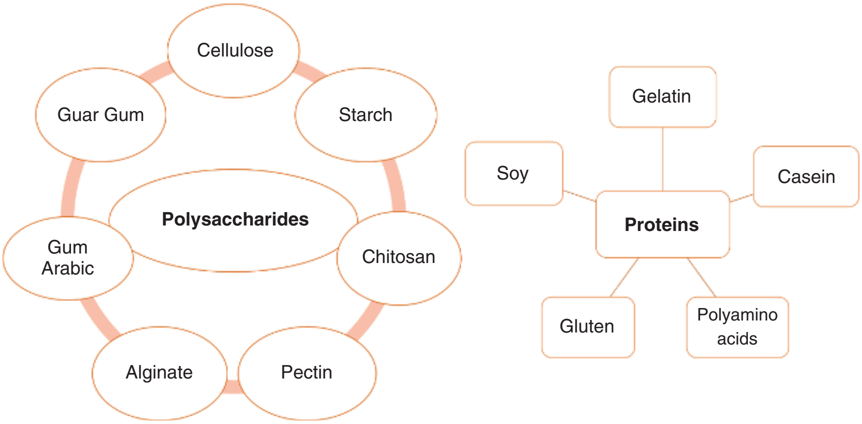


Figure 1.1 Different types of polysaccharides and proteins-based biopolymers reported as corrosion inhibitors.

characterized using spectral analysis methods, including Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) (^{1}H NMR, ^{13}C NMR), molecular weight analysis, and thermal stability using thermogravimetric analysis (TGA).

Chitosan is a polysaccharide extracted from chitin, which constitutes the exoskeleton of insects, molluscs, shrimps, etc. It was studied on copper corrosion for 0.5 M HCl [21]. Scanning electron microscopy (SEM) and FTIR analyses supported the inhibitor adsorption on the metallic surface. For mild steel substrate, chitosan was studied in 0.1 M HCl, wherein the inhibition efficiency (IE) increases with increasing the inhibitor concentration, and maximum efficiency of 68% was achieved [22]. Chitosan and carboxymethylcellulose were studied for API 5L X60 steel surface in the sweet environment via electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), and surface analysis [23]. The inhibitor performance was also compared with a commercial inhibitor formulation, and encouraging results were noted. Hydroxyethylcellulose was investigated for zinc surface in ammonium chloride [24]. Electrochemical and surface analysis evidenced the inhibitor adsorption on the metallic surface. The high inhibition efficiency was noticed with the thermodynamic parameters indicating the physical mode of adsorption. Sodium alginate is a polysaccharide carbohydrate extracted from seaweed (such as *sargassum*). It is biodegradable and nontoxic, has good biocompatibility, can reduce blood glucose and lipid levels, clean the intestinal tract, eliminate heavy metals, and have other functions beneficial to health. Sodium alginate is an unbranched binary copolymer of (1–4)-linked β-D-mannuronic acid (M) and α-l-guluronic acid (G) residues as monomers, constituting of M, G, and MG sequential block structures [25]. Sodium alginate as a corrosion inhibitor was evaluated for Mg alloy AZ31 in NaCl environment [26]. Surface analysis by SEM and FTIR supported the adsorption of sodium alginate on the metal surface. It was also studied for X60 carbon steel in the saline environment using weight loss and electrochemical measurements [27]. The inhibitor adsorption on the metal surface took place by the carboxylate oxygen groups and exhibited a physical mode of adsorption. Ultraviolet (UV)–vis and FTIR verified the adsorption of the corrosion inhibitor on the metallic substrate. Chitosan and carboxymethylcellulose were studied for API 5L X60 steel surface in sweet environment via EIS, PDP, and surface analysis [23]. The inhibitor performance was also compared with a commercial inhibitor formulation, and encouraging results were noted. Hydroxyethylcellulose was investigated for zinc surface in ammonium chloride [24]. Electrochemical and surface analysis evidenced the adsorption of hydroxyethylcellulose on the metallic surface. The high inhibition efficiency was noticed with the thermodynamic parameters indicating the physical adsorption.

Guar gum is a polysaccharide consisting of a straight chain of D-mannopyranose units joined by β-(1 → 4) linkage with a side-branching unit of a single D-galactopyranose unit joined to every other mannose unit by α-(1 → 6) linkages. It was analyzed for carbon steel corrosion in 1 M H_2SO_4 by applying weight loss and PDP tests [28]. Guar gum was also studied for pure aluminum in 1 M HCl, and 84.19% protection efficiency was noted at a dose of $0.4\,\mathrm{g\,l^{-1}}$ [29]. Gum acacia (GA) is a complex arabinogalactan, which contains a small proportion of proteinaceous materials and has been classified as arabinogalactan–protein complex. Gum acacia was analyzed for steel in 1 M HCl, resulting in 95% inhibition at $1\,\mathrm{g\,l^{-1}}$ [30]. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) evidenced the inhibitor adsorption, and the formation of a protective film on the metal surface further supported using the DFT-based computational studies. Gum arabic provided 83.5% inhibition efficiency at $5\,\mathrm{g\,l^{-1}}$ when evaluated for carbon steel 1018 [31].

Pectin is a structural heteropolysaccharide contained in the primary cell walls of terrestrial plants. It is produced commercially as a white to light brown powder, mainly extracted from citrus fruits. Electrochemical tests studied pectin as a corrosion inhibitor for X60 steel substrate in a 0.5 M HCl environment [32]. EIS revealed a charge-transfer control of the inhibition performance that was further supported with contact angle measurements, which exhibited an increment in the hydrophobicity with the inhibitor-adsorbed film providing evidence for the formation of inhibitor film on the steel surface. On the aluminum surface, pectin provided 92.1% protection at a dose of $2\,\mathrm{g\,l^{-1}}$ [33]. The $\Delta G^0{}_{\mathrm{ads}}$ values indicated spontaneous inhibitor adsorption with a primarily mixed type of inhibition. Starch is a natural polymer, available in abundance at low cost, renewable, and biodegradable. Chemically, it is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. All green plants produce starch as an energy store. It contains two structurally different components: amylose (15–20%) and amylopectin (80–85%). The amylose is composed of a large linear chain of a (1–4) linked α-D-glucopyranosyl residue, whereas amylopectin is a branching form of α-glycogen linked by a (1–6) linkage. Amylose was evaluated on mild steel in 0.1 M $H_2SO_{4,}$ and 64.78% protection was achieved at $500\,\mathrm{mg\,l^{-1}}$ [34]. The addition of cetyltrimethylammonium bromide (CTAB) surfactant produced a synergistic improvement in the corrosion inhibition performance. Tapioca starch was evaluated for AA6061 alloy in seawater medium using weight loss and electroanalytical measurements [35]. The inhibition efficiency was achieved at 96% at 1000 mg l^{-1}, and the adsorption of inhibitor was in agreement with Langmuir isotherm. SEM and energy-dispersive X-ray (EDX) analyses supported the inhibitor film formation on the metallic substrate that supported the surface protection.

Hydroxyethylcellulose (HEC) and sodium alginate (ALG)–based corrosion inhibitor formulations were used as inhibitors for Mg alloy AZ31 in NaCl environment [36]. HEC and ALG formulations provided effective performance with 80.56% and 77.43% efficiencies. Surface examinations using scanning electrochemical microscopy (SECM), AFM, SEM, and EDX revealed that the coexistence of $Mg(OH)_2$ and adsorbed inhibitor complexes protected the alloy surface. Dextran was used to inhibit corrosion of 6061 Al alloy in a 1 M HCl medium [37]. The inhibitor showed a mixed type of performance with physical adsorption and obeyed Langmuir adsorption isotherm. At a dose of 0.4 g l^{-1}, an inhibition efficiency of 74.6% was obtained. Some of the different polysaccharides that have been used as corrosion inhibitors for metals and alloys are listed in Table 1.1.

1.5 Proteins and Polyamino Acids as Corrosion Inhibitors

Mostly the animal and vegetable wastes are responsible for the protein sources. For example, slaughterhouse wastes can provide a reputable resource for the proteins of animal origin, such as gelatin. These wastes constitute the inedible tissues/parts of the animals that have been slaughtered for meat production [38]. Several reports are available in the literature on the application of protein-based biopolymers as corrosion inhibitors. Figure 1.1 lists the different proteins that have been used as corrosion inhibitors for metals and alloys [39]. Casein was studied as a corrosion inhibitor for mild steel in 0.1 M HCl solution in the range of 50–400 mg l^{-1} concentrations [40]. The corrosion rate decreased from 98.4 to 3.9 mpy in the presence of an inhibitor. EIS studies revealed a charge-transfer control of the electrochemical process, whereas the PDP measurements indicated a mixed mode of inhibition. Casein was also studied as an inhibitor for reinforcing steel 0.1 mol l^{-1} NaOH solution in the presence of varying concentrations of Cl^- ions with 82% inhibition efficiency [41]. Using weight loss and electrochemical measurements, gelatin was explored for X60 steel in a 15% HCl environment wherein the inhibition efficiency increased with increasing the inhibitor concentration [42]. Adding potassium iodide (KI) to gelatin as a synergistic component increased the inhibition efficiency from 70.42% to 84.51%. Gelatin was also evaluated for aluminum and aluminum–silicon alloys in 0.1 M NaOH solution using electrochemical measurements [43]. The inhibitor adsorption was in accordance with the Flory–Huggins isotherm. Gluten hydrolysate was analyzed on mild steel in 1 M HCl solution using weight loss and electrochemical measurements [44]. The inhibitor showed a mixed mode of inhibition performance by forming an inhibitive film on the metallic substrate. It also performed as a mixed mode of physical and chemical adsorption. A high inhibition efficiency of 93% was obtained even at an elevated temperature

Table 1.1 Performance of different polysaccharides as corrosion inhibitors.

Name	Metal surface/medium	Inhibition efficiency/ concentration	Adsorption isotherm/type	Reference
Chitosan	Cu/0.5 M HCl	93%/8 μM	Langmuir isotherm/mixed type	[21]
Chitosan	Mild steel/0.1 M HCl	68%/4 μM	Langmuir isotherm/mixed type	[22]
Carboxymethylcellulose	API 5L X60 pipeline steel/CO_2 saturated 3.5% NaCl	39%/100 mg l^{-1}	Langmuir isotherm/mixed type	[23]
Hydroxyethylcellulose	Zn/26% NH_4Cl	92.07%/300 mg l^{-1}	Langmuir isotherm/mixed type	[24]
Sodium alginate	Mg alloy AZ31/3.5% NaCl	86.62%/500 mg l^{-1}	Mixed type	[26]
Sodium alginate	API X60 steel/3.5% NaCl	87.23%/1000 mg l^{-1}	—	[27]
Guar gum	Carbon steel/1 M H_2SO_4	93.2%/1000 mg l^{-1}	Langmuir isotherm/mixed type	[28]
Guar gum	Aluminum/1 M HCl	83.19%/400 mg l^{-1}	Temkin isotherm/cathodic type	[29]
Gum acacia	Mild steel/1 M HCl	95%/1000 mg l^{-1}	Langmuir isotherm/mixed type	[30]
Gum arabic	Carbon steel 1018/oil-field water	94.2%/5000 mg l^{-1}	Langmuir isotherm/mixed type	[31]
Pectin	X60 steel/0.5 M HCl	78.7%/1000 mg l^{-1}	Langmuir isotherm/mixed type	[32]
Pectin	Aluminum/2 M HCl	92.1%/2000 mg l^{-1}	Langmuir isotherm	[33]
Starch	Mild steel/0.1 M H_2SO_4	66.21%/300 mg l^{-1}	Langmuir isotherm/mixed type	[34]
Tapioca starch	AA6061 alloy/seawater	91.41%/1000 mg l^{-1}	Langmuir isotherm/mixed type	[35]

Table 1.2 Performance of different protein-based biopolymers as corrosion inhibitors.

Name	Metal surface/ medium	Inhibition efficiency/ concentration	Adsorption isotherm/type	Reference
Casein	Mild steel/0.1 M HCl	96.41%/400 mg l^{-1}	Langmuir isotherm/ mixed type	[40]
Casein	Reinforcing steel/ synthetic concrete pore solution	82%/9.7×10^{-4} M	—	[41]
Gelatin	X60 steel/15% HCl	70.42%/2.5% w/v	Mixed type	[42]
Gelatin	Al alloy/0.1M NaOH	65.71%/2000 mg l^{-1}	Flory–Huggins isotherm/ Mixed type	[43]
Gluten hydrolysate	Mild steel/1 M HCl	92.8%/1000 mg l^{-1}	Langmuir isotherm/ mixed type	[44]
Maize-gluten meal extract	Steel/Simulated concrete pore solution in 3% NaCl	88%/2000 mg l^{-1}	Langmuir isotherm/ mixed type	[45]
Soy	Carbon steel/1 M H_2SO_4	89.51%/5000 mg l^{-1}	Langmuir isotherm/ mixed type	[46]

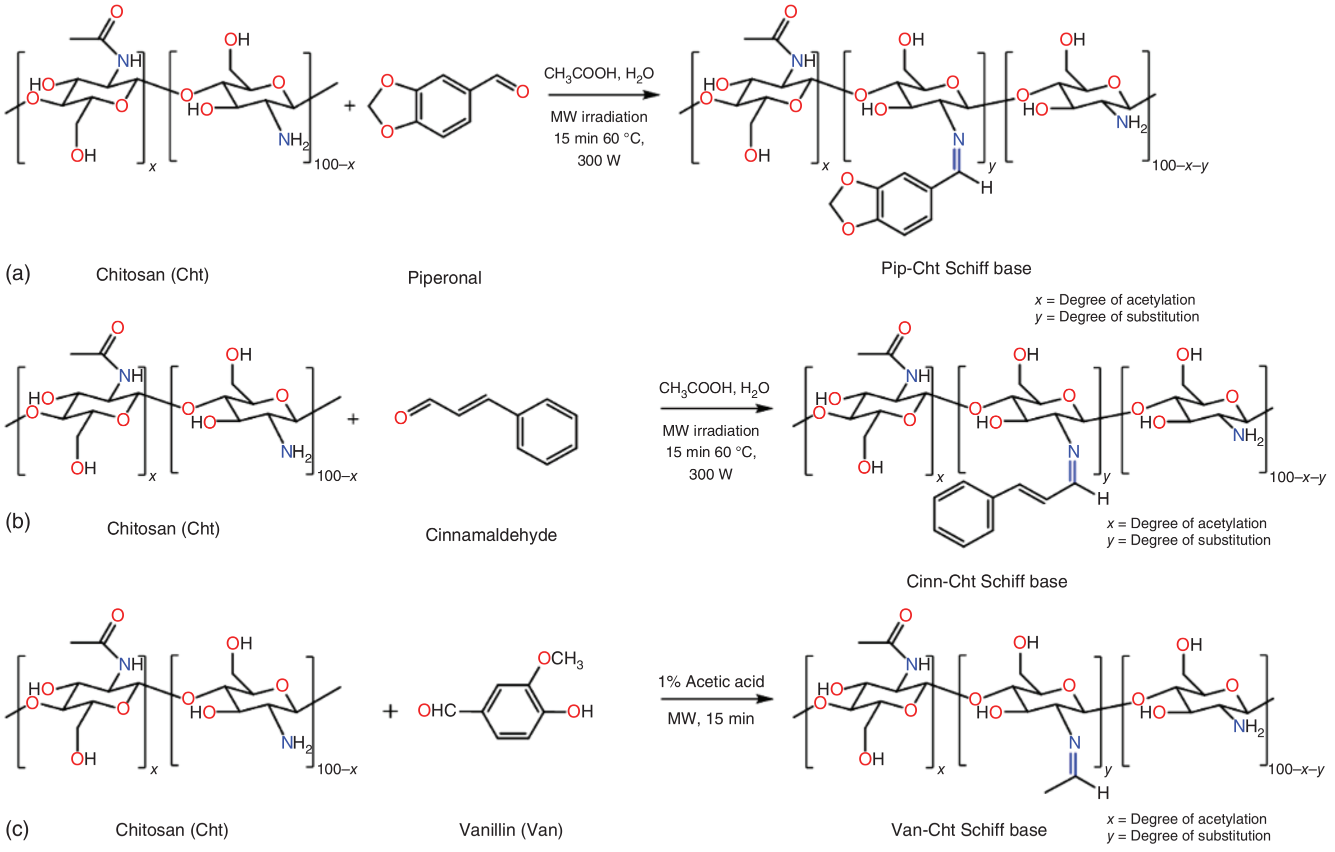
of 323 K. Maize-gluten meal extracts were analyzed for steel in simulated concrete pore solutions with 3% NaCl [45]. The inhibition efficiency rose from 69.12% to 88.10% in the concentration range of 0.25–2 g l^{-1}. The Langmuir isotherm provided the most appropriate fit of the data and the surface analysis via SEM and AFM studies. Soy polymer and polyvinyl pyrrolidinone were evaluated for carbon steel in a 1 M H_2SO_4 environment in the temperature range of 30–60 °C with high efficiency of 89.5% [46]. The inhibitor adsorption on the metal surface obeyed the Langmuir isotherm and the PDP studies revealed a mixed mode of inhibitor action. Table 1.2 lists some of the different protein-based biopolymers that have been used as corrosion inhibitors for metals and alloys.

Among polyamino acids, most of the available literature reports the application of polyaspartic acid as corrosion inhibitors. Polyaspartic acid (PAsp) was reported as a corrosion inhibitor in different molecular weights. Besides, a combination of polyaspartic acid and various amino acids, namely, tyrosine, histidine, phenylalanine, and leucine, resulted in detergent formulations without/with phosphate/silicate have also been reported as corrosion inhibitors [47]. The effect of pH, temperature, and rotation conditions was studied for PAsp as corrosion inhibitors by Silverman et al. [48]. PAsp accelerated the corrosion at pH values lower than neutral pH. In contrast, at the higher pH values, it facilitated corrosion inhibition at a concentration of 1–10% for iron and steel surfaces. In an amino sulfonic acid medium, PAsp was also reported as a corrosion inhibitor for copper surface wherein it provided a high efficiency of 89.8% at 1 g l^{-1} [49]. An amount of 0.5 g l^{-1} PAsp in a synergistic combination with the same imidazole concentration provided an inhibition efficiency of 95.7%. Synergistic corrosion inhibition was also introduced with iodide ions for mild steel in 0.5 M H_2SO_4, resulting in a rise in the inhibition efficiency from 87.9% to 96.3% [50]. At a pH value lower than an isoelectric point, the amino acid can get protonated in the corrosive solution, resulting in $PAspH^+$ species in the medium, which would directly adsorb on the metallic surface to provide protection from corrosion. In the presence of KI, I^- ions would first undergo adsorption on the metallic surface and would promote the electrostatic interaction with the protonated form of the polymer. In another study, a combination of polyaspartic acid with Zn^{2+} ions (0.01 $g\,l^{-1}$) produced the corrosion inhibition of 61% at 2 $g\,l^{-1}$ for mild steel in 3.5% NaCl medium [51]. It was proposed that the amide groups and the carboxylate species of the PAsp played a key role in the interaction of the PAsp with the metallic substrate. This was further evidenced by the DFT-based quantum chemical calculations and Monte Carlo simulations.

1.6 Chemically Modified Biopolymers as Corrosion Inhibitors

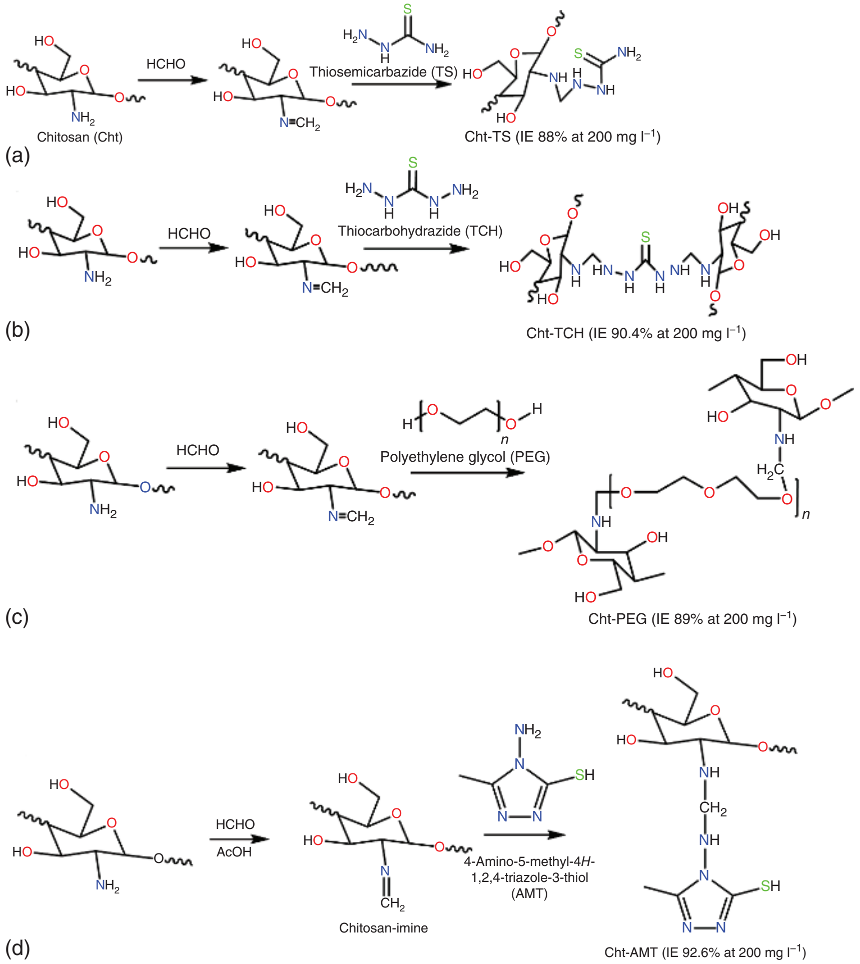
One of the issues associated with the naturally occurring carbohydrate-based polymers as corrosion inhibitors is their limited solubility in the corrosive solution. The high-molecular weights of these polymers that afford the appreciable surface coverage also render these molecules with limited solubility in the aqueous corrosive medium. A convenient strategy, in this case, is the chemical functionalization of the polymeric backbone using a suitable agent to improve the solubility and the inhibition performance. Herein we have discussed the corrosion inhibition behavior of several organic corrosion inhibitors based on chemically modified biopolymers in the aqueous corrosive media. The synthesis of some chemically modified chitosan-based inhibitors is shown in Scheme 1.2.

A most commonly adopted strategy for chemical modification of chitosan is the Schiff base formation. The pyranose ring present in the chitosan contains attached $–NH_2$ functional groups. These amine groups can be reacted with organic compounds containing free –CHO groups in a single-step reaction to introduce the imine (–HC=N–) linkage in the chitosan polymer. The imine (–HC=N–) linkage present in the Schiff base shows the ability to undergo adsorption on the metal surfaces. The choice of Schiff bases stems from the fact that they are nontoxic and can be synthesized easily, and the introduction of the imine linkage is expected to improve the film-forming capability and anticorrosion behavior [5, 55–58]. A significant advantage of using the chitosan Schiff bases is that the Schiff base preparation is a simple procedure requiring single-step reactions, and the azomethine (–CH=N) linkage is known to show strong adsorption over the metallic surface. Three Schiff bases of chitosan produced via microwave irradiation method using benzaldehyde (CSB-1), vanillin (CSB-2), and *N*,*N*-dimethylaminobenzaldehyde (CSB-3) were utilized as inhibitors against the corrosion of mild steel in 1 M HCl [5]. At a low dose of 50 $mg\,l^{-1}$, all the inhibitors showed high inhibition efficiencies among which, CSB-3 performed the best. The structural aspects in terms of $–N(CH_3)_2$



Scheme 1.2 Synthesis of chemically modified chitosans. Source: (a) Chauhan et al. [52]/Elsevier, (b) Chauhan et al. [53]/Elsevier, (c) Quraishi et al. [54]/Elsevier.

group afforded a planar orientation on the metallic substrate that allowed a better coverage and a superior corrosion inhibition. Two more Schiff bases of chitosan with Piperonal (Pip-Cht) [52] and cinnamaldehyde (Cinn-Cht) [53] were prepared using a single-step microwave synthesis method. They were utilized as corrosion inhibitors for carbon steel in 15% HCl solution. The thermal stability studies indicated both the inhibitors were stable up to 200 °C and revealed high efficiencies at low doses of 500 and 400 mg l^{-1}, respectively. In a subsequent study by the same group, vanillin–chitosan (Van–Cht) Schiff base was used as a corrosion inhibitor for carbon steel in 15% HCl solution [54]. Electrochemical studies and computation analyses revealed strong inhibitor adsorption over the metallic substrate. Another



Scheme 1.3 Structures and inhibition performance of different chemically modified chitosan-based inhibitors on mild steel in 1M HCl. Source: (a) Chauhan et al. [60]/Elsevier, (b) Chauhan et al. [60]/Elsevier, (c) Srivastava et al. [61]/Elsevier, (d) Chauhan et al. [62]/Elsevier.

Schiff base of chitosan was prepared using salicylaldehyde and studied for sweet corrosion of J55 steel [59]. At an elevated temperature of 65 °C, high inhibition efficiency of 95% was obtained at a concentration of 150 $\mathrm{mg\,l^{-1}}$. The structures and corrosion inhibition performance of different chemically modified chitosan derivatives are shown in Scheme 1.3.

Heterocyclic molecules are generally understood as effective corrosion inhibitors. Several heterocyclic corrosion inhibitors, e.g. azoles, pyridines, and pyrimidines, have been reported for different corrosive media [3]. In a study, chitosan was chemically functionalized using amino-mercapto triazole and utilized as corrosion inhibitor for 1 M HCl on carbon steel environment and in 3.5% NaCl on stainless steel [62, 63]. In both cases, high inhibition performances were obtained. Thiosemicarbazide (CS-TS) and thiocarbohydrazide (CS-TCH) were used to chemically functionalize the chitosan and used as mild steel inhibitors in 1 M HCl medium using gravimetric, electrochemical, and computational studies. The CS-TCH provided a more significant corrosion inhibition with preferential adsorption of the protonated form of the corrosion inhibitor [60]. Using EIS and PDP measurements, the same polymer was further investigated for stainless steel 3.5% NaCl [64]. Chitosan was also modified using polyethylene glycol and was evaluated as an inhibitor for steel surface in 1 M HCl and 1 M sulfamic acid solutions [61, 65]. High efficiencies were obtained at around 200 $\mathrm{mg\,l^{-1}}$ in both media. Two amino-acid-modified derivatives of dextran (LDT and S-LDT) were studied as inhibitors for corrosion of carbon steel in CO_2-saturated oilfield produce water [66].

1.7 Biopolymer Nanoparticles as Corrosion Inhibitors

Nanoparticles of chitosan were utilized for corrosion inhibition of mild steel substrate in 3.5% NaCl solution. A 90% protection was achieved with the inhibitor adsorption on the steel surface, obeying the Langmuir isotherm [67]. Nonionic amphiphilic chitosan nanoparticles were synthesized in aqueous medium employing surfactant-free protocol and used for steel surface protection in 1 M HCl. At 250 $\mathrm{mg\,l^{-1}}$, an inhibition efficiency of 93.5% was afforded [68]. Chitosan nanoparticles were also studied as inhibitors for A6063 alloy corrosion in 3.65% NaCl medium [69]. An inhibition performance of >70% was observed. Glycogen nanoparticles were synthesized via microwave irradiation and studied as corrosion inhibitors for zinc in sulfamic acid medium [70]. At a concentration of 0.20 $\mathrm{mg\,l^{-1}}$, an inhibition efficiency of 92% was obtained. Maltodextrin nanoparticles were evaluated as inhibitors against acid corrosion of zinc and at high efficiency of 93% was obtained at 50 $\mathrm{mg\,l^{-1}}$ of concentration [71].

1.8 Biopolymer Composites as Corrosion Inhibitors

Nanocomposites of chitosan were prepared with cobalt ($\mathrm{IE} > 95\%$) and SnS_2 ($\mathrm{IE} > 80\%$) and investigated for mild steel in 1 M HCl medium [72]. Chitosan composites were also prepared with silver nanoparticles using the simple reduction of silver by honey and were studied for ST37 steel in 15% HCl [73]. A mixed mode of physical and chemical adsorption was obtained at low temperatures, wherein chemical adsorption was observed at higher temperatures. A cathodic type of corrosion inhibition performance was observed at higher temperatures. The chitosan–AgNp composites when evaluated in 15% H_2SO_4 provided a 94% inhibition performance [74]. Chitosan (Ch) grafted with poly(ethylene glycol) (Ch-g-mPEG) was assembled over silver nanoparticles and evaluated for carbon steel in 1 M HCl using electrochemical and surface analytical measurements [75]. Starch–silver nanoparticle composites were studied as inhibitors for mild steel in 0.5 M HCl, and 82.806% efficiency was obtained at 70 °C [76]. At 30 °C, a high efficiency of 93.168% was observed. Dextran and its silver nanoparticle composites were utilized as corrosion inhibitors for ST37-2 steel surface in 15% H_2SO_4 using weight loss and electrochemical studies [77]. Synergistic effect of KI was also investigated at 25 °C (IE 94.21%) and 60 °C (IE 99.4%). A mixed type of inhibition behavior with predominance of the cathodic control of the reaction was observed.

1.9 Adsorption and Protection Mechanism of Biopolymers on the Metal Surface

A general mechanism of the adsorption of the biopolymer-based corrosion inhibitors on the surface of metals and the protection performance can be explained as follows. The gravimetric method of inhibitor analysis reveals the effect of the variation in the inhibitor concentration on the corrosion rate and the inhibition efficiency. The increase in the inhibition efficiency and a corresponding lowering in the corrosion rate with an increase in the inhibitor concentration suggests adsorption of the corrosion inhibitor on the metal surface. The inhibitor molecules adsorb on the metal surface and cover the corrosion active sites, thereby decreasing corrosion. The EIS studies show an increase in the resistance against the charge transfer with the increase in the inhibitor concentration [14]. The PDP method shows a lowering in the corrosion current densities with an increase in the inhibitor concentration. Thus, the EIS and PDP methods also support the inhibitor adsorption and corrosion inhibition. The shift in the corrosion potential can indicate the anodic, cathodic, or mixed type of inhibition behavior [14]. In a corrosive solution, a corrosion inhibitor can exist in the protonated form as shown below:

$$\text{Cinn} - \text{Cht}_{\text{neutral}} \rightleftharpoons \text{Cinn} - \text{Cht}_{\text{protonated}} \tag{1.1}$$

The inhibitor can adsorb on the metallic surface via displacement of the pre-adsorbed water molecules as follows:

$$\text{M}_{\text{H}_2\text{O}} + \text{Cinn} - \text{Cht} \rightleftharpoons \text{M}_{\text{Cinn}-\text{Cht}} + \text{H}_2\text{O} \tag{1.2}$$

The protonated form of corrosion inhibitor can adsorb on the metallic substrate and cover the cathodic sites, protecting them from corrosion. The neutral form

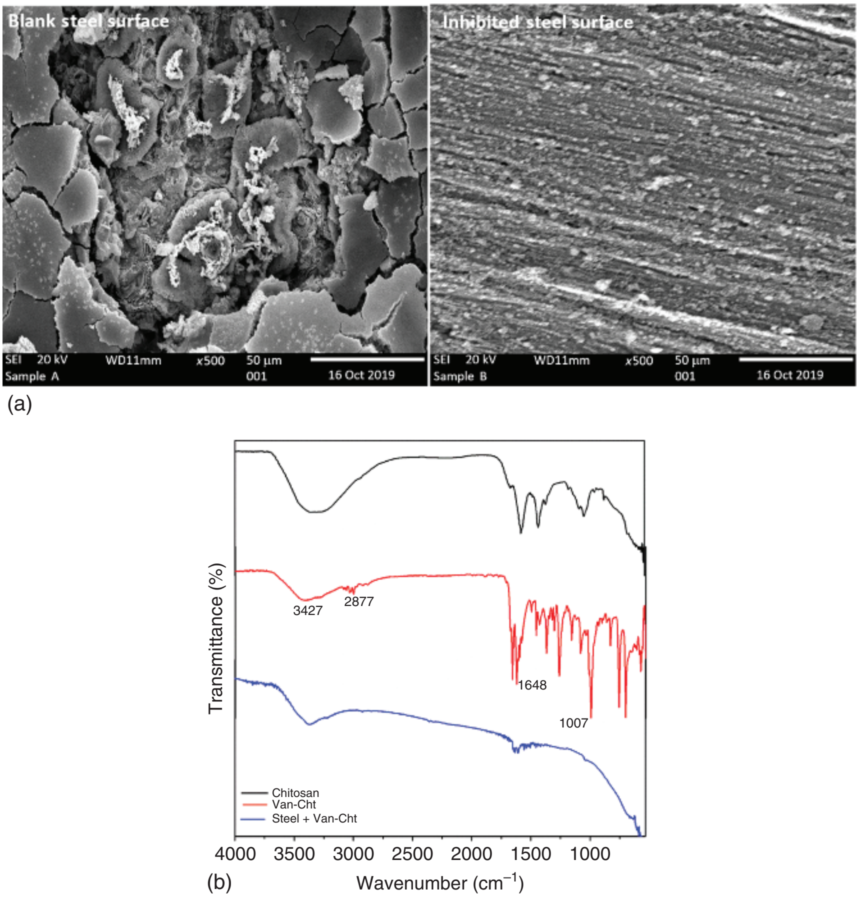


Figure 1.2 (a) Surface morphology (SEM) of carbon steel samples after immersion in 15% HCl in the absence (A) and the presence of (B) optimum concentration of Van–Cht for 6 h at 25 °C. (b) FTIR spectra of pure chitosan, Van–Cht, and film of Van–Cht adsorbed steel surface after immersion in 15% HCl for 6 h at 25 °C. Source: Quraishi et al. [54]/Springer Nature.

of the inhibitor can adsorb directly at the metal surface by the sharing of the π electrons or the lone pair of electrons. The filled d-orbitals of the metal surface can also back-donate the electrons to the inhibitor molecules. The surface analysis of the metal surface via electron microscopy and spectroscopic analysis can provide further support for inhibitor adsorption (Figure 1.2). The surface morphology of carbon steel substrate after immersion in 15% HCl in the absence and the presence of inhibitor Van–Cht is given in Figure 1.2a. The blank steel surface shows considerable damage, whereas the inhibited surface shows a smooth morphology indicating the adsorption and protection performance of inhibitor. The FTIR spectra of pure chitosan, Van–Cht, and Van–Cht inhibitor after adsorption on carbon steel surface following immersion in 15% HCl are given in Figure 1.2b. The characteristic absorbance maxima of Van–Cht can be seen in the range of 3300–3400 cm^{-1},

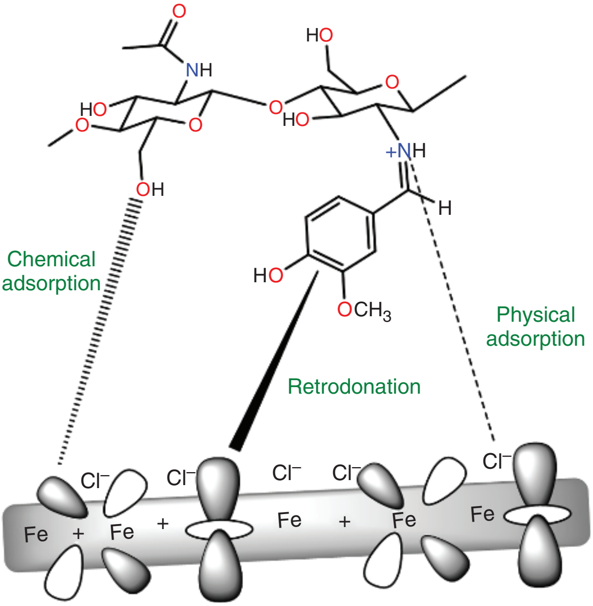


Figure 1.3 Mechanism of adsorption and inhibition behavior of vanillin-modified chitosan (Van–Cht) on carbon steel surface. Source: Quraishi et al. [54]/Springer Nature.

corresponding to N–H stretch. Small peaks of –HC=N– stretching in the region of 1598–1575 cm^{-1} can be observed in the adsorbed sample. Slight shift in the above band in the adsorbed sample compared to the pure Van–Cht with a lowering in the intensity indicates the involvement of this group in the adsorption of the inhibitor on the steel surface.

Further information can be obtained via computation analysis. The pK_a analysis can indicate the existence of the inhibitor in the protonated form [66]. This observation is supported by the DFT calculations and the molecular simulations, both of which can reveal the active sites present on the inhibitor molecule amenable to undergo adsorption and the inhibitor's preferred alignment on the metal surface [23]. Figure 1.3 shows a tentative mechanism of the adsorption and inhibition behavior of the corrosion inhibitor.

1.10 Conclusions and Prospects

Corrosion of metallic structures is a major issue causing significant economic concerns. Most of the available corrosion inhibitors belong to the class of nitrogen-based heterocyclic compounds. However, the use of these inhibitors leads to severe issues related to toxicity and environmental pollution. Therefore, there is a growing interest in the area of corrosion inhibitors based on environmentally benign molecules, such as natural extracts, drugs, and ILs. One of the primary categories is the polymeric corrosion inhibitors derived from carbohydrates and proteins.

The polymer-based corrosion inhibitors find application due to their large molecular size that can afford the considerable coverage of the metallic substrate on the target metal surface. The major categories are chitosan and the exudate gums, among the carbohydrate-based corrosion inhibitors. On the other hand, polyamino acids have found the major application as corrosion inhibitors among the protein-based corrosion inhibitors.

Furthermore, in recent years, to improve the adsorption and the inhibition effect of the polymeric corrosion inhibitors on the metallic surface, the chemical modification of the inhibitor backbone has been applied as a strategy. Namely, the single-step chemical modifications, nanocomposite formations, and copolymer formation are some of the methods commonly adopted to develop the modified polymeric materials with superior corrosion inhibition behavior. The comprehensive experimental studies have been well supported using appropriate computational modeling analysis of the corrosion inhibitors. In recent years, researchers have also targeted industry-relevant research areas, such as sweet corrosion and the oil-well acidizing environments using polymeric corrosion inhibitors. However, the collected literature also shows some knowledge gaps specifically in the realms of the influence of different functional groups, more detailed synergism studies, the effect of temperature, etc. Furthermore, another aspect is the development of inhibitor formulations using the desired surfactant, oil, synergistic agent, etc. as an additive along with the active corrosion inhibitors. Also, detailed comparisons of the newly developed corrosion inhibitors with the literature reported corrosion inhibitors must be carried out before they can be considered for the potential applications in industry.

Acknowledgment

MAQ wishes to thank the Deanship of Scientific Research (DSR), KFUPM, Saudi Arabia, for the financial assistance received under the project DF191051.

References

1. Sastri, V.S. (1998). *Corrosion Inhibitors: Principles and Applications*. Wiley.
2. Ansari, K.R., Chauhan, D.S., Singh, A. et al. (2020). Corrosion inhibitors for acidizing process in oil and gas sectors. In: *Corrosion Inhibitors in the Oil and Gas Industry* (ed. V.S. Saji and S.A. Umoren), 153–176. Wiley-VCH Verlag GmbH & Co. KGaA, ISBN 978-3-527-34618-9.
3. Quraishi, M.A., Chauhan, D.S., and Saji, V.S. (2020). *Heterocyclic Organic Corrosion Inhibitors: Principles and Applications*. Amsterdam: Elsevier Inc.
4. El-Hajjaji, F., Messali, M., Aljuhani, A. et al. (2018). Pyridazinium-based ionic liquids as novel and green corrosion inhibitors of carbon steel in acid medium: electrochemical and molecular dynamics simulation studies. *Journal of Molecular Liquids* 249: 997–1008.

5 Haque, J., Srivastava, V., Chauhan, D.S. et al. (2018). Microwave-induced synthesis of chitosan Schiff bases and their application as novel and green corrosion inhibitors: experimental and theoretical approach. *ACS Omega* 3: 5654–5668.

6 Singh, A., Ahamad, I., and Quraishi, M.A. (2016). Piper longum extract as green corrosion inhibitor for aluminium in NaOH solution. *Arabian Journal of Chemistry* 9: S1584–S1589.

7 Verma, C., Ebenso, E.E., Bahadur, I., and Quraishi, M.A. (2018). An overview on plant extracts as environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media. *Journal of Molecular Liquids* 266: 577–590.

8 Verma, C., Olasunkanmi, L., Ebenso, E.E., and Quraishi, M.A. (2018). Substituents effect on corrosion inhibition performance of organic compounds in aggressive ionic solutions: a review. *Journal of Molecular Liquids* 251: 100–118.

9 Verma, C., Ebenso, E.E., and Quraishi, M.A. (2017). Corrosion inhibitors for ferrous and non-ferrous metals and alloys in ionic sodium chloride solutions: a review. *Journal of Molecular Liquids* 248: 927–942.

10 Gece, G. (2011). Drugs: a review of promising novel corrosion inhibitors. *Corrosion Science* 53: 3873–3898.

11 Xhanari, K., Finšgar, M., Hrnčič, M.K. et al. (2017). Green corrosion inhibitors for aluminium and its alloys: a review. *RSC Advances* 7: 27299–27330.

12 Verma, C., Ebenso, E.E., and Quraishi, M.A. (2017). Ionic liquids as green and sustainable corrosion inhibitors for metals and alloys: an overview. *Journal of Molecular Liquids* 233: 403–414.

13 Likhanova, N.V., Domínguez-Aguilar, M.A., Olivares-Xometl, O. et al. (2010). The effect of ionic liquids with imidazolium and pyridinium cations on the corrosion inhibition of mild steel in acidic environment. *Corrosion Science* 52: 2088–2097.

14 El-Hajjaji, F., Salim, R., Messali, M. et al. (2019). Electrochemical studies on new pyridazinium derivatives as corrosion inhibitors of carbon steel in acidic medium. *Journal of Bio-and Tribo-Corrosion* 5: 4.

15 El-Hajjaji, F., Ech-chihbi, E., Rezki, N. et al. (2020). Electrochemical and theoretical insights on the adsorption and corrosion inhibition of novel pyridinium-derived ionic liquids for mild steel in 1 M HCl. *Journal of Molecular Liquids* 314: 113737.

16 Umoren, S.A. and Eduok, U.M. (2016). Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: a review. *Carbohydrate polymers* 140: 314–341.

17 El Ibrahimi, B., Jmiai, A., Bazzi, L., and El Issami, S. (2020). Amino acids and their derivatives as corrosion inhibitors for metals and alloys. *Arabian Journal of Chemistry* 13: 740–771.

18 Jha, A. and Kumar, A. (2019). Biobased technologies for the efficient extraction of biopolymers from waste biomass. *Bioprocess and Biosystems Engineering* 42: 1893–1901.

19 Martău, G.A., Mihai, M., and Vodnar, D.C. (2019). The use of chitosan, alginate, and pectin in the biomedical and food sector—biocompatibility, bioadhesiveness, and biodegradability. *Polymers* 11: 1837.

20 Obot, I., Macdonald, D., and Gasem, Z. (2015). Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: an overview. *Corrosion Science* 99: 1–30.

21 El-Haddad, M.N. (2013). Chitosan as a green inhibitor for copper corrosion in acidic medium. *International journal of Biological Macromolecules* 55: 142–149.

22 Umoren, S.A., Banera, M.J., Alonso-Garcia, T. et al. (2013). Inhibition of mild steel corrosion in HCl solution using chitosan. *Cellulose* 20: 2529–2545.

23 Umoren, S.A., AlAhmary, A.A., Gasem, Z.M., and Solomon, M.M. (2018). Evaluation of chitosan and carboxymethyl cellulose as ecofriendly corrosion inhibitors for steel. *International Journal of Biological Macromolecules* 117: 1017–1028.

24 Deyab, M. (2015). Hydroxyethyl cellulose as efficient organic inhibitor of zinc–carbon battery corrosion in ammonium chloride solution: electrochemical and surface morphology studies. *Journal of Power Sources* 280: 190–194.

25 Gombotz, W.R. and Wee, S. (1998). Protein release from alginate matrices. *Advanced Drug Delivery Reviews* 31: 267–285.

26 Dang, N., Wei, Y., Hou, L. et al. (2015). Investigation of the inhibition effect of the environmentally friendly inhibitor sodium alginate on magnesium alloy in sodium chloride solution. *Materials and Corrosion* 66: 1354–1362.

27 Obot, I., Onyeachu, I.B., and Kumar, A.M. (2017). Sodium alginate: a promising biopolymer for corrosion protection of API X60 high strength carbon steel in saline medium. *Carbohydrate Polymers* 178: 200–208.

28 Abdallah, M. (2004). Guar gum as corrosion inhibitor for carbon steel in sulfuric acid solutions, Portugaliae. *Electrochimica Acta* 22: 161–175.

29 Palumbo, G., Berent, K., Proniewicz, E., and Banaś, J. (2019). Guar gum as an eco-friendly corrosion inhibitor for pure aluminium in 1-M HCl solution. *Materials* 12: 2620.

30 Azzaoui, K., Mejdoubi, E., Jodeh, S. et al. (2017). Eco friendly green inhibitor Gum Arabic (GA) for the corrosion control of mild steel in hydrochloric acid medium. *Corrosion Science* 129: 70–81.

31 Shen, C., Alvarez, V., Koenig, J.D., and Luo, J.-L. (2019). Gum Arabic as corrosion inhibitor in the oil industry: experimental and theoretical studies. *Corrosion Engineering, Science and Technology* 54: 444–454.

32 Umoren, S.A., Obot, I.B., Madhankumar, A., and Gasem, Z.M. (2015). Performance evaluation of pectin as ecofriendly corrosion inhibitor for X60 pipeline steel in acid medium: experimental and theoretical approaches. *Carbohydrate Polymers* 124: 280–291.

33 Fares, M.M., Maayta, A., and Al-Qudah, M.M. (2012). Pectin as promising green corrosion inhibitor of aluminum in hydrochloric acid solution. *Corrosion Science* 60: 112–117.

34 Mobin, M., Khan, M., and Parveen, M. (2011). Inhibition of mild steel corrosion in acidic medium using starch and surfactants additives. *Journal of Applied Polymer Science* 121: 1558–1565.

35 Rosliza, R. and Nik, W.W. (2010). Improvement of corrosion resistance of AA6061 alloy by tapioca starch in seawater. *Current Applied Physics* 10: 221–229.

36 Umoren, S.A., Solomon, M.M., Madhankumar, A., and Obot, I.B. (2020). Exploration of natural polymers for use as green corrosion inhibitors for AZ31 magnesium alloy in saline environment. *Carbohydr Polym* 230: 115466.

37 Charitha, B., Rao, P.J.S.E., and Electrochemistry, A. (2017). Electrochemical and adsorption studies for the corrosion control of 6061 Al alloy using eco-friendly inhibitor. *Surface Engineering and Applied Electrochemistry* 53: 551–559.

38 Adhikari, B.B., Chae, M., and Bressler, D.C. (2018). Utilization of slaughterhouse waste in value-added applications: recent advances in the development of wood adhesives. *Polymers* 10: 176.

39 Nishinari, K., Fang, Y., Guo, S., and Phillips, G. (2014). Soy proteins: a review on composition, aggregation and emulsification. *Food Hydrocolloids* 39: 301–318.

40 Rabizadeh, T. and Asl, S.K. (2019). Casein as a natural protein to inhibit the corrosion of mild steel in HCl solution. *Journal of Molecular Liquids* 276: 694–704.

41 Zomorodian, A., Bagonyi, R., and Al-Tabbaa, A. (2021). The efficiency of eco-friendly corrosion inhibitors in protecting steel reinforcement. *Journal of Building Engineering* 38: 102171.

42 Haruna, K., Obot, I., Ankah, N. et al. (2018). Gelatin: a green corrosion inhibitor for carbon steel in oil well acidizing environment. *Journal of Molecular Liquids* 264: 515–525.

43 Abdallah, M., Kamar, E., El-Etre, A., and Eid, S. (2016). Gelatin as corrosion inhibitor for aluminum and aluminum silicon alloys in sodium hydroxide solutions. *Protection of Metals and Physical Chemistry of Surfaces* 52: 140–148.

44 Roy, P., Maji, T., Dey, S., and Sukul, D. (2015). Adsorption behaviour of gluten hydrolysate on mild steel in 1 M HCl and its role as a green corrosion inhibitor. *RSC Advances* 5: 61170–61178.

45 Zhang, Z., Ba, H., and Wu, Z. (2019). Sustainable corrosion inhibitor for steel in simulated concrete pore solution by maize gluten meal extract: electrochemical and adsorption behavior studies. *Construction and Building Materials* 227: 117080.

46 Nwanonenyi, S., Obasi, H., Chukwujike, I. et al. (2019). Inhibition of carbon steel corrosion in 1 M H_2SO_4 using soy polymer and polyvinylpyrrolidone. *Chemistry Africa* 2: 277–289.

47 Freeman, M.B., Hann, W.M., Paik, Y.H., and Swift, G. (1996). Method of inhibiting corrosion in aqueous systems using poly (amino acids), in, United States Patent, United States.

48 Silverman, D., Kalota, D., and Stover, F. (1995). Effect of pH on corrosion inhibition of steel by polyaspartic acid. *Corrosion* 51: 818–825.

49 Wang, H., Wu, Q., Li, C., and Gu, N. (2013). Copper corrosion inhibition by polyaspartic acid and imidazole. *Materials and Corrosion* 64: 347–352.

50 Qian, B., Wang, J., Zheng, M., and Hou, B. (2013). Synergistic effect of polyaspartic acid and iodide ion on corrosion inhibition of mild steel in H_2SO_4. *Corrosion Science* 75: 184–192.

51 Zeino, A., Abdulazeez, I., Khaled, M. et al. (2018). Mechanistic study of polyaspartic acid (PASP) as eco-friendly corrosion inhibitor on mild steel in 3% NaCl aerated solution. *Journal of Molecular Liquids* 250: 50–62.

52 Chauhan, D.S., Mazumder, M.J., Quraishi, M.A. et al. (2020). Microwave-assisted synthesis of a new Piperonal-Chitosan Schiff base as a bio-inspired corrosion inhibitor for oil-well acidizing. *International Journal of Biological Macromolecules* 158: 231–243.

53 Chauhan, D.S., Mazumder, M.J., Quraishi, M.A., and Ansari, K. (2020). Chitosan-cinnamaldehyde Schiff base: a bioinspired macromolecule as corrosion inhibitor for oil and gas industry. *International Journal of Biological Macromolecules* 158: 127–138.

54 Quraishi, M.A., Ansari, K.R., Chauhan, D.S. et al. (2020). Vanillin modified chitosan as a new bio-inspired corrosion inhibitor for carbon steel in oil-well acidizing relevant to petroleum industry. *Cellulose* 27: 6425–6443.

55 Ansari, K.R. and Quraishi, M.A. (2014). Bis-Schiff bases of isatin as new and environmentally benign corrosion inhibitor for mild steel. *Journal of Industrial and Engineering Chemistry* 20: 2819–2829.

56 Ansari, K.R., Quraishi, M.A., and Singh, A. (2014). Schiff's base of pyridyl substituted triazoles as new and effective corrosion inhibitors for mild steel in hydrochloric acid solution. *Corrosion Science* 79: 5–15.

57 Gupta, N.K., Verma, C., Quraishi, M.A., and Mukherjee, A.K. (2016). Schiff's bases derived from L-lysine and aromatic aldehydes as green corrosion inhibitors for mild steel: experimental and theoretical studies. *Journal of Molecular Liquids* 215: 47–57.

58 Singh, P. and Quraishi, M.A. (2016). Corrosion inhibition of mild steel using Novel Bis Schiff's Bases as corrosion inhibitors: electrochemical and surface measurement. *Measurement* 86: 114–124.

59 Ansari, K.R., Chauhan, D.S., Quraishi, M.A. et al. (2020). Chitosan Schiff base: an environmentally benign biological macromolecule as a new corrosion inhibitor for oil & gas industries. *International Journal of Biological Macromolecules* 144: 305–315.

60 Chauhan, D.S., Ansari, K.R., Sorour, A.A. et al. (2018). Thiosemicarbazide and thiocarbohydrazide functionalized chitosan as ecofriendly corrosion inhibitors for carbon steel in hydrochloric acid solution. *International Journal of Biological Macromolecules* 107: 1747–1757.

61 Srivastava, V., Chauhan, D.S., Joshi, P.G. et al. (2018). PEG-functionalized chitosan: a biological macromolecule as a novel corrosion inhibitor. *ChemistrySelect* 3: 1990–1998.

62 Chauhan, D.S., Quraishi, M.A., Sorour, A.A. et al. (2019). Triazole-modified chitosan: a biomacromolecule as a new environmentally benign corrosion inhibitor for carbon steel in a hydrochloric acid solution. *RSC Advances* 9: 14990–15003.

63 Chauhan, D.S., Mouaden, K.E., Quraishi, M.A., and Bazzi, L. (2020). Aminotriazolethiol-functionalized chitosan as a macromolecule-based bioinspired corrosion inhibitor for surface protection of stainless steel in 3.5% NaCl. *International Journal of Biological Macromolecules* 152: 234–241.

64 Mouaden, K.E.L., Chauhan, D.S., Quraishi, M.A., and Bazzi, L. (2020). Thiocarbohydrazide-crosslinked chitosan as a bioinspired corrosion inhibitor for protection of stainless steel in 3.5% NaCl. *Sustainable Chemistry and Pharmacy* 15: 100213.

65 Chauhan, D.S., Srivastava, V., Joshi, P.G., and Quraishi, M.A. (2018). PEG cross-linked Chitosan: a biomacromolecule as corrosion inhibitor for sugar industry. *International Journal of Industrial Chemistry* 9: 363–377.

66 Zhang, Q., Hou, B., Li, Y. et al. (2021). Dextran derivatives as highly efficient green corrosion inhibitors for carbon steel in CO_2-saturated oilfield produced water: experimental and theoretical approaches. *Chemical Engineering Journal* 130519: 130519.

67 Fayomi, O., Akande, I., Oluwole, O., and Daramola, D. (2018). Effect of water-soluble chitosan on the electrochemical corrosion behaviour of mild steel. *Chemical Data Collections* 17: 321–326.

68 Atta, A.M., El-Mahdy, G.A., Al-Lohedan, H.A., and Ezzat, A.-R.O. (2015). Synthesis of nonionic amphiphilic chitosan nanoparticles for active corrosion protection of steel. *Journal of Molecular Liquids* 211: 315–323.

69 Fayomi, O., Akande, I., and Popoola, A. (2018). Corrosion protection effect of chitosan on the performance characteristics of A6063 alloy. *Journal of Bio-and Tribo-Corrosion* 4: 1–6.

70 Pais, M., George, S.D., and Rao, P. (2021). Glycogen nanoparticles as a potential corrosion inhibitor. *International Journal of Biological Macromolecules* 182: 2117–2129.

71 Pais, M., George, S.D., and Rao, P. (2021). Interfacial adsorption of nanoparticles of maltodextrin for enhanced protection of metal surface. *Surfaces and Interfaces* 26: 101418.

72 Srivastava, M., Srivastava, S.K., Nikhil, G., and Ji, R.P. (2019). Chitosan based new nanocomposites for corrosion protection of mild steel in aggressive chloride media. *International Journal of Biological Macromolecules* 140: 177–187.

73 Solomon, M.M., Gerengi, H., Kaya, T., and Umoren, S.A. (2016). Performance evaluation of a chitosan/silver nanoparticles composite on St37 steel corrosion in a 15% HCl solution. *ACS Sustainable Chemistry & Engineering* 5: 809–820.

74 Solomon, M.M., Gerengi, H., Kaya, T., and Umoren, S.A. (2017). Enhanced corrosion inhibition effect of chitosan for St37 in 15% H_2SO_4 environment by silver nanoparticles. *International Journal of Biological Macromolecules* 104: 638–649.

75 Hefni, H.H., Azzam, E.M., Badr, E.A. et al. (2016). Synthesis, characterization and anticorrosion potentials of chitosan-g-PEG assembled on silver nanoparticles. *International Journal of Biological Macromolecules* 83: 297–305.

76 Paul, E., Egbuniwe, A., and Ekwumemgbor, P. (2018). The use of starch silver nanoparticles for the inhibition of mild steel corrosion using weight loss technique. *ATBU Journal of Science, Technology and Education* 6: 176–182.

77 Solomon, M.M., Umoren, S.A., Obot, I.B. et al. (2018). Exploration of dextran for application as corrosion inhibitor for steel in strong acid environment: effect of molecular weight, modification, and temperature on efficiency. *ACS Applied Materials & Interfaces* 10: 28112–28129.