

Review Article

Polymers Decorated with Functional Motifs for Mitigation of Steel Corrosion: An Overview

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Corrosion is a hazardous phenomenon having a devastating impact on technological and industrial applications, particularly in the oil and gas industries. Therefore, controlling the corrosion of metals is an important activity of technical, economical, environmental, and aesthetical importance in order to save huge expenses in materials, equipment, and structure. The use of corrosion inhibitors is one of the best options for controlling the metallic corrosion in various corrosive media. Numerous problems aroused with the use of inorganic and small molecule organic corrosion inhibitors, and the use of polymeric corrosion inhibitors came into limelight. This review article provides an overview of the recent development of different classes of corrosion inhibitors with special emphasis on different functional motifs of natural, synthetically modified natural, and synthetic polymeric materials. The significance, mechanism, and challenges of using polymeric materials as corrosion inhibitors are also highlighted in the review.

1. Significance of Corrosion

Corrosion is referred to as the deterioration of the materials by the chemical reactions between materials and their reactive ambience [1]. It is a hazardous phenomenon having a devastating impact on gas and oil manufacture and their subsequent transportation, triggered more or less by almost any aqueous environment and happens by means of redox reactions in gas and oil production, handling, and pipeline systems [2]. Technically, corrosion is considered a bounded electrochemical reduction-oxidation (redox) reaction taking place on the surface of materials, typically metals, prompting the release of electrons by the dissolution of metal and their successive transfer to another position on the surface causing the oxygenated water or hydrogen ions to be reduced and resulting in gradual deterioration and consequent failure of the host material. This corrosion process consists of a cathode, an anode, and an electrolyte. The anode is the location where the corrosion of metals takes place to generate free

electrons, which travel through the corrosive electrolytic medium to the cathode, where hydrogen ions (from an acidic corrodant) are reduced to hydrogen gas. Natural gas and crude oil usually contain several highly contaminated products, which are innately corrosive. Free water, carbon dioxide (CO₂), and hydrogen sulfide (H₂S) are well-established examples of extremely corrosive media in case of oil and gas wells and pipelines. Furthermore, oxygen contaminations in basic or neutral conditions lead to the production of hydroxyl ions through the reduction of oxygenated water by the current produced at the anodic site due to the oxidation process [3]. In general, upon exposure to metals, the chemical species, such as moisture/water (H₂O), acids (HNO₃, HCl, and H₂SO₄), bases (NaHCO₃, CaCO₃, and NaOH), table salts (NaCl), aggressive metal polishes, and gases (ammonia, formaldehyde, and sulfur-containing gases and liquid chemicals), perpetuate the degradation of the metals [4].

Corrosion is a huge concern for most of the industrialized countries. Even though oil companies around the world

spend a lot of money on tackling corrosion, casualties, economic losses, and environmental side effects still take place [5]. It has been reported that the maintenance cost of the corrosion-related issues in industries/establishments for any country is in the range of 1-5% of its gross national product (GNP) [6]. A study revealed by the National Association of Corrosion Engineers (NACE) in 2013 has shown that the global cost of corrosion was estimated to be US\$2.5 trillion, which was equivalent to 3.4% of the global gross domestic product (GDP) of that year [7]. The total cost of corrosion in the Gulf Cooperation Council (GCC) states was estimated to be US\$57.96 billion in 2011 [8]. Among the GCC states, the Kingdom of Saudi Arabia incurred the highest annual cost of corrosion. The United Kingdom suffered a corrosion cost of £13.65 billion in 1969 [9]. Corrosion has a severe impact on between a quarter and a half of all drinkable water primarily in France, particularly old ones that are made of cast iron or uncoated steel [5].

Since corrosion causes loss of economic, natural resources, and human lives in case of infrastructure collapses, it is of paramount importance to look into smart and developed corrosion mitigation techniques. Anodic protection [10], cathodic protection [11, 12], coating [13], and alloying are some of the approaches towards mitigating corrosion. Exploitation of chemical inhibitors [14, 15] is the most effective and practical method of corrosion prevention owing to its ease of use. Several authors have reported the uses of organic [16–19] and inorganic compounds [20–22] as corrosion inhibitors (CIs) and classified them depending on their mode of actions. Even though organic and inorganic inhibitors are efficient CIs at times, they pose a dangerous threat to health and ecology. Moreover, the contamination of the hydrocarbon stream might occur due to the fragmentation of the small molecule inhibitors at higher temperatures [23]. This has driven researchers towards the invention of nontoxic inhibitors that impart efficiency to the maximum extent and least impact on nature and humankind [24]. Different eco-friendly green CIs have been reported by several authors [25–27]. Nevertheless, novel approaches and current trends in CIs are in favor of use of polymers. Polymers, owing to the presence of a large number of binding sites, adsorb very well on the metal surface, hence impart superior inhibition efficiency (IE). Furthermore, multifunctionality, solubility, flexible viscosity, and the increased number of attachment points render polymers superior to their organic and inorganic counterparts. In this present investigation, we aim to review the uses of several classes of commonly used polymeric CIs in various corrosive environments.

2. Polymers as Corrosion Inhibitors

Synthesis of polymers as CIs is the current trend and considered a novel approach. Polymers can have various architectures such as branched, linear chains, hyperbranched, rotaxanes, cross-links, comb-like, and dendrimeric composed of long chains of repeating units. Polymers possess the advantages of multifunctionality, solubility, flexible viscosity, increased attachment points to metal surfaces, and better film-forming capabilities in comparison to the more

widely used small molecule (organic or inorganic) inhibitors [28]. Smart designing of repeating functional groups in the polymer backbone having a large surface area and large number of binding moieties makes polymers capable of forming complexes with metals, which lead to an efficient CI [3, 24]. The anchoring groups may be anionic, cationic, nonionic, or ampholytic in nature [24]. The reputation of having high thermal stability combined with the presence of heteroatoms such as O, N, and S that predominantly dictate the process of adsorption usually contributes superb corrosion IEs of polymers as well as plant extracts owing to the increased basicity and electron density [29]. In the following sections, we discuss different classes of polymers and their merits and demerits as CIs in various corrosive environments.

2.1. Naturally Occurring Polymers. Naturally occurring substances, also popularly known as “green inhibitors,” have continued to receive more attention over the years owing to the facts that they are cheap, are ecologically friendly, and possess no real threat to the environment. Furthermore, they are renewable sources of materials and readily available. We aim to discuss some common and readily available naturally occurring polymers and their role as CIs in this section of the review.

Polyamino acids, including polymers of amino acids like glutamic acid (Glu) and aspartic acid (Asp), have been explored for their applications as antiscalants and CIs. Corresponding salts of polyamino acids such as alkali metal salts, alkyl ammonium salts, ammonium salts, and aryl ammonium salts also possess these properties [3]. Polyaspartic acid (PASP), a water-soluble, biodegradable copolymer of acetacetamide and 3-carboxypropionamide, α - and β -forms of L-Asp, and occasionally containing cyclic imide (succinimide) moieties and Glu, is a polymer of this type that has been explored as a CI [30]. This biodegradable polymer has been found inhibiting sweet corrosion of mild steel (MSteel) in a simulated brine solution without dissolved oxygen. This polymer has reduced the corrosion of MSteel by 40% at room temperature, whereas the corrosion protection efficiency was found to be 70% at 50°C [3]. The corrosion IE of PASP for carbon steel (CSteel), at a concentration of 6 g/L, was found to be 80.3% after 72 h immersion in 0.5 M H₂SO₄ at 10°C. The inhibitor was found to follow the Freundlich isotherm [31].

Abd-El-Nabey and his research team studied cysteine (Cys) and methionine (Met) for their corrosion inhibition of MSteel in 1 N H₂SO₄ [32]. The IE increased with an increasing concentration of the inhibitor, and more than 60% inhibition was achieved with an amino acid concentration as low as 10⁻³ M. All of the amino acid inhibitors acted as a mixed-type inhibitor. The IE of alanine (Ala), Cys, and S-methylcysteine (S-MCys) was tested for iron in aerated stagnant 1 M HCl solutions by Tafel and impedance measurements [33]. Corresponding shifts in the corrosion potential (E_{corr}) values indicated that Ala acts mainly as a cathodic inhibitor, while S-MCys and Cys act as mixed-type inhibitors. Cys, containing a mercapto group in its molecular structure, was the most effective compared to the other inhibitors. The inhibitive effect of valine (Val), glycine (Gly), arginine

(Arg), lysine (Lys), and Cys was also studied using weight loss (WL) and electrochemical polarization measurements [34]. Cys was found to be the best inhibitor with an efficiency of 61% obtained at a meager concentration of 10^{-3} M. The influence of sulfur-containing amino acids, namely, Met, Cys, and *N*-acetylcysteine (*N*-ACys), on the corrosion behavior of MSteel in a highly concentrated solution of H_3PO_4 in the absence and presence of Cl^- , F^- , and Fe^{3+} ions has been investigated [35]. Ismail used electrochemical studies [36] to investigate the inhibitive effect of Cys on Cu metal in 0.6 M NaCl and 1.0 M HCl. The potentiodynamic polarization (PDP) study revealed that the presence of Cys affects mainly the cathodic process in both types of solutions, decreases the corrosion current to a great extent, and shifts the E_{corr} towards more negative values. The thermodynamic study revealed that the inhibitor follows the Langmuir adsorption isotherm and demonstrates a strong physical adsorption on the metal surface. Synergistic inhibitive effect of Cys and Cu(II) ions on Fe in 0.5 M H_2SO_4 has been investigated [37]. Electrochemical Impedance Spectroscopy (EIS) revealed a significant increase in the polarization resistance (R_p) of the iron/solution interface in the presence of Cys and Cu(II) ions instead of Cys alone.

The corrosion IE of Cys, *N*-ACys, and Met as environmentally safe inhibitors for the corrosion of Cu-10Al-5Ni alloy in 3.5 wt.% NaCl solution was studied [38]. Cys, at a meager concentration of 6.0 mM showed 96% IE of corrosion. Amino acids, namely, Gly, Ala, Val, Cys, Glu acid, and histidine (His), have been investigated for their corrosion inhibition of Pb in aqueous solutions with different pH. The corrosion IE of 87% was recorded with Glu at a concentration of 0.025 M [39]. The inhibitive action of Cys on Cu-30Ni alloy in aerated 0.5 M H_2SO_4 was explored [40]. An IE of 91% was obtained at an inhibitor concentration of 10^{-3} M. Badawy and coworkers demonstrated that Gly at a concentration as low as 0.1 mM can impart an IE of about 85% on Cu-Ni alloy in neutral chloride solution [41]. For low Ni content alloy (Cu-5Ni), a remarkably high efficiency of 96% was achieved at a low concentration of 2.0 mM Cys. Helal and Badawy studied the inhibitive action of some amino acids including phenylalanine (Phe) and Cys on Mg-Zn-Al alloy in stagnant naturally aerated chloride-free neutral solutions. Phe showed a very high efficiency of 93% at a concentration of 2×10^{-3} mol dm $^{-3}$. The corrosion inhibition process was found to depend on the concentration of amino acid molecules on the metal surface [42].

Carbohydrate polymers are commonly used as protective coatings and metal linings. These biopolymers represent a biodegradable, ecofriendly, and chemically stable set of inhibitors that have unique inhibiting strengths and mechanistic approaches to metal surface and bulk protection [43]. Umoren et al. investigated the inhibition effect of polyethylene glycol (PEG; a synthetic polymer) and gum arabic (GA; a naturally occurring polymer) in the absence and presence of halide ions on MSteel in 0.1 M H_2SO_4 [44]. In the absence and presence of 0.05 M KCl, KBr, and KI at 60°C, the IEs of GA were determined by WL measurements and were found to be 37.9, 38.7, 47.1, and 59.1%, respectively, while the IEs of PEG (1×10^{-3} M) were determined to be 40.2, 46.4, 52.5,

and 64.3%, respectively. This synergistic IE resulted from the increased surface coverage that appears from the ion pair interactions between the organic cations and the anions. The same research group also investigated the inhibitory effect of GA on AA1060 type aluminum sheets (98.5% purity) at 40°C. The IEs of GA (0.5 g/L) obtained from hydrogen evolution and thermometric methods were 74.2 and 75.9%, respectively [45]. A research group from Tanzania studied the IE of gum exudates from *Acacia seyal* var. *seyal* using EIS technique and PDP measurements on MSteel in chlorinated drinking water. The IE of gum exudates at 1000 ppm was determined to be 98.5% at 30°C. The acacia gum from *seyal* var. *seyal* showed an IE of 96.8% at an elevated temperature of 80°C at 600 ppm [46]. The inhibitory effect of guar gum (GG) on CSteel in 1 M H_2SO_4 was thoroughly studied, and the IE at 1500 ppm was found to be 93.8 and 93.6% from WL and PDP measurements, respectively [47]. It was proposed that GG acted as a mixed-type inhibitor in which adsorption takes place at the electrode/solution interface. GG is a polysaccharide composed of β 1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose having repeated heterocyclic pyran moiety. The presence of heteroatom oxygen makes it possible to produce a coordinate-type linkage to the steel surface and make a stable chelate five-membered ring with ferrous ions. Mobin and Rizvi from Corrosion Research Laboratory, India, investigated the inhibitory effect of xanthan gum (XG) as an eco-friendly CI for MSteel in 1 M HCl at 30, 40, 50, and 60°C, respectively. The maximum IE of 74.2% was achieved at a concentration of 1000 ppm at 30°C. The IE of XG enhanced upon the addition of very small amounts of surfactants sodium dodecyl sulfate, cetylpyridinium chloride, and Triton X-100. The increased efficiency of the XG in the presence of the surfactants was further corroborated by the quantum chemical calculations. The energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were found to be 0.05 eV and 0.02 eV in XG alone and XG plus the sodium dodecyl sulfate surfactant, respectively. The smaller the energy gap between LUMO and HOMO, the higher is the IE of the inhibitor. Ultraviolet-visible (UV-Vis) spectroscopic measurements suggested the formation of a complex between XG and Fe^{2+} ions released during corrosion reaction. An improvement in the surface morphology of inhibited MSteel compared with uninhibited MSteel was confirmed by scanning electron microscopy (SEM) studies [48].

The anticorrosive effect of a composite coating consisting of chitosan (CS; green matrix), oleic acid (OA), and graphene oxide (GO; nanofiller) was studied for corrosion protection of CSteel in 3.5 wt.% NaCl solution [49]. The corrosion resistance of the nanocomposite coating was monitored using PDP and EIS. The corrosion resistance of OA-modified CS/GO film (CS/GO-OA) was found to increase by 100-fold in comparison to the pure CS coating. The oxygen transmission rate measured for the CS/GO-OA was found to decrease by 35-fold in comparison to the pure CS film. This decreased permeability for the CS/GO-OA justifies the enhancement in corrosion protection of the composite coating because of the

development of a large barrier effect against the ingress of aggressive electrolyte species.

The corrosion inhibition and adsorption characteristics of hemicellulose- and cellulose-based elephant grass (*Pennisetum purpureum*) extract on MSteel in 1 M HCl solution were studied in detail [50]. The IEs were averagely above 95% at room temperature and increasing with the increasing concentration of the extract but decreasing with increasing temperatures. Fourier transform infrared spectroscopy (FT-IR) analysis of the extract showed the presence of the hydroxyl (O-H) and unsaturated (C=C) functional groups which are known to have inhibitory properties. However, FT-IR analysis of the corrosion product revealed a shift of the hydroxyl (O-H) group from 3379 to 3440 cm^{-1} and the unsaturated band from 1635 to 1640 cm^{-1} . These shifts in the bands indicated an interaction between the extract and the MSteel surface resulting in inhibition. The scanning electron micrograph of the substrate immersed in the HCl solution without the extract revealed pitting in the metal surface, whereas pitting was rarely present in the metal substrate immersed in a solution containing 0.5 g/L elephant grass extract. This proves the effectiveness of the extract in reducing the localized dissolution of the steel in HCl solution. The energy-dispersive spectroscopy (EDS) spectrum of the MSteel after immersion in HCl with the inhibitor showed a higher Fe peak than that of the MSteel in HCl without the inhibitor. This observation attests to the lower rate of iron dissolution in the acidic solution containing the extract.

El-Haddad studied the inhibition effect of hydroxyethylcellulose (HEC) for 1018 CSteel corrosion in 3.5 wt.% NaCl solution using PDP, electrochemical frequency modulation (EFM), and EIS techniques. The PDP study revealed that HEC acts as a mixed-type inhibitor. The adsorption behavior of HEC on the steel surface was found to follow the Langmuir adsorption isotherm. The optimized geometry of HEC obtained by *DMol*³ quantum chemical calculations suggested that oxygen atoms of HEC have Mulliken atomic charges with higher electron densities. This implied that the oxygen atoms donate the unshared pair of electrons to the vacant *d*-orbitals of iron. Maximum IEs of 96.7, 94.8, and 95.5% were measured by PDP, EFM, and EIS techniques, respectively, for the inhibitor concentration of 0.5 mM at 25°C [51]. Researchers have been working extensively on the carbohydrate-based biopolymers to evaluate them as green CIs, and accommodating all of them in detail in this review is difficult. We have searched for recent literatures, listed many of them that explored and evaluated as CIs to arrest corrosion of different metals and alloys, and presented them in Table 1.

Polyphenol compounds are characterized by diverse structures that lend them various biological and chemical activities such as antioxidant activity and antibiotic and antifouling actions. The coumarin derivatives of polyphenolic compounds are characterized by at least one aromatic ring. On the contrary, regarding the flavonoid family, the two aromatic cycles are linked by a heterocycle containing oxygen atoms. Its hydroxyl group, the aromatic ring, and the π -electrons make these compounds chelate with the empty *d*-orbitals of the metal atoms. Veys-Renaux et al.

studied the morphological, structural, and electrochemical effects of three polyphenolic compounds esculetol, esculin, and rutin on steel in a weak acidic medium containing 10^{-3} M NaCl at pH 4 [52]. SEM, Raman spectroscopy, and synchrotron X-ray absorption spectroscopy (XAS) proved that a surface film was formed because of the formation of iron polyphenolate conversion products, in which Fe^{3+} is likely coordinated with free catechol groups. Of all the three inhibitors, esculetol formed a compact layer and acted as both anodic and cathodic inhibitors. On the contrary, rutin formed a nonflat layer and esculin formed no layer that led them to function as weaker inhibitors. Nardeli et al. studied tannin, which is a complex mixture of nontoxic and biodegradable polyphenolic compounds [53]. In this study, tannin was derived from the flavon-3-ol structure that resulted from the aqueous leaching of bark from black acacia, *Acacia mearnsii* de Wild. This work was aimed at investigating the effect of tannin as CI of bare and coated aluminum alloys 1200. Attenuated total reflectance Fourier transform infrared spectroscopy (FT-IR-ATR) was used to characterize tannin, and its corrosion inhibition behavior was investigated using density functional theory (DFT), open circuit potential (OCP), EIS, and scanning vibrating electrode technique (SVET). The electrochemical results revealed that tannin acted as an effective inhibitor by giving both coated and uncoated aluminum alloy samples more protection than when they were in an inhibitor less 3.5 wt.% NaCl solution. SVET measurements demonstrated that the presence of inhibitor improved the corrosion resistance of the exposed metal when both coatings were damaged.

Plant *Tragia involucrata* L., which is a known source for many active components like flavonoids, tannins, alkaloids, sterols, and volatile oils, has been studied recently for its corrosion mitigation properties of low CSteel against 1 M HCl [54]. Before the initiation of the corrosion study, the plant was tested for the total phenolic and flavonoid content and antioxidant activity and they were found to be significant. Scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX), atomic force microscopy (AFM), UV-Vis, and FT-IR studies were used to study the surface morphology. At a concentration of 0.25g/L, the inhibitor showed an efficiency of 74.8 and 88.0% in Tafel and EIS measurements, respectively. Leaf and bark extracts of *Acacia tortilis* have been evaluated as CIs of MSteel in seawater [55]. The extracts were found to contain polyphenols, phenolic compounds, and flavonoids. Both PDP curves and EIS studies were performed to gauge the IE of the inhibitors. The PDP study revealed that both types of extracts acted as mixed-type inhibitors. The adsorption of the inhibitors on the steel surface follows the Langmuir adsorption isotherm model and involves competitive physisorption and chemisorption mechanisms. The maximum achievable IEs were 87.6 and 72.9% for leaf and bark extracts measured by EIS, respectively. Moreover, IEs revealed by Tafel and WL techniques were in accordance with the findings revealed by the EIS study.

2.2. Synthetic Polymers. Synthetic polymers are referred to as polymers that are synthesized in the laboratory to serve as a better replacement of the natural polymers. Natural

TABLE 1: Effectiveness of various carbohydrate-based natural polymers as CIs of different metals and alloys.

Inhibitor	Concentration	Material	Test conditions	Maximum efficiency	Test technique	References
Inulin	1.0 g/L	6061 Al alloy	0.025 M HCl, 30°C	69.0%	Tafel	[121]
Inulin	1.0 g/L	6061 Al-15% _(v) SiC _(p)	0.025 M HCl, 30°C	93.9%	Tafel	[121]
HEC	2000 mg/L	MSteel	0.5 M H ₂ SO ₄ , 30°C	93.9%	WL	[122]
HEC	2000 mg/L	AA 1060 (98%)	0.5 M H ₂ SO ₄ , 30°C	65.5%	WL	[122]
Hydroxypropyl methylcellulose (HPMC)	2000 mg/L	AA 1060 (99%)	0.5 M H ₂ SO ₄ , 30°C	60.4%	WL	[123]
<i>Ficus benjamina</i> gum	0.5 g/L	Al (96.65%)	0.1 M H ₂ SO ₄ , 60°C	87.5%	WL	[124]
Exudate gum	0.5 g/L	AA 1060 (98.5%)	2 M HCl, 30°C	42.0%	WL	[125]
<i>Raphia hookeri</i>	0.5 g/L	AA 1060 (98.5%)	2 M HCl, 30°C	56.3%	WL	[126]
<i>Raphia hookeri</i> -halide mixture	Exudate (0.5 g/L)+KI	Al sheet	0.1 M HCl, 30°C	70.5%	WL	[125]
Iota-carrageenan-peffloxacin mixture	i-carrageenan (1600 ppm)+peffloxacin (400 ppm)	Al sheet (99.7%)	2 M HCl, 10°C	74.2%	WL	[127]
Pectin	8.0 g/L	Al sheet (99.7%)	2 M HCl, 10°C	90.0%	WL	[128]
Polymeric pectate	0.06 M	Al (99.9%)	3 M HCl, 40°C	70.1%	WL	[129]
Starch	0.8 g/L	6061 Al-15% _(v) SiC _(p)	0.25 M HCl, 50°C	83.4%	Tafel	[130]
CS	0.028 g/L	Pure Al	0.1 M HCl, 30°C	90.6%	EIS	[131]
Dextran	0.4 g/L	6061 Al-15% _(v) SiC _(p)	1 M HCl, 30°C	91.3%	Tafel	[132]
Dextran	0.4 g/L	Epoxy coated 6061 Al-15% _(v) SiC _(p)	1 M HCl, 30°C	92.7%	Tafel	[132]
Dextran	0.4 g/L	6061 Al alloy	1 M HCl, 30°C	77.9%	EIS	[133]
Dextran	0.4 g/L	6061 Al-15% _(v) SiC _(p)	0.25 M HCl, 50°C	79.5%	Tafel	[134]
Glucomannan+bisquaternary ammonium salt	80 mg/L	MSteel	0.5 M NaCl, 50°C, pH = 8.0	99.1%	Tafel	[135]
GA of Iraqi apricot tree	0.3 g/L	MSteel	1 M HCl, 40°C	73.6%	WL	[136]
Tender arcanut seed extract	4.5 g/L	Al-63400	0.5 M HCl, 30°C	96.2%	EIS	[137]
Agarose	700 ppm	Al (98.5%)	1 M HCl	81.3%	EIS	[138]
Agarose	700 ppm	Al (98.5%)	0.5 M H ₂ SO ₄	64.7%	EIS	[138]
Agarose	700 ppm	Al (98.5%)	0.5 M H ₃ PO ₄	61.8%	EIS	[138]
HPMC phthalate	580 μm thick coating	High-speed steel	0.5 M NaCl, RT	96.9%	Tafel	[139]
HPMC acetate succinate	360 μm thick coating	High-speed steel	0.5 M NaCl, RT	94.7%	Tafel	[139]
Extract of <i>Thevetia peruviana</i>	300 ppm	CSteel	1 M HCl, 25°C	90.3%	EIS	[140]
GG	0.5 g/L	MSteel	15% HCl, 25°C	86.5%	WL	[141]
Cationic GG	0.5 g/L	MSteel	15% HCl, 25°C	96.4%	WL	[141]

polymers, though environmentally benign, are not always soluble in the aqueous medium that renders its use disadvantageous at times. So designing new polymers to mimic the properties of existing natural polymers or synthetically modified natural polymers, if necessary, can contribute to enhanced solubility and adsorption of inhibitors hence enhanced performance. Some synthetic polymers classified by their nature are commonly used as an efficient CI as discussed below.

Because of the environmentally benign nature of Cys and Met, they would probably never cease to be used as CIs in their original form or as derivatives. The cyclopolymerization of SO_2 and *N,N*-diallyl methionine ethyl ester hydrochloride in dimethyl sulfoxide *via* Butler's copolymerization protocol led to the formation of an environmentally benign CI, which showed an IE of impressive 99% *via* WL technique at a concentration of 25 ppm [56]. The authors further oxidized this polymer in the presence of 1 and 2 equivalents of H_2O_2 to create copolymers that contained sulfoxide and sulfone moieties, respectively [57]. The polymer that contained a sulfoxide moiety showed maximum IE of 97% at a concentration of 175 μM . The IEs of these polymers obtained *via* different corrosion measurement techniques were consistent with each other, and all inhibitors acted as mixed-type. When the monomer *N,N*-diallyl methionine ethyl ester hydrochloride was homopolymerized and oxidized subsequently in the presence of H_2O_2 , it was still the polymer that contained a sulfoxide moiety to impart maximum IE of 97% at a concentration of 70.3 μM [58]. An amazing IE was obtained when the ester functionality of the copolymer obtained *via* cyclopolymerization of SO_2 and *N,N*-diallyl methionine ethyl ester hydrochloride was hydrolyzed. A simultaneous presence of sulfide, sulfoxide, and carboxylate moieties along the chain length made the polymer impart an astonishing efficiency of 99.6% *via* Tafel method at a low concentration of 20 ppm [59]. Cys-based diallylamine salts were copolymerized with diallyldimethylammonium chloride [60] showed an impressive efficiency of 99.5% at a concentration of 100 ppm. The fact that all these Met- and Cys-based polymers showed these IEs in aggressive electrolyte 1 M HCl and at temperature as high as 60°C and that all of them are environmentally benign makes them suitable for industrial acid cleaning and descaling processes.

It is well known that sweet corrosion, caused by the presence of dissolved carbon dioxide during the enhanced oil recovery phase, can corrode J55 and N80 CSteel structures in the petrochemical industry. While nitrogen-based imidazoline inhibitors, amines and triazoles, are frequently used to tackle this issue, they are harmful and toxic, and imidazoline inhibitors can cause the anodic dissolution of CSteel to make the matter worse. Of all the classes and subclasses of naturally occurring or green CIs, CS happens to be one of the most heavily researched inhibitors because of its low-toxic nature. However, its poor solubility and effective inhibition only at high concentration make its application restricted; therefore, chemical functionalization is a practical way to overcome these drawbacks. Ansari et al. [61] synthesized salicylaldehyde-chitosan Schiff base (SCSB) by the reaction of CS and salicylaldehyde to find its corrosion inhibition

effect in 3.5 wt.% NaCl solution saturated with CO_2 at 65°C. WL, EIS, and PDP techniques were explored to find out the IE. A maximum IE of 95.4% was achieved through WL technique at a concentration of 150 mg/L. The PDP study revealed that the inhibitor acted as mixed-type, and EIS measurement suggested that the corrosion inhibition process was kinetically controlled. Computational studies corroborated the understanding that the introduction of a salicylaldehyde moiety increased the size of the resulting SCSB molecule and also resulted in a planar structure. This increased size and structural planarity aided SCSB imparting better corrosion IE. There are numerous examples of chemically functionalized CS being tested for corrosion inhibition efficacy (Figure 1). Some very recent examples with their performances are mentioned in Table 2.

The application of paint or organic coating is the most common corrosion prevention technique and, ideally, would protect the metal substrate for a long time. However, sometimes a coating may not be able to provide long-lasting protection when defects appear during a metal's service lifetime. Recently, conducting polymers (CPs) have grabbed huge attention as smart coatings owing to their ability to safeguard the bare metallic surface even in defect areas when it is exposed to the corrosive environment. CPs can exist in both conducting and nonconducting states and are capable of interchanging between them in response to appropriate conditions [62]. It was shown back in 1985 that CP polyaniline (PANI) could induce a passive state in 400 series SSteel in H_2SO_4 solutions. CPs are capable of maintaining the surface potential of the substrate into the passive state where a protective oxide film is formed on the metal substrates. The CP charge that is consumed by metal oxidation is replenished by oxygen reduction within the CP layer. Thus, the corrosion process is prevented when the potential turns into the passive state after CP switches into the oxidation state [63]. Various CPs, such as PANI, polythiophene (PTh), polypyrrole (PPy), and polycarbazole (PCz), are chemically and electrochemically synthesizable and commercially available. CPs' ease of synthesis coupled with their electrical conductivity makes them very attractive anticorrosive materials, and they have been in use since the 1980s [64–66].

PANI is usually considered an ideal CI because of the copiousness of nitrogen atoms in the chemical structure and the π -electrons in the benzene rings [3]. PANIs are CPs, and their electronic properties can be varied by changing the number of electrons, protons, or both in their chemical structure (Figure 2(a)). Their conductivity increases when PANI and its derivatives are protonated at $-\text{N}-$ sites below pH 4. The protonated species easily adsorb on the metal surface and produce an effective barrier that hinders the diffusion of aggressive ions to a greater extent [24]. PANIs have been regarded as very efficient anticorrosive coatings, and it has been reported that PANI-containing coatings with scratches and pinholes are capable of protecting steels in neutral and acidic environment by repassivation of exposed areas [67].

A new PANI from aniline was synthesized by persulfate oxidation (Figure 2(b)) and demonstrated its merits over the monomeric counterpart by conducting corrosion studies

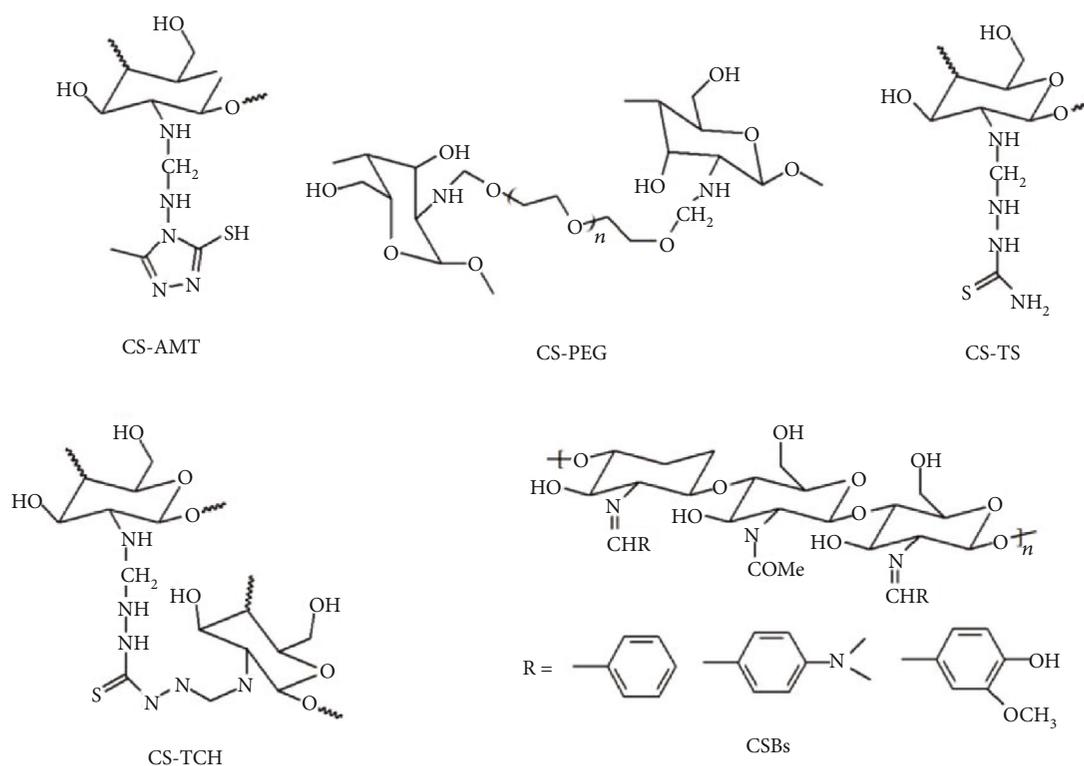


FIGURE 1: Chemically functionalized chitosan inhibitors.

TABLE 2: Functionalized chitosan as eco-friendly CIs in different corrosive media.

Inhibitor	Concentration	Material	Test conditions	Maximum efficiency	Test technique	References
CS	200 ppm	MSteel	1 M H ₃ NSO ₃ , 35°C	73.8%	WL	[142]
CS+KI	200 ppm (CS)+5 ppm (KI)	MSteel	1 M H ₃ NSO ₃ , 35°C	91.7%	Tafel	[142]
CS-TS	200 ppm	MSteel	1 M HCl, 35°C	92.5%	EIS	[143]
CS-TCH	200 ppm	MSteel	1 M HCl, 35°C	93.2%	EIS	[143]
CS-PEG	200 ppm	MSteel	1 M HCl, 35°C	93.9%	Tafel	[144]
CS-PEG	250 ppm	MSteel	1 M H ₃ NSO ₃ , 35°C	94.0%	Tafel	[145]
CSB-1 ^a	150 ppm	MSteel	1 M HCl, 30°C	88.5%	WL	[146]
CSB-2 ^b	150 ppm	MSteel	1 M HCl, 30°C	89.9%	WL	[146]
CSB-3 ^c	150 ppm	MSteel	1 M HCl, 30°C	91.7%	WL	[146]
CS-AMT	250 ppm	MSteel	1 M HCl, 35°C	96.6%	EIS	[147]
CS-TCH	1000 ppm	Stainless steel (SSteel)	3.5% NaCl, RT	98.0%	Tafel	[148]
CS-EN	0.1%	CSteel	5% HCl	90.0%	WL	[149]
CS-MAA-TN	0.1%	CSteel	5% HCl	84.0%	EIS	[149]

^aBenzaldehyde-CSB, ^b4-(dimethylamino)benzaldehyde-CSB, and ^c4-hydroxy-3-methoxybenzaldehyde-CSB.

on pure Fe against 0.5 M H₂SO₄ in simulating industrial operations including descaling, cleaning, and pickling [28]. The study of monomeric aniline for the corrosion inhibition of pure Fe samples in 0.5 M H₂SO₄ for 30 min immersions revealed that the corrosion current decreased slightly, which started from 410 μA·cm⁻² for the blank to the monomeric aniline concentration of 250 ppm. Afterwards, the corrosion current showed an increasing trend and reached 569 μA·cm⁻² at 1000 ppm. The R_p near the vicinity of steady-state corrosion

potential in the current-potential (η - I) plots showed a decreasing trend starting from 34 Ωcm² for the blank to 20 Ωcm² for 1000 ppm, which was in line with the results obtained from the Tafel extrapolation method. Furthermore, EIS measurements revealed that the values of charge transfer resistance (R_{ct}) decreased and double-layer capacitance (C_{dl}) increased with increasing concentration of aniline. This opposing trend to what aniline was supposed to do has been attributed to the delocalization of the lone pair of electrons

have been used as CIs of various metals and alloys to impart about 90% corrosion IE. Some of these PANI-based substances along with their corresponding IEs are listed and summarized in Table 3.

Most of the PANI-based substances have been used in the acid medium. Manivel et al. showed that the IEs of PANIs are highly contingent upon the concentrations of H^+ and Cl^- ions. They demonstrated the IEs for 500 ppm of PANI in the presence of 1.0, 0.5, 0.1, and 0.05 M H^+ ions by Tafel extrapolation method were 95.6, 63.8, 60.2, and 59.9%, respectively, while in the presence of 1.0, 0.5, and 0.1 M Cl^- ions were reported to be 62.9, 57.7, and 55.3%, respectively. The lower IE in the lower concentration of H^+ ions has been attributed to the dominant neutral form of PANI, while the presence of higher concentrations of H^+ ions helps in increasing the cationic form of PANIs, i.e., anilinium cations, which undergo strong adsorption on the negatively charged metal surface. In case of Cl^- ions, it is believed that Cl^- ions are preferentially adsorbed on the iron electrode surface to make the surface more negative and assist the adsorption of aromatic amines. The results also showed that PANI blocked both anodic and cathodic processes of iron dissolution in 1 M HCl and it followed Langmuir's adsorption isotherm [75].

A water-soluble sulfonated PANI (Figure 2(c)) has been synthesized [76] to improve the compatibility of PANI in a wider range of brine solutions. This polymer was thermally stable up to 251°C. The compensated sulfonated PANI made in NaOH at a concentration of 500 ppm showed an IE of 98.4% after 30 minutes of immersion in 1 M HCl. KOH- and LiOH-compensated forms of the sulfonated PANI also demonstrated good IEs, although with slightly lower values. This high efficiency shown by the polymer is attributed to the presence of quaternary ammonium nitrogen and π -electrons from the aromatic nucleus that aid the polymer to be adsorbed strongly on the metal surface by minimizing the van der Waals repulsive forces between neighboring monomeric units. The sulfonated group in the polymer backbone is believed to stay facing the electrolyte to prevent it from reaching the metal surface, thus increasing the IE.

Aniline-based polymeric compounds are usually very efficient inhibitors in acidic media owing to the high degree of adsorption of the protonated form. Secondary forces, such as van der Waals forces, dispersion, or dipole interactions, dictate the interaction at the metal/solution interfaces. However, the insolubility of PANIs in aqueous and organic solvents limits their use in the alkaline/neutral medium and cooling water systems [24].

Recently, a PPy-coated CSteel surface was studied for its improved anticorrosion and antimicrobial resistance properties [77]. Galvanostatic and CV techniques in sodium salicylate solution performed the electrosynthesis of the coating on the steel surface. The electrodeposition, morphology, and stability of the coating were studied by XPS, SEM, and Raman spectroscopy. OCP, EIS, and atomic absorption spectroscopy (AAS) studies revealed the coating's anticorrosion properties. OCP studies showed that the potential of the uncoated steel reached steady state after 48 hours of immersion and a yellow precipitate was found on the surface that confirmed the

oxidation of the uncoated steel in a 3% NaCl medium. On the contrary, the coated steel showed an anodic shift in the E_{corr} that induced an anodic protection of the surface after 140 hours of immersion. This indicates that a passive oxide layer has been formed between the polymer coating and the metal surface or in the holes of the polymer coating that provides protection against aggressive Cl^- ions in the salt medium. The EIS study revealed that the diameter of the semicircle kept increasing with the prolonged presence of the coated steel in the corrosive solution. This increased R_p can be attributed to the slow redox reaction of the polymer coating that helps to maintain the electrode of the steel to be in the passive state.

PTh films were electrosynthesized on SSteel in boron trifluoride diethyl etherate solution through potentiostatic method for its anticorrosive properties study [78]. The structure, morphology, and thermal stability of the PTh films were studied by means of SEM and UV-Vis diffusing method. Tafel and EIS studies were explored to find out the anticorrosive properties of the films in 3.5 wt.% NaCl solution. An efficiency of 87.4% was obtained by Tafel study after 1400 s of deposition time. For the EIS study, Nyquist plots were recorded for different soaking time of the PTh-modified electrodes. Collection of Nyquist plots kept going on until 1773 hours after having the first one at 40 minutes of starting the experiment. After 1773 hours, the R_{ct} was the lowest indicating that the protecting ability of the film is diminished now. However, this study indicates that PTh films can provide good corrosion resistance for SSteel in saltwater.

Trachli et al. electropolymerized 3-amino 1,2,4-triazole on a copper substrate in alkaline methanol solution to produce a homogenous and adherent polyamino 1,2,4-triazole (PATA) film [79]. They tested the corrosion IE of this polymer film towards copper metal in aerated 0.5 M NaCl using EIS. It is worth mentioning that the copper has a wide range of usage in microelectronic and industrial applications such as wiring technology, heat exchangers, electrostatic dissipation technology, and electromagnetic interference shielding. It is believed that the formulation of a protective layer on copper imparts good corrosion resistance. Immersion of a bulky copper electrode in aerated 0.5 M NaCl for 2 hrs without any polymer film produced a film resistance of $150 \Omega cm^2$. In case of uncoated copper, the cuprous oxide Cu_2O film is formed on the copper electrode in the solution open to the air or the formulation of chloride salt. On the other hand, PATA-coated copper, prepared by polarizing the copper electrode at a constant potential ranged between 0.6 and 1.4 V and also by CV, after one-month immersion in aerated 0.5 M NaCl, showed a R_{ct} of more than $200 k\Omega cm^2$ provided the film-forming potential less than 1.4 V. Thus, the protective effectiveness of this film was calculated to be greater than 99%. It is important to mention that the R_{ct} decreased from two to seven days, then increased progressively, which attributed to the initial damage of the PATA film caused by the corrosive electrolyte followed by gradual recovery due to the formation of the protective Cu_2O film.

An ideal corrosion-resistant coating is supposed to protect the metals from aqueous conditions. The coating should adhere to a wet surface, resist temperature and moisture

TABLE 3: PANI-based CIs for various metals and alloys.

Inhibitor	Concentration	Material	Test conditions	Maximum efficiency	Test technique	References
HCl-doped poly(<i>o</i> -ethoxy aniline)	200 ppm	Pure Fe	1 M HCl, RT	92%	LPR	[150]
Sulfamic acid-doped poly(<i>o</i> -ethoxy aniline)	75 ppm	Pure Fe	1 M HCl, RT	93%	WL	[150]
HCl-doped poly(<i>o</i> -methoxy aniline)	200 ppm	Pure Fe	1 M HCl, RT	91%	LPR	[151]
Sulfamic acid-doped poly(<i>o</i> -methoxy aniline)	75 ppm	Pure Fe	1 M HCl, RT	92%	LPR	[151]
Poly(styrene sulfonic acid)-doped PANI	70 ppm	MSteel	1 M HCl, 30 °C	85%	Tafel	[152]
Low-MW poly(<i>o</i> -ethoxyaniline)	100 ppm	CSteel	1 M HCl, 60 °C	96%	Tafel	[153]
Self-doped polyanthranilic acid	60 ppm	MSteel	0.5 M HCl, 60 °C	94%	EIS	[154]
PANI and PDDMAC blend	150 ppm	Pure Fe	1 M HCl, RT	59%	Tafel	[155]
Poly(aniline-co-2-isopropylaniline)	80 ppm	Pure Fe	1 M HCl, RT	72%	Tafel	[156]
LiSIPA-doped poly(aniline-co-2-isopropylaniline)	80 ppm	Pure Fe	1 M HCl, RT	72%	Tafel	[157]
Poly(aniline-formaldehyde)	10 ppm	MSteel	1 M HCl, 35 °C	98%	WL	[158]
Poly(vinyl alcohol- <i>o</i> -methoxy aniline) composite	2000 ppm	MSteel	1 M HCl, RT	91%	EIS	[159]
Poly(<i>p</i> -chloroaniline-formaldehyde)	15 ppm	MSteel	1 M HCl, 35 °C	98%	WL	[160]
Sulfonated chitosan-doped PANI	40 ppm	MSteel	0.5 M HCl, RT	92%	EIS	[161]
PANI-polyacrylic acid (PAA) composite	200 ppm	316 SSteel	0.5 M HCl, RT	92%	EIS	[162]
PANI-palm oil blend	1.5×10^{-1} M	MSteel	3% NaCl, RT	90%	EIS	[163]
<i>p</i> -Toluene sulfonic acid-doped PANI	2×10^{-3} M	Copper	0.1 M HCl, RT	89%	EIS	[164]
PANI/modified SiO ₂ composite coating	50 μm thick coating	Q235 CSteel	0.1 M H ₂ SO ₄ , RT	99%	Tafel	[165]
PANI-graphene nanocomposite film	6.9 μm thick coating	310 SSteel	Aerated 5000 ppm NaCl, RT	97%	EIS	[166]
PANI/poly(methyl methacrylate) (PMMA) coating	40-48 μm thick coating	Q235 CSteel	0.1 M H ₂ SO ₄ , RT	99%	Tafel	[167]
Poly(aniline-co-phenetidine)/SiO ₂	65-75 μm thick coating	MSteel	3.5% NaCl, 25 °C	99%	Tafel	[168]
Poly(aniline-co-2-pyridylamine-co-2,3-xylylidine)/ZnO nanocomposite	11.05-13.30 μm thick coating	MSteel	0.1 M HCl, 30 °C	99%	Tafel	[169]
Poly(aniline-co-N-methyl aniline)	—	CSteel	0.1 M HCl	81%	Tafel	[170]

TABLE 4: Some recently reported polyamine-based corrosion inhibitors.

Inhibitor	Concentration	Material	Test conditions	Maximum efficiency	Test technique	References
Poly(benzoxacine-urethane)	—	MSteel	3.5% NaCl	99%	Tafel	[171]
Poly(3-aminobenzoic acid)/PANI	—	430 SSteel	3.5% NaCl	88%	Tafel	[172]
PAPEMP	20 ppm	CSteel	Soft water	88%	Tafel	[173]
Poly(cyanurateamine)	2 ppm	MSteel	0.5-3 M HCl	98%	Tafel	[174]
Poly(2-aminothiazole)	—	MSteel	0.5 M HCl	97%	EIS	[175]

changes, bind to metals as well as siliceous materials under wet conditions, and resist autoclaving. A new series of poly(amino-quinones) (PAQ) were prepared from di-, triamines, and quinines [80, 81]. They are very efficient in protecting metallic surfaces. They instantly bind to the metal surface with sufficient affinity to displace water. One of the major advantages of this class of polymers is its preparation from a host of readily available amines and quinones. The PAQ polymer showed IEs of 94.7 and 83.4% towards MSteel at 500 ppm *via* WL technique, whereas 92.9 and 86.1% at 300 ppm *via* Tafel extrapolation method and 89.2 and 84.9% at 300 ppm by EIS measurements in 1 N H₂SO₄ and 1 N HCl, respectively. The trend of shift in the E_{corr} values suggested that the polymer acted as a mixed-type inhibitor. The phenomenon of more efficiency in H₂SO₄ has been attributed to the lesser adsorption of SO₄²⁻ ions on the metal surface in comparison to the Cl⁻ ions and hence more space for the inhibitors to adsorb and provide better efficiency. However, the adsorption of the PAQ polymer on the MSteel surface in both types of acids followed Temkin's adsorption isotherm.

The poly(*o*-toluidine) (POT) coatings were synthesized on copper substrates under cyclic voltametric conditions from an aqueous solution of sodium oxalate, and the POT coatings were examined for corrosion protection of Cu in an aqueous solution of 3.5 wt.% NaCl at room temperature by PDP and CV [82]. The comparative study of bare Cu, copper oxalate-coated Cu, and POT-coated copper revealed the superior protection efficiency of POT-coated copper in the salt medium. The corrosion current for the bare Cu in the salt medium was measured to be 24.06 $\mu\text{A}\cdot\text{cm}^{-2}$. The measured corrosion current (I_{corr}) for the oxalate-coated Cu was 69.5 $\mu\text{A}\cdot\text{cm}^{-2}$, which is higher than the bare Cu. This observation revealed that the copper oxalate coating provides poor corrosion protection to Cu. On the other hand, the I_{corr} decreased from 25 $\mu\text{A}\cdot\text{cm}^{-2}$ for bare Cu to 0.62 $\mu\text{A}\cdot\text{cm}^{-2}$ for POT-coated Cu, and the E_{corr} increased from -234 mV *vs.* the saturated calomel electrode (SCE) for bare Cu to -163 mV for POT-coated Cu. This positive shift of E_{corr} indicates the protection of Cu by POT coating. Actually, the corrosion rate of POT-coated Cu was found to be $\sim 0.007\text{ mm}\cdot\text{y}^{-1}$, which was ~ 40 times lower than the bare Cu. Furthermore, the PDP study of POT-coated Cu after storing them in air at 25°C for 7 days revealed an increase in corrosion IE with a slight lower shift in E_{corr} . This excellent IE of this coating has been ascribed to the adherent and uniform coverage of the metal surface as *confirmed* by the SEM study and the strong adsorption facilitated by the delocalized π -electrons in the polymer. Some recently reported

polyamine-based corrosion inhibitors and their IEs in different corrosive media are listed in Table 4.

The research group led by Sekine investigated the behavior of corrosion inhibition of MSteel by various cationic and anionic polymers, namely, polyethyleneimine (PEI) and its derivative (PEID), polydicyanodiamide derivative (PDCDA), and polyarylamine (PAAm) as cationic polymers and poly-maleic acid (PAA) derivative (PMAD) and polyacrylic acid derivative (PAAD) as anionic polymers (Figure 3) in different concentrations of CaCl₂. Cationic polymers showed to be deficient in inhibition abilities, whereas anionic polymers demonstrated better scale-forming corrosion inhibition of MSteel [83].

A research conducted by Zhang et al. reported a cationic polyelectrolyte (quaternary polyethyleneimine) as CI of Fe in H₂SO₄. The polymer behaved as a mixed-type inhibitor and proved to be an excellent CI, and the IE showed an increasing tendency with increasing cationic degree [84]. Quaternary PEI was also reported by same group, and its corrosion IE was tested in H₂SO₄ for low CSteel [85]. The PEIs with different molar masses (1300-750000 Da) as potential CIs for the American Iron and Steel Institute (AISI) 430 SSteel have been studied in a 3.5 wt.% NaCl solution [86]. WL and LPR measurements showed that all of the selected polymers protect this type of SSteel against uniform corrosion, whereas PEI with a molar mass of 2000 Da provides the best corrosion protection against localized corrosion, as demonstrated by cyclic polarization measurements. PEI as CI of the American Society for Testing and Materials (ASTM) 420 SSteel in 3 wt.% aqueous NaCl solution was also studied. Cyclic polarization measurements showed that PEI can act as an inhibitor against pitting corrosion. The WL test revealed that PEI can show remarkable IE against uniform corrosion. Furthermore, it has also been shown that once the protective layer is formed, it becomes very stable even in a noninhibited NaCl solution [87].

The corrosion inhibiting action of the polyphosphate derivative of guanidine and urea copolymer (PGUC) (Figure 4) for Armco Fe in 1 M HCl at 30°C was studied using EIS. The experimental results revealed that the inhibitor imparted an efficiency of 91.0% at a concentration of 11.5 g/L. The adsorption of PGUC followed Temkin's isotherm, and the low negative values of the standard free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) indicated that the adsorption of PGUC took place through physisorption [88]. Furthermore, the authors explored the antibacterial activity of PGUC against both Gram-positive and Gram-negative bacteria to have insight into the possibility of PGUC being used

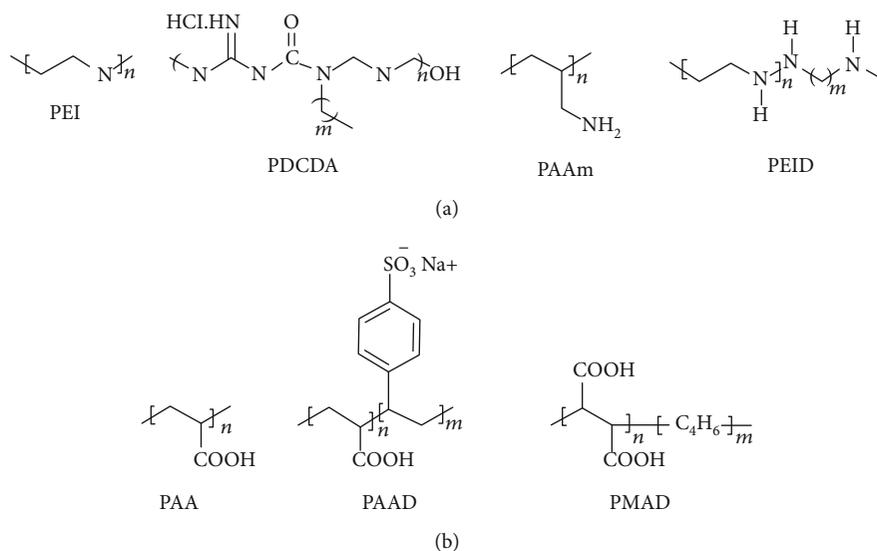


FIGURE 3: (a) Cationic and (b) anionic polymers as corrosion inhibitors.

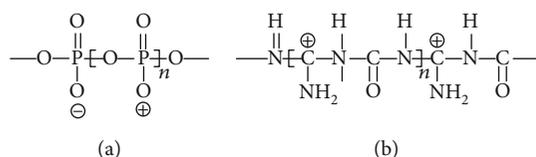


FIGURE 4: The molecular structure of the (a) polyphosphate derivative of guanidine and (b) urea copolymer (PGUC).

as a biocorrosion agent. The minimal inhibition concentration (MIC) measurements showed that the inhibitor is more efficient against the Gram-positive bacteria than Gram-negative bacteria. The MIC measured for the Gram-positive bacteria *Staphylococcus aureus* was of ca. 6-fold lower than the efficient inhibitory concentration of PGUC (11.5 g/L). On the contrary, the MICs measured for the Gram-negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa* were of ca. 2.7-fold and of ca. 10.9 higher than this concentration.

A surface-active water-soluble hyperbranched polyamide-ester (Hb-PAE) was synthesized through bulk polycondensation reaction between maleic anhydride and diisopropylamine [89]. Hb-PAE was tested as a CI of plain CSteel in neutral (distilled water) and acidic (1 N HCl) media using WL technique. The inhibitor showed an efficiency of 88.6% and 92.9% at a concentration of 0.1 M in the acidic and neutral media, respectively. Al-Sabagh et al. synthesized a new polyamide based on thiourea and tartaric acid, as a CI of CSteel in a 1 M HCl acidic medium [90]. The IE was measured using WL, PDP, and EIS techniques. The inhibitor imparted maximum efficiency of 90.6% at a concentration of 250 ppm. The results obtained from different IE measurement techniques were in good agreement. The adsorption of the inhibitor molecule on the steel surface was found to obey the Langmuir isotherm model, and both SEM and EDX proved the existence of a protective film on the MSteel surface techniques.

A new series of thiazole-based polyamides containing a diarylidencyclohexanone moiety was synthesized by Aly and

Hussein using low-temperature solution polycondensation technique [91]. The polymers were synthesized by the reaction of a thiazole-based monomer, namely, bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone, with different aliphatic and aromatic diacid chlorides using *N*-methylpyrrolidone, and in the presence of anhydrous LiCl as a catalyst. Polymers made with terephthaloyl chloride (Figure 5(a)) and biphenyldicarbonyl chloride (Figure 5(b)) were tested as CIs of CSteel in 0.5 M H₂SO₄ at 40°C using the Tafel extrapolation method. The polymer carrying a terephthaloyl chloride moiety imparted an efficiency of 98.2% at a concentration of 1.0 mg·L⁻¹, and the polymer carrying a biphenyldicarbonyl chloride moiety imparted an efficiency of 87.7% at a concentration of 0.5 mg·L⁻¹.

The high reactivity of vinyl monomers makes them easily polymerized by either anionic, cationic, irradiation, or free radical initiators. The water solubility of vinyl monomers facilitates the polymerization in water. Vinyl polymers containing polar substituents such as pyrrolidones and pyridines show ionic and thermal conductivity both in doped and undoped states [24]. The corrosion inhibition of poly(4-vinylpyridine-poly(3-oxide-ethylene)tosyle) for Fe in H₂SO₄ at 80°C using WL, PDP, and EIS measurements was studied [92]. The efficiencies obtained from different corrosion measurement techniques were in good agreement. Surprisingly, the polymer showed very high efficiencies of 100, 98, and 100% at 2.5 × 10⁻⁸ M in WL, Tafel extrapolation, and EIS measurements, respectively. The IE of poly(4-vinylpyridine isopentyl bromide) was studied by the same research group for pure Fe in 1 M H₂SO₄. At 10⁻⁵ M concentration, the polymer showed IEs of 100 and 97% in WL and Tafel extrapolation methods, respectively [93].

The corrosion protection efficiency of the poly(*N*-vinylpyrrolidone)-*b*-polyurethane-*b*-poly(*N*-vinylpyrrolidone) (PNVP-PU) triblock copolymer on MSteel in a 0.5 M H₂SO₄ medium was studied [94]. The copolymer showed a maximum efficiency of 98% at 1600 ppm, and the EIS

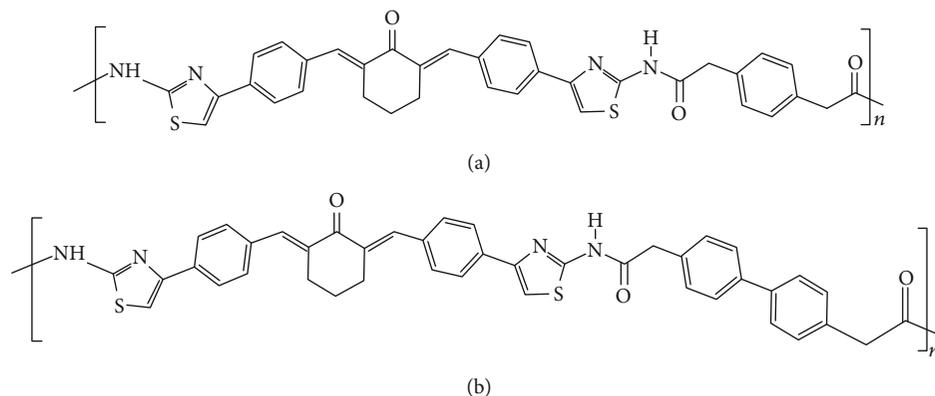


FIGURE 5: Copolymer of bis(2-aminothiazol-4-ylbenzylidene) cyclohexanone and (a) terephthaloyl chloride and (b) biphenyldicarbonyl chloride.

measurements revealed that the polymer inhibits MSteel corrosion by adsorbing on the MSteel surface to form the pseudocapacitive interface. The adsorption of the polymer on the MSteel surface obeyed the Langmuir adsorption isotherm and involves both the physisorption and chemisorption mechanisms. AFM and SEM analyses showed that the polymer established a protective film on the MSteel surface. Quantum chemical calculations revealed that the HOMO of PNVP-PU is distributed over the entire aromatic ring of the diurethane (dicarbamate) group. This implies that PNVP-PU can interact with the metal atom by donating charges from the electron-rich phenyl-diurethane centers to the suitable vacant orbitals of the metal. The LUMO of PNVP-PU was found to be distributed over the π -electron centers of the pyrrolidinone group and also on the neighboring Br heteroatom and the adjacent carboxylate group. This suggests that PNVP-PU can accept charges using the electron-deficient centers around the unsaturated pyrrolidinone group and the electronegative Br atom. Molecular dynamic simulation studies computed the energy of interaction between PNVP-PU and Fe (110) surface to be -365.2 kcal/mol. The equilibrium configuration of PNVP-PU revealed that the molecule adopts near-flat orientation on the Fe (110) surface. This ensures strong interaction between the inhibitor molecule and Fe. The anticorrosive property of Lumiflon (LU; fluoroethylene/vinyl ether alternating copolymer)/xylene/ TiO_2 coating on electronic boards was investigated [95]. The anticorrosive properties of the coatings were studied using a PDP technique depositing the coatings on a model substrate, aluminum alloy AA 2024. The cathodic current densities of the LU/xylene coatings and the LU/xylene/ TiO_2 coatings were found to be 10^{-9} and 10^{-10} A/cm², respectively. This implies that the addition of TiO_2 nanoparticles contributed to the protective properties of the coatings. The contact angles were also determined for LU/xylene and LU/xylene/ TiO_2 coatings deposited on AA 2024 alloy. It was found that the addition of TiO_2 nanoparticles increased the contact angle value for LU/xylene coatings from 80° to 90° for LU/xylene/ TiO_2 coatings. Moreover, optical microscopy and Raman spectroscopy were used to study the coverage of the most critical spots of the electronic

boards, and it was found that the boards coated with eight layers of LU/xylene/ TiO_2 coating were entirely covered and did not show any cracks.

The IE of PEG and polyvinylpyrrolidone (PVP) and synergistic effect of polyethylene-PVP blends for MSteel corrosion in 0.5 M H_2SO_4 at temperature range of 30 - 60°C were explored. It was found that the IE increased with increasing concentration of the homopolymers and decreased with increasing temperature. IE was found to be increasing with an increase in the concentration of the blends and determined to be highest for the (PEG:PVP) blending ratio of $1:3$ [96]. The inhibition effect of PVP10 (MW = $10,000$ Da) and PVP45 (MW = $45,000$ Da) on the corrosion of 316 SSteel was studied by Khaled. The IE was found to increase with increasing MW of PVP [97].

The inhibiting effects of 2,6-ionen and 2,10-ionen type polyvinylbenzyltrimethyl-ammonium chloride and latex on low CSteel in 0.1 M HCl by PDP and EIS techniques over the temperature range of 20 - 60°C at different inhibitor concentrations were investigated [98]. The efficiency was found to increase with increasing concentration. The degree of shift in E_{corr} values revealed that the studied inhibitors behaved as anodic inhibitors. Umoren et al. explored the IE and adsorption characteristics of two water-soluble polymers, namely, PEG and polyvinyl alcohol (PVA), on MSteel in 0.1 M H_2SO_4 at 60°C . The IE increased with increasing concentrations and temperatures. The inhibitors (PVA and PEG) were found to obey the Langmuir, Temkin, and Freundlich adsorption isotherms at all concentrations and temperatures studied. PEG was found to be a better inhibitor than PVA [45].

Acrylic acid is an embryo toxin, and acrylamide is a neurotoxin, while their respective polymers are found to be non-hazardous [24]. An array of acrylic-based polymers has been synthesized as hydrogels and has been exploited for different applications based on their sensitivity towards heat, light, and pH. In this context, corrosion protection properties of some acryl-based polymers have been highlighted. The effect of static and hydrodynamic conditions (0 - 2000 rpm) on corrosion inhibition of a water-based acrylic terpolymer, methyl methacrylate (MMA)/butyl acrylate/acrylic acid, was investigated [99]. The study was carried out on the Society

of Automotive Engineers (SAE) 1018 steel in simulated sour petroleum corrosive solution (NACE 1D196) by alternate current/direct current (AC/DC) electrochemical tests. Increase in rotation speed increased the corrosion rate; however, the corrosion IE also increased which was ascribed to the enhanced mass transport of inhibitor molecules to the metal surface. The thermodynamic study disclosed that the terpolymer obeys the Langmuir adsorption isotherm and adsorbs chemically onto the surface. The efficiency of the dispersed magnetite core-shell nanogel polymer poly(2-acrylamido-2-methylpropane sulfonic acid) and its copolymers with acrylic acid and acrylamide magnetic nanogels was studied as CIs. The study was conducted for carbon steel in 1 M HCl employing various electrochemical techniques, such as PDP and EIS. The results revealed that the nanogels showed increasing efficiency with increasing concentrations and temperatures and acted as mixed inhibitors. The thermodynamic study revealed that the adsorption of nanogel particles was found to fit the Langmuir isotherm and followed chemisorption [100]. Umoren and his team studied the corrosion inhibition behavior of bulk nanocrystalline ingot iron (BNII) which was fabricated from coarse polycrystalline ingot iron (CPII) by PAA in 0.1 M H₂SO₄ using EIS and PDP techniques. The results revealed that PAA inhibited the acid-induced corrosion of both types of metal specimens with greater effect noted for BNII. Microstructures of the iron samples have contributed to the variation in IE shown by PAA. Synergistic inhibition effect, upon the addition of iodide ions to PAA, was observed in case of CPII, while for BNII IE was marginally increased [96].

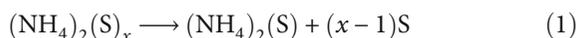
The different feed ratios of *N*-(methacryloyloxymethyl)-benzotriazole (MMBT) and MMA were used to synthesize different forms of copolymers, and their role as CIs of MSteel was studied in 0.1 M HCl using PDP and EIS methods. Variation in the composition of the copolymers showed different corrosion protection efficiencies. The copolymer obtained from the 1:1 molar ratio of MMBT and MMA exhibited better protection efficiency than other combinations [101]. Palmitic acid PAAm was synthesized by Han and Liu and used to study the corrosion inhibition of X-65 CSteel [102]. The result showed maximum IE of 78.1% at 0.1 g/L inhibitor concentration *via* WL method, and the inhibition was of cathodic-type. The inhibitive effect of PAAm grafted with fenugreek mucilage (Fen), a natural grade polysaccharide, on the corrosion of MSteel in 0.5 M H₂SO₄ has been investigated by EIS, PDP, and WL methods [103]. The polymer, Fen-g-PAAm, showed an IE of 78% at a meager concentration of 1 ppm and efficiency as high as 96% at 100 ppm. The polarization study revealed that the polymer acted as a predominantly cathodic inhibitor. The adsorption of this inhibitor on the MSteel surface obeyed the Langmuir adsorption isotherm.

Unlike the nitrogen-containing polymeric CIs, which adsorb on the metal surface, polysulfides react with Fe to form Fe disulfides that can abate the corrosion rate in very harsh corrosive environment. The metal disulfide coating can be continuously replenished by the continuous addition of reactants (either disulfide source or ferrous ions), which provides a more dynamic solution to corrosion. Polysulfides

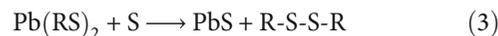
are one of the well-recognized polymeric CIs in the petrochemical industry. Additionally, polysulfides can also prevent a dangerous phenomenon named “hydrogen blistering” or “hydrogen attack” that results when process streams with hydrogen sulfide pass through ferrous ion pipes with liquid water. Though the mechanism was not completely understood, it is believed that the hydrogen sulfide reacts with Fe to form Fe sulfide and atomic hydrogen. The atomic hydrogen is not deleterious for the system in itself but can pose a significant threat when it reaches and concentrates on areas with some imperfections and exerts pressure after combining with another atomic hydrogen to create a molecular hydrogen. The pressure that builds up inside causes blistering [3].

Polysulfides not only act as CIs; their presence in the process stream can also cause synergistic advantages for the inhibition [104]. It can prevent the hydrogen embrittlement by controlling CN⁻ concentration, which causes the formation of HCN amine salts. HCN, in the upper part of regeneration towers, decomposes to form H⁺ ions that infiltrate the metal to yield molecular hydrogen that causes hydrogen embrittlement. Moreover, polysulfides react with arsenic and mercury to produce insoluble species that can be filtered out from the stream. Organic polysulfides of the type R-(S)_x-R' have demonstrated corrosion protection against naphthenic acid at very high temperatures [105]. Naphthenic acids cause severe corrosion damage in the refining distillation units at temperatures ranging from 400 to 790°F. While amine and amide-based CIs have been quite ineffective in fighting naphthenic acid corrosion, organic polysulfides, on the contrary, perform well in these conditions.

Polysulfides, in spite of having good corrosion protection efficiencies, can decompose to free sulfur and mono- or hydrosulfides when present in excessive amount at higher temperatures as shown in the reactions (1) and (2) below:



The produced sulfur can form mercaptans that are difficult to remove even by caustic washing. In addition to this, olefins can interact with these species at temperatures higher than 325°F. Lead oxide, lead salts of the lower alkyl mercaptans, sodium polysulfide, or any other agent capable of combining with sulfur (reaction (3)) can be employed to adsorb or wash the process stream to address this dilemma.



Moreover, the free sulfur can produce an organic disulfide, which can combine with the hydrocarbon stream and is not as precarious as the free sulfur.

Carboxylic acid derivatives and fatty acids are well-renowned CIs for the oil and gas industries. Long-chain fatty acids of OAs are reacted with alkylene polyamines to yield polyamide CIs that are widely used in the petrochemical industries [106]. Azelaic and sebacic acids can be reacted with ammonia, di- and triethanol amines, ethanol amine, and *N,N*-diethyl-ethanol amine to produce beneficial

carboxylate salt inhibitors in aqueous systems for drilling operations [107]. Polymaleic acids have been reacted with amines to form oil-soluble inhibitors with good anticorrosion properties and have been tested in H₂S and CO₂ environments [106, 108]. Aside from the typical inhibitors produced from fatty acid polyamine reactions, polycarboxylic acids or other carboxylic acid-functionalized materials themselves are widely used CIs in various industries [3]. CIs made from polycarboxylic acids are mostly based on PAAs or polymaleic acids that have been frequently used in cooling water systems [109, 110]. Polycarboxylic acid CIs can also be made from some unsaturated carboxylic acids such as α -haloacrylic acid, methacrylic acid, maleic anhydride, itaconic acid or anhydride, allyl acetic acid, vinyl acetic acid, β -carboxyethylacrylate, fumaric acid, and their salts [3].

3. Mechanism of Corrosion Inhibition by Polymeric Inhibitors

Corrosion is a spontaneous process, and the extent of spontaneity, i.e., the relative rate of corrosion, is contingent upon the change in standard Gibbs free energy (ΔG°). The more negative the value of ΔG° , the higher the rate of corrosion [111]. Metals and alloys corrode to form stable corrosion products when exposed to the environment [112]. In general, CIs are used to mitigate corrosion. Interestingly, rust and scale that form because of the corrosion can also act as CIs. This is because they act as physical protective barriers after accumulating on the surface. Adsorption of an inhibitor is the first step in forming a corrosion protective film or coating in the presence of an aggressive medium that causes corrosion on the active sites. The type of interaction between the inhibitor and the metal surface is best revealed by the Langmuir adsorption isotherm [113]. If the value of $\Delta G^\circ_{\text{ads}}$ is $-20 \text{ kJ}\cdot\text{mol}^{-1}$ or less negative, the type of interaction is known as physisorption, which arises due to the electrostatic interaction between the charged centers of inhibitor molecules and the charged metal surface. However, chemisorption occurs when the bonding strength becomes much larger where the value of $\Delta G^\circ_{\text{ads}}$ is around $-40 \text{ kJ}\cdot\text{mol}^{-1}$ or more negative [1]. In chemisorption, transfer or sharing of electron occurs from the inhibitor molecules to the metal's empty *d*-orbital through the formation of a coordinate covalent bond. Sometimes, mixed-type inhibition can occur as well, which is considered ideal for effective corrosion inhibition. Umoren and Solomon [114] pointed out that most polymers exist as polycations in widely studied acid media as proved by extensive research works. This makes it difficult for the polycations to get adsorbed onto the surfaces of positively charged metal ions. In this circumstance, anions in the aqueous medium with a smaller degree of hydration can bring more negative charges in the interface to facilitate the adsorption of polycations further *via* electrostatic interaction or physisorption. According to Umoren et al. [115], the inhibitor molecules exist as protonated species in equilibrium with the corresponding neutral species when chemisorption prevails. These inhibitor molecules then displace water molecules from the interface to get adsorbed onto the metal

surfaces by donating the lone pair of electrons from their heteroatoms.

It is widely accepted that the presence of heteroatoms, such as O, N, S, and P, in an inhibitor increases its basicity and electron density and intensifies its IE. The lone pair of electrons on these heteroatoms and π -electrons help the inhibitors form a coordinate covalent bond with the empty *d*-orbitals of the metal atoms and facilitate adsorption of the inhibitors on the metal surface. The bond formed this way is known as chemisorption, and the electron density on the donor atom and the polarizability of the functional groups that contain the heteroatoms dictate the strength of this bond. Additionally, the presence of hydrophilic functional groups, replacement of H atoms attached to the C in a ring by the -NH₂, -CHO, -COOH, or -NO₂ groups, and presence of carbon numbers up to 10 in a chain are some other factors that help the inhibitors adsorb well on the metal surface [29].

In addition to the features mentioned in the preceding paragraph, some additional parameters make polymers superior to their traditional organic and inorganic counterparts. Polymers form complexes with the metal surface through their functional groups, and these complexes occupy a large surface area, thereby blanketing the surface better than other types of inhibitors and providing the metals with excellent protection in corrosive solutions [116]. Because of the presence of multiple attachment groups repeated along with the polymeric chain length, the polymeric inhibitors are better adsorbed. However, the situation becomes complex when it comes to tracing the inhibition mechanism of naturally occurring polymeric plant extracts. Because these extracts oftentimes contain multiple chemical species, it is difficult to know which one contributed more than others in corrosion prevention.

4. Conclusions

This review has highlighted the significance of corrosion along with different classes of CIs with a particular emphasis given to the common classes of polymers that have been widely used as CIs of various types of metals in different corrosive media. The corrosion inhibition approach has been discussed using different conducting and nonconducting polymers, copolymers, terpolymers, composites, polymer blends, doped polymers, and naturally occurring polymers. Corrosion inhibition by polymeric materials is one of the most economically viable corrosion mitigation techniques because these materials can be exploited through batch and/or continuous treatments and can lower the chance of partial or complete shutdowns even if used at a meager concentration. Even though the research on polymeric CIs bloomed a long ago, they were not successfully taken to onsite application since the performance of organic CIs thwarted the emergence of polymeric CIs. Some remarkable and innate features of these macromolecular inhibitors such as several possible attachment points, highly versatile derivatization, and better film-forming capability along with the eco-harmful nature of the inorganic inhibitors laid the foundation for the development of environmentally benign

polymeric CIs. Mechanisms of inhibition are mainly ascribed to adsorption and contingent upon the metal, physiochemical properties of the molecule such as steric factors, functional groups, electronic structure, aromaticity at the donor atom, and *p* orbital character of donating electrons. To put it another way, the efficiency of polymers as CIs relies not only on the corrosive environment in which it functions, the nature of the metal surface, and the electrochemical potential at the interface but also on the structure of the inhibitor itself, i.e., the number of adsorption active centers in the molecule and their charge density, the mode of adsorption, the molecular size, and the projected area of the inhibitor on the metallic surface leading to the formation of metallic complexes. It is usually desirable that a successful polymeric CI will contain heteroatoms, such as O, N, S, and P, which will increase its basicity, and the increased electron density will help increase polymers' corrosion inhibition potential. These heteroatoms are the active centers for the process of adsorption on the metal surface with the IE supposed to follow the sequence O<N<S<P. Most inhibitors adsorb on the surface of the metal by displacing the water molecules and forming a compact barrier. Availability of nonbonded (lone pair) and π -electrons facilitates the formation of a coordinate covalent type of bond through which the transfer of electrons from the inhibitor molecule to the metal surface could happen. The strength of this chemisorption bond relies on the polarizability of the functional group and the electron density on the donor atom. Replacement of the H atom attached to the C in the ring by a substituent group, such as the $-\text{NO}_2$, $-\text{NH}_2$, $-\text{CHO}$, or $-\text{COOH}$ group, culminates in a change of electron density in the metal at the point of attachment that causes retardation of anodic and cathodic reactions. The presence of multiple cationic and anionic sites within a polymer chain along with the presence of highly polarizable heteroatoms, such as N, P, and S, causes the polymer to undergo strong adsorption on the metal surface. The presence of a hydrophobic hydrocarbon chain is highly desirable since it displaces the water molecules from the surface of the metal, makes a compact barrier, and prevents the metal from coming into contact with the corrosive water molecules any further. The advent of new technologies that will make the polymerization process more controllable to produce other architectures, such as branched, hyperbranched, and dendrimeric, will surely open up new frontiers in corrosion research.

5. Future Outlook/Challenges

Corrosion is a stochastic, probabilistic phenomenon, which can be tackled well by interdisciplinary approaches of electrochemistry, surface science, thermodynamics and kinetics, hydrodynamics, mechanics, metallurgy/materials science, and chemistry. The oil and gas industries lose tens of billions of dollars income and expense as treatment costs every year [2]. Corrosion inhibition is one of the most practical and cost-effective approaches in confronting corrosion. However, the chemical, refinery, and petrochemical industries need to face the challenge of dealing with corrosion issues, such as the selection and development of corrosion-resistant mate-

rials, environment friendly inhibitors, and coatings. A better understanding of the corrosion mechanism in these environments is a first-order priority [117]. Importantly, chromium has been ubiquitous in our life for over a century finding applications ranging from wood treatments to corrosion prevention. However, hexavalent chromium and chromate compounds have been found to induce lung cancer and genotoxicity, respectively. Even though the health risks associated with the chromium-based inhibitors being well known and extensive research has been underway since the 1980s to date, hexavalent chromium remains the benchmark corrosion preventive compound in essentially all industries [118].

In this circumstance, it is extremely important that corrosion inhibition researchers guide their focus on finding appropriate green CIs, the more the better, for appropriate conditions. Fortunately, in recent years, there has been a surge in the corrosion inhibition research community in investigating various green inhibitors. As polymers are better CIs than their organic and inorganic counterparts, corrosion researchers remain much enthusiastic in investing time on experimenting different amino acid- and carbohydrate-based polymers as both scale and CIs. Even though much progress has been attained in the chemistry of inhibitors, the study of these inhibitors in different corrosive systems remains very challenging. The two main challenges associated with the inhibitors being adsorbed on the metal surface are as follows: (1) metal-inhibitor interactions and (2) transport of the CI from bulk solution to the surface of the metal. The immobilization of CIs into micro-/nanocontainers could help overcome these issues [119].

The concept of this type of coating is having nanocontainers with controlled permeability of the shell and loaded with CIs or other active agents. This technology provides an excellent opportunity of combining passive functionalities like color or barrier and active ones that are responsive to local pH, temperature, humidity, cracks, and electrochemical potential. An autonomic response to corrosion or any other defects in the coating is a big advantage of such self-healing coatings. There are scores of publications that demonstrated this concept of nanocontainers with single functionality, i.e., the release of one CI using one triggering mechanism. Nevertheless, a lot of research works need to be done on extending this idea for developing multifunctional nanocontainers that are able to encapsulate several active materials and respond to different triggering impacts. The transformation of the current research achievements to the technology level is another big challenge that needs to be tackled in a priority basis as well [120].

Abbreviations

AAS:	Atomic absorption spectroscopy
AC:	Alternate current
AFM:	Atomic force microscopy
AISI:	American Iron and Steel Institute
Ala:	Alanine
AMT:	4-Amino-5-methyl-1,2,4-triazole-3-thiol
Arg:	Arginine
Asp:	Aspartic acid

ATR:	Attenuated total reflectance	PANI:	Polyaniline
β_a :	Anodic beta (Tafel) coefficient	PAPEMP:	Polyamino polyether methylene phosphonate
β_c :	Cathodic beta (Tafel) coefficient	PAQ:	Poly(amino-quinone)
BNII:	Bulk nanocrystalline ingot iron	PASP:	Polyaspartic acid
C_{dl} :	Double-layer capacitance	PATA:	Poly(3-amino-1,2,4-triazole)
CI:	Corrosion inhibitor	PCz:	Polycarbazole
CP:	Conducting polymer	PDCDA:	Polydicyanoamide derivative
CPII:	Coarse polycrystalline ingot iron	PDDMAC:	Poly(diallyldimethylammonium chloride)
CS:	Chitosan	PDP:	Potentiodynamic polarization
CSB:	Chitosan Schiff base	PEG:	Polyethylene glycol
CSteel:	Carbon steel	PEI:	Polyethyleneimine
CV:	Cyclic voltammetry	PEID:	Polyethyleneimine derivative
Cys:	Cysteine	PFOA:	Perfluorocaprylic acid
ΔG° :	Gibbs free energy	PGUC:	Polyphosphate derivative of guanidine and urea copolymer
ΔG°_{ads} :	Gibbs free energy of adsorption	Phe:	Phenylalanine
DC:	Direct current	PMAD:	Polymaleic acid derivative
DFT:	Density functional theory	PMMA:	Poly(methyl methacrylate)
E_{corr} :	Corrosion potential	PNVP-PU:	Poly(<i>N</i> -vinylpyrrolidone)-polyurethane
EDS:	Energy-dispersive spectroscopy	POA:	Poly(<i>o</i> -anisidine)
EDX:	Energy-dispersive X-ray spectroscopy	POT:	Poly(<i>o</i> -toluidine)
EFM:	Electrochemical frequency modulation	PPy:	Polypyrrole
EN:	Ethylene diamine	PS:	Polystyrene
Fen:	Fenugreek mucilage	PTh:	Polythiophene
FESEM:	Field emission scanning electron microscopy	PVA:	Polyvinyl alcohol
FT-IR:	Fourier transform infrared spectroscopy	PVP:	Polyvinylpyrrolidone
GA:	Gum arabic	R_{ct} :	Charge transfer resistance
GCC:	Gulf Cooperation Council	R_p :	Polarization resistance
GDP:	Gross domestic product	SAE:	Society of Automotive Engineers
GG:	Guar gum	SCE:	Saturated calomel electrode
Glu:	Glutamic acid	SCSB:	Salicylaldehyde-chitosan Schiff base
Gly:	Glycine	SEM:	Scanning electron microscopy
GNP:	Gross national product	S-MCys:	S-Methylcysteine
GO:	Graphene oxide	SSteel:	Stainless steel
Hb-PAE:	Hyperbranched polyamide-ester	SVET:	Scanning vibrating electrode technique
HEC:	Hydroxyethylcellulose	TCH:	Thiocarbohydrazide
His:	Histidine	TS:	Thiosemicarbazide
HOMO:	Highest occupied molecular orbital	UV-Vis:	Ultraviolet-visible
HPMC:	Hydroxypropyl methylcellulose	Val:	Valine
I_{corr} :	Corrosion current	WL:	Weight loss
IE:	Inhibition efficiency	XAS:	X-ray absorption spectroscopy
LiSIPA:	Lithiumsulfisophthalic acid	XG:	Xanthan gum
LPR:	Linear polarization resistance	XPS:	X-ray photoelectron spectroscopy
LU:	Lumiflon	XRD:	X-ray diffraction.
LUMO:	Lowest unoccupied molecular orbital		
Lys:	Lysine		
MAA-TN:	Methyl acrylate-triethylene tetramine		
Met:	Methionine		
MIC:	Minimal inhibition concentration		
MMA:	Methyl methacrylate		
MMBT:	<i>N</i> -(methacryloyloxymethyl)benzotriazole		
MSteel:	Mild steel		
MW:	Molecular weight		
NACE:	National Association of Corrosion Engineers		
<i>N</i> -ACys:	<i>N</i> -Acetylcysteine		
OA:	Oleic acid		
OCP:	Open circuit potential		
PAA:	Polyacrylic acid		
PAAD:	Polyacrylic acid derivative		
PAAm:	Polyarylamine		

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

N. A. Aljeaban and L. K. M. O. Goni contributed equally to this work.

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