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Green Corrosion Inhibitors, Past, Present, and Future

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Abstract

Green corrosion inhibitors are of interest because there has been an increase in environmental awareness and a change in regulations that restrict regular corrosion inhibitors due to their toxicity. Natural products are a good source of green corrosion inhibitors, where most of their extracts containing the necessary elements such as O, C, N, and S, which are active in organic compounds, assist in adsorption of these compounds on metals or alloys to form a film that protects the surface and hinders corrosion. Numerous natural products and their application in different processes, especially in steel reinforcement embedded in concrete, are discussed. Development of green chemistry and green chemical technologies offers novel synthetic methods for ionic liquids, which are considered as new corrosion green inhibitors, and their mechanism of adsorption, how these green inhibitors act in different media, and their protective role for different metals and alloys are discussed. Finally, industrial applications of vapor-phase inhibitors and their mechanisms are presented.

Keywords: green inhibitors, corrosion protection, green chemistry, ionic liquid, vapor-phase inhibitors

1. Introduction

Corrosion is a natural phenomenon where metals and alloys try to revert to their more stable thermodynamics form due to reaction with the environment that surrounds them. Corrosion is expensive due to loss of materials or their properties, which leads to loss of time during maintenance, the shutting down of systems, and severe failure of some structures, which in some cases may be hazardous and cause injury.

To protect metals or alloys from corrosion, approaches such as isolating the structure from aggressive media (using coatings or film-forming chemicals) or compensating for the loss of electrons (corrosion is an oxidation process) from the corroded structure (e.g. cathodic protection by impressed current or by using active sacrificial anodes) are employed.

Corrosion inhibition may include organic or inorganic compounds that adsorb on the metallic structure to isolate it from its surrounding media to stop the oxidation-reduction process. Organic inhibitors create their inhibition by adsorbing their molecules on the metal or alloy surface to form a protective layer [1]. Alternatively, inorganic inhibitors act as anodic inhibitors and their metallic atoms are enclosed in the film to improve their corrosion resistance. Most investigated corrosion inhibitors are toxic and cause severe environmental hazards upon disposal. Therefore, their use has been limited by environmental regulations. Nevertheless, inhibitors still play a critical role in corrosion prevention. Inhibitors are classified according to:

- Three types of electrode process, namely, anodic, cathodic, and mixed;
- The chemical nature of the environment to acid inhibitors (organic or inorganic), neutral inhibitors, alkaline inhibitors, and vapor-phase inhibitors.

Hazards caused by toxicity of regular inhibitors have led to the use of new green corrosion inhibitors. Most of these inhibitors derived from natural products act as anticorrosion agents, which are eco-friendly and harmless upon disposal. Other green inhibitors such as rare earths and organic polymers are not focused on in this chapter and further information may be found elsewhere [2–4]. This chapter will focus on green inhibitors from natural products, ionic liquids, and safety vapor-phase inhibitors, with a brief description of their mechanisms of action.

Green inhibitors act when they are added in very low concentrations to treat the surface of metals or alloys in a corrosive environment. Plant extracts are deemed to be rich, naturally synthesized chemical compounds [5] that affect the corrosion rate by adsorption of effective species on metal surfaces when added to many industrial systems through:

- Changing the rate of anodic and/or cathodic reactions;
- Effecting the diffusion rate of aggressive ions interacting with metallic structures;
- Increasing electrical resistance of the metal surface by forming a film (coat) on it.

During corrosion, metal ions move into the solution at active areas (the anode) and pass electrons from the metal to an acceptor at less active areas (the cathode); the cathodic process requires the presence of an electron acceptor such as oxygen, oxidizing agents, or hydrogen ions. Corrosion can be minimized by retarding or completely stopping the anodic or cathodic reactions, or both. Inhibitors are adsorbed on the metal surface, forming a protective barrier, and interact with anodic and/or cathodic reaction sites to decrease the oxidation and/or reduction of corrosive reactions [6].

There are several different, common cathodic reactions in corrosive media:

Reduction reaction is hydrogen gas evolution as follows:

In Eq. (3) hydrogen ions adsorbed on the metal surface are catalyzed in combination with other hydrogen ions hold hidden giving evolved hydrogen gas on cathode surface, in presence inhibitor amount of hydrogen bubble refer to ability of inhibitor to prevent this reaction and protected metal from corrosion [7]. The action of inhibitors molecules occurs due to their adsorption on an exposed metal surface in the form of neutral molecules instead of hydrogen ions adsorbed from the metal surface.

or by displacement of water molecules on the surface, as described in Eq. (2). Green inhibitors have adsorptive properties, known as site-blocking elements [8, 9].

Figure 1 shows the interest shown in green inhibitors in the last few decades, as explained by the number of publications in that period. We summarize the research focused on using natural products that have been used as green inhibitors in various aggressive media for corrosion protection of different alloys and metals as depicted in **Table 1**. The table shows the numerous studies arranged in chronological order and discussed in the reference next to each type of inhibitor. Each inhibitor’s percentage of inhibition efficiency is reported at the maximum

Figure 1. The interest in green inhibitors versus corrosion as indicated by number of publications. Keywords of corrosion and green inhibitors were used to retrieve the data from Web of Knowledge®.

Source of natural products	Metal/alloy studied	Agg. media studied	Efficiency (%)	References
Flour and yeast	Iron	Acid media	65–82	[10]
Furit—peels of pomegranate	Aluminum	Acid media	83	[11]
<i>Hibiscus sabdariffa</i> extract	Al and Zn	HCl	85	[12]
Tobacco leaves	Mild steel and Aluminum	Neutral then acidic media	87.5 (steel), 77.5 (Al)	[13]
Castor seeds			71.0 (steel), 45.9 (Al)	
Black pepper			87.5 (steel), 65.8 (Al)	
Soya bean			65.5 (steel), 27.1 (Al)	
Gum (acacia)			NA (steel), 21.8 (Al)	
Catechu			50.0 (steel), 6.3 (Al)	
Opium (0.1%)			NA (steel), 42.7 (Al)	
Opuntia extract	Steel, Aluminum, Zinc and Copper	Acid media	75 (steel), 70 (Al), 55 (Zn), 56 (Cu)	[14]
<i>Aloe eru</i> leaves			80 (steel), 64 (Al), 43 (Zn), 43 (Cu)	
Orange peels			80 (steel), 59 (Al), 59 (Zn), NA (Cu)	
Mango peels			82 (steel), 82 (Al), 80 (Zn), 30 (Cu)	
Pomegranate fruit shell			65 (steel), 81 (Al), 71 (Zn), 73 (Cu)	
<i>Papaia</i>			94	
<i>Poinciana pulcherrima</i>			96	
<i>Cassia occidentalis</i>	Mild steel	Acid media	94	[15]
<i>Datura stramonium</i> seeds			93	
<i>Calotropis procera</i>			98	
<i>Azadirachta indica</i>			84	
<i>Auforpio turkiale</i> sap			69	
<i>Swertia angustifolia</i>			75–96	
<i>A. indica</i>			88–96	
<i>A. indica</i>	Mild steel	NaCl	86.1	[18]
<i>Punica granatum</i>	Mild steel	Acid media	79.2	[16]
<i>Momordica charantia</i>			82.4	
<i>Pongamia glabra</i> , <i>Annona squamosa</i>			89–95	
<i>Acacia arabica</i>			93–97	
Natural honey			82–91	
<i>Rosmarinus officinalis</i>			75	
Mimosa tannin			66–87	
Vanillin	Carbon steel	Acid media	93–98	[24]
Dodecanohydrazide, cis-9-octadecanohydrazide and 10-undecanohydrazide derived from fatty acids	Mild steel	Acid media	85	[25]

Source of natural products	Metal/alloy studied	Agg. media studied	Efficiency (%)	References
Herbs (thyme, coriander, hibiscus, anis, black cumin, and garden cress)	Steel	Acid media	37–92	[26]
Reducing saccharides fructose and mannose	Aluminum and Zinc	Alkaline media	92	[27]
Opuntia extract	Aluminum	Acid media	76–96	[28]
<i>Vernonia amygdalina</i>	Al alloys	Acid media	49.5–72.5	[29]
<i>Allium cepa</i> , <i>Allium sativum</i> , <i>M. charantia</i>	Mild steel	Acid media	86–94	[30]
Guar gum	Carbon steel	Acid media	75–93.88	[31]
<i>Zanthoxylum alatum</i>	Mild steel	Acid media	76–95	[32]
<i>Nypa fructicans</i>	Mild steel	Acid media	75.11	[33]
Caffeine–Mn ²⁺	Carbon steel	Chloride ions	50	[34]
Caffeine and nicotine			80–90	[107]
Eugenol from cloves	Steel	Acid media	80	[35]
<i>acetyleugeno</i>			91	
<i>Ricinus communis</i> leaves	Mild steel	NaCl	43–84	[36]
Berberine extracted from <i>Coptis chinensis</i>	Mild steel	Acid media	79.7	[37]
Halfabar	Steel	Acid media	90.50	[38]
Chamomile			92.97	
Black cumin			88.43	
<i>Kidney bean</i>			88.43	
<i>Sansevieria trifasciata</i>	Aluminum	Acid and alkaline media + halides	94.3 (HCl) 95.3 (KOH)	[39]
Exudate gum from <i>Dacryodes edulis</i>	Aluminum	Acid media	42	[40]
Gum arabic			80	
Exudate gum from <i>Raphia hookeri</i>	Aluminum	Acid media + halide	56.3	[41]
Exudate gum from <i>Pachylobus edulis</i>	Mild steel	Acid media	56	[42]
<i>Bambusa arundinacea</i>	Steel rebar	Chloride and nitrite	85	[43]
Parts of the kola tree (leaves, nuts, and bark) and tobacco	Steel rebar	NaCl	70–91	[44]
<i>Artemisia pallens</i>	Mild steel	Acid media	93–98	[45]
<i>V. amygdalina</i>	Steel rebar	NaCl	90.8	[46]
<i>Chamaerops humilis</i> L.	Steel rebar	Alkaline media	42.2	[47]
Mangrove tannin	Copper	Acid media	82.4	[48]
Chitosan	Copper	Acid media	93	[49]
<i>Myrtus communis</i>	Copper	Acid media	>85	[50]
<i>Tagetes erecta</i>	Copper	Acid media	98.07	[51]

Source of natural products	Metal/alloy studied	Agg. media studied	Efficiency (%)	References
<i>Morinda lucida</i>	Steel rebar	NaCl	92.8	[52]
<i>Opuntia ficus indica</i>	Carbon steel	Acid media	70–91	[53]
<i>Alhagi maurorum</i> plant extract	Copper	Acid media	33–83	[54]
Egyptian licorice extract	Copper	Acid media	89.55	[55]
<i>Tridax procumbens</i> <i>Chromolaena odorata</i>	Stainless steel	Oilfield environment	82.03 95.6	[56]
<i>Corchorus olitorius</i>	Mild steel	Acid media	93	[57]

Table 1. Natural products and their anticorrosive properties on metals or alloys in different aggressive.

value when different conditions are applied, according to conditions of study in each reference (temperature, concentration of inhibitors, concentration of aggressive media, conditions of study, and adsorption isotherm).

Figure 2 shows examples for the most used natural green corrosion inhibitors from past to present times as a real image.

Figure 2. Various sources for natural green corrosion inhibitors.

Figure 3. Usage of green corrosion inhibitors in various industries.

Figure 3 presents the importance of green corrosion inhibitors in large industrial applications. Most of these inhibitors contain functional groups and/or π -electrons in conjugation with triple or double bonds, which affect organic compounds by specific interaction between necessary elements such as nitrogen, sulfur, and oxygen through free lone pairs of electrons, which are adsorbed on the metal surface or by supplying electrons through π -orbitals [58].

2. Mechanism of green inhibitors as corrosion inhibitors

Corrosion is a spontaneous process; the relative rate of corrosion is related to the change in standard Gibbs free energy (ΔG°). A more negative value of ΔG° is related to higher spontaneous reaction, i.e. higher corrosion rate [59]. Metals and alloys when exposed to the environment corrode to form stable corrosion products [60]. Utilization of additive corrosion inhibitors is necessary to mitigate corrosion rate. Corrosion products such as rust and scale can also act as corrosion inhibitors because they can accumulate on the surface and act as physical protective barriers; however, the relative rate of corrosion of any particular metal depends on the Pilling–Bedworth ratio [61, 62], which is used at high-temperature oxidation (corrosion); the ratio is defined as:

$$\frac{M \cdot d}{n \cdot m \cdot D} \quad (5)$$

where m and d are the atomic weight and density of the metal, respectively, M and D are the molecular weight and density of scale (corrosion product) accumulated on the metallic surface, and n denotes the number of metallic atoms in the molecular formula of the corrosion product. The magnitude of the Pilling–Bedworth ratio can be used to explain the status of

surface film, i.e. whether it will be protective or not. When the volume of corrosion product is smaller than the volume of metal from which it is formed, then $Md/nmD < 1$ and in this situation it is expected that the surface film of the corrosion product contains pores and cracks that would be relatively nonprotective. When the volume of the corrosion product is larger than the volume of metal for $Md/nmD > 1$, it is expected that the surface film of the corrosion product is relatively more compressed and compact than would result in a more protective film.

Adsorption is the first step in forming a corrosion protective film or coat in the presence of aggressive media that occurs on metallic surfaces on the active sites. Several factors affect the adsorption of inhibitor on the metallic surface and isolate it including adsorption mode, chemical and electronic characteristics of the inhibitor, temperature, type of electrolyte employed, steric effects, and the nature and surface charge of metals [63]. The Langmuir adsorption isotherm is the most favorable to clarify interaction between the inhibitor and metal surface [53]. Adsorption on the corroded surfaces approximates to a steady-state adsorption that may be physical adsorption (physisorption) or chemical adsorption (chemisorption), or a mixed adsorption mechanism that is considered ideal for effective corrosion inhibition.

Physical adsorption is related to the standard free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$ in aqueous solution. If its value is -20 kJ.mol^{-1} or less negative it is associated with an electrostatic interaction between charged centers of molecules and the charged metal surface, which results in a dipole interaction of the molecules and metal surface [64]. However, chemical adsorption is a process that involves the transfer or sharing of electrons from the inhibitor to the metallic surface and results in the formation of a coordinate covalent bond. The bonding strength is much larger than physical adsorption where the value of $\Delta G_{\text{ads}}^{\circ}$ is around -40 kJ.mol^{-1} or more negative [65, 66]. Adsorption of green corrosion inhibitor retards corrosion by detraction of the active metallic surface area, leaving inactive sites on the surface exposed to corrosive media. Green inhibitors are more efficient at room temperature or low temperatures, while inhibition efficiency is decreased with an increase in temperature in most cases.

The action of green inhibitors depends on the structure of the active ingredient; many researchers have postulated numerous theories to explain the mechanism of their effect. The active ingredient derived from natural inhibitors changes from one plant species to another but their structures are closely related to their organic coordinate. As an example, garlic contains allyl propyl disulfide, mustard seeds contain an alkaloid berberine that has a long chain of aromatic rings and an N atom in the ring, carrot contains pyrrolidine, and castor seed contains the alkaloid ricinine. Eucalyptus oil contains monomtrene-1,8-cineole. Lawsonia extract contains 2-hydroxy-1,4-naphthoquinone resin and tannin, coumarin, gallic acid, and sterols. Gum exudate contains hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, and reducing and nonreducing sugars. Garcinia kola seed contains primary and secondary amines, unsaturated fatty acids, and bioflavonoids. Calyx extract contains ascorbic acid, amino acids, flavonoids, pigments, and carotene [67]. The corrosion inhibition activity of these plant extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids, etc.

3. Green inhibitors for rebar embedded in concrete

Kundu et al. [68] reviewed green inhibitors' effect in rebar embedded into concrete under an alkaline environment of nearly pH 12–13 to protect rebar from premature deterioration. Its

mechanism depends on the strong hydrophobic effect of *Bambusa arundinacea* that supports the formation of a product layer of two faced oxides (Fe_2O_3 and Fe_3O_4) adherent to the steel surface [69] or as spinel $\alpha\text{-Fe}_3\text{O}_4\text{-}\gamma\text{-Fe}_2\text{O}_3$ solid solution, which is proposed to form a passive film on steel [43]. Moreover, efficiency of *B. arundinacea* was due to its strong adsorption parallel to the metal surface, which restricted the number of surface active sites available for chloride ion ingress. In another investigation, Eyu et al. [70] studied the effect of *Vernonia amygdalina* extract within 70 days of immersion on carbon steel reinforcement in concrete exposed to a chloride-laden environment to compare efficiencies of other inhibitors, while Loto et al. [44] studied plant extract by a potentiometric method to compare the percentage of efficiency between tobacco and extract of kola nut, leaves, and bark in 5% NaCl. Okeniyi et al. [71, 72] studied the bark extract of the *Rhizophora mangle* L. plant for rebar in concrete in an acidic environment.

4. Green corrosion inhibitor based on ionic liquids

Nowadays, worldwide growing ecological awareness and strict environmental protocols prevent synthesis and utilization of hazardous traditional volatile corrosion inhibitors. So, there is a vital need for improvement in synthetic and engineering chemistry by environmentally friendly materials. Use of alternative synthetic strategies toward green synthesis [73, 74] has become necessary as multicomponent reactions (MCRs) in combination with ultrasonic (sonochemical) and microwave irradiation. So, scientists have been directed to develop drugs from plant extracts that are characterized by their natural and biological origins and nontoxic nature [75] to act as green corrosion inhibitors. Pathak et al. [76] studied different classes of drugs in different media; their effectiveness depends on their chemical composition, molecular structure, and affinities for metallic surfaces. The most effective of them depend on heteroatoms like nitrogen, oxygen, and phosphorus.

However, extraction and purification of plant extracts is tedious, exhausting, and extremely expensive as well as time consuming, and requires relatively large amounts of organic solvents that may adversely affect the environment and living beings; high temperature can also decompose the active constituents and thereby decrease relative inhibition efficiency. For these reasons the use of drugs as corrosion inhibitors for ferrous and nonferrous metals is also limited [75]. Therefore, there is a need to develop green inhibitors by proper design of the synthesis, which can be achieved by using cheap and environmentally friendly products. This is onset of green chemistry as ionic liquids that are eco-friendly and sustainable solvents composed of ions that can displace a wide range of inorganic and organic compounds. Ionic liquids follow the principles of green chemistry proposed by Anastas and Warner [77]. Ionic liquids have a promising future in the field of green chemistry, and have attracted great attention because they are widely used in various applications [78, 79]. **Figure 4** shows important properties of ionic liquids and their applications as green corrosion inhibitors [80–82]. They show high performance to adhere to the surface of steel with the formation of thin films to protect steel [78], copper [83], zinc [84], titanium, and aluminum substrates [85].

Chitosan is a linear copolymer of (1-4)-2-amido-2-deoxy-d-glucan (glucosamine) and (1-4)-2-acetamido-deoxy-d-glucan (*N*-acetylglucosamine), which are considered sources for ionic liquids [86]. Chitosan is extracted from crab shell [87] based on aminopolysaccharides and is used to produce several new materials [88]. Their high ability for functionalization makes them applicable to apply in several industrial applications because of their better solubility

Figure 4. Important properties of ionic liquids and their impact as green corrosion inhibitors for many applications.

in organic solvents and water than chitosan itself. This chemical functionality is extremely relevant when chitosan is used as a corrosion inhibitor [89]. Chitosan can inhibit the corrosion of copper in acidic media because HCl is used as a mixed-type inhibitor, which follows a Langmuir isotherm [49]. Chitosan possesses unique physicochemical properties, namely, biocompatibility, antimicrobial activity, biodegradability, and excellent film-forming ability. Indeed, it can be used to form thin coatings to protect metallic surfaces.

Ionic liquids have been classified into 11 categories according to Hajipour and Refiee [90], namely, neutral ionic liquids, acid ionic liquids, basic ionic liquids, ionic liquids with amphoteric anions, functionalized ionic liquids, protic ionic liquids, chiral ionic liquids, supported ionic liquids, bio-ionic liquids, poly-ionic liquids, and energetic ionic liquids, and have described common features and properties of these ionic liquids. However, Angell et al. [91] classified ionic liquids in four classes, including aprotic, protic, inorganic, and solvate (chelate) ionic liquids. Their adsorption on metallic surfaces takes place via chemisorption, which obeys the Langmuir adsorption isotherm as reported by Verma et al. [92] in their recent review, which showed several ionic liquids and their properties as green corrosion inhibitors for different metals and alloys such as mild steel, aluminum, copper, zinc, and magnesium in several electrolytic media. A similar observation has been reported by other authors for different metals including copper, nickel, and stainless steel [93], while Shetty et al. [94] have reviewed adsorption of ionic liquids on an aluminum surface that obeyed the Temkin adsorption isotherm.

Inhibition of metallic corrosion in the presence of ionic liquids involves blocking of anodic oxidative metallic dissolution as well as cathodic hydrogen evolution reactions [95] described as follows:

where M is the anodic dissolution of metals in aqueous corrosive solution, and $ILsC^+$ and X^- represent the cationic counterpart of the ionic liquid and anionic counterpart of the ionic liquid, respectively. Both anionic charged species attract positively charged cationic counterparts of the ionic liquids ($ILsC^+$) by electrostatic force of attraction (physisorption) and form a monomolecular layer as an insoluble complex on the metallic surface [95]. The adsorption of the $ILsC^+$ on the metallic surface causes a change in the surface polarity, which induces the adsorption of $ILsC^+$ and X^- ions again, which results in a multimolecular layer [95]. The multimolecular layers are stabilized by van der Waal's cohesion force acting between organic moieties of the ionic liquids, which causes a more closely adsorbed film at metal/electrolyte interfaces. Generally, the cationic part ($ILsC^+$) interacts with the metallic surface and forms the multimolecular layers, while the rest of the ionic liquids form hydrophobic hemimicelles, admicelles, and/or surface aggregation [95, 96]. The adsorbed multimolecular layers of the ionic liquids isolate the metal (M) from the corrosive environment and protect it from corrosive dissolution.

During cathodic hydrogen evolution reactions, hydronium ions are adsorbed on the metallic surface by the Volmer mechanism followed by discharge of hydrogen gas by the Heyrovsky and Tafel mechanism [97, 98], represented as follows:

The cationic part of ionic liquids ($ILsC^+$) starts competing with hydrogen ions for electrons; however, $ILsC^+$ has a larger molecular size so replaces a greater number of water molecules from the metallic surface. After their adsorption the cationic part of the ionic liquids accepts electrons from the metal (M), which results in the formation of electrically neutral ionic liquids (inhibitors). The neutral species transfer (donation) their nonbonding (of heteroatoms) and π -electrons into the d-orbitals of the surface metallic atoms resulting in the formation of coordinate bonds between metal and ionic liquids (chemisorption) as reported for several organic conventional inhibitors [95]. However, metals are already electron-rich species; this type of donation causes interelectronic repulsion, which results in the transfer of electrons from d-orbitals of the surface metallic atoms to antibonding molecular orbitals of the ionic liquids (retrodonation). Both donation and retrodonation strengthen each other through synergism [99].

Development of corrosion inhibitors requires correlating the inhibition efficiency of the inhibitors with their molecular properties through study interactions between inhibitors and the metallic surface and describing the adsorption behavior of ionic liquids on the metallic surface. This is achieved by density functional theory (DFT). DFT is one of the most important methods

used in theoretical chemistry for corrosion inhibition to accurately predict the inhibition efficiencies based on the calculations provided by mechanistic information about metal–inhibitor interactions and can be performed for inhibitor molecules even before their synthesis [100–105].

5. Vapor-phase inhibitors

Vapor-phase inhibitors (VPI) are volatile corrosion inhibitors. They are considered a revolution in green inhibitors and are required in many fields covering electronics, packaging, industrial processing, reinforced concrete, coatings, and metalworking fluids due to their nontoxic properties. They are free of nitrites, halogens, and phosphates, and are completely safe to handle. In addition, they also inhibit the corrosion of ferrous and nonferrous metals. In a review of the literature, Bastidas et al. [106] studied various factors influencing VPI performance and mechanisms. Nanovapor-phase inhibitors made from renewable agricultural by-products do not destabilize the natural balance of the environment. Their impact depends on their diffusion, filling all void spaces and active areas with protective vapor molecules that

Figure 5. Accessibility of green corrosion inhibitors from nature with approximated cost of extraction and percentage of efficiency according to the cited literature [109–117].

are attracted to metallic surfaces and adsorbed physically and/or chemically onto the resulting formation of a nanoprotective barrier layer [107, 108].

Several factors must be considered to control the cost of extractions, which sometimes may be very high when the quantities needed are high. Also, the estimated percentage of an inhibitor's efficiency must be controlled, including temperature, concentration of inhibitors, type of metallic surface exposed to aggressive environments, etc. **Figure 5** summarizes the accessibility of green corrosion inhibitors from nature with approximate estimations of cost of extraction between low, medium, and expensive, and the percentage of efficiency according to the cited literature.

The objective of this chapter was to review natural compounds as effective green corrosion inhibitors because of their biodegradability, easy availability, and nontoxic nature. The literature revealed that natural plant extracts are effective green corrosion inhibitors against various metals and alloys. In addition, the chapter focused on why the efficiency of green and sustainable inhibitors of ionic liquids for the corrosion of metals and alloys is preferred compared to traditional corrosion inhibitors because of their advantageous physiochemical properties. Finally, attention was given to the adsorption behavior of ionic liquids generally, following the Langmuir isotherm, the Temkin adsorption isotherm, and in particular the adsorption behavior of ionic liquids on metallic surfaces using DFT-based quantum chemical calculations. Quantum chemical calculations (DFT) provide a good insight into the inhibition mechanism and experimental order of inhibition efficiency. The tendency to explore vapor-phase corrosion inhibitors and green nanoinhibitors is a new area for future research.

A lot of potential is still untapped, especially computational modeling of the major extract components of various metals and alloys. Further research should also be focused on plant extraction methods and their active constituents as well as scale-up experiments for industrial applications that are needed to commercialize these natural extracts to effectively replace conventional chemicals.

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References

- [1] Hefter GT, North NA, Tan SH. Organic corrosion inhibitors in neutral solutions; part 1—inhibition of steel, copper, and aluminum by straight chain carboxylates. *Corrosion*. 1997;**53**(8):657-667. DOI: 10.5006/1.3290298
- [2] Bethencourt M, Botana FJ, Calvino JJ, Marcos M, Rodriguez-Chacon MA. Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: A review. *Corrosion Science*. 1998;**40**(11):1803-1819. DOI: 10.1016/S0010-938X(98)00077-8

- [3] Sabirneeza AAF, Geethanjali R, Subhashini S. Polymeric corrosion inhibitors for iron and its alloys: a review. *Chemical Engineering Communications*. 2015;**202**(22):232-244. DOI: 10.1080/00986445.2014.934448
- [4] Branzoi F, Branzoi V, Licu C. Corrosion inhibition of carbon steel in cooling water systems by new organic polymers as green inhibitors. *Materials and Corrosion—Werkstoffe und Korrosion*. 2014;**65**(6):637-647. DOI: 10.1002/maco.201206579
- [5] Krishnaveni K, Ravichandran J. Effect of aqueous extract of leaves of *Morinda tinctoria* on corrosion inhibition of aluminium surface in HCl medium. *Transactions of Nonferrous Metals Society of China*. 2014;**24**(8):2704-2712. DOI: 10.1016/S1003-6326(14)63401-4
- [6] Singh P, Srivastava V, Quraishi MA. Novel quinoline derivatives as green corrosion inhibitors for mild steel in acidic medium: electrochemical, SEM, AFM, and XPS studies. *Journal of Molecular Liquids*. 2016;**216**(1):164-173. DOI: 10.1016/j.molliq.2015.12.086
- [7] Oguzie EE. Inhibition of acid corrosion of mild steel by *Telfaria occidentalis* extract. *Pigment & Resin Technology*. 2005;**34**(6):321-326. DOI: 10.1108/03699420510630336
- [8] Sanatkumar BS, Nayak J, Shetty AN. Influence of 2-(4-chlorophenyl)-2-oxoethyl benzoate on the hydrogen evolution and corrosion inhibition of 18 Ni 250 grade weld aged maraging steel in 1.0 M sulfuric acid medium. *International Journal of Hydrogen Energy*. 2012;**37**(11):9431-9442. DOI: 10.1016/j.ijhydene.2012.02.165
- [9] Manamela KM, Murulana LC, Kabanda MM, Ebenso EE. Adsorptive and DFT studies of some imidazolium based ionic liquids as corrosion inhibitors for zinc in acidic medium. *International Journal of Electrochemical Science*. 2014;**9**(6):3029-3046
- [10] Baldwin J. British Patent. 1895:2327
- [11] Saleh RM, El-Hosary AA. Corrosion inhibition by naturally occurring substances. Effect of Pomegranate Juice and the Aqueous Extracts of Pomegranate Fruit Shells, Tamarind Fruits and Tea Leaves on the Corrosion of Al. In: El-Hosary, editor. *Electrochemistry*; 13th ed.; Karaikudi. CECRI; 1972
- [12] El-Hosary AA, Saleh RM, El Din AMS. Corrosion inhibition by naturally occurring substances: the effect of *Hibiscus subdariffa* (karkade) extract on the dissolution of Al and Zn. *Corrosion Science*. 1972;**12**(12):897-904. DOI: 10.1016/S0010-938X(72)80098-2
- [13] Srivastav K, Srivastava P. Studies on plant materials as corrosion inhibitors. *British Corrosion Journal*. 1981;**16**(4):221-223. DOI: 10.1179/000705981798274788
- [14] Saleh RM, Ismail AA, El Hosary AA. Corrosion inhibition by naturally occurring substances: VII. The effect of aqueous extracts of some leaves and fruit-peels on the corrosion of steel, Al, Zn and Cu in acids. *British Corrosion Journal*. 1982;**17**(3):131-135. DOI: 10.1179/000705982798274345
- [15] Zucchi F, Omar IH. Plant extracts as corrosion inhibitors of mild steel in HCl solutions. *Surface Technology*. 1985;**24**(4):391-399. DOI: 10.1016/0376-4583(85)90057-3
- [16] Zakvi SJ, Mehta GN. Acid corrosion of mild steel and its inhibition by *Swertia angustifolia*—study by electrochemical techniques. *Transactions of the SAEST*. 1988;**23**(4):407-410

- [17] Ekpe UJ, Ebenso EE, Ibok UJ. Inhibitory action of *Azadirachta indica* leaves extract on the corrosion of mild steel in H_2SO_4 . Journal of West African Journal of Biological and Applied Chemistry. 1994;**37**:13-30
- [18] Quraishi MA, Farooqi IH, Saini PA. Investigation of some green compounds as corrosion and scale inhibitors for cooling systems. Corrosion. 1999;**55**(5):493-497. DOI: 10.5006/1.3284011
- [19] Sakthivel P, Nirmala PV, Umamaheswari S, Antony AAA, Paruthimal Kalaigan G, Gopalan A, Vasudevan T. Corrosion inhibition of mild steel by extracts of *Pongamia glabra* and *Annona squamosa* in acidic media. Bulletin of Electrochemistry. 1999;**15**(2):83-86
- [20] Verma SA, Mehta GN. Effect of acid extracts of *Acacia arabica* on acid corrosion of mild steel. Bulletin of Electrochemistry. 1999;**15**(2):67-70
- [21] El-Etre AY, Abdallah M. Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water. Corrosion Science. 2000;**42**(4):731-738. DOI: 10.1016/S0010-938X(99)00106-7
- [22] Klišćić M, Radošević J, Gudic S, Katalinic V. Aqueous extract of *Rosmarinus officinalis* L. as inhibitor of Al–Mg alloy corrosion in chloride solution. Journal of Applied Electrochemistry. 2000;**30**(7):823-830
- [23] Martinez S, Štern I. Inhibitory mechanism of low-carbon steel corrosion by mimosa tannin in sulphuric acid solutions. Journal of Applied Electrochemistry. 2001;**31**(9):973-978
- [24] El-Etre AY. Inhibition of acid corrosion of aluminum using vaniline. Corrosion Science. 2001;**43**(6):1031-1039. DOI: 10.1016/S0010-938X(00)00127-X
- [25] Quraishi MA, Jamal D. Approach to corrosion inhibition by some green inhibitors based on oleochemicals. Bulletin of Electrochemistry. 2002;**18**(7):289-294
- [26] Khamis E, Alandis N. Herbs as new type of green inhibitors for acidic corrosion of steel. Material Wissenschaft und Werkstofftechnik. 2002;**33**(9):550-554. DOI: 10.1002/1521-4052
- [27] Müller B. Corrosion inhibition of aluminium and zinc pigments by saccharides. Corrosion Science. 2002;**44**(7):1583-1591. DOI: 10.1016/S0010-938X(01)00170-6
- [28] El-Etre AY. Inhibition of aluminum corrosion using *Opuntia* extract. Corrosion Science. 2003;**45**(11):2485-2495. DOI: 10.1016/S0010-938X(03)00066-0
- [29] Avwiri GO, Igbo FO. Inhibitive action of *Vernonia amygdalina* on the corrosion of aluminium alloys in acidic media. Material Letters. 2003;**57**(22):3705-3711. DOI: 10.1016/S0167-577X(03)00167-8
- [30] Parikh KS, Joshi KJ. Natural compounds onion (*Allium cepa*), garlic (*Allium sativum*) and bitter gourd (*Momordica charantia*) as corrosion inhibitors for mild steel in hydrochloric acid. Transactions—Society for the Advancement of Electrochemical Science and Technology. 2004;**39**(1/2):29-35
- [31] Abdallah M. Guar gum as corrosion inhibitor for carbon steel in sulfuric acid solutions. Portugaliae Electrochimica Acta. 2004;**22**(2):161-175

- [32] Gunasekaran G, Chauhan LR. Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium. *Electrochimica Acta*. 2004;**49**(25):4387-4395. DOI: 10.1016/j.electacta.2004.04.030
- [33] Orubite KO, Oforka NC. Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of *Nypa fruticans* Wurmb. *Materials Letters*. 2004;**58**(11):1768-1772. DOI: 10.1016/j.matlet.2003.11.030
- [34] Anthony N, Malarvizhi E, Maheshwari P, Rajendran S, Palaniswamy N. Corrosion inhibition of caffein-Mn²⁺ system. *Indian Journal Chemical Technology*. 2004;**11**(May):346-350
- [35] Chaieb E, Bouyanzer A, Hammouti B, Benkaddour M. Inhibition of the corrosion of steel in 1 M HCl by eugenol derivatives. *Applied Surface Science*. 2005;**246**(1):199-206. DOI: 10.1016/j.apsusc.2004.11.011
- [36] Sathiyathan R, Maruthamuthu S, Selvanayagam M, Mohanan S, Palaniswamy N. Corrosion inhibition of mild steel by ethanolic extracts of *Ricinus communis* leaves. *Indian Journal Chemical Technology*. 2005;**12**(May):356-360
- [37] Li Y, Zhao P, Liang Q, Hou B. Berberine as a natural source inhibitor for mild steel in 1 M H₂SO₄. *Applied Surface Science*. 2005;**252**(5):1245-1253. DOI: 10.1016/j.apsusc.2005.02.094
- [38] Abdel-Gaber AM, Abd-El-Nabey BA, Sidahmed IM, El-Zayady AM, Saadawy M. Inhibitive action of some plant extracts on the corrosion of steel in acidic media. *Corrosion Science*. 2006;**48**(9):2765-2779. DOI: 10.1016/j.corsci.2005.09.017
- [39] Oguzie EE. Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract. *Corrosion Science*. 2007;**49**(3):1527-1539. DOI: 10.1016/j.corsci.2006.08.009
- [40] Umoren SA, Obot IB, Ebenso EE, Obi-Egbedi N. Studies on the inhibitive effect of exudate gum from *Dacryodes edulis* on the acid corrosion of aluminium. *Portugaliae Electrochimica Acta*. 2008;**26**(2):199-209
- [41] Umoren SA, Obot IB, Ebenso EE, Obi-Egbedi NO. The inhibition of aluminium corrosion in hydrochloric acid solution by exudate gum from *Raphia hookeri*. *Desalination*. 2009;**247**(1-3):561-572
- [42] Umoren SA, Ekanem UF. Inhibition of mild steel corrosion in H₂SO₄ using exudate gum from *Pachylobus edulis* and synergistic potassium halide additives. *Journal Chemical Engineering Communications*. 2010;**197**(10):1339-1356
- [43] Abdulrahman AS, Ismail M. Green plant extract as a passivation-promoting inhibitor for reinforced concrete. *International Journal of Engineering Science and Technology*. 2011;**3**(Aug.):6484-6489
- [44] Loto CA, Loto RT, Popoola API. Electrode potential monitoring of effect of plants extracts addition on the electrochemical corrosion behaviour of mild steel reinforcement in concrete. *International Journal of Electrochemical Science*. 2011;**6**(Aug):3452-3465

- [45] Garai S, Garai S, Jaisankar P, Singh JK, Elango A. A comprehensive study on crude methanolic extract of *Artemisia pallens* (Asteraceae) and its active component as effective corrosion inhibitors of mild steel in acid solution. *Corrosion Science*. 2012;**60**:193-204. DOI: 10.1016/j.corsci.2012.03.036
- [46] Loto CA, Joseph OO, Loto RT, Popoola API. Inhibition effect of *Vernonia amygdalina* extract on the corrosion of mild steel reinforcement in concrete in 3.5M NaCl environment. *International Journal of Electrochemical Science*. 2013;**8**:11087-11100
- [47] Left DB, Zertoubi M, Khoudali S, Benaissa M, Irhzo A, Azzi M. Effect of methanol extract of *Chamaerops humilis* L. leaves (MECHLL) on the protection performance of oxide film formed on reinforcement steel surface in concrete simulated pore solution. *International Journal of Electrochemical Science*. 2013;**8**(10):11768-11781
- [48] Shah AM, Rahim AA, Hamid SA, Yahya S. Green inhibitors for copper corrosion by mangrove tannin. *International Journal of Electrochemical Science*. 2013;**8**:2140-2153
- [49] El-Haddad MN. Chitosan as a green inhibitor for copper corrosion in acidic medium. *International Journal of Biological Macromolecules*. 2013;**55**:142-149. DOI: 10.1016/j.ijbiomac.2012.12.044
- [50] Bozorg M, Shahrabi Farahani T, Neshati J, Chaghazardi Z, Mohammadi Ziarani G. *Myrtus communis* as green inhibitor of copper corrosion in sulfuric acid. *Industrial & Engineering Chemistry Research*. 2014;**53**(11):4295-4303. DOI: 10.1021/ie404056w
- [51] Mourya P, Banerjee S, Singh MM. Corrosion inhibition of mild steel in acidic solution by *Tagetes erecta* (marigold flower) extract as a green inhibitor. *Corrosion Science*. 2014;**85**(Aug.):352-363. DOI: org/10.1016/j.corsci.2014.04.036
- [52] Okeniyi JO, Loto CA, Popoola API. *Morinda lucida* effects on steel-reinforced concrete in 3.5% NaCl: implications for corrosion-protection of wind-energy structures in saline/marine environments. *Energy Procedia*. 2014;**50**:421-428. DOI: 10.1016/j.egypro.2014.06.051
- [53] Flores-De los Ríos JP, Sánchez-Carrillo M, Nava-Dino CG, Chacón-Nava JG, González-Rodríguez, Huape-Padilla E, Neri-Flores MA, Martínez-Villafañe A. *Opuntia ficus-indica* extract as green corrosion inhibitor for carbon steel in 1 M HCl solution. *Journal of Spectroscopy*. 2015;**2015**:14692-14701/714692. DOI: 10.1155/2015/714692
- [54] Abd-El-Nabey BA, El-Housseiny S, El-Naggar GA, Matter EA, Esmail G. Inhibitive action of *Alhagi maurorum* plant extract on the corrosion of copper in 0.5 M H₂SO₄. *Physical Chemistry*. 2015;**5**(3):49-62. DOI:10.5923/j.pc.20150503.01
- [55] Deyab MA. Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution. *Journal of Industrial and Engineering Chemistry*. 2015; **22**(Feb.):384-389. DOI: org/10.1016/j.jiec.2014.07.036
- [56] Aribi S, Olusegun SJ, Ibhadiyi LJ, Oyetunji A, Folorunso DO. Green inhibitors for corrosion protection in acidizing oilfield environment. *Journal of the Association of Arab Universities for Basic and Applied Sciences*. 2016 (In Press). DOI: 10.1016/j.jaubas.2016.08.001

- [57] Gobara M, Zaghloul B, Baraka A, Elsayed M, Zorainy M, Mokhtar Kotb M, Elnabarawy H. Green corrosion inhibition of mild steel to aqueous sulfuric acid by the extract of *Corchorus olitorius* stems. *Materials Research Express*. 2017;**4**(4):046504. DOI: 10.1088/2053-1591/aa664a
- [58] Shehata OS, Khorshed LA, Mandour HS. Effect of acetamide derivative and its Mn-complex as corrosion inhibitor for mild steel in sulphuric acid. *Egyptian Journal of Chemistry*. 2017;**60**(2):243-259. DOI: 10.21608/ejchem.2017.674.1014
- [59] Manimegalai S, Manjula P. Thermodynamic and adsorption studies for corrosion inhibition of mild steel in aqueous media by *Sargassum swartzii* (brown algae). *Journal of Material and Environmental Science*. 2015;**6**(6):1629-1637
- [60] Roh Y, Lee SY, Elless MP. Characterization of corrosion products in the permeable reactive barriers. *Environmental Geology*. 2000;**40**(1-2):184-194. DOI: 10.1007/s002540000178
- [61] Xu C, Gao W. Pilling-Bedworth ratio for oxidation of alloys. *Materials Research Innovations*. 2000;**3**(4):231-235. DOI: 10.1007/s100190050008
- [62] Bedworth RE, Pilling NB. The oxidation of metals at high temperatures. *Journal of the Institute of Metals*. 1923;**29**(3):529-582
- [63] Maayta AK, Al-Rawashdeh NAF. Inhibition of acidic corrosion of pure aluminum by some organic compounds. *Corrosion Science*. 2004;**46**(5):1129-1140. DOI: 10.1016/j.corsci.2003.09.009
- [64] Damaskin BB, Petrii OA, Batrakov VV. Adsorption. New York: Plenum Press; 1971
- [65] Roberge PR. Handbook of corrosion engineering. McGraw-Hill; 2000
- [66] Martinez S, Štern I. Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel/mimosa tannin/sulfuric acid. *Applied Surface Science*. 2002;**199**(1):83-89. DOI: 10.1016/S0169-4332 (02) 00546-9
- [67] Rani BE, Basu BB. Green inhibitors for corrosion protection of metals and alloys: an overview. *International Journal of Corrosion*. 2011;**2012**:15. DOI: 10.1155/2012/380217
- [68] Kundu M, Prasad SK, Virendra K. A review article on green inhibitors of reinforcement concrete corrosion. *International Journal of Emerging Research in Management & Technology*. 2016;**5**:42-46
- [69] Asipita SA, Ismail M, Majid MZA, Abdullah CS, Mirza J. Green *Bambusa arundinacea* leaves extract as a sustainable corrosion inhibitor in steel reinforced concrete. *Journal of Cleaner Production*. 2014;**67**:139-146. DOI: 10.1016/j.jclepro.2013.12.033
- [70] Eyu DG, Esah H, Chukwuekezie C, Idris J, Mohammad I. Effect of green inhibitor on the corrosion behaviour of reinforced carbon steel in concrete. *ARON Journal of Engineering and Applied Science*. 2013;**8**(5):326-332
- [71] Okeniyi JO, Loto CA, Popoola API. Corrosion inhibition performance of *Rhizophora mangle* L. bark-extract on concrete steel-reinforcement in industrial/microbial simulating-environment. *International Journal Electrochemical Science*. 2014;**9**(8):4205-4216

- [72] Okeniyi JO, Loto CA, Popoola API. *Rhizophora mangle* L. effects on steel-reinforced concrete in 0.5 M H₂SO₄: implications for corrosion-degradation of wind-energy structures in industrial environments. *Energy Procedia*. 2014;**50**:429-436. DOI: 10.1016/j.egypro.2014.06.052
- [73] Carp O, Visnescu D, Patrinoiu G, Tirsoaga A, Paraschiv C, Tudose M. Green synthetic strategies of oxide materials: Polysaccharides-assisted synthesis. Part 1. Polysaccharide Roles in Metal Oxides Synthesis. *Revue Roumain de Chimie*. 2010;**55**(10):705-709. DOI: 10.1002/chin.201139239
- [74] Hulsbosch J, De Vos DE, Binnemans K, Ameloot R. Biobased ionic liquids: solvents for a green processing industry? *ACS Sustainable Chemistry & Engineering*. 2016;**4**(6):2917-2931. DOI: 10.1021/acssus chem eng.6 b00553
- [75] Verma C, Chauhan DS, Quraishi MA. Drugs as environmentally benign corrosion inhibitors for ferrous and nonferrous materials in acid environment: an overview. *Journal of Materials and Environmental Sciences (JMES)*. 2017;**8**(11):4040-4051
- [76] Pathak RK, Mishra P. Drugs as corrosion inhibitors: a review. *International Journal of Science and Research (IJSR)*. 2016;**5**(4):671-677
- [77] Anastas PT, Warner JC. *Green Chemistry: Theory and Practice*. New York: Oxford University Press; 2000
- [78] Kowsari E, Payami M, Amini R, Ramezanzadeh B, Javanbakht M. Task-specific ionic liquid as a new green inhibitor of mild steel corrosion. *Applied Surface Science*. 2014;**289**:478-486. DOI: 10.1016/j.apsusc.2013.11.017
- [79] Scendo M, Uznanska J. The effect of ionic liquids on the corrosion inhibition of copper in acidic chloride solutions. *International Journal of Corrosion*. 2011;**2011**:3. DOI: 10.1155/2011/718626
- [80] Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*. 2005;**30**(1):38-70. DOI: 10.1016/j.progpolymsci.2004.11.002
- [81] Ng LT, Swami S. IPNs based on chitosan with NVP and NVP/HEMA synthesised through photoinitiator-free photopolymerisation technique for biomedical applications. *Carbohydrate Polymers*. 2005;**60**(4):523-528. DOI: 10.1016/j.carbpol.2005.03.009
- [82] Ham-Pichavant F, Sèbe G, Pardon P, Coma V. Fat resistance properties of chitosan-based paper packaging for food applications. *Carbohydrate Polymers*. 2005;**61**(3):259-265. DOI: 10.1016/j.carbpol.2005.01.020
- [83] Scendo M, Uznanska J. The effect of ionic liquids on the corrosion inhibition of copper in acidic chloride solutions. *International Journal of Corrosion*. 2011;**2011**:13. DOI: 10.1155/2011/718626
- [84] Manamela KM, Murulana LC, Kabanda MM, Ebenso EE. Adsorptive and DFT studies of some imidazolium based ionic liquids as corrosion inhibitors for zinc in acidic medium. *International Journal of Electrochemical Science*. 2014;**9**(6):3029-3046

- [85] Wang YC, Lee TC, Lin JY, Chang JK, Tseng CM. Corrosion properties of metals in dicyanamide-based ionic liquids. *Corrosion Science*. 2014;**78**:81-88. DOI: 10.1016/j.corsci.2013.09.002
- [86] Shukla SK, Mishra AK, Arotiba OA, Mamba BB. Chitosan-based nanomaterials: a state-of-the-art review. *International Journal of Biological Macromolecules*. 2013;**59**:46-58. DOI: 10.1016/j.ijbiomac.2013.04.043
- [87] Paul W, Sharma CP. Chitosan, a drug carrier for the 21st century: A review. *STP Pharma Science*. 2000;**10**(1):5-22
- [88] Yao Z, Zhang C, Ping Q, Yu L. A series of novel chitosan derivatives: synthesis, characterization and micellar solubilization of paclitaxel. *Carbohydrate Polymers*. 2007;**68**(4):781-792. DOI: 10.1016/j.carbpol.2006.08.023
- [89] Mima S, Miya M, Iwamoto R, Yoshikawa S. Highly deacetylated chitosan and its properties. *Journal of Applied Polymer Science*. 1983;**28**(6):1909-1917. DOI: 10.1002/app.1983.070280607
- [90] Hajipour AR, Refiee F. Recent progress in ionic liquids and their applications in organic synthesis. *Organic Preparations and Procedures International*. 2015;**47**(4):249-308. DOI: 10.1080/00304948.2015.1052317
- [91] Angell CA, Ansari Y, Zhao Z. Ionic liquids: past, present and future. *Faraday Discussions*. 2012;**154**:9-27. DOI: 10.1039/C1FD00112D
- [92] Verma C, Ebenso EE, Quraishi MA. Ionic liquids as green and sustainable corrosion inhibitors for metals and alloys: an overview. *Journal of Molecular Liquids*. 2017;**233**:403-414. DOI: 10.1016/j.molliq.2017.02.111
- [93] Lin PC, Sun IW, Chang JK, Su CJ, Lin JC. Corrosion characteristics of nickel, copper, and stainless steel in a Lewis neutral chloroaluminate ionic liquid. *Corrosion Science*. 2011;**53**(12):4318-4323. DOI: 10.1016/j.corsci.2011.08.047
- [94] Shetty SK, Shetty AN. Ionic liquid as an effective corrosion inhibitor on 6061 Al-15 Vol. Pct. SiC (p) composite in 0.1 M H₂SO₄ medium—an ecofriendly approach. *Canadian Chemical Transactions*. 2015;**3**:41-64. DOI: 10.13179/canchemtrans.2015.03.01.0160
- [95] Likhanova NV, Domínguez-Aguilar MA, Olivares-Xometl O, Nava-Entzana N, Arce E, Dorantes H. The effect of ionic liquids with imidazolium and pyridinium cations on the corrosion inhibition of mild steel in acidic environment. *Corrosion Science*. 2010;**52**(6):2088-2097. DOI: 10.1016/j.corsci.2010.02.030
- [96] Fuchs-Godec R. The adsorption, CMC determination and corrosion inhibition of some N-alkyl quaternary ammonium salts on carbon steel surface in 2M H₂SO₄. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006;**280**(1):130-139. DOI: 10.1016/j.colsurfa.2006.01.046
- [97] Gennero de Chialvo MR, Chialvo AC. Hydrogen evolution reaction: analysis of the Volmer-Heyrovsky-Tafel mechanism with a generalized adsorption model. *Journal of Electroanalytical Chemistry*. 1994;**372**(1-2):209-223. DOI: 10.1016/0022-0728(93)03043-O

- [98] Gennero de Chialvo MR, Chialvo AC. The Tafel–Heyrovsky route in the kinetic mechanism of the hydrogen evolution reaction. *Electrochemistry Communications*. 1999;**1**(9):379-382
- [99] Migahed MA. Electrochemical investigation of the corrosion behaviour of mild steel in 2 M HCl solution in presence of 1-dodecyl-4-methoxy pyridinium bromide. *Materials Chemistry and Physics*. 2005;**93**(1):48-53. DOI: 10.1016/j.matchemphys.2005.02.003
- [100] Verma C, Olasunkanmi LO, Ebenso EE, Quraishi MA, Obot IB. Adsorption behavior of glucosamine-based, pyrimidine-fused heterocycles as green corrosion inhibitors for mild steel: experimental and theoretical studies. *Journal of Physical Chemistry C*. 2016;**120**(21):11598-11611. DOI: 10.1021/acs.jpcc.6b04429
- [101] Verma C, Olasunkanmi LO, Obot IB, Ebenso EE, Quraishi MA. 2,4-Diamino-5-(phenylthio)-5H-chromeno [2,3-b] pyridine-3-carbonitriles as green and effective corrosion inhibitors: gravimetric, electrochemical, surface morphology and theoretical studies. *RSC Advances*. 2016;**6**(59):53933-53948. DOI: 10.1039/c6ra04900a
- [102] Verma C, Olasunkanmi LO, Obot IB, Ebenso EE, Quraish MA. 5-Arylpyrimido-[4,5-b] quinoline-diones as new and sustainable corrosion inhibitors for mild steel in 1 M HCl: a combined experimental and theoretical approach. *RSC Adv*. 2016;**6**(19):15639-15654. DOI: 10.1039/C5RA27417F
- [103] Suresh SJS. Recent advances in ionic liquids: green unconventional solvents of this century: part I. *Green Chemistry Letters and Reviews*. 2011;**4**(4):289-310. DOI: doi.org/10.1080/17518253.2011.572294310
- [104] Murulana LC, Singh AK, Shukla SK, Kabanda MM, Ebenso EE. Experimental and quantum chemical studies of some bis(trifluoromethyl-sulfonyl) imide imidazolium-based ionic liquids as corrosion inhibitors for mild steel in hydrochloric acid solution. *Industrial & Engineering Chemistry Research*. 2012;**51**(40):13282-13299. DOI: 10.1021/ie300977d
- [105] Yadav DK, Quraishi MA. Application of some condensed uracils as corrosion inhibitors for mild steel: gravimetric, electrochemical, surface morphological, UV–visible, and theoretical investigations. *Industrial & Engineering Chemical Research*. 2012;**51**(46):14966-14979. DOI: 10.1021/ie301840y
- [106] Bastidas DM, Cano E, Mora EM. Volatile corrosion inhibitors: a review. *Anti-Corrosion Methods and Materials*. 2005;**52**(2):71-77. DOI: 10.1108/00035590510584771
- [107] Subramanian A, Natesan M, Muralidharan VS, Balakrishnan K, Vasudevan T. An overview: vapor phase corrosion inhibitors. *Corrosion*. 2000;**56**(2):144-155. DOI: 10.5006/1.3280530
- [108] Vuorinen E, Kálmán E, Focke W. Introduction to vapour phase corrosion inhibitors in metal packaging. *Surface Engineering*. 2004;**20**(4):281-284. DOI: 10.1179/026708404225016481
- [109] Honarmand E, Mostaanzadeh H, Motaghedifard MH, Hadia M, Khayadkashanic M. Inhibition effect of opuntia stem extract on corrosion of mild steel: a quantum computational assisted electrochemical study to determine the most effective components in

- inhibition. *Protection of Metals and Physical Chemistry of Surfaces*. 2017;**53**(3):560-572. DOI: 10.1134/S20702511703008X
- [110] Ating EI, Umoren SA, Udousoro II, Ebenso EE, Udoh AP. Leaves extract of *Ananas sativum* as green corrosion inhibitor for aluminum in hydrochloric acid solution. *Green Chemistry Letters and Reviews*. 2010;**3**(2):61-68. DOI: 10.1080/17518250903505253
- [111] Subhashini S. Corrosion inhibition study of mild steel in acid media by extract of some leguminous seeds as eco-friendly inhibitors. *Journal Camel Practice Research*. 2004;**11**(1):27-34
- [112] Espinoza-Vázquez A, Rodríguez-Gómez FJ. Caffeine and nicotine in 3% NaCl solution with CO₂ as corrosion inhibitors for low carbon . *RSC Advances*. 2016;**6**(74):70226-70236. DOI: 10.1039/C6RA07673D
- [113] Loto CA, Popoola API. Effect of tobacco and kola tree extracts on the corrosion inhibition of mild steel in acid chloride. *International Journal of Electrochemical Science*. 2011;**6**(Aug):3264-3276
- [114] Oukhrib R, El Ibrahim B, Bourzi H, El Mouaden K, Jmiai A, El Issami S, Bammou L, Bazzi L. Quantum chemical calculations and corrosion inhibition efficiency of biopolymer "chitosan" on copper surface in 3% NaCl. *Journal of Material and Environmental Sciences*. 2017;**8**(1):195-208
- [115] Kasshanna S, Rostron P. Novel synthesis and characterization of vegetable oil derived corrosion inhibitors. *Journal of Material and Environmental Sciences*. 2017;**8**(12):4292-4300
- [116] Verma C, Chauhan DS, Quraishi MA. Drugs as environmentally benign corrosion inhibitors for ferrous and nonferrous materials in acid environment: an overview. *Journal of Material and Environmental Sciences*. 2017;**8**(11):4040-4051
- [117] Kumar H, Saini V, Yadav V. Study of vapour phase corrosion inhibitors for mild steel under different atmospheric conditions. *International Journal of Engineering and Innovative Technology*. 2013;**3**(3):206-211