Chapter 9

Case-Studies on Green Corrosion Inhibitors

M. Ramesh^{1*}, L. Rajeshkumar²

¹Department of Mechanical Engineering, KIT-Kalaignarkaranidhi Institute of Technology,
Coimbatore-641402, Tamil Nadu, India

²Department of Mechanical Engineering, KPR Institute of Engineering and Technology,
Coimbatore-641407, Tamil Nadu, India

*mramesh97@gmail.com

Abstract

Corrosion in metals and its alloys is an inevitable phenomenon but can be controlled by suitable classical methods like process control, cathode protection, surface treating methods, impurity reduction in metals and addition of metals to form alloys. Nevertheless, the employment of corrosion inhibitors is still a noteworthy and simplest of all the above processes in protecting the metals and alloys especially in acidic media. Protection of metals against corrosion not only prevents corrosion but also is beneficial in terms of money loss as far as industrial equipment, surfaces and vessels are concerned. Since the use of organic and inorganic inhibitors are highly discouraged due to their high cost and toxicity, necessity has adequately aroused the development of corrosion inhibitors which are natural and green. Trends, nowadays, focussed in controlling corrosion in various metals and alloys through green corrosion inhibitors consisting of natural elements alone. In contrast to the inorganic inhibitors, green corrosion inhibitors are characterized by biodegradability, low cost and meagre toxicity. Several researchers are now turning themselves towards the research of green inhibitors which are of no threat to humans and the ecosystem. The current discussion is focussed on the fundamentals of corrosion, corrosion inhibition, materials used for it and case studies of green inhibitors used for corrosion control in various conventional and monolithic metals.

Keywords

Corrosion, Green Inhibitors, Inhibition, Biodegradability, Plant Extracts

Contents

Case-Studies on Green Corrosion Inhibitors	204
1. Introduction.....	205
2. Corrosion inhibitors	207
3. Use of green corrosion inhibitors	209
4. Plant extracts as corrosion inhibitors	210
4.1 Corrosion inhibitors for low carbon steel	210
4.2 Corrosion inhibitors for mild steel.....	211
4.3 Corrosion inhibitors for aluminium in corrosion media.....	213
4.4 Natural gums as corrosion inhibitors for metals.....	215
4.5 Ionic liquids as green corrosion inhibitors	216
Conclusion.....	217
References	218

1. Introduction

When a reaction between metals and alloys with the environment takes place then it could be termed as corrosion. Usually at the time of corrosion the chemical or electrochemical reaction of the metals and alloys, used in different environments and applications, end up in the depletion of the top layer of the substrate due to its contact with acidic or aqueous environments. Corrosion of metal results in the loss of the metal considerably due to its environment. It is also a fact that corrosion is a never ending problem that requires sole attention but could not be eliminated completely. Its priority of addressing is very important such that it has direct influence over the conservation, safety and economic aspects in numerous applications like natural, medical, metallurgical and chemical engineering. Corrosion also affects the design of mechanical elements in various sizes and functions and also their lifespan. Corrosion induces heavy losses in terms of finance by directly affecting the safety, product loss, leakage, renewal and replacement of affected metals and alloy structures and ultimately resulting in environmental pollution and loss of efficiency. Depletion of metal substrate is often associated with heavy loss in productivity because of the faulty operation of corroded products and industrial instruments due to their presence in aqueous medium. Corrosion becomes one of the main problems that must be

eliminated to avoid such harmful effects and if left unobserved, may result in equipment failure by all means [1].

National Association of Corrosion Engineers (NACE) performed an analysis in the year 1998 and concluded that a huge sum of 276 billion dollars was pumped into the economy for controlling corrosion which roughly approximates to 3.1 % of GDP of the USA. The amount magnified to 2.2 trillion dollars during the year 2011 for the US. During the Global Corrosion Summit that took place in New Delhi during the year 2011, it was declared that an amount of Rs. 2 lakh crore was spent on corrosion. Aforementioned data were possibly outdated, recent analysis of NACE during the year 2017 revealed that the global corrosion cost was 2.5 trillion US dollars approximately and it holds upto 3.4 % of global GDP [2]. A survey of NACE showed that approximate corrosion cost in South Africa was also approximately 130 billion US dollars approximately. All these corrosion costs could be easily reduced by 15 % to 35 % if the current prevention methods of corrosion are appropriately employed. Such prevention may also contribute for rise in GDP of all countries and thus globally.

Corrosion could easily and practically be prevented which is rather simpler than purging completely. Phenomenon of corrosion is slow until the top or protective passive layer of the metal gets worn off and then gets accelerated. Process of corrosion takes place along with numerous reactions between the metal substrate and its surrounding. For instance, the reaction could possibly be the local pH changes, oxide formation, electrochemical potential or/and metal cation penetration into coating of the substrate metal. Prevention of these reactions is the key function of an inhibitor. Specifically, while using acid solution in industries for functions like acid descaling, oil well acidizing, acid cleaning and acid pickling, the above reactions could be kept within limits by the use of a proper inhibitor and protect the metallic substrates [3]. Corrosion may not only end up in degradation or metal loss but also produces effects like resource wastage, reduction in yield, contamination of metal leading to loss of product, elevated cost of maintenance, safety hazards and slowing down the scientific progress of a nation. Larger structures like nuclear waste dispensation facilities, pipelines, tank trucks, storage tanks, ships, hazardous materials transport units and wagons would also be affected by corrosion heavily. Corrosion abates these structures and even compromises public safety and wellbeing.

Factors like deformation temperature of a metal substrate during its preparation, composition of the alloy, structure of metallic grain influences the affinity of a metal towards corrosion. Since the mechanism of corrosion is dependent on various factors like working metal, its environment and its interaction with the surrounding, understanding of corrosion mechanism is considered to be mystical and hence prevention of corrosion according to the environment would be more feasible than trying to eliminate it. Some

factors which are to be addressed for corrosion prevention includes presence of electrolyte, sulphur dioxide, carbon dioxide, air and moisture [4]. Various types of corrosion, depending on the above said factors, are briefly described in Table 1.

Table 1. Corrosion Classification [5].

Type	Narrative
Uniform corrosion	Corrosion takes place over the entire surface reducing its overall thickness
Galvanic corrosion	Takes place in between various metals having different corrosion potential in presence of an electrolyte
Pitting Corrosion	Induced on a surface at some specific points due to random attacks resulting in formation of pits. Develops as the undamaged surface acts as cathode while the pits acts as cathode
Stress corrosion cracking	Arises when a corrosive environment is acted upon stresses
Corrosion fatigue	Occurs due to combined action of corrosion and load reversal
Intergranular corrosion	Takes place mostly at the metal grain boundaries
Crevice corrosion	Occurs due to entrapment of corrosive liquids within the metal gaps due to concentration corrosion
Filiform corrosion	Occurs in surfaces of metals coated with organic film
Erosion corrosion	Occurs on surface of metals due to flow of corrosive liquids containing abrasives
Fretting corrosion	Another form of erosion corrosion which occurs due to metal fretting

2. Corrosion inhibitors

An inhibitor is the combination of elements supplemented in smaller proportions to shield the exposed metallic surface from a corrosion atmosphere and it reduces or eliminates the corrosion in metals [6]. Corrosion inhibitor is said to be a chemical agent of preventing corrosion when it is present in the medium of corrosion at a concentration which does not pose much change in the other corrosive agent concentration. Rate of corrosion depends on the acidic-basic nature, agents of the environment, moisture and micro-dust particles.

Inhibitor substances reduce the rate of corrosion by absorbing the molecules and ions from the substrate metal [7]. By the formation of a passivating layer around the molecules, the interaction of the metal substrate with the surrounding environment is reduced. Usually corrosion inhibitors are added to metal substrates in ppm concentrations and these elements can have adsorption of substrate atoms at the physical and chemical levels which hinders the direct contact between corrosion agents and metal surfaces. Process of working of corrosion inhibitors is depicted in Fig. 1 [8].

Figure 1 Corrosion inhibition mechanism [8].

Currently due to high toxic nature and being a foe to environments, uses of organic and inorganic inhibitors are reduced widely and the uses of green corrosion inhibitors are encouraged. These green inhibitors are the extracts from various parts of a plant and are environmentally friendly as they are not constituted with heavy metallic or toxic compounds. Green inhibitors usually possess biocompatibility with the environment and nature [9]. The following are the ways by which these inhibitors reduce the rate of corrosion: i) Ions/molecules of the inhibitor elements gets adsorbed by the substrate of the metal, ii) Reaction with cathode and/or anode may be increased or decreased, iii) slowing down the rate of diffusion of the reactant into the metal surface, iv) minimizing the electrical confrontation of the metal substrate, v) choosing an easily applicable green inhibitor which has an advantage of in situ processing. Besides these, choice of inhibitor plays a significant role which could be done by considering factors like availability, cost, environmental safety and flora type [10].

Such choice of inhibitors may orient the researcher to consider the following facts: i) Inhibitor material has to act effectively even at minimal concentrations and should impede dissolution of metal, ii) Inhibitor should have an indifference towards the intake of hydrogen along with thermal stability and inertness towards chemicals, iii) Attributes to acts as surfactant and foaming properties should be better, iv) Inhibitor chosen should be easily available, cheap and non-toxic. When the above factors were considered simultaneously at the time of choosing, usage of green inhibitors becomes more feasible and reliable [11].

3. Use of green corrosion inhibitors

Corrosion of metals can be readily prevented by the use of green corrosion inhibitors. Currently, the inhibitors in existence were prepared from carbon compounds with long chain and aromatic heteroatoms or from raw materials of low quality. Such inhibitors were highly toxic in nature which slowly promoted the use of green corrosion inhibitors. Inhibitors like *Delonix regia* and *Opuntia* extracts prevented corrosion of aluminium in HCL medium [12] while corrosion of aluminium and magnesium alloy in 3 % NaCl medium was prevented by extracts prepared from rosemary leaves. Extracts of natural honey inhibited the copper corrosion while *Khillah* seed extracts had an appreciable inhibitive effect over 316 stainless steel in acidic environments [13]. Extracts from African bush pepper rendered ethanol which inhibited the corrosion of mild steel and the neem leaves extract prevented corrosion of the same metal in sulphuric acid environments. Corrosion inhibition of steel in acidic environments was appreciable given by extracts like *Auforpio turkiale* sap, *Papaia*, *Azadirachta indica*, *Poinciana pulcherrima*, *Calotropis procera*, *Cassia occidentalis*, *Datura stramonium* seeds and *Papaya* with an overall efficiency of 95 %. Corrosion inhibition mechanism in all the above cases was due to the formation of highly insoluble complexes with iron as cations. Better corrosion inhibition of the above plants was purely due to the protein hydrolysis reaction [14-20]. Measurements of corrosion inhibition were normally made by potentiodynamic polarization studies and weight loss methods. Fig. 2 depicts the possibilities of using plants for the extraction of green inhibitors.

Figure 2 Green corrosion inhibitors from plants [21].

4. Plant extracts as corrosion inhibitors

4.1 Corrosion inhibitors for low carbon steel

Nik et al. [22] performed experiments on Henna extracts and exhibited that the Henna extracts were behaving mostly as cathodic side inhibitor and as a mixed type. Most of the researchers found the extracts of Henna to be used as inhibitors for aluminium alloy 5083. The inhibitor effect of henna is mainly due to one of its constituents namely Lawsone. Singh et al. [23] considered *Bacopa monnieri* as a corrosion inhibitor for aluminium metal in an alkaline environment and measured the rate of corrosion by weight reduction estimations and polarization techniques. Experiments revealed that the inhibiting effect of *Bacopa monnieri* extract has high efficiency and the comparison between the rate of corrosion between weight loss and polarization techniques rendered almost the same results. *Bacopa monnieri* extract behaved as a mixed-type inhibitor on aluminium metal in alkaline environments and the reaction between cathode and anode was avoided by using it. These facts were observed from potentiodynamic polarization test results. Johnsirani et al. [24] examined the inhibition efficiency (IE) of aqueous extracted Henna leaves by applying them upon carbon steel placed in sea water. Experiments were conducted by weight loss method and the results depicted that the compound comprising 25 ppm of Zn^{2+} mixed with 8 ml of henna extract possesses an efficiency of 94%. Same experiments were repeated by Polarization method and the results were almost aligned revealing the inhibitor to be a mixed type. Characterization techniques like SEM, FTIR, EIS and AFM were used to analyse the metal surface and it was found that a protective film was formed by the inhibitor over the metal substrate.

Nour et al. [25], analysed the corrosion inhibition of carbon steel by employing various concentrations of aqueous extracted henna leaves in an acidic solution of HCl. Corrosion

rate was determined by weight loss and potentiodynamic polarization techniques. Besides this the corrosion behaviour of carbon steel at a temperature range of 20 to 60°C was also analysed. IE increased with inhibitor concentration while it decreased with raise in temperature. The physical adsorption mechanism of carbon steel with henna extracts was braced by the activation of free energies. The adsorption on the carbon steel surface was compatible with the Langmuir's adsorption isotherm, endothermic and spontaneous. Potentiodynamic polarization measurements demonstrate that the henna extraction shows as mixed inhibitor. Surface analysis and protective film characterization was carried out by using; Fourier transforms infrared (FTIR), spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and X-ray diffraction (XRD) analysis. It could be observed from the experiments that the order of occurrence was Langmuir adsorption isotherm and then adsorption.

4.2 Corrosion inhibitors for mild steel

A seaweed termed as *Leucaena leucocephala* (commonly known as River tamarind) was reported to have better inhibition towards corrosion for the components in seawater. The statistics taken by the transportation department of USA, within a span of six years from 1994 to 1999, reported that almost 26 % of mild steel pipeline accidents occurred mainly because of corrosion [26]. Dry powder of river tamarind was bought from Secret Barn Sdn. Bhd. and used directly. It was soaked in ethanol and filtered using a vacuum pump. The powder was then evaporated using rotovap and then stored in the refrigerator until used. Mild steel specimens were cut into 25 mm × 25 mm × 3 mm and polished using sandpaper until mirror finish. They were finally cleaned using acetone and stored in a desiccator for further use. Immersion test was carried out in seawater for 240 hours and the characteristics were studied using electron impedance spectroscopy (EIS) and SEM [27].

The coating produced by integrating the extract of river tamarind with a local paint proved to be successful and able to protect the mild steel against the damage of corrosion to a certain extent when immersed in seawater. Analysis via FTIR confirms the presence and the involvement of several functional groups such as hydroxyl and carbonyl groups which proposedly supplies the neutral molecules for the inhibition mechanism. Fig. 3 shows a plot of corrosion of mild steel specimens when immersed in sea water. The analysis conducted through electrochemical studies as shown in Fig. 4, indicate the efficiency of the coating increases with the increase of LLE concentration until a certain limitation or optimum value is achieved [28].

Figure 3 Nyquist plot for coated and uncoated mild steels immersed in seawater [27].

Figure 4 Potentiodynamic polarization curves of low carbon steel in Henna solution [28].

On the other hand, the study also implies that the coating acts as a mixed type coating where it reduces the progress of corrosion on both anodic and cathodic sites. Based on the observation via SEM, as shown in Fig. 5, the surface of the coating with the optimum concentration of LLE shows a smooth and well distributed layer with no sign of cracks and

pores indicating the improvement in its capabilities when compare to the observation of the same coating without the presence of extract. This demonstrates a remarkable use of natural resources as a viable method in improving the present corrosion inhibitor [29].

Figure 5 SEM images of cross-sectional area of (a) freshly polished mild steel coupon, (b) naked mild steel and (c) mild steel after 240 hours of immersion in seawater [29].

4.3 Corrosion inhibitors for aluminium in corrosion media

Owing to a better technological impact arising from an uninterrupted necessity in industries, aluminium and its alloys have incessantly engrossed industrialists, metallurgists and researchers. They are applied in food packing, electrical transmission, thermal reservoirs and light-weight transport sectors. Aluminium and its alloys are characterized by a unique feature of formation of passivating oxide layer over their surface which makes them highly resistant towards oxidation. This layer is usually spontaneously formed either as anodic or cathodic film. But compounds containing alkali elements and concentrated base or acidic solutions easily penetrate within the passivating layer inducing corrosion. However, Neutral solutions pose no threat to the protective oxide layer over aluminium metal within a pH range of 4.0–8.5. Hence plant extracts or parts of any plants are believed to act as a corrosion inhibitor with high efficiency because they contain nearly analogous molecular and electronic structures of emblematic organic inhibitors and active phytochemical compounds. These plant extracts are sturdily close at dynamic locations of aluminium at the time of corrosion and indorses anti-corrosion then. *Borassus flabellifer* (BF) is an eco-friendly and biodegradable fiber and the BF extracts comprises abundant hemicelluloses, cellulose and lignin contents [30]. These fiber extracts possess elemental functional groups that will strappingly stick to metal substrate and protect them from its corrosion in any acidic or in alkaline corrosive environment. Several parts of BF namely coir, fruits, shell, seeds, flowers, leaves and roots were derived from the plant and analysed by various researchers.

Analysis was also carried out on BF dust (BFD) derived out of water and methyl alcohol and was considered to be a biodegradable, minimal cost and environmental friendly inhibitor of corrosion for aluminium metals in hostile acid solutions. Furthermore, it was revealed from the experiments that the efficiency of corrosion inhibition surges with increase of BFD content and maximum IE was noted to be 67 % and 52 % in the case of BFD mined from methyl alcohol (BFDME) and water (BFDWE), respectively. Both the materials were derived at a similar concentration of 0.41 g/l. Likewise, polarization graphs portray that the extracts implement a mixed nature with somewhat dominant on adjacent cathode. Meanwhile, adsorption isotherm and thermodynamic calculations illustrates that materials were adsorbed by both physisorption and chemisorption on metallic aluminium surface which also obeys Langmuir adsorption isotherm. Micrograph and morphological studies by SEM portrays the ability of BFDME and BFDWE on corrosion inhibition on aluminium while kept in 1M H_2SO_4 and could be readily recommended for industrial use [31].

Figure 6 SEM image of aluminium: (a) before absorption; (b) after absorption in 1M H_2SO_4 ; (c) after absorption in 0.4 g/l BFDME+ 1M H_2SO_4 ; (d) after absorption in 0.4 g/l BFDWE+ 1M H_2SO_4 [31].

IE of BFDME and BFDWE was observed to increase with the increase in concentration of inhibitor added to the metal substrate. According to the weight-loss method test results, maximum IE was obtained as 66% and 51% for both of the above extracted materials at a temperature of 30°C in the same concentrations. SEM images also shows that inhibition of corrosion in aluminium alloys by the addition of BFDME and BFDWE was due to the formation of a passivating top layer on the metal substrate. The SEM micrographs of bare and inhibited aluminium specimens are shown in Fig. 6 [31].

4.4 Natural gums as corrosion inhibitors for metals

Gums are the natural elements obtained from the trunks or stem of various plants and they mostly contain polysaccharides which are soluble in water. When they are kept in water, due to their hydrophilic nature, they absorb water and get swollen up to form a gel like element. However they are insoluble in solvents and oils like alcohol, hydrocarbons and ether. The constituents of gum are normally complex and when they undergo hydrolysis reaction they render simple sugar compounds like glucuronic acid, mannose, arabinose and galactose. If the trunk or stem of a tree is injured pathologically in a gradual manner or by boring of insects or accidentally then the phenomenon is described as exudation. Gums are formed in the stems or root of trees at the time of exudation. When the seed endosperm portions were separated from them, then seed gums were formed. Apart from the application of gums towards corrosion inhibition they are also used in various other applications like pharmaceutical, food and other technical applications. Because of dominant stabilizing, emulsifying, suspending and thickening characteristics, gums are widely used in food and drinks applications in the food industry. On the other hand, gums are used as emulsifying agents for lotions and creams, tablet binding agents and in some other medical fields including dental in pharmaceutical industries. Above all, it could be seen that gums are excellent and effective corrosion inhibitors.

Eddy et al. [32] stated that gums were excellent corrosion inhibitors due to some of the reasons including: i) Gums form complex metal ions on the surface of the metals with the aid of their functional groups, ii) The so formed metal complexes protect the metal substrate from the causal agents of corrosion by inhabiting a large surface area thereby sheltering the surface, iii) Adsorption behaviour of gums are primarily due to presence of compounds like glucoprotein, sucrose, polysaccharides, arbinogalactan and oligosaccharides as these are constituted primarily with nitrogen and oxygen, iv) Adsorption mechanism of the gums were enhanced by the transfer of charge and electrons as they are rich in CO-OH organic groups, v) Usually like many other green inhibitors gums are also environmental friendly and low in toxicity. Some of the commonly used gums are Gum Arabic, Locust Bean gum, Guar gum, Albizia gum, Excudated gum Raphia

hookeri, *Dacryodes edulis*, *Ficus glumosa* gum, *Commiphora keatingii* gum, exudated gum *Pachylobus edulis*, *Ficus Benjamina* gum, *Anogessius leocarpus* gum, *Commiphora pendunculata* gum, *Ficus platyphylla* gum, *Ficus tricopoda* gum, *Daniella olieverri* gum, *Ficus thonningii* gum, *Khaya ivorensis* gum, *Gloriosa superba* gum.

4.5 Ionic liquids as green corrosion inhibitors

Though iron and its alloys are cheap in cost and easy to produce, they are more prone to corrosion in acidic media especially during acid cleaning and the acid pickling process. Restrictions, due to ecological balance maintenance and stringent consciousness towards environment, are unavoidable when the toxic inhibitors of corrosion were used for metals. Hence depletion of ionic liquids to act as inhibitors for corrosion is emerging as an inevitable substitutive technique for the prevention of corrosion by green methods. These liquids have numerous better properties like high polarity, chemical stability, lower vapour pressure, lower melting point (lower than 100°C), high thermal stability and low toxicity render them to be an ideal alternative for conventional toxic inhibitors of corrosion. Fig. 7 depicts various applications of the ionic liquids for using them as green corrosion inhibitors [33]. The ionic liquids considered here inhibit corrosion in metallic substrates by adsorbing the molecules of metal obeying the Langmuir adsorption isotherm. Phenomenon of adsorption was supported by scanning electron microscopy, energy dispersive X-ray spectroscopy and atomic force microscopic analysis. Polarization analysis depicted that the ionic liquids considered had acted as an inhibitor of mixed type.

Copper and its alloys were broadly utilized for various applications such as coinages, electronics, ornamental, electricity and building construction industries and also in manufacturing of equipment owing to better corrosion resistance, electrical and thermal and mechanical properties [34]. Nonetheless, in occurrence of belligerent anionic elements like nitrates, sulphates and chlorides, copper and alloys may be severely attacked making them corrosion prone and ending up with loss of materials. Similarly, zinc and its alloys are widely used in chemical and petroleum industries [35]. But these industries are considered to have a constant fluctuation of pH values between maximum and minimum which results in degradation of mechanical properties due to corrosion. 1-butyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide, 1-hexyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide, and 1-propyl-2,3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide were the most preferably used synthesized green inhibitors for copper and zinc alloys. Results showed that both the ionic liquids acted as good corrosion inhibitors and their inhibition efficiency increases with increasing their concentrations.

Figure 7. Applications of ionic liquids [33].

Conclusion

Efforts to prevent corrosion of metals are in force these days by employing green corrosion inhibitors. It could be stated from the above case studies that usage of plant excerpts as green inhibitors towards corrosion is much feasible and effective for a wide range of metals. When the metals were present in hydrochloric or sulphuric acid environments, then potentiodynamic polarization, weight loss and electrochemical impedance methods could be readily used to analyse the inhibition of corrosion. Though most of the inhibitors which are processed in the laboratories has exhibited better efficiency, their usage in industries is very limited due to their toxic nature. This shifted the focus of various researchers towards the processing and application of inhibitors that are environmental friendly. In spite of its successful processing, application of green inhibitors in real industrial sectors has to be explored more. Corrosive atmospheres involving harmful gases like hydrogen sulphide, carbon dioxide and sulphur dioxide are to be analysed more for the application of green inhibitors in such environments. All green inhibitors derived from plant oils are characterized by non-toxicity, renewable, cheap and high efficiency. Nevertheless efforts for finding out the compound responsible for the inhibition property in any plant are rarely reported. When the inhibitor is considered to be a mixture of compounds having better inhibition efficiency, they experience synergistic effects. In this way, such green inhibitors

are exhibiting an efficiency of nearly 98%. Hence the excerpts of plants are good corrosion inhibitors that could be positively used on an industrial level. Yet concentration could be given further on the numerical modelling of the inhibition mechanism by green inhibitors which may be helpful in instituting the mechanism of inhibition in detail. It may also open many avenues for finding suitable alternatives.

References

- [1] M. Sangeetha, S. Rajendran, T.S. Muthumegala, A. Krishnaveni. Green corrosion inhibitors-an overview, *Zastita Materijala*. 52(1) (2011) 3-19.
- [2] J.T. Stephen, A. Adebayo, Inhibition of corrosion of mild steel in hydrochloric acid solution using akee apple seed extract. *J. Fail. Anal. Prev.* 18 (2018) 350–355. <https://doi.org/10.1007/s11668-018-0431-7>
- [3] H. Habeeb, H.M. Jwad, T.A. Luaibi, R.M. Abdullah, A.A. Dakhil, H. Kadhum, A.A. Al-Amiery, Case study on thermal impact of novel corrosion inhibitor on mild steel, *Case Stud. Therm. Eng.* 12 (2018) 64-68. <https://doi.org/10.1016/j.csite.2018.03.005>
- [4] B.E. Rani, B.J.B. Bharathi, Green inhibitors for corrosion protection of metals and alloys: an overview. *Int. J. Corros.* 2012 (2012) 380217. <https://doi.org/10.1155/2012/380217>
- [5] D.K. Singh, S. Kumar, G. Udayabhanu, R.P. John. 4(N,Ndimethylamino) benzaldehyde nicotinic hydrazone as corrosion inhibitor for mild steel in 1M HCl solution: An experimental and theoretical study, *J. Mol. Liq.* 216 (2016) 738–746. <https://doi.org/10.1016/j.molliq.2016.02.012>
- [6] K.K. Alaneme, S.J. Olusegun, O.T. Adelowo. Corrosion inhibition and adsorption mechanism studies of *Hunteria umbellata* seed husk extracts on mild steel immersed in acidic solutions, *Alex. Eng. J.* 55(1) 2016) 673–681. <https://doi.org/10.1016/j.aej.2015.10.009>
- [7] A. Harmaoui, H. Bourazmi, M.E. Fal, M. Boudalia, M. Tabyaoui, A. Guenbour, A. Bellaouchou, Y. Ramli, E.M. Essassi, Study of triazolotiazepinon as a corrosion inhibitor in 1M hydrochloric acid, *Environ. Sci.*, 6(9) (2015) 2509-2519.
- [8] W. Belmaghraoui, A. Mazkour, H. Harhar, M. Harir, S. El-Hajjaji, Investigation of corrosion inhibition of C38 steel in 5.5 M H₃PO₄ solution using *Ziziphus lotus* oil extract: an application model, *Anti-Corros. Meth. Mater.* 66(1) (2019) 121-126. <https://doi.org/10.1108/ACMM-02-2018-1901>

- [9] R. Rajalakshmi, A. Prithiba, S. Leelavathi, An overview of emerging scenario in the frontiers of eco-friendly corrosion inhibitors of plant origin for mild steel, *J. Chem. Acta* 1(1) (2012) 6-13.
- [10] G. Ting, P. Su, X. Liu, J. Zou, X. Zhang, Y. Hu, A composite inhibitor used in oilfield: MA-AMPS and imidazoline. *J. Petrol. Sci. Eng.* 102 (2013): 41-46.
<https://doi.org/10.1016/j.petrol.2013.01.014>
- [11] F.J. Schwinn, Ergosterol biosynthesis inhibitors. An overview of their history and contribution to medicine and agriculture, *Pestic. Sci.* 15(1) (1984) 40-47.
<https://doi.org/10.1002/ps.2780150107>
- [12] S. Abdoul-Azize, Potential benefits of jujube (*Zizyphus Lotus* L.) bioactive compounds for nutrition and health, *J. Nutr. Metabol.* (2016) 2867470.
<https://doi.org/10.1155/2016/2867470>
- [13] H. Saufi, A. Al-Maofari, A. El Yadini, L. Eddaif, H. Harhar, S. Gharby, S. El-Hajjaji, Evaluation of vegetable oil of nigel as corrosion inhibitor for iron in NaCl 3% medium, *J. Mater. Environ. Sci.* 6(7) (2015) 1845-1849.
- [14] R.T. Vashi, N.I. Prajapati, Corrosion Inhibition of Aluminium in hydrochloric acid using bacopa monnieri leaves extract as green inhibitor, *Int. J. ChemTech Res.* CODEN (USA) IJCRGG 10(15) (2017) 221-231.
- [15] E.E. Oguzie, Corrosion inhibitive effect and adsorption behaviour of Hibiscus Sabdariffa extract on mild steel in acidic media, *Port. Electrochem. Acta* 26 (2008) 303–314. <https://doi.org/10.4152/pea.200803303>
- [16] E.E. Oguzie, K.L. Iyeh, A.I. Onuchukw, Inhibition of mild steel corrosion in acidic media by aqueous extracts from Garcinia kola seed. *Bull. Electrochem.* 22(2) (2006) 63–68.
- [17] M.S. Kumar, K. Sudesh, R. Ratnani, S.P. Mathur, Corrosion inhibition of aluminium by extracts of Prosopis cineraria in acidic media, *Bull. Electrochem.* 22(2) (2006) 69–74.
- [18] A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, Corrosion inhibition of some metals using lawsonia extract, *Corros. Sci.* 47(2) (2005) 385–395.
<https://doi.org/10.1016/j.corsci.2004.06.006>
- [19] A. Bouyanzer, L. Majidi, B. Hammout, Effect of eucalyptus oil on the corrosion of steel in 1 M HCl, *Bull. Electrochem.* 22(7) (2006) 321–324.
- [20] M.J. Sanghvi, S.K. Shuklan, A.N. Misra, M.R. Padh, G.N. Mehta, Inhibition of hydrochloric acid corrosion of mild steel by aid extracts of Embilica officianalis,

- Terminalia bellirica* and *Terminalia chebula*, Bull. Electrochem. 13(8–9) (1997) 358–361.
- [21] P.B. Raja, M. Ismail, S. Ghoreishiamiri, J. Mirza, M.C. Ismail, S. Kakooei, A.A. Rahim, Reviews on corrosion inhibitors: a short view, Chem. Eng. Comm. 203(9) (2016) 1145–1156. <https://doi.org/10.1080/00986445.2016.1172485>
- [22] W.B.W. Nik, F. Zulkifli, R. Rosliza, M.M. Rahman, Lawsonia Inermis as green inhibitor for corrosion protection of aluminium alloy, Int. J. Mod. Eng. Res. 1(2) (2011) 723–728.
- [23] E.E. Singh, Ebenso, M.A. Quraishi, Stem extract of Brahmi (*Bacopa monnieri*) as green corrosion inhibitor for Aluminum in NaOH solution, Int. J. Electrochem. Sci. 7 (2012) 3409–3419.
- [24] V. Johnsirani, J. Sathiyabama, S. Rajendran, A.S. Prabha, Inhibitory mechanism of carbon steel corrosion in sea water by an aqueous extract of henna leaves, Int. Sch. Res. Network ISRN Corros. (2012) 574321. <https://doi.org/10.5402/2012/574321>
- [25] A.H. Nour, S. El-Gendy, Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium, Egypt. J. Petrol. 22(1) (2013) 17–25. <https://doi.org/10.1016/j.ejpe.2012.06.002>
- [26] I. Adejoro, F. Ojo, S. Obafemi, Corrosion inhibition potentials of ampicillin for mild steel in hydrochloric acid solution, J. Taibah Univ. Sci., 9(2) (2015) 196–202. <https://doi.org/10.1016/j.jtusci.2014.10.002>
- [27] W.M.K.W.M. Ikhmal, M.F.M. Maria, W.A.W. Rafizah, W.N.W.M. Norsani, M.G.M. Sabri, Corrosion inhibition of mild steel in seawater through green approach using *Leucaena leucocephala* leaves extract, Int. J. Corros. Scale Inhib. 8(3) (2019) 628–643. <https://doi.org/10.17675/2305-6894-2019-8-3-12>
- [28] Al Hasan, N.H. Jasim, H.J. Alaradi, Z.A. Khadhim Al Mansor, A.H.J. Al-Shadood, The dual effect of stem extract of Brahmi (*Bacopamonnieri*) and Henna as a green corrosion inhibitor for low carbon steel in 0.5 M NaOH solution, Case Stud. Construct. Mater. 11 (2019) 00300. <https://doi.org/10.1016/j.cscm.2019.e00300>
- [29] D. Jeroundi, H. Elmsellem, S. Chakroune, R. Idouhli, A. Elyoussfi, A.E. Dafali, E.M. Hadrami, A. Ben-Tama, R.Y. Kandri. Physicochemical study and corrosion inhibition potential of dithiolo[4,5-b][1,4] dithiepine for mild steel in acidic medium, Environ. Sci. 7(11) (2016) 4024–4035.
- [30] S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan, G. Bouet, Novel thiophene symmetrical Schiff base compounds as corrosion inhibitor for mild steel in

acidic media, *Corros. Sci.* 53 (2011) 1484–1488.

<https://doi.org/10.1016/j.corsci.2011.01.022>

- [31] R.S. Nathiya, S. Perumal, V. Murugesan, V. Raj, Evaluation of extracts of *Borassus flabellifer* dust as green inhibitors for aluminium corrosion in acidic media, *Mater. Sci. Semicond. Process.* 104 (2019) 104674.
<https://doi.org/10.1016/j.mssp.2019.104674>
- [32] N.O. Eddy, E.E. Ebenso, Adsorption and inhibitive properties of ethanol extracts of *Musa sapientum* peels as a green corrosion inhibitor for mild steel in H_2SO_4 , *Afr. J. Pure. Appl. Chem.* 2(6) (2008) 46–54.
- [33] C. Verma, E.E. Ebenso, M.A. Quraishi. Ionic liquids as green and sustainable corrosion inhibitors for metals and alloys: An overview, 233 (2017) 403-414.
<https://doi.org/10.1016/j.molliq.2017.02.111>
- [34] H. Tavakoli, T. Shahrabi, M.G. Hosseini. Synergistic effect on corrosion inhibition of copper by sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoxazole, *Mater. Chem. Phys.* 109 (2008) 281-288.
<https://doi.org/10.1016/j.matchemphys.2007.11.018>
- [35] M.A. Elmorsi, A.M. Hassanein, Corrosion inhibition of copper by heterocyclic compounds, *J. Corros. Sci.*, 41 (1999) 2337-2352. [https://doi.org/10.1016/S0010-938X\(99\)00061-X](https://doi.org/10.1016/S0010-938X(99)00061-X)