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Recent developments in sustainable corrosion inhibitors: design, performance and industrial scale applications

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Recently, research studies in the fields of science and engineering are directed towards the synthesis, design, development, and consumption of environment-friendly chemical species to replace traditional toxic chemicals. This is because of the escalating demands of conservation understanding and stringent ecological rules. Currently, various environment-friendly alternatives derived from natural resources such as biopolymers, plant extracts, chemical medicines (drugs), *etc.* are widely used to replace toxic corrosion inhibitors. Moreover, various biopolymers in their pure and modified forms are extensively employed as environment-friendly corrosion inhibitors. Compounds derived through multicomponent reactions (MCRs), and microwave (MW) and ultrasound (US) irradiations are also considered as environment-friendly alternatives. Polyethylene glycol (PEG) and ionic liquids (ILs) possess low vapor pressure and are regarded as designer environment-friendly alternatives. The chemicals synthesized using green solvents such as water, ILs and supercritical CO_2 can also be regarded as environment-friendly chemical species. A comprehensive literature survey reveals that these compounds are extensively utilized as metallic corrosion inhibitors in various corrosive electrolytes. Overall, this review provides a summary of several major reports on environment-friendly corrosion inhibitors.

1. Introduction

1.1. Corrosion inhibition: current trends and challenges

Metallic materials are widely used for various applications, for example, as constructional materials, especially in the petroleum, oil and gas industries.[1,2] However, most of the metals in their pure form are thermodynamically unstable, and therefore they readily undergo corrosive degradation by the reaction of constituents of the surrounding environment. Corrosion causes huge safety concerns and economic damage. According to the recent estimation of the NACE (National Association of Corrosion Engineers), the global cost of corrosion is around US$2.5 trillion, which constitutes about 3.5% of the world's GDP. The cost of corrosion may be of direct or indirect type.[3–5] The direct cost of corrosion includes the repair, storage and replacement of the corroded metallic equipment, modifying alloys into metals and *vice versa*. The cost associated with nickel plating and galvanization can also be regarded as the direct cost of corrosion.[6,7] Apart from the above, economic losses associated with the synthesis, characterization and application of compounds as corrosion inhibitors are also integrated as the direct cost of corrosion. The indirect costs of corrosion include the leakage of liquids (petroleum) and gases from transport pipelines that adversely affect the performance of machineries and transport efficiency. Contamination of rusts and scales (corrosion products) can also adversely affect the quantity of the materials (liquids and gases) to be transported. These corrosion products can also reduce transport efficiency and the performance of machineries by choking the valves and joints. Obviously, the leakage of the transported petroleum based liquids and gases is associated with various environment related problems because of their toxicity.

In view of the above, several methods of corrosion mitigation have been developed by corrosion scientists and engineers. One of the oldest (before 1960) methods of corrosion mitigation was the implementation of inorganic compounds, mainly nitrites, chromates, borates, molybdates, silicates and zinc salts.[8] These compounds become effective by forming a highly effective passive film over metal surfaces (passivators) through their adsorption. However, they were replaced by more economical alternatives such as phosphonic acid, gluconates, polyacrylates,

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surface active chelates, polyphosphates, polyphosphonates, phosphonates and carboxylates during 1960–1980.[8] Generally, these compounds precipitate at the interface of the metal and environment and therefore they are called precipitating inhibitors (precipitators). Nevertheless, after that, ecological considerations came into play and toxic chemicals were replaced by natural alternatives including natural and bio-polymers, bio-surfactants, vitamins, tannins and natural compounds during 1980–1995. Recently (1995 to present), environment-friendly approaches such as the use of rare earth metals (REM), polyfunctional compounds, the synergism of organic/inorganic compounds using REM and the encapsulation of inhibitors are the main areas of focus.[9] Obviously, these alternatives exhibit very low or no toxicity and high protection effectiveness.

Currently, organic compounds are established as one of the most effective and profitable methods of corrosion inhibition because of their association with E4 (efficiency, economy, ecology and environmental friendliness).[10–12] Organic corrosion inhibitors are used for different industrial applications (Fig. 1). However, there are numerous challenges of using these compounds. One of the biggest challenges of using organic corrosion inhibitors is their limited solubility, especially in polar electrolytes.[13,14] Because of their hydrophobic nature, organic corrosion inhibitors, especially compounds containing aromatic rings and non-polar hydrocarbon chains, show limited solubility that adversely affects their protection efficiency. Therefore, current research studies in corrosion science and engineering are oriented towards the development of corrosion inhibitors that contain hydrophilic polar functional substituents in their molecular structures.

The electron rich polar functional substituents enhance the bonding efficiency between the metal surface and organic compounds either directly participating in coordination bonding or increasing the electron density over the active sites of inhibitor molecules.[15–17] The polar substituents also triggered the protection effectiveness of the organic inhibitors by increasing their hydrophilicity and solubility in polar electrolytes.[16,17] The nature of the substituents plays a significant role in designing effective corrosion inhibitors. Electron donating substituents (EDS) with a negative Hammett substituent constant are expected to increase the inhibition effect of organic compounds.[15,18–20] On the other hand, electron withdrawing substituents (EWS) with a positive Hammett substituent constant are expected to decrease the protection effectiveness of the inhibitors. Nevertheless, EWS such as –CN, $-NO_2$, –COOH, $-SO_3H$, *etc.* enhance the corrosion

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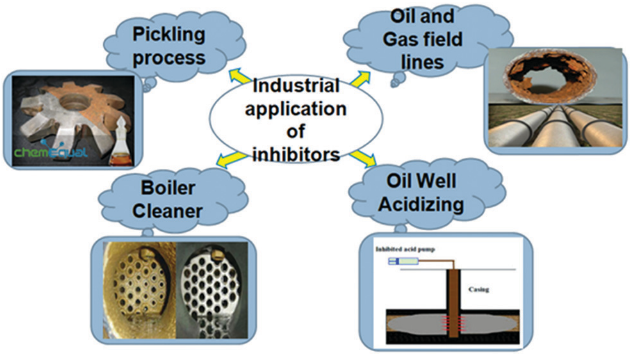

Fig. 1 Applications of organic corrosion inhibitors in different industrial sectors.

inhibition effectiveness of macromolecules and polymers by increasing their solubility in polar electrolytes.

Thermal decomposition represents another challenge of using organic compounds as inhibitors against metallic corrosion. The inhibition efficiency of most of the organic compounds decreases on increasing the temperature.[21,22] This type of decrease in the inhibition efficiency is attributed to the acid or base catalyzed decomposition and/or rearrangement of the inhibitor molecules, especially at high temperatures.[23,24] Obviously, the increase in the kinetic energy of the inhibitor molecules on increasing the temperature results in the corresponding decrease in the attractive force between the inhibitor molecules and the metallic surface.[23,24] This observation reveals that the bonding between the inhibitor molecules and the metallic surface is mostly electrostatic, *i.e.* physisorption. However, the increase in protection efficiency on increasing the temperature has also been documented.[25–27] The increase in the inhibition efficiency with the rise in temperature suggests that the interaction between the metal surface and the inhibitor molecules involves chemical bonding, *i.e.* chemisorption. The literature observation suggests that most of the organic corrosion inhibitors adsorb using a mixed mode of adsorption, *i.e.* physiochemisorption.[28–30]

1.2. Assessment of sustainable corrosion inhibitors: OSPAR and REACH commissions

Because of the rising environmental consciousness and severe ecological policies, decent advancements in the field of corrosion science and engineering are oriented towards the development, synthesis, design and implementation of environment-friendly alternatives to the conventional toxic corrosion inhibitors.[31–33] Obviously, the environmentally benign nature of a chemical species (or corrosion inhibitor) can be determined by assessing its bioaccumulation ability, biodegradability and the impact of its toxicity on the environment.[33–35] The Oslo and Paris Commission (OSPAR) and Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) are the international commissions for the assessment of the above parameters. REACH is a European Union Regulation (EUR) that was dated on 18 December 2006 and came into force on 7 June 2007.[36,37] The 849-page EUR addresses the production, design and implementation of chemical substances as well as their impact on the environment and human health. OSPAR, which was formed on 22 September 1992, combines and updates the 1972 Oslo Convention on dumping of wastes at sea and 1974 Paris Convention on marine pollution resulting through land-based sources.[38–40] These commissions set up some guidelines and indices, in terms of which the toxicity, biodegradability and bioaccumulation ability and their impact on human health and the environment of chemical compounds can be assessed. The toxicity of a chemical compound to be used as a corrosion inhibitor can be assessed using its lethal and ethical

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concentrations designated as LC_{50} and EC_{50}, respectively.[41,42] LC_{50} represents the concentration of the substance that causes the demise of 50% of the living population and EC_{50} denotes the chemical concentration that adversely affects the growth of the living population.[43–45] Obviously, an inferior LC_{50}/EC_{50} magnitude indicates superior sensitive toxicity and *vice versa*. A chemical with a LC_{50}/EC_{50} value greater than 10 mg kg^{-1} is considered non-toxic.[43–45] Most of the chemicals spontaneously undergo degradation by microorganisms called decomposers though the process is quite slow and takes several days, months or even years.[46] A chemical can be categorized as environment-friendly if it decomposes 60% or more in 28 days.[47,48] Bioaccumulation is the ability of a chemical to gather in a living organism when the source of the chemical is exclusively water.[49–51] Generally, it is measured in terms of the partition coefficient, designated as log K_{OW} or D^{OW}. Generally, K_{OW} or D^{OW} represents the ratio of concentrations of a compound in an assortment of two immiscible solvents at equilibrium. Bioaccumulation is a measure in a mixture of water and octanol. For an environment-friendly compound, the K_{OW} or D^{OW} value should be equal to or less than 3.[52]

1.3. Computational chemistry tools for corrosion inhibition studies

Numerous chemical, electrochemical and surface morphological techniques are widely used for the evaluation of the inhibition performance of corrosion inhibitors.[53–55] However, these experimental methods have several shortcomings. Generally, these experimental methods are associated with expensive synthesis and the use of toxic chemicals that adversely affect the surrounding environment.[56–58] These chemicals are synthesized using toxic and expensive starting materials and catalyst using multistep reactions that consume huge amounts of solvents for purification and work-up processes. Discharge of excess amounts of organic solvents and toxic catalysts into the environment causes severe environment related issues. Because of the multistep nature, the syntheses of corrosion inhibitors are associated with the formation of several undesirable side products that can also pollute the environment. Instead of their highly toxic and expensive synthesis, most of the compounds do not give fruitful results and fail in experimental trials.[28,59,60] In view of this, recently computational chemistry tools have come into play for determining the corrosion inhibition effectiveness of corrosion inhibitors.[5,61,62] The environment-friendly nature of these techniques is associated with the fact that the inhibition effectiveness of compounds can be theoretically predicted before their toxic and expensive synthesis.[5,62–64] Unlike experimental methods, computational modeling involves the use of computational software for predicting inhibitory efficiency instead of highly expensive instruments.[65–67]

Recently, several computational methods, especially density functional theory (DFT), molecular dynamics (MD) and Monte Carlo (MC) simulations, have emerged as powerful computational chemistry tools for corrosion monitoring.[5,61,62] DFT simulations represent the most powerful computational tool, which give some vital indices including the energy of frontier molecular orbitals (FMOs; E_{HOMO} and E_{LUMO}) and numerous correlation parameters such as energy band gap ($E_{LUMO} - E_{HOMO} = \Delta E$), hardness ($\eta$), electronegativity ($\chi$), dipole moment ($\mu$), softness ($\sigma$), fraction of electron transfer (ΔN), *etc.*, in terms of which the adsorption ability and corrosion inhibition effectiveness of a compound can be explained.[5,61,62,68] DFT studies are mostly used to correlate the relative inhibition effect of a series of compounds having similar molecular structures. In general, higher E_{HOMO}, softness (σ) and dipole moment (μ) and lower E_{LUMO}, ΔE, electronegativity (χ) and hardness (η) values are associated with high inhibition efficiency.[61,62] One of the most significant indices is the energy band gap ΔE ($E_{LUMO} - E_{HOMO}$) and its lower value is associated with a higher inhibition efficiency.[69,70] By studying the anticorrosive effect of chitosan (CH) modified with 4-amino-5-methyl-1,2,4-triazole-3-thiol (AMT), the authors reported that both CH and AMT separately have higher ΔE values as compared to the ΔE value of AMT modified CH (CH–AMT). This observation suggests that CH–AMT is relatively more reactive towards its absorption on the metallic surface as compared to CH and AMT separately (Fig. 2).[71] An increase in protection efficiency for a series of corrosion inhibitors with a decrease in the ΔE value has been reported extensively.

It is important to mention that, during metal and inhibitor interactions, some parts of the inhibitor molecules are involved in bonding with the metallic surface. These parts are called active or adsorption centers. Among the several experimental and computational techniques, the implementation of DFT is established as one of the most significant methods for identifying the active centers of the inhibitor molecule.[61,62] Localized regions in FMOs (HOMO and LUMO) represent the electron rich centers (active centers) that actively contribute to charge sharing with the metallic surface.[72–74] Generally, these electron rich centers are aromatic ring(s) and/or polar functional groups. However, the contribution of FMOs in charge sharing with the metallic surface depends greatly on the nature of substituents.[15,19] In general, substituents with a negative Hammett (σ) or Taft (σ^*) constant (electron donating) show an increased FMO contribution with an increase in electron density.[15,19] In contrast, substituents with a positive Hammett (σ) or Taft (σ^*) constant (electron withdrawing) show a decreased FMO contribution to charge sharing.[15,19]

A study on the inhibitive effect of 2-amino-4-arylquinoline-3-carbonitriles (AACs) on mild steel in acidic medium showed that the presence of –OH (AAC-3) increases the inhibition efficiency and the presence of a $-NO_2$ substituent (AAC-1) decreases the inhibition efficiency as compared to the non-substituted compound (AAC-2).[75]

DFT studies revealed that the $-NO_2$ substituent decreases the HOMO contribution, whereas the –OH substituent increases the HOMO contribution. The FMOs of the AACs are presented in Fig. 3. The negative sign of the Hammett constant for –OH indicates that it is an electron donor in nature and therefore increases the electron donor (HOMO) contribution and the converse is true for the $-NO_2$ substituent. A similar finding was also observed when studying the inhibition effect of 5-aryl-pyrimido-[4,5-*b*]quinoline-diones (APQDs) for MS corrosion in acidic medium. DFT analyses showed that the $-NO_2$ substituent with a positive Hammett constant (σ = +0.78) decreases the

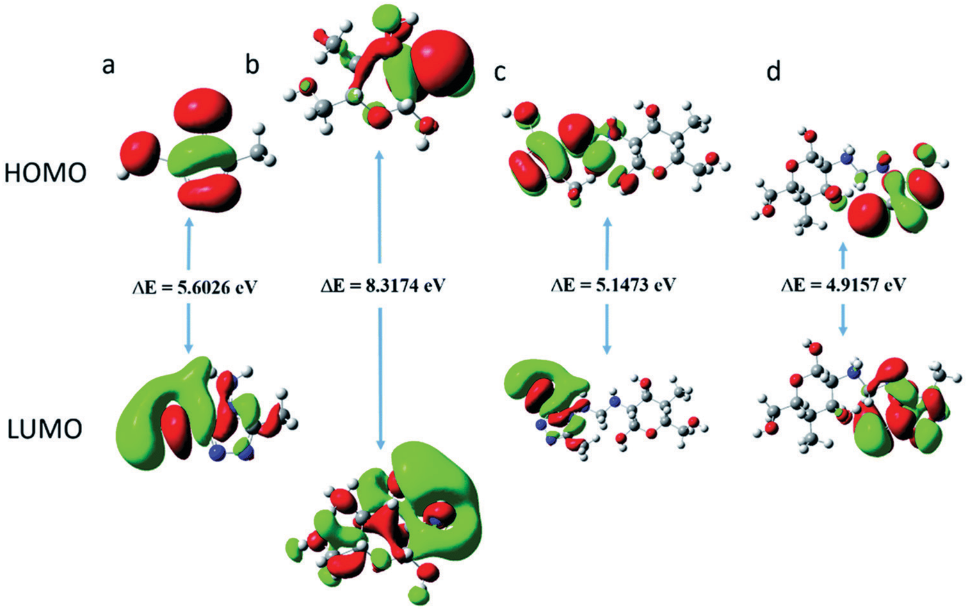


Fig. 2 Presentation of energy band gaps (ΔE: $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) for (a) 4-amino-5-methyl-1,2,4-triazole-3-thiol (AMT), (b) chitosan (CH), (c) neutral AMT modified CH and (d) protonated AMT modified (CH-MAT).[71]

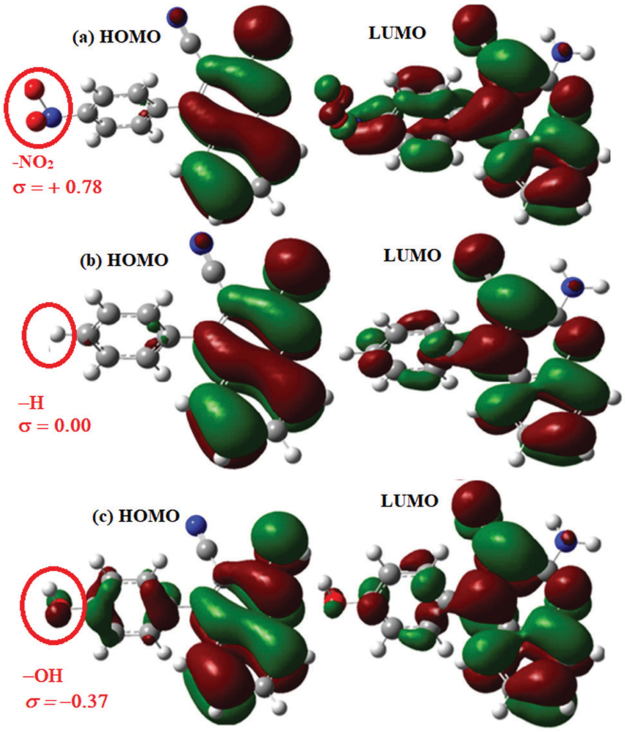


Fig. 3 Frontier molecular orbitals (FMOs) of (a) AAC-1 (–NO_2), (b) AAC-2 (–H) and (c) AAC-3 (–OH) derived using the Gaussian 09 software package.[75]

HOMO and LUMO contributions by decreasing the electron density.[76] Very interestingly only nitrophenyl (–Ph–NO_2) moieties are involved in the LUMO because of the electron withdrawing nature of –NO_2 (APQD-4). In contrast, the presence of one and two –OH substituent(s) in APQD-3 and APQD-4, respectively, increase the contributions of both the HOMO and LUMO because of the electron donating nature of –OH ($\sigma = -0.37$).[76] The frontier molecular orbital images of APQDs are shown in Fig. 4. A similar finding was also reported in other studies.[17,77]

Other significant computational techniques are molecular dynamics (MD) and Monte Carlo (MC) simulations.[5,78–80] Using these techniques one can determine the orientation of the inhibitor on the metallic surface. Measurement of the orientation of the inhibitor on the metal surface is an important aspect of corrosion monitoring as an inhibitor with planar orientation covers a larger part of the metallic surface and acts as a superior corrosion inhibitor to an inhibitor with vertical orientation. When an inhibitor approaches the metallic surface, due to the effect of different attractive and repulsive forces it gets polarized and acquires a specific orientation depending upon the nature of the electronic structure of the inhibitor molecules. Nevertheless, substituents play a significant role in determining the orientation of the inhibitor molecules over the metal surface. Generally, electron donating substituents force the inhibitor molecules to obtain vertical orientation and *vice versa*.

The orientations of four 5-arylpyrimido-[4,5-*b*]quinoline-diones (APQDs) and glucosamine-based, pyrimidine-fused heterocycles (CARBs) are shown in Fig. 5 and 6. It can be clearly observed that in the presence of the electron withdrawing –NO_2 substituent the extent of adsorption (yellow circle) decreased with respect to the adsorption extent of inhibitors with electron donating substituents.

1.4. Design of effective corrosion inhibitors based on experimental and computational studies

From the above discussion it is clear that substituents play a significant role in determining the corrosion inhibition effect of organic corrosion inhibitors. Obviously, because of their

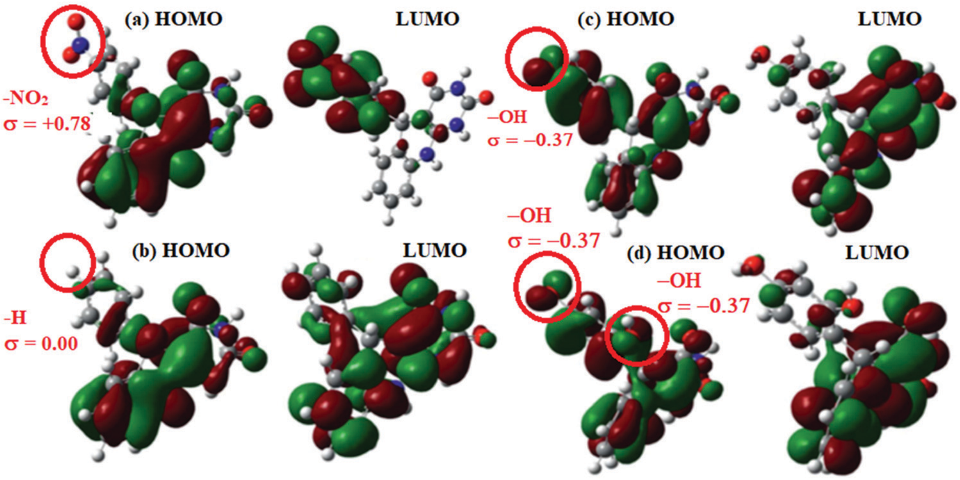


Fig. 4 Frontier molecular orbital images of (a) APQD-1 ($-NO_2$), (b) APQD-2 (–H), (c) APQD-3 (–OH) and (d) APQD-4 (2× –OH) derived using the Gaussian 09 software package.[76]

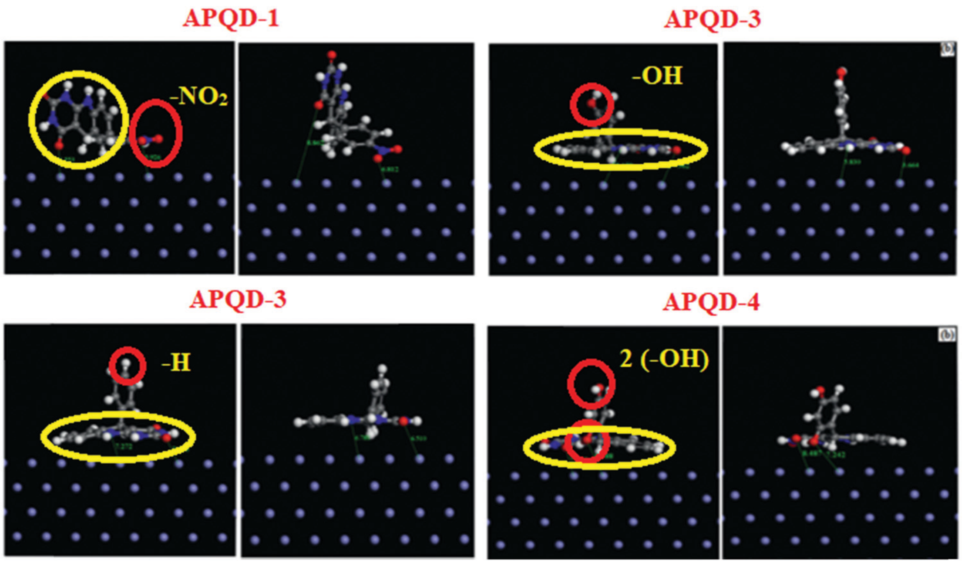


Fig. 5 Top and side views of APQD-1 ($-NO_2$), APQD-2 (–H), APQD-3 (–OH) and APQD-4 (2× –OH) on the Fe(110) surface derived using molecular dynamics simulations.[76]

electron donating or electron withdrawing nature, these substituents affect the overall electron density at the donor site(s) of the inhibitor molecules. It is important to mention that the interaction of organic corrosion inhibitors with the metallic surface involves the donor–acceptor (charge sharing) phenomenon. The effect of substituents on the electron sharing tendency of corrosion inhibitors can be assessed through DFT analysis (Fig. 3 and 4). On the other hand, the effect of substituents on the orientation of corrosion inhibitors over the metal surface can be easily assessed through MD or MC simulations (Fig. 5 and 6). Besides computational chemistry tools, the effect of electron donating as well as electron withdrawing substituents on the inhibition efficiency of the substituted aromatic corrosion inhibitors can also be determined using the Hammett substituent constant (σ) (or Taft substituent constant, σ^*-for aliphatic cyclic and linear compounds). The various forms of the Hammett equations are presented below:[15]

$$\log\frac{K_R}{K_H} = \rho\sigma \tag{1}$$

$$\log\frac{1-\eta\%_R}{1-\eta\%_H} = \rho\sigma \tag{2}$$

$$\log\frac{\eta\%_R}{\eta\%_H} = \log\frac{C_{rH}}{C_{rR}} = \rho\sigma - \log\frac{\theta_R}{\theta_H} \tag{3}$$

In the above equations, K, $\eta\%$, θ and C_r represent the equilibrium constant, percentage inhibition efficiency, surface coverage and corrosion rate, respectively. Subscripts "H" and "R" represent the absence and presence of the substituent, "–R". ρ is the

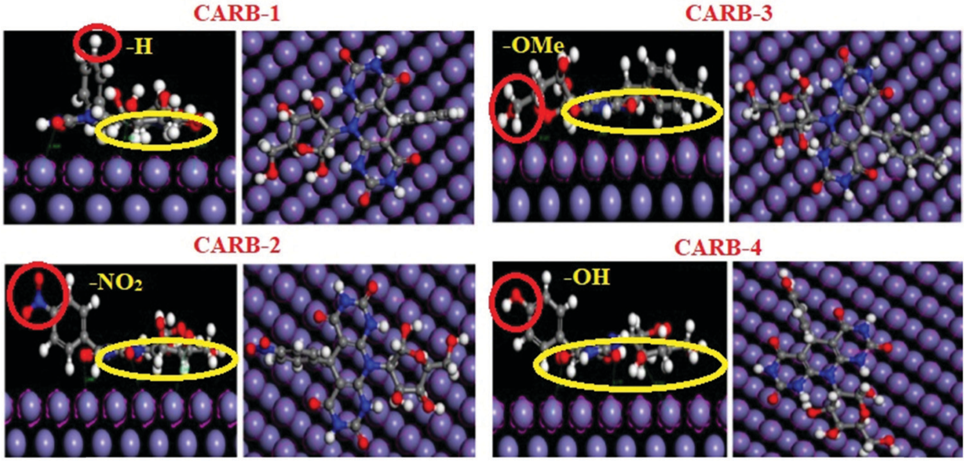


Fig. 6 Top and side views of CARB-1 (–H_2), CARB-2 (–NO_2), CARB-3 (–OH) and APQD-4 (–OMe) on the Fe(110) surface derived using Monte Carlo simulations.[17]

reaction parameter and its value mainly depends upon the nature of reaction. σ is the Hammett substituent constant and its value reflects the total electron density at the donor (adsorption) site(s). Generally, the negative sign of the Hammett constant is consistent with the electron donating ability of the substituents and *vice versa*.

It is extensively reported that electron donating substituents such as –OH (hydroxyl), –NH_2 (amino; 1°-amine), >NH (2°-amine), >N– (3°-amine), –CH_3 (methyl), –OCH_3 (methoxy), *etc.* generally increase the corrosion inhibition efficiency of organic compounds, whereas the converse is true for electron withdrawing substituents including –CN (nitrile), –NO_2 (nitro) and –COOH (carboxyl).[15] Moreover, the addition of a substituent also affects the overall molecular size of the compound to be used as the corrosion inhibitor. An organic compound with a larger molecular size is expected to be a more effective corrosion inhibitor as compared to the molecule that has a relatively smaller molecular size. Therefore, the effects of the molecular size and substituent on the inhibition efficiency for a specified class of organic compounds differ from case to case. Nevertheless, in most of the previous reports, it is observed that the presence of electron donating substituents increases the corrosion inhibition efficiency of organic compounds and the converse is true for electron withdrawing substituents.

M. Abdallah *et al.*[81] studied the inhibition efficiency of five 5-arylazothiazole derivatives for 1018 carbon steel corrosion in 0.5 M H_2SO_4 using experimental methods. These compounds differed in the nature of substituents and were designated as compound 1 (–NO_2), compound 2 (–Br), compound 3 (–H), compound 4 (–CH_3) and compound 5 (–OCH_3). The results derived through weight loss study showed that, as compared to the non-substituted 5-arylazothiazole derivative (compound 3), compounds 4 and 5 having electron donating substituents showed superior corrosion inhibition efficiency and compounds 1 and 2 having electron withdrawing substituents showed inferior corrosion inhibition efficiency. The weight loss study was further supported by electrochemical studies. The order of inhibition efficiencies derived from electrochemical studies was consistent with the order of weight loss. The analysis showed that the 5-arylazothiazole derivative containing the most electron withdrawing nitro substituent (compound 1) exhibited the lowest inhibition efficiency and the 5-arylazothiazole derivative containing the most electron donating methoxy substituent (compound 5) exhibited the highest inhibition efficiency (compound 1) toward 1018 carbon steel corrosion in 0.5 M H_2SO_4.

The effect of the substituents on the corrosion inhibition effectiveness of organic corrosion inhibitors is also investigated in various other reports.[15,82] Our research group also widely reported the effect of substituent on the corrosion inhibition effectiveness of organic compounds for mild steel in acidic hydrochloric acid solution. Findings from the literature investigation suggest that the inhibition efficiency of organic corrosion inhibitors is greatly dependent upon the nature of substituents. Therefore, it is important to notice that compounds that contain electron donating substituents would be preferred to be used as corrosion inhibitors as compared to compounds that contain electron withdrawing substituents in their molecular structures.

1.5. Corrosion inhibitors for industrial processes

Various industrial processes involve the utilization of highly concentrated acidic solutions.[83–85] One of the most significant and widely known acidic processes is acid pickling which involves the removal of rusts and surface impurities of metal plates, wires and pipelines and metal equipment in various industrial sectors including heat exchange, heat transfer, cooling systems and boilers. Acidic solutions of hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, sulfamic acid, citric acid, and hydrofluoric acid are commonly used in acid pickling and descaling processes to remove surface metal oxide based rusts and scales.[86] Because of their highly aggressive nature acidic solutions cause corrosion related failure of metallic structures during these processes. In addition, during these processes hydrogen gas is produced which can penetrate the interior of metal structures and can induce hydrogen embrittlement.[87]

Therefore, these industrial processes need the addition of some suitable chemical species called corrosion inhibitors. It is important to mention that most of the effective acid pickling based corrosion inhibitors are organic, especially heterocyclic compounds.[87] The addition of corrosion inhibitors not only avoids metallic corrosion but can also extend the service duration of metallic equipment and diminish the amount of acid used.

Organic compounds, especially organic amines, quaternary ammonium salt, urea and thiourea derivatives, rosin amine, acetylenic compounds, alkaloids, Mooney alkali and so on, are widely used as corrosion inhibitors for pickling in sulfuric acid solution.[88–90] On the other hand, acid pickling of various metallic alloys, especially mild steel and carbon steel, in hydrochloric acid mainly employs heterocyclic organic compounds containing N, O, P and S atoms.[91–95] Ammonia and thiourea based organic compounds are extensively used as corrosion inhibitors for pickling in hydrochloric acid based solutions. Metal oxides and boiler scales are extremely soluble in nitric acid. Nitric acid solutions are highly oxidizing in nature and therefore a relatively lower number of corrosion inhibitor formulations have been developed for pickling in nitric acid. Nevertheless, a mixture of hydrazine (C_8H_7N) and Na_2S or NH_4SCN and a mixture of thiourea and Na_2S are extensively used as corrosion inhibitors for pickling in nitric acid.[87] The pickling process in phosphoric acid solutions involves the consumption of various heterocyclic compounds including triazole, benzotriazole and urea derivatives, polyvinylpyrrolidone (PVP), sulfonated imidazoline, polyethyleneimine (PEI), *etc.*[96–99] along with the inorganic and their mixed-formulations. Organic compounds are also used as corrosion inhibitors for pickling in other acidic solutions. These compounds become effective by adsorbing on the metallic surface using their electron rich centers called adsorption sites. It is important to mention that lower concentrations of acidic solutions are used for the descaling process, whereas highly concentrated acidic solutions are used for the acid pickling process.

Another industrial process that requires the use of highly concentrated acidic solution is oil-well acidification in the petroleum industry.[100,101] In this process, a highly concentrated acidic solution of hydrochloric acid (mostly 15–28%) is injected into the well through a metallic pipeline to enhance the flow of oil. Tubing of these highly acidic solutions causes extensive corrosion of the metallic surface during the acidization process. Therefore, some external additives known as corrosion inhibitors are added into the acidizing solution. A literature study showed that most of the previously used inhibitors for the acidization process are heterocyclic compounds containing heteroatoms, especially N and O. Obviously, these compounds become effective by adsorbing on the metallic surface using their electron rich centers called adsorption centers. This type of adsorption results in the formation of a protective film which isolates the metal surface from aggressive solutions and protects from corrosive damage.

Most of the previously used industrially useful corrosion inhibitors are not environment-friendly because of their toxic nature and synthesis using toxic chemicals and solvents. However, because of the increasing ecological awareness and strict environmental regulations, the use of environment-friendly compounds as corrosion inhibitors derived through environment-friendly synthetic approaches and natural resources would be preferred. In view of this, compounds derived from amino acids are used as corrosion inhibitors for pickling, descaling and acidization processes.[102,103] Organic compounds (especially heterocyclic ones) derived from one-step multicomponent reactions (MCRs) with and without MW and US irradiations can be used as environment-friendly corrosion inhibitors for these industrial processes.[104–106]

2. Environment-friendly corrosion inhibitors: literature survey

2.1. Biopolymers as environment-friendly corrosion inhibitors

Biopolymers are natural polymers produced by the cells of animals and plants. Because of their natural (animal and plant) origin, biopolymers are considered as environment-friendly alternatives to be used for different biological and industrial applications. Moreover, unlike synthetic polymers, biopolymers are biodegradable and non-bioaccumulative. Some of the common biopolymers are polysaccharides (starch, cellulose, chitosan, *etc.*), polypeptides, nucleic acids (RNA & DNA), natural rubber, lignin, *etc.* Because of the increasing ecological awareness and environmental regulations, the use of environment-friendly biopolymers would be preferred. In view of this, various reports have been published describing the anticorrosive effect of biopolymers. It is important to mention that almost all kinds of biopolymers are evaluated as corrosion inhibitors; however, in the present study we described the corrosion inhibition effect of carbohydrate based polymers, especially chitosan and cellulose and their derivatives as they are the most frequently used biopolymer based corrosion inhibitors.

Chitosan is a linear polysaccharide of randomly distributed *N*-acetyl-D-glucosamine and D-glucosamine connected together by a β-1,4-glycosidic linkage.[107–109] *N*-Acetyl-D-glucosamine and D-glucosamine are called acetylated and deacetylated units, respectively.[107–109] Generally, the synthesis of chitosan is achieved by deacetylation of chitin as shown in Fig. 7. Chitosan possesses numerous industrial and biological applications and commercially fashioned by the partial deacetylation of chitin which is a structural constituent of the exoskeleton of crustacea (such as shrimps and crabs) and the cell walls of fungi.[110–112] Commercially useful chitosan acquires a degree of deacetylation (%DD) of 60–100 and a molecular weight of 3800–20 000 Da.[113,114] Polar substituents such as $-CH_2OH$ (hydroxymethyl), $-NHCOCH_3$ (acetyl), –OH (hydryl), $-NH_2$ (amine) and –O– (ether) present in the molecular structure of chitosan can effectively form bonding with the metallic surface. The anticorrosive effect of chitosan for metals and alloys is widely reported.[115–118] Because of their natural origin, chitosan based corrosion inhibitors are considered as environment-friendly.[119–121] Generally, chitosan modified with various organic compounds exhibits a higher corrosion inhibition efficiency than pure chitosan.

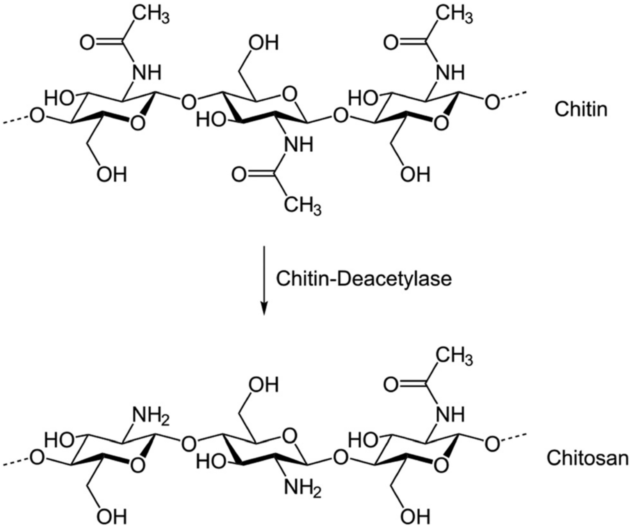


Fig. 7 Schematic illustration of the synthesis of chitosan from chitin.

Umoren *et al.*[122] reported the corrosion inhibition effect of chitosan for MS in HCl medium using chemical, surface characterization and electrochemical methods. Studies revealed that CH showed reasonably good efficiencies of 96% and 93% at 60 °C and 70 °C, respectively. Adsorption of CH followed the Langmuir adsorption isotherm model. Electrochemically it was derived that CH behaved as an interface- and mixed-type inhibitor for MS acidic corrosion. The anticorrosive effect of CH for MS in 1 M HCl has also been reported elsewhere.[123] Generally, chitosan acts as a mixed-type corrosion inhibitor by retarding the anodic as well as cathodic half-cell reactions. Recently, our research team described the influence of the inhibition of CH for MS corrosion in sulfamic acid medium.[124] Numerous experimental methods were employed to determine the inhibition efficiency of CH with and without potassium iodide, KI (5 ppm). The authors observed that at a 200 ppm concentration CH manifests 90% and 73.8% inhibition efficiencies with and without KI, respectively.[124] In all the experimental conditions CH behaves as a mixed-type inhibitor. The adsorption mechanism of CH on the MS surface was studied by means of SEM and AFM methods. The outcomes of this study showed that the presence of KI significantly improved the corrosion inhibition effectiveness of CH. An increase in the inhibition efficiency of organic corrosion inhibitors by the addition of other chemical species, especially salts (*e.g.* KI & $ZnCl_2$), is known as synergism. Synergism or the synergistic effect is widely investigated in the field of corrosion inhibition using organic compounds. CH is also used as a corrosion inhibitor for copper in acidic[125] and NaCl[126,127] electrolytes. Harmami and coworkers[128] demonstrated the inhibition effect of water soluble chitosan (WSC) derived from shrimp and mussel shells for tinplate in 2% NaCl medium. Protection efficiency was determined at different concentrations ranging from 10 to 1500 mg L^{-1}. The weight loss and PDP methods revealed that WSC derived from shrimp shell waste showed the highest efficiencies of 72.73% and 91.41%, respectively, whereas WSC derived from mussel shells showed the highest efficiency of 54.55% at a 1300 mg L^{-1} concentration. WSC derived from shrimp and mussel shell waste acted as mixed-type inhibitors (PDP analyses).

Although chitosan shows reasonably good anticorrosive properties in salt solutions and acidic electrolytes, its anticorrosive effect and solubility in aqueous electrolytes can be further enhanced by its functionalization using several species.[129–137] It is important to mention that this type of functionalization not only increases chitosan's solubility in polar electrolytes but also enhances its corrosion inhibition effectiveness by increasing the number of donor (active) sites responsible for interaction/adsorption with the metallic surface. Generally, this type of functionalization also increases the molecular size which results in a higher protection efficiency of chitosan derivatives as compared to chitosan itself. An inhibitor molecule with a larger molecular size acts as a better corrosion inhibitor as compared to the molecule with a smaller molecular size. Table 1 presents the functionalization of chitosan and its derivatives and their use in corrosion inhibition.

Recently, various reports dealing with the anticorrosive effect of Schiff bases (SBs) derived from aromatic aldehydes and chitosan have been published.[133] SBs show remarkably high solubility and protection efficiency in polar electrolytes as compared to pure chitosan. The increase in the protection effectiveness on adding organic moieties in the molecular structure of chitosan is attributed to the increased number of active centers and enhanced solubility. Haque *et al.*[138] synthesized three chitosan based SBs (CSBs) from benzaldehyde (CSB-1), 4-(dimethylamino)-benzaldehyde (CSB-2) and 4-hydroxy-3-methoxybenzaldehyde (CSB-3) and they were evaluated for their ability to prevent metallic corrosion in 1 M HCl. Among the tested CSBs, CSB-3 showed the highest protection efficiency of 90.65% at a 50 ppm concentration. SEM, EDX and FT-IR analyses were conducted to demonstrate the adsorption nature of corrosion protection. Electrochemical studies validated the mixed and interface-type nature of the tested CSBs. DFT and MD simulation studies indicated that the CSBs interact with the metal surface in the donor–acceptor mode and acquire planar orientations on the Fe(100) surface. CSBs are also reported as anticorrosive materials in other studies.[139,140] Most of the investigated SBs behave as mixed-type corrosion inhibitors as they adversely affect the anodic as well as cathodic Tafel reactions. Through EIS studies, it can be observed that SBs act as interface-type corrosion inhibitors as they become effective by adsorbing at the interface of metal and electrolyte.

Currently, cross-linking of chitosan with organic compounds and their relevance as corrosion inhibitors is gaining particular attention. Cross-linking of chitosan results in the joining of two or more polymeric chains (of chitosan) through an organic linker. This type of cross-linking increases the solubility as well as protection efficiency of chitosan derivatives.[141,142] Recently, Chauhan and coworkers[143] cross-linked chitosan with PEG (Cht-PEG) and evaluated its ability to act as a corrosion inhibitor for mild steel in 1 M sulfamic acid. Cht-PEG showed the highest protection of 93.9% at a 200 mg L^{-1} concentration. The Cht-PEG

Table 1 Chemical name, abbreviation, nature of adsorption, metal and electrolyte system, method of corrosion measurements, highest inhibition efficiency and optimum concentration of some chitosan derivatives evaluated as corrosion inhibitors

S. no.	Moiety attached from chitosan & abbreviation	Nature of adsorption	Electrolyte and metal	Method of corrosion monitoring	IE% and conc.	Ref.
1	Chitosan–cinnamaldehyde (Cinn-Cht)	Langmuir isotherm & mixed-type inhibitor	15% HCl/carbon steel	WL, EIS, PDP, SEM, DFT and MCS	87.72% at 600 ppm & 92.67% at 600 ppm + 10 mM KI	134
2	Carboxymethyl-chitosan-benzaldehyde (CMChi-B) & carboxymethyl-chitosan–urea-glutaric acid (CMChi-UGLU)	—	2% NaCl and 1–3 M HCl/steel	Fluidization techniques	CMChi-B (80.82%) > CMChi-UGLU (80.62%)	133
3	CH-Benzaldehyde (CSB-1), CH-4 (dimethylamino)benzaldehyde (CSB-2) & 4-hydroxy-3-methoxy benzaldehyde (CSB-3)	Langmuir isotherm & slight cathodic-type inhibitor	1 M HCl/mild steel	WL, EIS, PDP, SEM, EDX, FT-IR, DFT and MDS	CSB-3 (91.43%) > CSB-2 (89.87%) CSB-1 (88.63%) at 100 ppm	138
4	Chitosan–vanillin (Van-Cht)	Langmuir isotherm & mixed-type inhibitor	15% HCl/carbon steel	WL, EIS, EFM, PDP, SEM, FT-IR and DFT	92.72% at 500 mg L^{-1}	139
5	Chitosan–salicylaldehyde (CHSA)	Temkin adsorption isotherm/mixed-type inhibitor	1 M HCl/mild steel	WL, EIS, PDP, EDX and SEM	70.08% at 1500 ppm	140
6	Chitosan–thiosemicarbazide (TSFCS) & chitosan–thiocarbohydrazide (TCFCS)	Mixed-type inhibitors	2% Acetic acid/ 304 steel	PDP	TCFCS (92%) at 60 mg L^{-1}	141
7	Chitosan–poly(vinyl butyral) (PVB-Ch)	—	0.3 M salt solution/ carbon steel	EIS, PDP, SEM, EDX and Raman spectroscopy	—	142
8	Chitosan–polyethylene glycol (Cht-PEG)	Langmuir isotherm & slight cathodic-type inhibitor	1 M sulfamic acid/ mild steel	WL, EIS, PDP, SEM, FT-IR and DFT	93.9% at 200 ppm	143
9	Chitosan–polyethylene glycol (CS-PEG)	Langmuir isotherm & slight cathodic-type inhibitor	1 M HCl/mild steel	WL, EIS, PDP, AFM and DFT	93.9% at 200 mg L^{-1}	145
10	Chitosan–polyaniline (PANI/CTS)	Mixed-type inhibitor	0.5 M HCl/Q235 steel	EIS, PDP, SEM and DFT	79.02% at 200 ppm	146
11	Chitosan–methyl acrylate–ethylene diamine (CS-MAA-EN) & chitosan–methyl acrylate–triethylene tetramine (CS-MAA-TN)	—	5% HCl/carbon steel	WL, EIS, PDP and SEM	CS-MAA-EN (88.06%) > CS (84.22%) > CS-MAA-TN (69.46%) at 0.3%	135
12	Chitosan–polyaspartic acid (PASP/CS)	Anodic-type inhibitor	3.5% NaCl/ carbon steel	WL, EIS, PDP and SEM	87.56% at 20 ppm	136
13	Carboxymethyl chitosan (CMC)	Langmuir adsorption isotherm/mixed-type inhibitor	3.5% NaCl/1020 carbon steel	PDP, EIS	85.57% at 80 ppm	137

adsorption obeyed the Langmuir adsorption isotherm model. The polarization study validated the mixed and slightly cathodic dominance behavior of Cht-PEG. Cht-PEG interacts with the MS surface using the donor–acceptor mechanism. Recently, our research team reported the cross-linking of chitosan with thiocarbohydrazide (TC-Cht) and tested it as an anticorrosive material for stainless steel in 3.5% NaCl medium.[144] TC-Cht showed more than 94% efficiency at a 500 mg L^{-1} concentration. Similar to Cht-PEG, TC-Cht adsorption obeyed the Langmuir isotherm model and exhibited slightly cathodic behavior. SEM and EDX studies were performed to demonstrate the adsorption nature of corrosion protection.

The above chitosan based composite materials are also used extensively as corrosion inhibitors for different metals and alloys in various electrolytes. It is important to mention that these formulations exhibit superior anticorrosive properties to pure chitosan. Kong *et al.* synthesized a chitosan–polyaniline (PANI/CTS) and tested its anticorrosive effect for Q235 steel in acidic medium.[146] Electrochemical studies demonstrate that PANI/CTS manifests a mixed-type nature. Interactions of PANI/CTS with the Q235 steel surface take place through the donor–acceptor mode. SEM studies suggested that PANI/CTS adsorbs on the Q235 steel surface and improves the surface morphology of the inhibited metal specimen. Fig. 8 shows the SEM images of the Q235 steel surface after 2 h corrosion in 0.5 M HCl. It can be clearly seen that PANI/CTS remarkably smoothened the surface morphology of Q235 steel. This observation suggests that PANI/CTS forms an inhibitive film through adsorption on the Q235 steel surface. Other chitosan based composites such as chitosan–Zn nanoparticles,[147–150] chitosan–Ag nanoparticles,[151,152] chitosan–Cu, Ni, Au, and F,[153–155] chitosan/TiO_2,[156–158] chitosan–hydroxyapatite,[159–163] chitosan–polyamines,[135] chitosan–drug,[164] chitosan–polymer,[142,146,165,166] chitosan–boron nitrile,[167] chitosan–nanocomposites,[168–170] carboxymethyl chitosan grafted poly(2-methyl-1-vinylimidazole),[171,172] sulfonated chitosan,[173,174] chitosan–polymer blends,[142,175] *etc.* are also widely used as anticorrosive materials. Generally, the above chitosan based formulations showed a higher protection efficiency as compared to pure chitosan. Therefore, it is recommended that in future studies, instead of using pure chitosan, its derivatives would be preferred. Obviously, these compounds become effective by adsorbing on the metallic surface following the Langmuir adsorption isotherm model. Using potentiodynamic

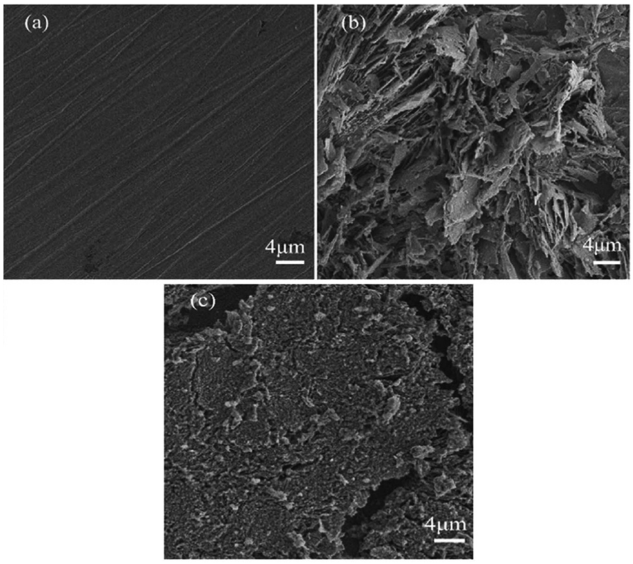


Fig. 8 SEM micrographs of Q235 steel (a) before and (b) after 2 h corrosion in 0.5 M HCl without PANI/CTS and (c) after 2 h corrosion in 0.5 M HCl with PANI/CTS.[146]

polarization studies, it can be observed that most of the chitosan based formulations act as mixed-type corrosion inhibitors as they become effective by retarding both anodic as well as cathodic Tafel (polarization) reactions.

Cellulose is another biologically and industrially useful carbohydrate based polymer. It is a linear chain polysaccharide composed of D-glucose units joined together by a β → 1–4-glycosidic linkage.[176,177] Cellulose has the general formula of $(C_5H_{10}O_5)_n$ and it is a structural component of plant cell walls, algae and oomycetes. Cellulose is one of the most plentiful polymers on the earth and around 90%, 40–5% and 57% of cellulose is present in cotton, wood and hemp, respectively.[178–181] Cellulose is widely used for various industrial and biological applications. However, its use as an anticorrosive material is scarce because of its limited solubility in most of the polar electrolytes. However, its derivatives are widely used either as corrosion inhibitors in aqueous electrolytes or as coating phase inhibitors.[182] Similar to other polysaccharides, cellulose and its derivatives can be regarded as environment-friendly alternatives to be used as corrosion inhibitors. The environment-friendly nature of cellulose and its derivatives is attributed to their biological origin and/or properties of biodegradation and non-bioaccumulation. Derivatization of cellulose has been widely reported; however, carboxymethyl cellulose (CMC) and hydroxymethyl cellulose (HEC) are most frequently utilized as corrosion inhibitors. Table 2 presents a summary of cellulose derivatives used as corrosion inhibitors.[183–199] Umoren *et al.*[183] reported the inhibition effect of CMC for MS corrosion in 2 M H_2SO_4 using weight loss (WL) and hydrogen evolution (HE) methods. The results showed that the adsorption of CMC obeyed the Langmuir adsorption isotherm model. The protection efficiency of CMC was measured at different temperatures in the absence and presence of KCl, KBr and KI (5 mM). Studies showed that significant improvement in the inhibition effectiveness was observed in the presence of halide salts, except in the case of KCl. The inhibition efficiency of CMC with halide salts followed the order: KI > KBr > KCl. CMC (0.5 g L^{-1}), CMC + KCl (5 mM), CMC + KBr (5 mM) and CMC + KI (5 mM) showed protection effectiveness of 56%, 48%, 63% and 85%, respectively.

The same group of authors reported the synthesis, characterization and corrosion inhibition effectiveness of the CMC and Ag nanoparticle (AgNP) composite (CMC/AgNPs) for St37 steel in 15% H_2SO_4 using chemical, electrochemical and surface morphological measurements.[184] The results showed that CMC/AgNPs inhibited corrosion by adsorption and its adsorption was reinforced by SEM, EDX, AFM and FT-IR methods. The SEM study showed that the surface morphology of the metal is improved significantly in the presence of CMC/AgNPs which validated the adsorption mechanism of corrosion inhibitors. This observation was further supported by the change in elemental composition in the EDX spectra of St37 steel recorded with and without CMC/AgNPs after 25 h immersion. The SEM and EDX spectra of the St37 surface after 25 h immersion in 15% H_2SO_4 with and without CMC/AgNPs are shown in Fig. 9. The corrosion inhibition properties of cellulose derivatives are also extensively reported in other studies for carbon and mild steel in acidic[4,6,13,14] and NaCl[3,14] electrolytes. They are also used as corrosion inhibitors for aluminum[7,8,11,12,15,18] and copper.[5,10,16] The synergistic effect of halide ions on the anticorrosive effect of cellulose derivatives for aluminum is also studied widely.[8,11]

Starch, consisting of linear amylose and branched-chain amylopectin, is also used as an effective corrosion inhibitor for metals and alloys. However, because of its limited solubility, its application in corrosion inhibition is limited. Therefore, chemically and physically modified starch is widely employed as a corrosion inhibitor for metals. Brindha *et al.*[200] demonstrated the anticorrosive properties of starch modified with 2,6-diphenyl-3-methylpiperidin-4-one (DPMP) for mild steel in acidic medium. Several chemical and electrochemical methods were employed and it was observed that the protection efficiency of modified starch was dependent on immersion time and temperature. The protection effectiveness of starch modified with sodium dodecyl sulfate (DS) and cetyltrimethylammonium bromide (CMAB) was reported using chemical and electrochemical techniques.[201] Later on, several other studies dealing with the anticorrosive effect of starch,[202–204] pectin,[205–210] dextrin & cyclodextrin,[13,211–215] pectate,[216,217] alginates[218,219] and exudate gums[220–225] are reported for metals and alloys in different electrolytes. The synergistic effect of halide ions is also reported for different classes of biopolymers.[226–229] Similar to chitosan, cellulose and their derivatives, these polymeric carbohydrates also behave as mixed-type corrosion inhibitors. They become effective by retarding the anodic and cathodic Tafel polarization reactions.

2.2. Plant extracts as environment-friendly corrosion inhibitors

Recently, the use of plant based materials is gaining particular attention because of their environmentally benign nature. Because of the natural and biological origin, plant based materials including

Table 2 Chemical name, abbreviation, nature of adsorption, metal and electrolyte system, method of corrosion measurements, highest inhibition efficiency and optimum concentration of some cellulose derivatives evaluated as corrosion inhibitors

S. no.	Moiety attached from chitosan & abbreviation	Nature of adsorption	Electrolyte and metal	Method of corrosion monitoring	IE% and conc.	Ref.
1	Carboxymethyl cellulose (CMC)	Langmuir adsorption isotherm	2 M H_2SO_4/mild steel	WL and hydrogen evolution	CMC (65% at 0.5 g L^{-1})	183
2	Hydroxyethyl cellulose (HEC)	Langmuir isotherm & mixed-type inhibitor	3.5 NaCl/1018 c-steel	PDP, EIS, EFM, SEM, EDX and DFT	95.5% at 0.5 mM	185
3	Hydroxyethyl cellulose (HEC)	Freundlich isotherm & mixed-type inhibitor	0.5 M H_2SO_4/mild steel	WL, EIS, PDP, DFT and MDS	70.35% at 2000 mg L^{-1} (333 K)	186
4	Hydroxyethyl cellulose (HEC) 2017	Langmuir isotherm & mixed-type inhibitor	1 M HCl/A1020 carbon steel	WL, PDP, EIS, SEM, EDX, AFM and DFT	91.62% at 500 ppm	187
5	Ethyl hydroxyethyl cellulose (EHEC)	Langmuir isotherm & slightly cathodic-type inhibitor	1 M H_2SO_4/mild steel	WL, EIS, PDP and DFT	68.19% (EHEC) and 91.05% (EHEC + KI) at 2.5 g L^{-1}	188
6	Hydroxyethyl cellulose (HEC)	Langmuir isotherm & mixed-type inhibitor	2% NH_4Cl, zinc–carbon battery	PDP, EIS, SEM and FT-IR	92.07% at 300 ppm	189
7	Hydroxypropyl cellulose (HPC)	Langmuir isotherm & mixed-type inhibitor	0.5 M HCl and 2 M H_2SO_4/aluminum	WL, PDP and DFT	92.54% (H_2SO_4) & 80.33% (HCl) at 5 g L^{-1}	190
8	Hydroxyethyl cellulose (HEC) & hydroxypropyl methylcellulose (HPMC)	Slightly cathodic-type inhibitors	1 M HCl/aluminum	WL, PDP, EIS and DFT	HEC (83.25%) and HPMC (84.68%) at 2000 mg L^{-1} (1 day)	191
9	Hydroxyethyl cellulose (HEC)	Langmuir isotherm & mixed-type inhibitor	0.5 M H_2SO_4/mild steel & aluminum	WL, EIS, PDP, DFT and MDS	93.61% (mild steel) 64.18% (Al) at 2000 mg L^{-1}	192
10	Cellulose acetate	—	0.5, 1, 2 & 3 M HCl/aluminum	WL and SEM	55.71%	193
11	Sodium carboxymethyl cellulose (Na-CMC) 2020	Freundlich adsorption isotherm	1 M HCl/aluminum	WL	86.0% at 1 g L^{-1} (at 35 °C)	194
12	Hydroxyethyl cellulose (HEC)		0.5 M HCl/mild steel & aluminum	WL	67.94% at 2.5×10^{-3} M	195
13	Carboxymethyl cellulose/AgNPs composite (CMC/AgNPs)	Langmuir isotherm & mixed-type inhibitor	15% H_2SO_4/St37 steel	WL, EIS, PDP, SEM, EDX, AFM and FT-IR	96.37% at 1000 ppm (at 60 °C)	184
14	Chitosan (CH) and carboxymethyl cellulose (CMC)	Langmuir isotherm & mixed-type inhibitors	3.5% NaCl + CO_2/API 5 L X60 pipeline steel	EIS, PDP and SEM	88% (Commercial inh.), 45% (CH) and 39% (CMC) at 100 ppm	196
15	Hydroxyethyl cellulose (HEC)	Mixed-type inhibitor	1 M HCl and 0.5 M H_2SO_4/copper	WL, EIS, PDP, DFT and MDS	95% at 2000 mg L^{-1}	197
16	Sodium carboxymethyl cellulose (Na-CMC)	Langmuir isotherm & slightly cathodic-type inhibitor	Simulated water (NaCl)/copper	PDP, EIS, AFM, FT-IR, DFT and MDS	83.34% at 5 mg L^{-1}(at 20 °C)	198
17	NEC, NMCC & NCMC	Mixed-type inhibitors	3.5% NaCl/copper	PDP, EIS, SEM and EDX	94.7% (NEC), 33.2% (NMCC) & 83.4% (NCMC) at 100 ppm	199

plant extracts are environment-friendly alternatives to be used as metallic corrosion inhibitors for different biological and industrial applications.[230–234] Generally, each plant extract contains several complex phytochemicals containing several electron rich centers that can act as adsorption centers during metal–inhibitor interactions.[230,235–237] The electron rich centers include polar functional groups such as hydroxyl (–OH), amino (–NH_2), ester (–$COOC_2H_5$), amide (–$CONH_2$), acid chloride (–COCl), dimethyl amino (–NMe_2), methoxy (–OMe), ether (–O–), *etc.* and multiple bonds such as $>C{=}C<$, $>C{=}N–$, $>C{=}O$, $–N{=}O$, $–C{\equiv}C–$, $–C{\equiv}N$, $–N{=}N–$, *etc.*

Although most of the phytochemicals are complex molecules, they are readily soluble in polar electrolytes because of their association with high peripheral functionalities in the form of polar functional groups. Plant extracts are extensively used as environment-friendly corrosion inhibitors for different metals and alloys in different electrolytic systems. The protection efficiency of extracts that have a relatively lower protection efficiency against metallic corrosion can be further enhanced by using inorganic salts such as KI that affect inhibition protectiveness through synergism.[238–240] Because of their huge availability at the cost-effective and commercial level, the development and consumption of plant extracts are increasing day by day. Extracts of several parts of plants such as leaves, barks, fruits, peels, flowers, *etc.* are widely used as corrosion inhibitors.[241] Generally, extracts of plants are prepared in a biphasic system consisting of an organic and an aqueous phase. A schematic illustration of the preparation of extracts is shown in Fig. 10. Before application, the prepared plant extracts should be stored in a refrigerator at low temperature. Table 1 presents a summary of some major works on extracts as corrosion inhibitors.

Among the different parts of plants, the extracts of leaves are most commonly tested as they showed the highest protection efficiency. In most of the plants, the synthesis of phytochemicals mostly takes place in leaves and therefore leaves are the part of plants that are richest in phytochemicals.

Similar to organic corrosion inhibitors, phytochemicals are generally rich in electron donor sites called active or adsorption sites. These electron rich sites of phytochemicals include polar functional groups and multiple bonds. Using these electron rich sites, phytochemicals form strong bonding with the metallic surface, especially through coordination bonding, and behave as

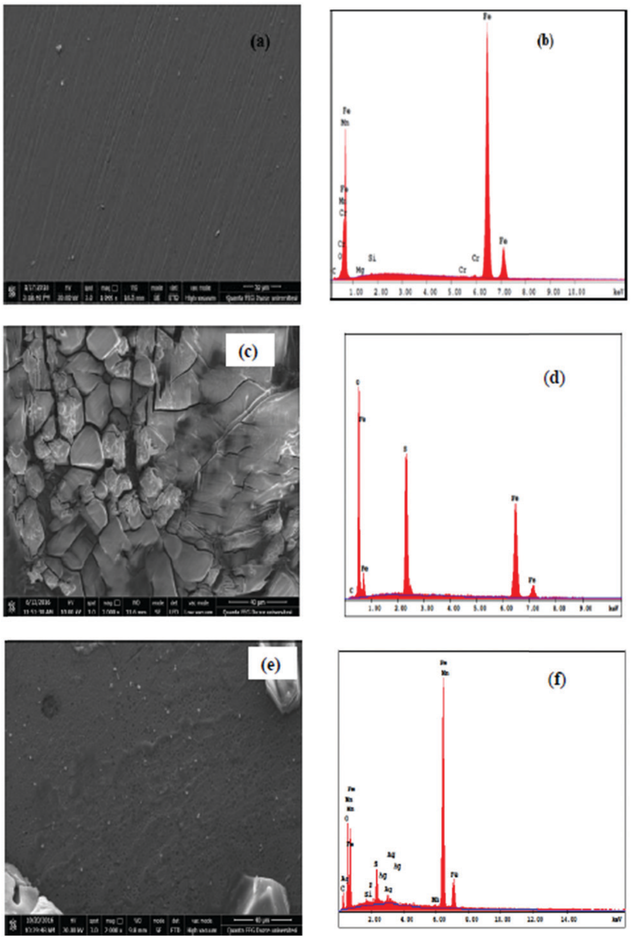


Fig. 9 SEM and EDX spectra of (a and b) abraded St37 surface, (c and d) corroded St37 surface in 15% H_2SO_4 without CMC/AgNPs for 25 h at 25 °C and (e and f) corroded St37 surface in 15% H_2SO_4 with 1000 ppm of CMC/AgNPs for 25 h at 25 °C. The morphology of the St37 steel surface is significantly improved in the presence of CMC/AgNPs.[184]

strong ligands. Table 3 presents a collection of major leaf extracts evaluated as corrosion inhibitors. Mehdipour *et al.*[242] reported the corrosion inhibition effect of aloe vera leaf extract as an effective corrosion inhibitor for stainless steel in sulfuric acid medium using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and scanning electron microscopy (SEM). The polarization study revealed that the extract retards both anodic and cathodic reactions and behaves as a mixed-type corrosion inhibitor. However, the authors observed slight anodic predominance. EIS studies showed that the extract becomes effective by controlling the charge transfer process. This finding suggested that the extract acted as an interface-type corrosion inhibitor as it becomes effective by adsorbing at the interface of the metal and electrolyte. The SEM analysis showed that, in the absence of the extract, the metallic surface was extremely damaged because of the unrestricted acidic attack. However, in the presence of the extract, the metallic surface became smooth and was protected significantly. This observation suggested that the phytochemicals present in the extract adsorbed and formed a corrosion protective film over the metallic surface. A similar finding has also been reported using plant extracts as corrosion inhibitors for metals and alloys in various electrolytes (Table 3).

2.3. Chemical medicines as environment-friendly alternatives

Chemical medicines or drugs represent another class of environment-friendly alternatives to the traditional toxic corrosion inhibitors. Several reports dealing with the inhibition effect of drugs have been published.[318–321] Chemical medicines are ideal environment-friendly alternatives as they are derived from biological and natural resources. Further, most of the drugs are bio-tolerable, bio-compatible and non-bioaccumulative in nature and therefore they offer environmentally sustainable alternatives.[322,323] Generally, drugs are complex molecules with several electron rich centers in the way of polar functional groups and multiple bonds through which they acquire a high anticorrosion ability. Because of their macromolecular nature, most of the drugs provide a large surface coverage and a high protection efficiency. Possessing numerous polar functional groups along with enhanced protection efficiency, they synergize the solubility of drug molecules in polar electrolytes. In view of their high efficiency, high solubility in polar electrolytes and environmental sustainability, numerous classes of drug molecules are evaluated as effective corrosion inhibitors for numerous metals and alloys in versatile electrolytes. Although the use of chemical medicines is an environmentally sustainable alternative method of corrosion inhibition, most of the drug molecules are highly expensive. Their high cost is associated with their multistep synthesis and ultra-purification processes. In view of this, corrosion scientists have started to use expired drugs as corrosion inhibitors.[324,325] Most of the expired drugs are thrown out as they are useless after their expiry. Although the application of such drugs in the biological system is not possible, they can be effectively used in industries for various applications. One of the greatest uses of expired drugs is in metallic corrosion inhibition. The use of expired drugs as corrosion inhibitors represents an environment-friendly and cost-effective approach.[325] Because of this, several articles and research papers have been published on expired drugs as corrosion inhibitors.[326,327] Various new and expired drugs are tested as effective corrosion inhibitors for different metals and alloys in various electrolytes. A summary of some major reports on the anticorrosive effect of drug molecules is provided in Table 4. Most of the drug molecules contain highly complex structures that enable them to be effective species to act as good corrosion inhibitors. They become effective by adsorbing on the metallic surface. The adsorption of drug molecules on the metallic surface mostly followed the Langmuir adsorption isotherm model. Using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), it can be observed that drug molecules mostly behaved as mixed- and interface-type corrosion inhibitors. The adsorption of drug molecules on the metallic surface is mainly supported by SEM, AFM and FT-IR spectroscopy studies.

2.4. Ionic liquids as environment-friendly corrosion inhibitors

Ionic liquids are salts in a liquid (molten) state.[358] Ionic liquids are composed of organic cations and inorganic anions and they

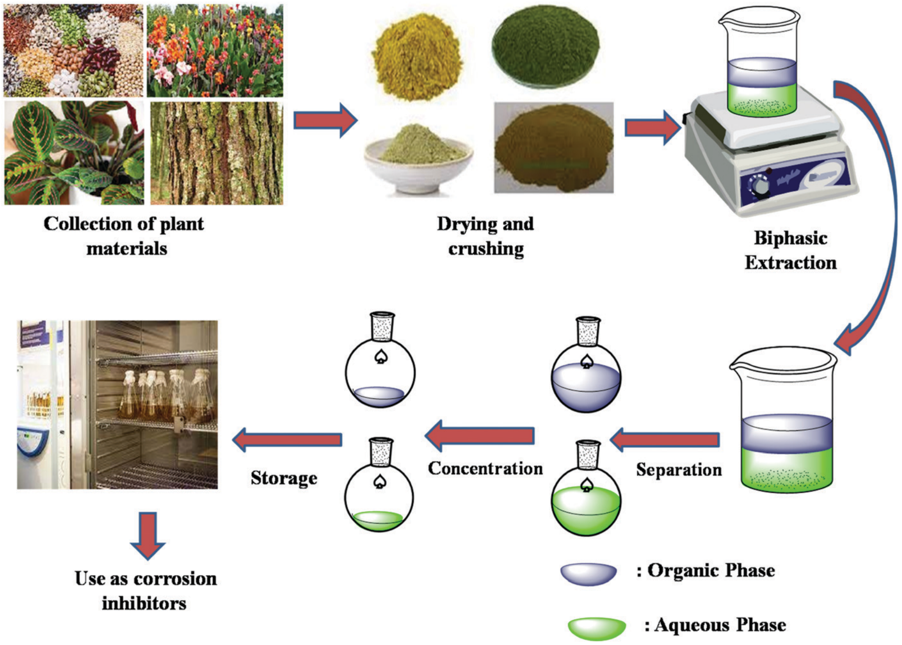


Fig. 10 Schematic illustration of the collection, drying, crushing, separation, extraction, concentration and storage of plant extracts.

are liquid at or below 100 °C.[359,360] Ionic liquids are also called ionic glasses, ionic melts, liquid fluids, ionic electrolytes or fused salts. Ethylammonium nitrate (MP: 12 °C) was the first reported ionic liquid (in 1914).[361,362] After that, several classes of ionic liquids have been developed and used for industrial and biological applications.[363–366] Ionic liquids are characterized by their ability to dissolve a wide range of organic and inorganic compounds. Because of their association with several environment-friendly properties including low toxicity, low melting point, high polarity, low vapor pressure and high resistivity for thermal and chemical treatment, ionic liquids are ideal environmentally benign alternatives to the traditional corrosion inhibitors.[57,367,368] Unlike traditional organic compounds, ionic liquids are readily soluble in polar electrolytes and manifest reasonably high protection effectiveness. Ionic liquids are rightly called designer corrosion inhibitors as their inhibition effect can be suitably tailored using a proper combination of cations and anions.[9,57] The chemical structures of major cations and anions are presented in Fig. 11. Ionic liquids can be classified as neutral, basic, acidic, functionalized or supported type.[369–371]

The literature study showed that several classes of ionic liquids are used as effective corrosion inhibitors for different metals and alloys.[57,367,372–374] Imidazolium based ionic liquids are most frequently used as corrosion inhibitors.[368,375–377] Likhanova *et al.*[378] proposed that the cationic and anionic moieties of ILs differently adsorb on cathodic and anodic active sites and inhibit the corrosion. The cationic part of ionic liquids mainly adsorbs on cathodic sites and anionic moieties mainly adsorb at anodic sites. While studying the corrosion inhibition effect of three imidazolium based liquids for mild steel corrosion in 1 M HCl, the authors observed that the inhibition effect was largely dependent on the nature of anions present in the investigated ionic liquids.[379] Imidazolium based ionic liquids interact with the metal surface through donor–acceptor interactions and acquire planar orientations. The polarization study showed that the tested ionic liquids behaved as mixed-type corrosion inhibitors, *i.e.* the tested ionic liquids adversely affect the rate of cathodic and anodic Tafel reactions. Polarization curves for mild steel corrosion in 1 M HCl with and without the evaluated ionic liquids are shown in Fig. 12. The observation of Fig. 12 shows that the shapes of both anodic and cathodic curves are affected by the presence of ionic liquids which validated the finding that ionic liquids adversely affect the rate of corrosion reactions. The adsorption mechanism was reinforced using SEM and AFM studies. SEM and AFM micrographs of the mild steel surface corroded in 1 M HCl for 3 h are shown in Fig. 13. It can be seen from the SEM and AFM images of the black specimen that the surface of the specimen is highly corroded because of free acid attack. However, in the presence of ionic liquids, the surface morphologies of the metallic specimens are greatly improved because of their anticorrosive effect. The order of metallic surface smoothness is consistent with the order of corrosion inhibition effect of ionic liquids. The average surface roughness of non-protected metallic surface was 372 nm. The average surface roughness in the presence of [bmim][Cl], [bmim][CF_3SO_3] and [bmim][Ac] 187, 134 and 114 nm, respectively.

Table 5 presents a summary of some major reports published on the anticorrosive effect of imidazolium based ionic liquids.[380–401] Several experimental and computational methods are employed to demonstrate the anticorrosive effect of imidazolium ionic liquids. It can be observed that most of the ionic liquids become effective against metallic corrosion by adsorbing on the metallic surface. Adsorption of imidazolium ionic liquids mostly follows the Langmuir adsorption isotherm; however, other adsorption isotherm mechanisms have also been reported. Adsorption of ionic

Table 3 Chemical name and metal and electrolyte system of some plant extracts evaluated as corrosion inhibitors

Plant name	System	Ref.	Plant name	System	Ref.
Leaf extracts as corrosion inhibitors in H_2SO_4					
Aloe vera	Fe/1 M H_2SO_4	242	*Spondias cytherea*	Fe/5 M H_2SO_4	243
Citrus aurantium	Fe/1 M H_2SO_4	244	*Combretum bracteosum*	Fe/2& 5 M H_2SO_4	245
Sida acuta (leaf and stem)	Fe/1 M H_2SO_4	246	*Hyptis suaveolens*	Fe/1 M H_2SO_4	247
African parquetina	Fe/2 M H_2SO_4	248	*Polyalthia longifolia*	Fe/1 M H_2SO_4	249
Emblica leaves	Fe/2 M H_2SO_4	250	*Buddleia perfoliata*	Fe/0.5 M H_2SO_4	251
Cassia tora	Fe/0.5 M H_2SO_4	252	*Bambusa glaucescens*	Fe/2 M H_2SO_4	253
Nicotiana tabacum	Fe/2 M H_2SO_4	254	*Vernonia amygdalina*	Fe/1.5 M H_2SO_4	255
Mango (Mangifera indica)	Fe/1 M H_2SO_4	256	*Cassava (Manihot esculenta)*	Fe/0.5 M H_2SO_4	257
Achyranthes aspera	Fe/0.5 M H_2SO_4	258	*Oxystelma esculentum*	Fe/0.5 M H_2SO_4	259
African breadfruit	Fe/1 M H_2SO_4	260	*Stachytarpheta indica*	Fe/1 M H_2SO_4	261
Jatropha curcas	Fe/0.5 M H_2SO_4 and 0.5 M NaCl	262	*Sida acuta*	Fe/1 M H_2SO_4	263
Wrightiatinctoria, Clerodendrumphlomidis, Ipomoeatriloba	Fe/0.5 M H_2SO_4	264	*Nauclea latifolia (leaf, bark, root)*	Fe/1 M H_2SO_4	265
Leaf extracts as corrosion inhibitors in HCl					
Olea europaea	Fe/2 M HCl	266	*Azadirachta excelsa*	Fe/1 M HCl	267
Tabernaemontana divaricata	Fe/1 M HCl	268	*Boscia senegalensis*	Fe/1 M HCl	269
Phyllanthus amarus	Fe/1 M HCl	270	*Acalypha indica*	Fe/1 M HCl	271
Eleusine aegyptiaca and Croton rottlerin	Fe/1 M HCl	272	*Phoenix dactylifera*	Fe/1 M HCl	273
Pimenta dioica	Fe/0.5 M and 1.0 M HCl	274	*Ruta graveolens*	Fe/1 M HCl	275
Thyme	Fe/2 M HCl	276	*Annona muricata L.*	Fe/1 M HCl	277
(Guatteria ouregou and Simira tinctoria)	Fe/1 M HCl	278	*Michelia alba*	Fe/mild steel 1 M HCl	279
Morusalba pendula	Fe/1 M HCl	280	*Anthocleista djalonensis*	Fe/1 M HCl	281, 282
Ficus hispida	Fe/1 M HCl	283	*Morinda tinctoria*	Fe/1 M HCl	282
Solanam xanthocarpum	Fe/1 M HCl	284	*Vitex negundo*	Fe/1 M HCl	285
Gliricidia sepium	Fe/1 M HCl	286	*Gymnema sylvestre*	Fe/1 M HCl	287
Rosmarinus officinalis L.	Fe/0.1 M HCl	288	*Argemone mexicana*	Fe/1 M HCl	289
Eichhornia crassipes	Fe/5 M HCl	290	*Acalypha torta*	Fe/1 M HCl	291
Murraya koenigii (curry leaves)	Fe/1 M HCl	292	*Podranea ricasoliana*	Fe/1 M HCl	293
Petroselinum crispum (parsley), Eruca sativa (Arugula), Anethum graveolens	Fe/1 M HCl	99	*Passiflora foetida*	Fe/1 M HCl	294
Emblica officinalis	Fe/1 M HCl	295	*Funtumia elastica*	Fe/1 M HCl	296
Pterocarpus soyauxii	Fe/1–2.5 M HCl	297	*Tithonia diversifolia*	Fe/1 M HCl	298
Plumeria alba, Blighia sapida, Secamone afezeli	Fe/1 and 2 M HCl	299	*Gnetum africana*	Fe/1 M HCl	300
Emblica officinalis	Fe/1 M HCl	301	*Lactuca sativa, etc.*	Fe/1 M HCl	302
Sesbania sesban	Fe/1 M HCl	303	*Bryophyllum pinnatum*	Fe/0.5 M HCl	304
Sansevieria trifasciata	Al/2 M HCl & 2 M KOH	305	*Piper longum*	Al/1 M NaOH	306
Gossypium hirsutum (leaf and seed)	Al/2 M NaOH	307	*Nicotiana tabacum*	AA3003Al/0.1 M HCl	308
Phyllanthus amarus	Al/2 M NaOH	309	*Cannabis sativa (CS)*	Al/1 M NaOH	310
Jasminum nudiflorum Lindl.	Al/1 M HCl	311	*Vernonia amygdalina*	Al/1 M HCl	312
Raphia hookeri	Al/0.02–2 M HCl	223	*Tender arecanut*	Al/0.5 M HCl	313
Thymus algeriensis	Al/1 M HCl	314	*Breadfruit*	Al/0.5 M H_2SO_4	260
Cocos nucifera	Al/0.5 M HCl	315	*Maesobatrya barteri*	Al/0.5 M and 2 M HCl	316
Morinda tinctoria	Al/0.5 M HCl	317			

liquids results in an increase in the value of charge transfer resistance that occurs in the form of an effective anticorrosive barrier. Most of the evaluated ionic liquids behave as interface-type corrosion inhibitors. Imidazolium based ionic liquids containing hydrophobic alkyl chain(s) exhibit a reasonably good anticorrosive effect relative to those without hydrophobic chain(s). In this case, it can be expected that the polar and electron rich hydrophilic imidazole ring interacts with the metal surface and forms a protective film, whereas hydrophobic alkyl chains float and prevent the water from coming into contact with the metal surface. Therefore, an increase in the length of the hydrophobic chain is expected to increase the inhibition effect of ionic liquids. Nevertheless, an increase in hydrophobicity can adversely affect the solubility of such ionic liquids in polar electrolytes. Therefore, a proper combination of hydrophilicity and hydrophobicity is highly essential while designing effective corrosion inhibitors.[389,402] The anticorrosive effect of pyridinium,[378,403–405] pyrrolidinium,[406–408] ammonium[9,409–412] and phosphonium[409,413] based ionic liquids has also been reported in the literature.

Because of their high solubility and environmentally benign nature ionic liquids are also tested as anticorrosive agents for other metals and alloys. Zhang and Hua[414] demonstrated three imidazolium based ionic liquids designated as BMIC, HMIC and OMIC for aluminum in 1 M HCl using chemical and electrochemical methods. BMIC, HMIC and OMIC inhibit Al corrosion by adsorbing on the metallic surface, which followed the Langmuir adsorption isotherm model. The inhibition effect followed the order: BMIC < HMIC < OMIC. All the tested ionic liquids acted as mixed type corrosion inhibitors. In another report,[415] the anticorrosive effect of an ionic liquid, designated as OPEIB, was evaluated for the 6061 Al-15 alloy in 0.5 M H_2SO_4

Table 4 Chemical structures and names of some major drugs that have been tested as corrosion inhibitors for different systems

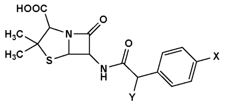
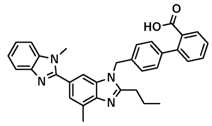
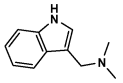
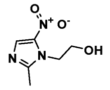
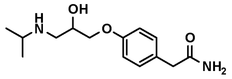
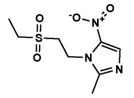
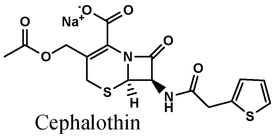
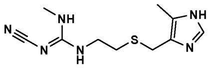
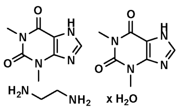
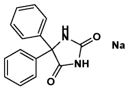
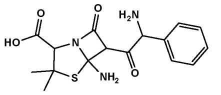
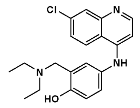
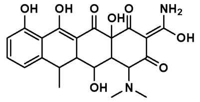
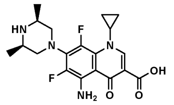
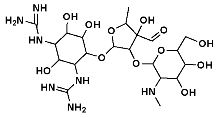
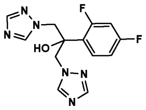
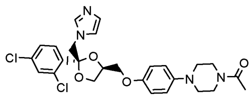
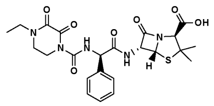
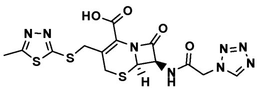
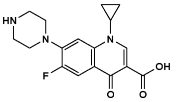
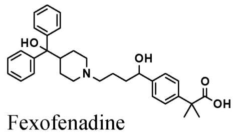
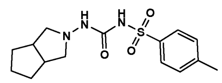
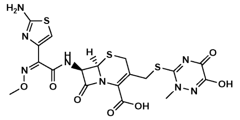
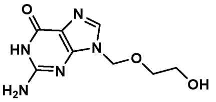
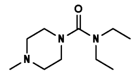
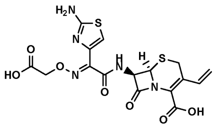
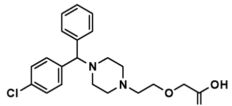
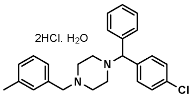
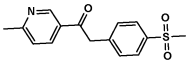
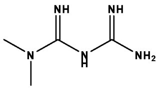
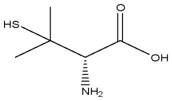
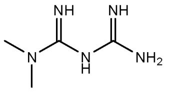
Drug name and structure	System	Ref.	Drug name and structure	System	Ref.
 Penicillin G (X, Y=H);ampicillin (X=H, Y=-NH$_2$); amoxicillin (X=-OH, Y=-NH2)	Fe/1 M HCl	328	 Telmisartan	Fe/1 M HCl	329
 Donaxine	Fe/1 M HCl	330	 Metronidazole	Fe/0.5 M HCl	331
 Atenolol	Fe/1 M HCl	332	 Tinidazole	Fe/1 M HCl	333
 Cephalothin	Fe/1 M HCl	334	 Cimetidine	Fe/1 M HCl	335
 Aminophylline	Fe/1 M HCl	336	 Phenytoin	Fe/1 M HCl	324
 Ampicillin	Fe/0.1 M H_2SO_4	337	 Amodiaquine	Fe/1 M HCl	338
 Doxycycline	Fe/1 M HCl	339	 Sparfloxacin	Fe/2.5 M HCl	340
 Streptomycin	Fe/1 M HCl	341	 Fluconazole	Fe/2.5 M HCl	340
 Ketoconazole	Fe/0.1 M H_2SO_4	342	 Piperacillin Sodium	Fe/1 M HCl	343
 Cefazolin	Fe/1 M HCl	344	 Ciprofloxacin	Fe/1 M HCl	345
 Fexofenadine	Fe/1 M HCl	346	 Gliclazide	Fe/1 M HCl	347
 Ceftriaxone	Fe/1 M HCl	348	 Acyclovir	Fe/1 M HCl	349

Table 4 (*continued*)

Drug name and structure	System	Ref.	Drug name and structure	System	Ref.
 diethylcarbamazine	Fe/1 M HCl	350	 Cefixime	Fe/1 M HCl	351
 Cetirizine	Fe/1 M HCl	352	 Meclizine hydrochloride	Fe/1 M HCl	353
 Ketosulfone	Fe/1 M HCl	354	 Metformin	Fe/1 M HCl	355
 d-penicillamine	Fe/1 M HCl	356	 Metformin (expired)	Fe/15% HCl	357

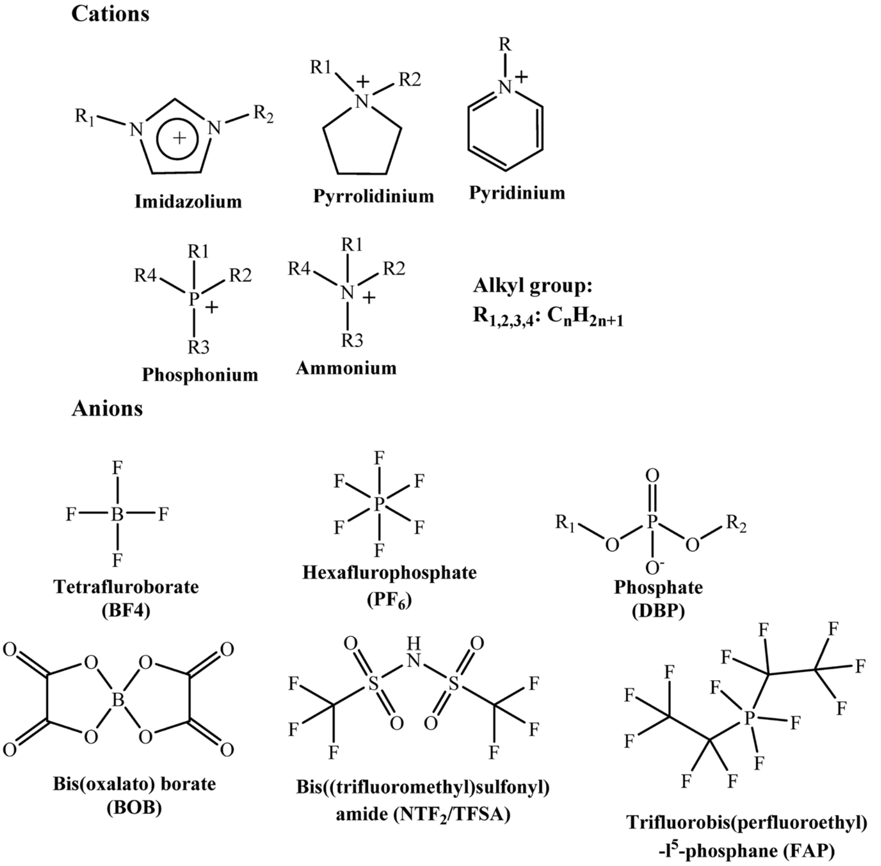


Fig. 11 Chemical structures of some common cations and anions of ionic liquids that can be used for anticorrosive applications.

using electrochemical and surface analyses. OPEIB acted as a mixed type inhibitor and its adsorption obeyed the Temkin adsorption isotherm model. The anticorrosive effect of ionic liquids for aluminum including the inhibition effect of three poly(ionic liquids) for the 6061 Al-15 alloy in 0.1–1 M HCl[416] and quaternary ammonium based surfactants ($CmC_6Cm(Et)\cdot 2Br$: m = 10, 12, 14, 16) for the Al/1 M HCl system,[417] *etc.* has been widely reported in the literature.[418–420] Ionic liquids are

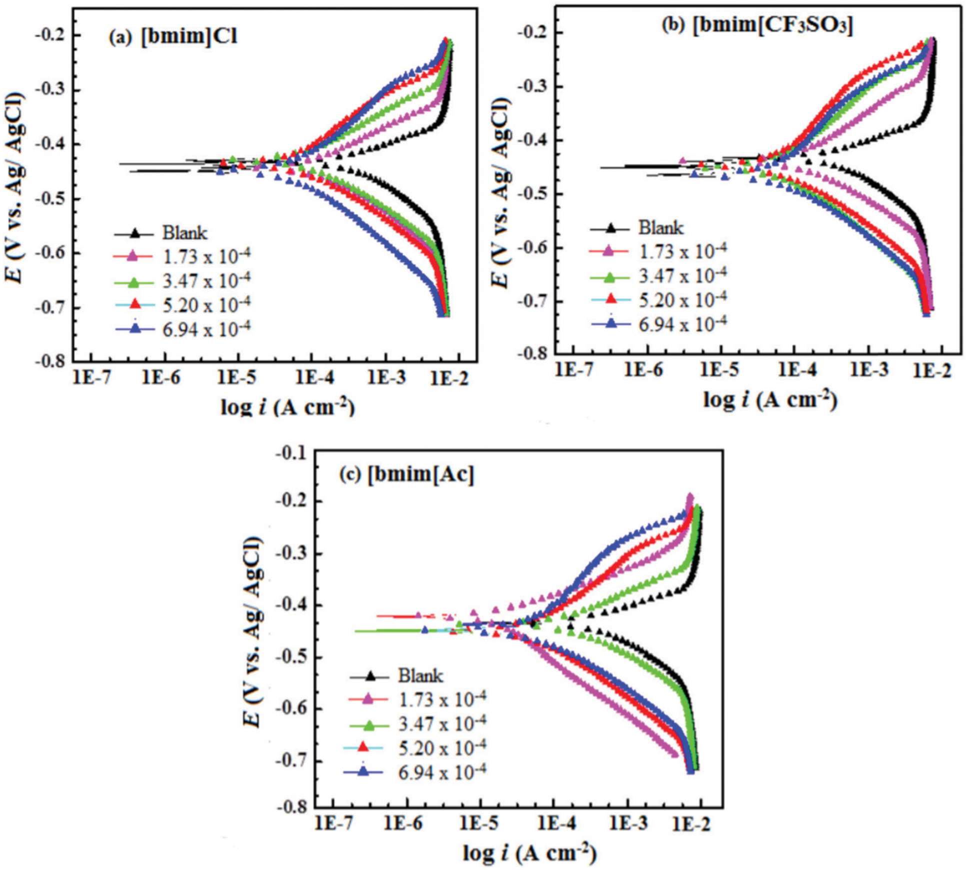


Fig. 12 Potentiodynamic polarization curves for mild steel corrosion in 1 M HCl in the absence and presence of (a) [bmim][Cl], (b) [bmim][CF$_3$SO$_3$] and (b) [bmim][Ac] at different concentrations.[379]

also widely used as corrosion inhibitors for zinc[421,422] and copper[401,422–424] in various electrolytes. In most of the studies, ionic liquids acted as mixed-type corrosion inhibitors and their adsorption followed the Langmuir adsorption isotherm model. Using the EIS technique, it was observed that most of the investigated ionic liquids behaved as interface-type corrosion inhibitors as they become effective by forming a protective film over the metallic surface.

2.5. Polyethylene glycols as environment-friendly corrosion inhibitors

Polyethylene glycols (PEGs) represent a special class of industrially and biologically useful compounds. PEGs are connected with several advantages including low flammability, vapor pressure, cost and environmental toxicity.[425] PEGs are available in different molecular weights varying from 200 to tens of thousands.[425,426] Low molecular weight PEGs (200–600 D) are in the liquid form at room temperature. PEGs having a molecular weight of 600–800 D are water soluble viscous materials. PEGs having a molecular weight greater than 800 D are in the form of solids. The solubility of PEG polymers decreases with the increase in the molecular weight as PEGs-200–600 D are fully soluble in water, whereas PEG-2000 shows only 60% solubility (at 20 °C) in water. Because of their environment-friendly nature, biocompatibility, high molecular weight and great solubility in polar electrolytes, PEGS are widely used as corrosion inhibitors for metals and alloys. Because of their polymeric nature, PEGs provide massive surface coverage and protection and therefore behave as effective corrosion inhibitors. Although several review articles dealing with the various aspects of PEGs are published, no review on the anticorrosive effect of PEGs has been published yet.[425,427–429] The literature survey demonstrates that PEGs possess a strong ability to interact with the metallic surface as they form strong coordination bonding with the metallic substrate.[430] Unlike the traditional corrosion inhibitors, PEGs are nonvolatile, nonflammable and biodegradable which are the requirements for being environmentally benign.[431–433] PEGs are relatively stable for chemical and thermal treatments and therefore they can be used as effective corrosion inhibitors at high temperature over a wide pH range.[434–436] PEGs are almost insusceptible to H_2O_2 oxidation and reduction *via* $NaBH_4$. PEGs possess the ability to recover from the medium they use.[437,438]

PEGs are widely employed as corrosion inhibitors in different electrolytes. Ashassi-Sorkhabi and Ghalebsaz-Jeddi[439] reported the anticorrosive properties of PEGs with molecular weights in the range of 200–10 000 g mol^{-1} for carbon steel in 3 N using chemical and electrochemical methods. It was observed that PEGs exhibited greater than 90% efficiency at a 10^{-1} M

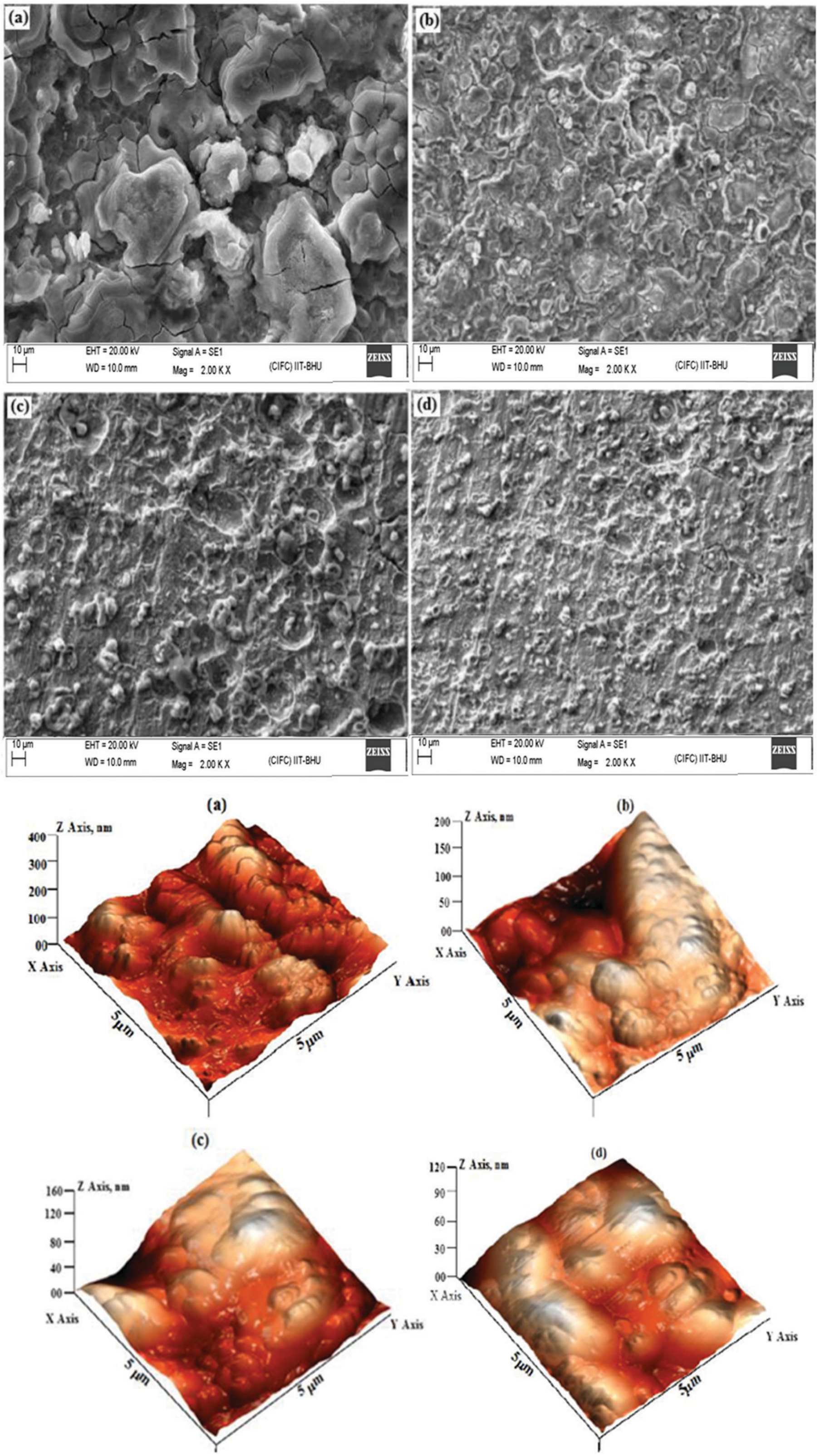


Fig. 13 SEM (above) and AFM (below) micrographs of the mild steel surface in the (a) absence and presence of (b) [bmim][Cl], (c) [bmim][CF_3SO_3] and (d) [bmim][Ac] at different concentrations.[379]

concentration. The interfacial behavior of PEGs was determined using the EIS method. These authors also reported the anticorrosive effect of PEGs-400–10 000 g mol^{-1} under the same experimental conditions (carbon steel/3 N H_2SO_4).[440] SEM

Table 5 Chemical structures, abbreviation, nature of adsorption, metal and electrolyte system, method of corrosion measurements, highest inhibition efficiency and optimum concentration of some ionic liquids evaluated as corrosion inhibitors

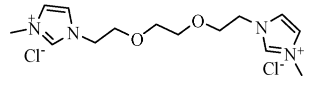
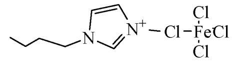
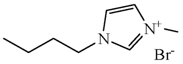
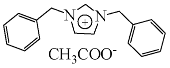
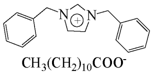
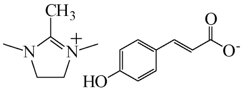
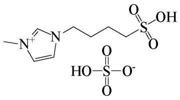
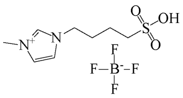
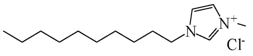
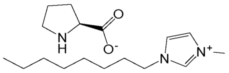
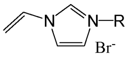
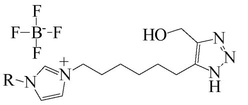
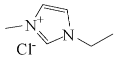
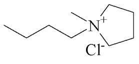
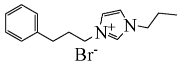
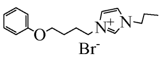
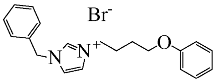
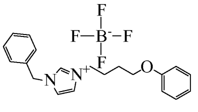
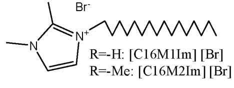
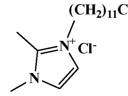
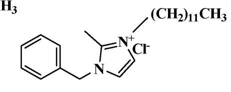
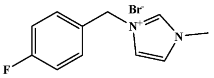
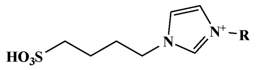
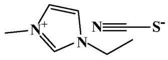
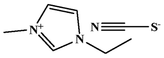
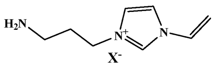
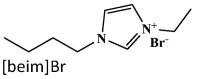
S. no.	Chemical structure and abbreviation	Nature of adsorption	Electrolyte and metal	Method of corrosion monitoring	IE% and conc.	Ref.
1	 (TSIL)	Langmuir isotherm, mixed type	1 M HCl/carbon steel	WL, PDP, EIS, SEM, AFM & CA	78.7% at 100 mg L^{-1}	380
2	 ([C_4C_1im][$FeCl_4$])	—	Open/A36 mild steel	WL, EIS, PDP, SEM & DFT	—	381
3	 [BMIM]Br	Langmuir isotherm, mixed type	1 M HCl/mild steel	WL, PDP & EIS	92% at 20 mM	382
4	  (DBImL) (DBImA)	Langmuir isotherm, mixed type	1 M HCl & 1 M H_2SO_4/API 5LX52 steel	PDP, EIS & SEM	DBImL (30%: H_2SO_4; 88% HCl)	383
5		—	0.01 M NaCl/ mild steel	EIS, PDP, SEM, OM and FT-IR	86% MeHImn 4-OHC (4 mM)	385
6	  ([BsMIM]-[HSO_4]) [BsMIM][BF_4]),	Langmuir adsorption isotherm	1 M H_2SO_4/304 S steel	WL, PDP, EIS & SEM	[BSMIM][HSO_4] (98.48%) & [BSMIM][BF_4] (98.29%) at 10^{-2} M	386
7	 (DMICL)	—	NaCl (3.8 & 6.8 pH)/mild steel	OCP, EIS, PDP, SEM, EDX and XPS	98.2% (3.8 pH) & 84.3% (6.8 pH)	387
8	 [Omim]Lpro	Flory–Huggins isotherm, mixed type	0.5 M H_2SO_4/ mild steel	WL, PDP, EIS, SEM & DFT	76.9% at 10 mM	388
9	 R= IL1:C_4H_9; IL2:C_8H_{17}; IL3:$C_{12}H_{25}$; IL4:$C_{18}H_{37}$; IL5: $C_{22}H_{45}$	Langmuir isotherm, mixed type	1 M H_2SO_4/ carbon steel	WL, PDP, SEM, EDX & AFM	90% at 10^{-4} M (IL4)	389
10	 R= -CH3 (I); -C4H8 (II); -C8H9 (III)	—	Ethanol/tinplate	PDP, SEM and XPS	$I_{corr} = 2.33 \times 10^{-7}$ A cm^{-2}	390
11	 ,  ([EMIm]Cl) ([Py1,4]Cl)	Mixed type inhibitors	Cast iron/gulf sea water	WL, OCP, PDP and EIS	R_p = 1376 ([EMIm]) & 1364 ([Py1,4]) at 5 mM	391
12	  (PPIB1) (PPIB4)	Langmuir isotherm, mixed type	1 M HCl/carbon steel	WL, PDP & EIS	92.3% (PPIB1) & 94.2% (PPIB4) at 10^{-2}	392
13	  (MA1) (MA2)	Langmuir isotherm	1 M HCl/mild steel	WL and DFT	94.6% (MA1) & 97.6% (MA2) at 10^{-2} M	393
14	 R=-H: [C16M1Im] [Br] R=-Me: [C16M2Im] [Br]	Langmuir isotherm, mixed type	1 M HCl/mild steel	WL, PDP, EIS, SEM, AFM, EDX & UV-vis	66.2% [$C_{16}M_1$Im] [Br] & 71.8% [$C_{16}M_2$Im] [Br] at 250 ppm	394

Table 5 (*continued*)

S. no.	Chemical structure and abbreviation	Nature of adsorption	Electrolyte and metal	Method of corrosion monitoring	IE% and conc.	Ref.
15	 ([DDMIM]Cl)  [BDMIM]Cl	Langmuir isotherm, mixed type	15% HCl/N80 steel	STT, WL, EIS, PDP, SEM, AFM, DFT & MDS	75.3% [DDMIM]C & 98.1% [BDMIM]Cl at 100 ppm	395
16	 [FBMIm]Br	Langmuir isotherm, mixed type	0.5 M H_2SO_4/ mild steel	PDP, EIS, SEM, AFM, DFT & MDS	98.9% at 0.01 M (298 K)	396
17	 C_2-IMIC$_4$-S: R=-C2H5; C_{10}-IMIC$_4$-S: R=-$C_{10}H_{21}$;	Langmuir isotherm, mixed type	0.5 M HCl/ carbon steel	PDP, EIS, CA, SEM, UV-vis, XPS, DFT and MDS	80.8% (C2-IMIC$_4$-S) & 97.9% (C10-IMIC4-SR = –$C_{10}H_{21}$)	397
18	 (EMIM) (SCN)–	Langmuir isotherm, mixed type	0.5 MH_2SO_4/API 5 L X52	WL, OCP, EIS, PDP, SEM, E-DX, UV, XPS, AFM, DFT & MDS	93.1% at 10 ppm (55 °C)	398
19	 (EMIM) (SCN)−	Langmuir isotherm, mixed type	0.5 M HCl & H_2SO_4/API 5 L X52	WL, EIS, PDP, SEM-EDX, AFM, XPS & MDS	69% (HCl) & 90 (H_2SO_4) at 75 ppm	399
20	 [VAIM][PF6]:[PF6]; [VAIM][BF4]:[BF4]	EI-Awady kinetic-thermodynamic, mixed type	1 M HCl/Q235 carbon steel	WL, PDP, EIS, CA, SEM, EDX and MDS	90.53%: [VAIM]PF6) & 54.01 [VA-IM]PF4) 0.8 mM	400
21	 [beim]Br	Langmuir isotherm, mixed type	0.01 M Na_2SO_4/ copper	WL, PDP, EIS, CA, SEM,	91.29% at 100 ppm	401

analyses revealed that the presence of PEGs enhances the smoothness of the surface and this enhancement was consistent with the molecular weight of PEGs. Umoren *et al.* extensively studied the corrosion inhibition effect of PEG in correlation with the anticorrosive effect of polyvinyl alcohol (PVA) and natural polymer (gum Arabic; GA).[441–444] They observed that PEG exhibited a better anticorrosive effect. The adsorption of PEG and GA obeyed the Temkin adsorption isotherm model. The authors observed a synergistic effect in the presence of halide ions and their relative order of effectiveness is as follows: KI > KBr > KCl. The corrosion inhibition effect of PEG with halide ions has been reported elsewhere.[445] The literature survey showed that PEGs are widely used as inhibitors for metals in H_2SO_4 medium.[446–448]

PEGs are also used as metallic corrosion inhibitors in HCl medium. Ashassi-Sorkhabi *et al.*[449] manifested the inhibition properties of PEGs (400–10 000 g mol^{-1}) for carbon steel in 0.5 M HCl. PEGs behave as mixed-type corrosion inhibitors. An analysis in which the comparative inhibition effect of PEG and ciprofloxacin is evaluated for aluminum in acidic medium showed that PEG showed better protection effectiveness.[450] The presence of ciprofloxacin synergistically enhanced the protection effect of ciprofloxacin. In another study Awad *et al.*[451] demonstrated the anticorrosive properties of PEGs (300–600) for aluminum in the acidic medium of HCl. The results showed that PEGs behaved as mixed-type inhibitors. Recently, the inhibition effect of chitosan modified PEG was reported for mild steel in 1 M HCl.[145] PEGs are also widely used as corrosion inhibitors in NaCl[452–454] and MOH (metal oxide)[455–457] solutions.

2.6. Environment-friendly alternatives derived from MCRs

The use of organic compounds is one of the most profitable methods of corrosion mitigation. However, most of the synthetic inhibitors are toxic in nature because they are synthesized using toxic chemicals, catalysts and solvents.[13,458] Nevertheless, corrosion inhibitors synthesized using one-step multicomponent reactions (MCRs) have recently gained particular advancement towards the development of environmentally benign synthesis methods for chemicals to be used for different industrial applications including corrosion inhibition. MCRs possess several advantages that make them environment-friendly.[459–462] Unlike the synthesis of traditional toxic corrosion inhibitors, MCRs are easy to proceed, profitable, and are associated with high yield and selectivity. In fact, in association with ultrasound (US) and microwave (MW) energy heating, MCRs have emerged as one of the greenest synthetic protocols.[462] MCRs are characterized by chemical syntheses that employ the reactions between three or more reactants in one step. These types of reactions are generally quick, highly selective and consume less time to complete. Several compounds synthesized using MCRs are evaluated as inhibitors against metallic corrosion inhibitors. The synthetic schemes of MCRs for some classes of corrosion inhibitors are shown in Table 4. A careful observation showed that most of the corrosion inhibitors derived from MCRs are heterocyclic compounds, especially those containing N and O heteroatoms. It can be observed from the table that nitrogen based heterocyclic compounds such as imidazole, indole, pyridine, *etc.* are derived using MCRs that offer strong bonding with the metallic surface. On this basis, it can be concluded that MCRs act as a potential medium for the synthesis of heterocyclic compounds that can be used as corrosion inhibitors. Along with MCR syntheses, mechanochemical mixing (MCM)[463,464] and solid supported syntheses (SSSs)[465,466] are also regarded as environment-friendly synthetic approaches because of their easy application, cost-effective nature and easy and lower number of purification and work-up steps (Table 6).

2.7. Environment-friendly alternatives derived from US and MW irradiations

Generally, conventional heating methods offer very slow and non-uniform heating of reaction vessels that allow slow activation of the reactant molecules.[503,504] Therefore, completion of the reactions carried out using conventional heating methods requires several minutes, hours or even days to complete. In the last three decades, the use of non-conventional heating sources mainly through ultrasound (US) and microwave (MW) irradiations gained significant attention.[505,506] Chemical reactions using these non-conventional heating methods can proceed within a fraction of a second or minute, which require several hours to complete when using conventional heating methods. The literature study showed that MW and US irradiations cause sudden and instantaneous heating that activates most of the reactant molecules together and the reaction proceeds quickly.[507–509] The MW and US irradiations are associated with several advantages that are closely related with the principles of green chemistry. Several theories are proposed to describe the activation of reactant molecules using MW and US irradiations. Generally, MW/US irradiation is used to catalyze MCR reactions.[510,511] In connection with MCRs, US and MW irradiations offer the greenest synthetic protocol. Along with increasing the rates of chemical reactions, US and MW irradiations can also enhance the selectivity of the reactions.[512,513] Moreover, MW and US irradiations also act as catalysts for chemical transformations. Several biologically and industrially useful compounds, especially heterocyclic compounds, are synthesized using MW and US irradiations. Heterocyclic compounds derived from MW and US irradiations have also been evaluated as inhibitors against metallic corrosion.[12] Synthetic schemes and chemical structures of some major heterocyclic compounds derived from MW or US irradiation are presented in Table 5. The observation of the table shows that MW/US catalyzed reactions are related with the synthesis of heterocyclic compounds. Although chemical transformations can be catalytically and efficiently catalyzed using MW/US irradiation, their implementation for the synthesis of corrosion inhibitors should be further explored (Table 7).

2.8. Environment-friendly alternatives derived using green solvents

Solvents play a significant role in the progress of numerous reactions.[521] There are several aspects of green chemistry and green synthesis, one of which is the use of environmentally benign and inexpensive solvents. It is well established that polar protic solvents such as alcohol (ROH) and amines (RNH_2, R_2NH and R_3N) favor SN_1 reactions and polar aprotic solvents such as THF (tetrahydrofuran), DMSO (dimethyl sulfoxide), and DMF (dimethyl formamide) favor SN_2 reactions.[522,523] Nevertheless, most of the traditional solvents used for chemical transformations are toxic and non-environment-friendly in nature.[524,525] Generally, after their use, they are discharged into the surrounding environment without adequate treatment, thereby causing pollution.

Although ''the best solvent is no solvent'', there are some environmentally benign alternatives that can be used for the synthesis of organic compounds in the place of traditional toxic and volatile solvents.[431] One of such solvents is water. Water is regarded as the best alternative to the traditional toxic solvents. Because of its bio-susceptibility, cost-effectivity, unique redox potential, high dielectric constant and huge availability, water represents one of the greenest solvents for chemical transformations.[524–526] Several chemical transformations have been carried out using water as a solvent. The literature study showed that water has also been used as a medium for the synthesis of compounds used as corrosion inhibitors.

Toxicity of most of the traditional organic solvents is attributed to their high vapor pressure. Therefore, chemical compounds with a lower vapor pressure that exist in a wide liquid range can also be used as environmentally benign solvents for chemical transformations. One such example is ionic liquids. The high polarity, low vapor pressure and high chemical and thermal stability of ionic liquids make them one of the best alternative environment-friendly solvents.[521,527] Several transformations have been carried out in ionic liquids to be used as effective corrosion inhibitors for metals and alloys.[57,528] In fact, ionic liquids can themselves be effectively used as corrosion inhibitors for different systems. Because of their ionic nature, most of the ionic liquids are freely soluble in aqueous media and therefore they are mainly used as aqueous phase corrosion inhibitors,[529,530] although they have also been tested as corrosion inhibitors in the coating phase. The inhibition effectiveness of ionic liquids can be suitably tailored by proper selection of cations and/or anions. In this sense, ionic liquids can be regarded as designer corrosion inhibitors. Imidazolium and pyridinium based ionic liquids are extensively used as corrosion inhibitors; however, other classes of ionic liquids are also used.[57]

Another such alternative is supercritical CO_2 that has very low vapor pressure; however, it is not a good solvent for high molecular weight compounds.[531,532] Therefore, supercritical CO_2 is mostly used in combination with other cosolvents (polar and non-polar). CO_2 philic (loving) ligands and highly CO_2 soluble surfactants can also be used to enhance the solubility of supercritical CO_2.[533,534] Supercritical CO_2 is extensively used for a variety of chemical transformations, as an extraction solvent, and as a solvent in polymer production, purification and processing, powder production and processing and semiconductor processing.

Table 6 Synthetic schemes for some major corrosion inhibitors derived through MCRs

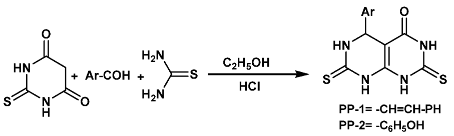
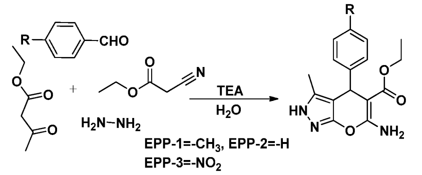
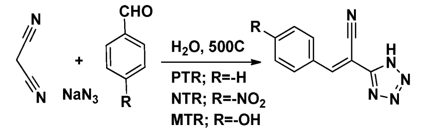
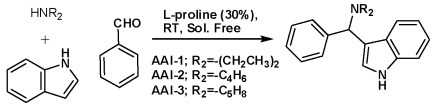
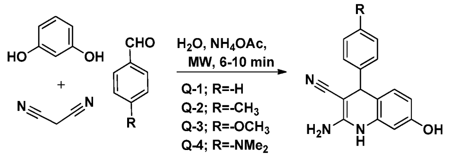
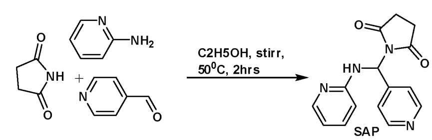
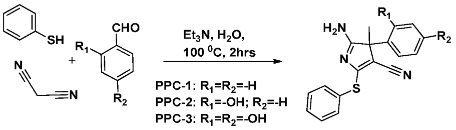
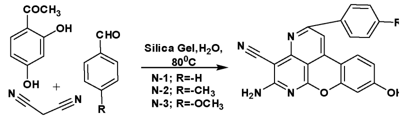
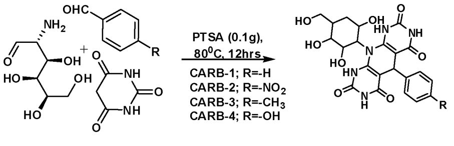
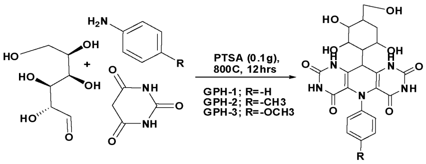
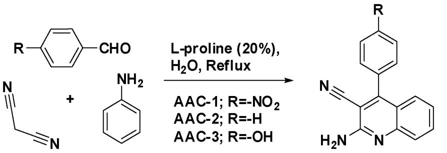
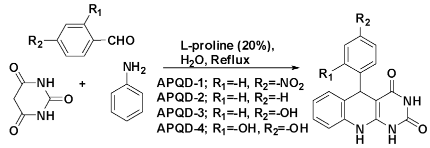
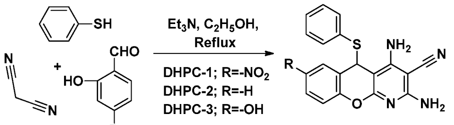
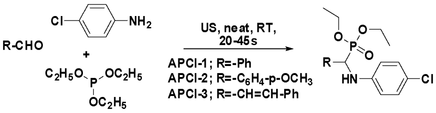
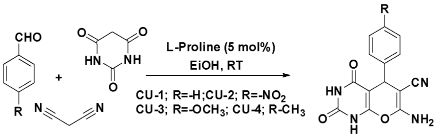
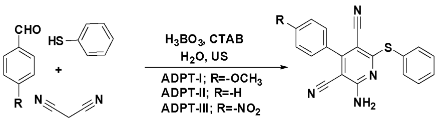
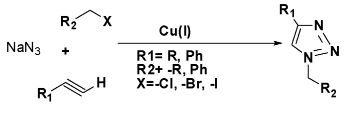
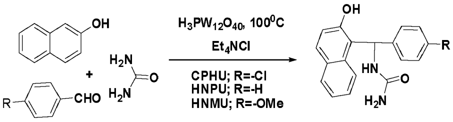
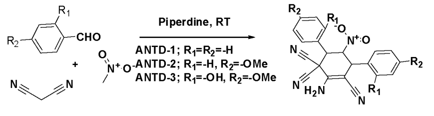
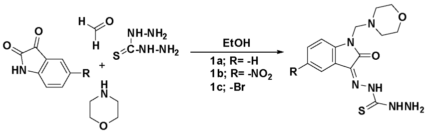
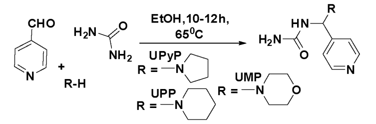
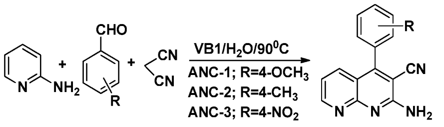
MCR synthetic scheme	System	Ref.	MCR synthetic scheme	System	Ref.
	Fe/15% HCl,	467		Fe/1 M HCl	468
	Fe/1 M HCl	469		Fe/1 M HCl	470
	Fe/1 M HCl	471		Fe/1 M HCl	472
	Fe/1 M HCl	23		Fe/1 M HCl	16
	Fe/1 M HCl	17		Fe/1 M HCl	473
	Fe/1 M HCl	75		Fe/1 M HCl	474
	Fe/1 M HCl	77		Fe/1 M HCl	475
	Fe/1 M HCl	53		Fe/1 M HCl	476
	Fe/1 M HCl	60		Fe/0.5 M HCl	477
	Fe/1 M HCl	478		Fe/0.5 M HCl	479
	Fe/1 M HCl	480		N80/15% HCl	481

Table 6 (*continued*)

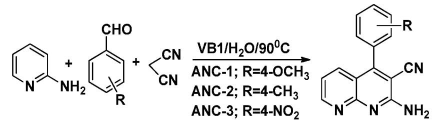
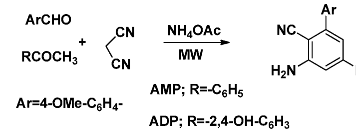
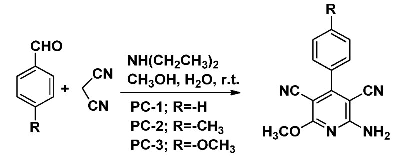
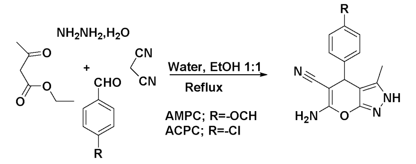
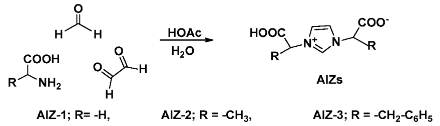
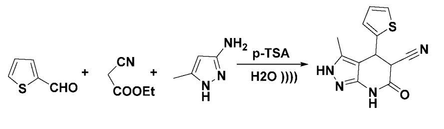
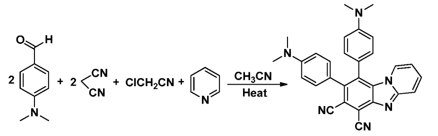
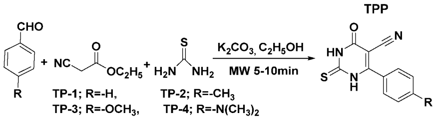
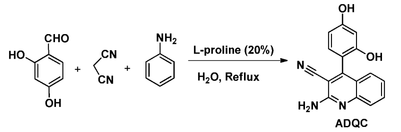
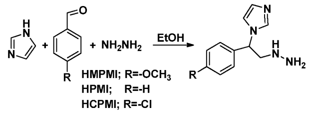
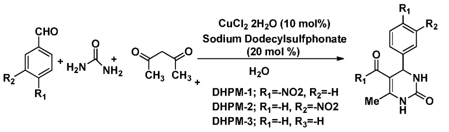
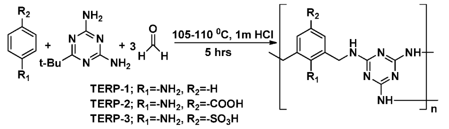
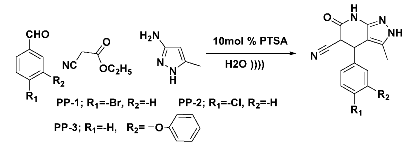
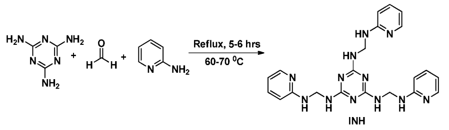
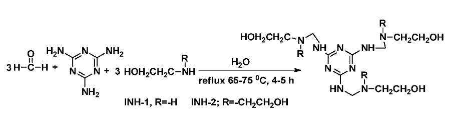
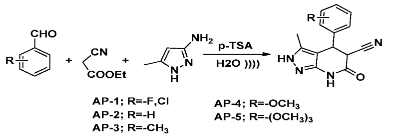
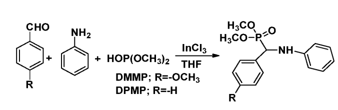
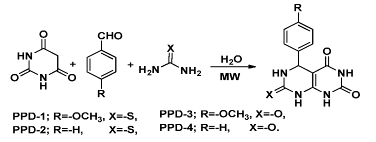
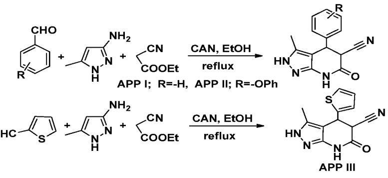
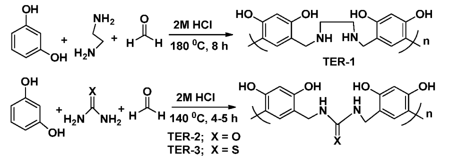
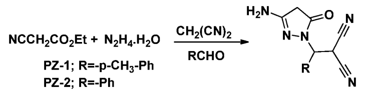
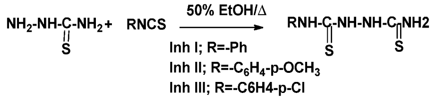
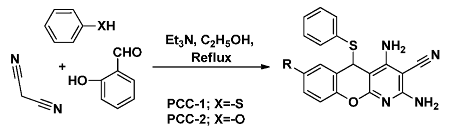
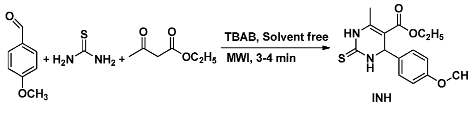
MCR synthetic scheme	System	Ref.	MCR synthetic scheme	System	Ref.
	Fe/1 M HCl	482		N80/15% HCl	483
	Fe/1 M HCl	484		Fe/15% HCl	468
	Fe/1 M HCl	485		Fe/1 M HCl	486
	Fe/1 M HCl	487		Fe/1 M HCl	488
	Fe/1 M HCl	489		N80/15% HCl	73
	Fe/1 M HCl	490		Fe/1 M HCl	491
	Fe/1 M HCl	492		Fe/1 M HCl	493
	Fe/1 M HCl	494		Fe/1 M HCl	495
	N80/15% HCl	496		Fe/1 M HCl	497
	Cu/0.5 M HCl	498		Fe/1 M HCl	499
	N80/15% HCl	500			91
	N80/15% HCl	501			502

Table 7 Synthetic schemes and chemical structures of some major heterocyclic compounds synthesized using MW or US irradiation and tested as corrosion inhibitors

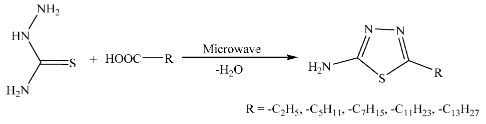
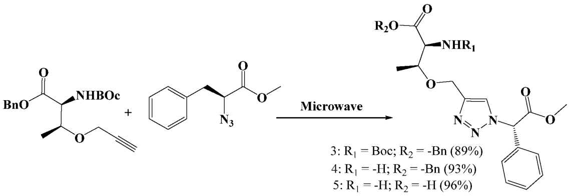
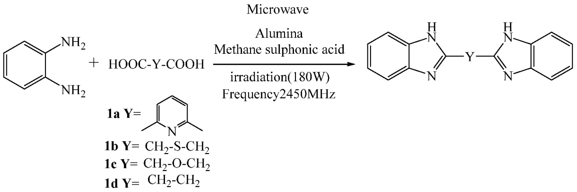
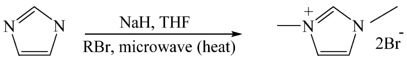
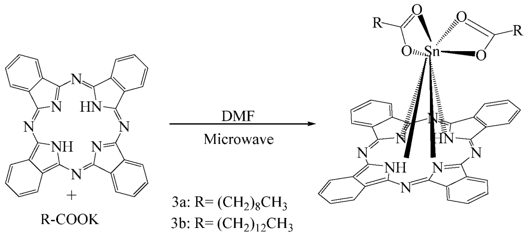
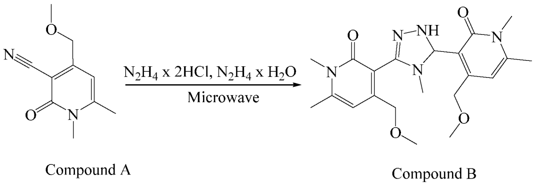
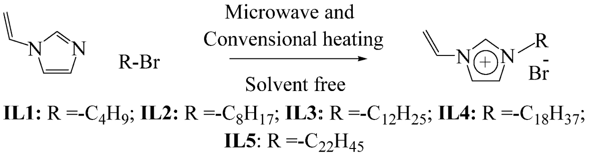
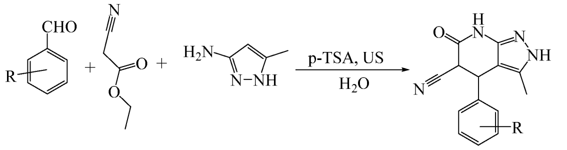
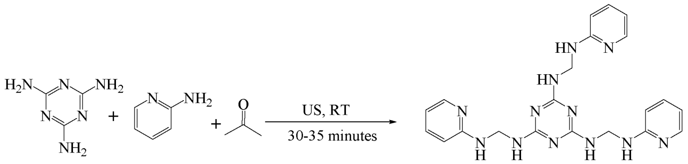
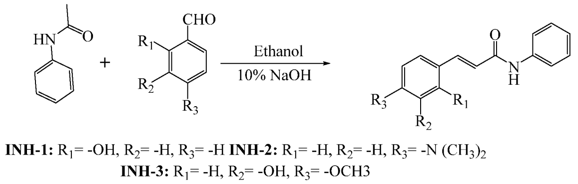
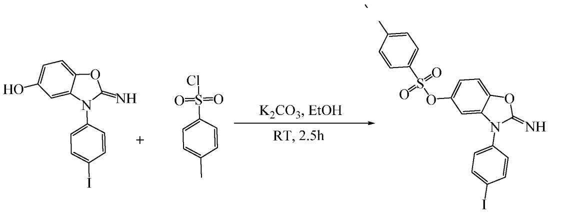
Synthetic scheme	System	Ref.
 Scheme 1	Fe/1 M H_2SO_4	514
 Scheme 2:	Fe/1 M HCl	515
 Scheme 3:	Fe/20% H_2SO_4	516
 Scheme 4:	Fe/1 M HCl	378
 Scheme 5:	Fe/H_2S medium	517
 Scheme 6:	Al-3Mg/0.5 M and 1 M HCl	518
 **IL1:** R =$-C_4H_9$; **IL2:** R =$-C_8H_{17}$; **IL3:** R =$-C_{12}H_{25}$; **IL4:** R =$-C_{18}H_{37}$; **IL5**: R =$-C_{22}H_{45}$ Scheme 7:	Fe/1 M H_2SO_4	60
 Scheme 8:	Fe/1 M HCl	495

Table 7 (*continued*)

Synthetic scheme	System	Ref.
 Scheme 9:	Fe/1 M HCl	493
 Scheme 15:	Fe/1 M HCl	519
 Scheme 16:	Fe/1 M HCl	520

3. Summary and outlook

The present review provides a summary of environmentally sustainable alternatives for traditional toxic corrosion inhibitors. The literature survey shows that several classes of pure and modified natural or bio-polymers have been widely reported as environment-friendly alternatives to traditional toxic corrosion inhibitors. With growing demand for green and sustainable technologies, the implementation of environment-friendly alternatives should be further explored. Among the natural environment-friendly alternatives, plant extracts and chemical medicines (drugs) are frequently used as corrosion inhibitors. Because of their natural and biological origin and property of non-bioaccumulation, they are regarded as environment-friendly alternatives to traditional toxic corrosion inhibitors. Due to their complex molecular structures that contain numerous electron rich centers including polar functional groups and multiple bonds, the drug molecules and phytochemicals present in plant extracts act as effective metallic corrosion inhibitors. Because of their natural and biological origin they are treated as environmentally sustainable chemicals. However, recently the use of drug molecules has been slightly restricted because of their high cost which promoted the idea of consuming expired drugs as environment-friendly corrosion inhibitors. The use of expired drugs as corrosion inhibitors should be further explored. Currently, compounds derived through multicomponent reactions (MCRs), mechanochemical mixing (MCM), and solid supported syntheses (SSSs) and chemicals derived through microwave (MW) and ultrasound (US) irradiations are widely used as environment-friendly alternatives to traditional toxic corrosion inhibitors. These synthetic methods provide several advantages over the traditional multistep reactions (MSRs), such as high yields, low reaction times, high selectivity, easy execution and handling, being cost-effective and a lower number of purification and work-up steps. The literature study shows that numerous environment-friendly alternatives derived from MCRs and MW/US irradiations are tested as corrosion inhibitors; however, the implementation of such types of chemicals should be further enhanced. Apart from the above, there are numerous solvents that are demonstrated as environment-friendly, and chemicals derived using these solvents as reaction media are also regarded as environment-friendly. Examples of such types of solvents include water, ILs, polyethylene glycol (PEG) and supercritical CO_2. In the literature, numerous chemicals derived from these solvents are widely used as environment-friendly corrosion inhibitors. Carbohydrates, amino acids (AAs) and their derivatives are other representatives of environment-friendly corrosion inhibitors; however, they are not covered herein as several review articles dealing with their anticorrosion behavior have already been published.

Conflicts of interest

The authors declare that there is no conflict of interest.

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