Chapter 5

Green Organic Inhibitors for Corrosion Protection

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Abstract

Plants are a rich source of different varied organic compounds. Due to the important applications of naturally occurring chemicals their derivatives are also pursued for modifying and potentiating the activities of natural products. Metallic corrosion is a natural process resulting in heavy losses in various fields. Non hazardous and non toxic corrosion inhibitors gained significance due to the environmental regularities and guidelines issued in the course of saving the pristine nature of environment and to maintain the sustainability of our earth. Green corrosion inhibitors play a potential role for the above said cause. Recent research contributions on green corrosion inhibitors from the active researchers in the concerned expertise are presented briefly here to give an idea about the current research activity across the world.

Keywords

Phytochemicals, Surfactants, Protective Film, Inhibition Efficacy, Corrosion Inhibition, Physisorption, Chemisorption, Corrosion Rate, Inhibitor Concentration, Electrochemical Impedance Spectroscopy

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1. Introduction

Metals and alloys react with the surrounding environment and undergo corrosion overtime, causing loss of material and their property. Corrosion process caused by either cathodic or anodic process can be controlled by the application of corrosion inhibitor on the metal or alloy surface. Inhibitors are adsorbed on the metal surface to provide an active barrier layer between metal and degrading and aggressive environment. Corrosion inhibition can be initiated by coating the concerned metallic surface with organic or inorganic compounds which can stop the oxidation-reduction process. Many inhibitors are toxic and hazardous. These can be cathodic, anodic or mixed type.

Due to the current environment regularities and guidelines with an aim to maintain the sustainability of the environment and to reduce the toxicity of chemical applications presently research is being focussed to find greener and more effective corrosion inhibitors which can deliver higher corrosion inhibition efficiency. Many plant extracts, compounds derived from natural products, synthetic organic compounds and ionic liquids come under this category. Plant extracts are generally rich in organic compounds containing functional groups, π -electrons in conjugation with double or triple bonds and the presence of hetero atoms like oxygen, nitrogen, or sulphur. During the adsorption process the active compounds present in the inhibitor layer interact with the metal surface involving electrons. Herbs like hibiscus, and thyme, saccharides like fructose, natural products like guar gum, nicotine, caffeine, eugenol, berberine, chamomile and gum Arabic were examined for their efficacy as corrosion inhibitors. Among metals steel, aluminium and copper were under study. Generally, the green corrosion inhibitors reduce or affect corrosion rate by increasing electrical resistance of the metal surface with the formation of a protective layer, by changing rate of anodic/cathodic reactions or by changing the diffusion rate of aggressive ions interacting with metallic structures.

The present review is intended to showcase the recent research findings on green corrosion inhibitors reported by enthusiastic researchers actively pursuing the field of corrosion inhibitors. The focus of the write-up is to expose the work from the angle of organic molecular structural point of view. Moreover, the available literature is classified

into two parts, a. plant/animal extract applications, b. application of organic compounds for the convenience of readers.

2. Examples from recent literature

2.1 Plant/animal extract applications

Rodriguez – Torres et al. examined [1] the extract of *Prunus persica* leaves for corrosion inhibition against AISI 1018 carbon steel in presence of 0.5 M sulphuric acid solution at 25 °C. It was reported that inhibitory efficiency was directly proportional to the inhibitor concentration, reaching the maximum effect at 600 ppm (97%). Authors observed negligible damage to the steel surface on protecting with *P.Persica* extract. *P.Persica* extract is a well-known Chinese plant, abundant in phenolic compounds such as hydroxycinnamic acid, anthocyanins, flavonoids and procyanidins. By GC-MS analysis authors identified several natural products in the extracts such as α -tocopherol, β -pinene, β -sitosterol, α -terpinene, squalene, β -myrcene, β -Cymene, α -Pinene and Linoleic acid. In view of the abundance of α -tocopherol and β -sitosterol as well as the experimental data obtained, these phytochemicals are considered to be responsible for the CIE against AISI 1018 carbon steel in H₂SO₄. To ensure that these phytochemical green corrosion inhibitors to be also eco-friendly, authors assessed the toxicity of these extracts.

G. Subramanian et al. examined [2] the efficacy of a new corrosion inhibitor – *Pithecollobium dulce* – leaves extract for mild steel surfaces in presence of 1 M HCl and 3.5% NaCl solutions with the help of electrochemical techniques and weight loss measurements. It was observed that the corrosion inhibition efficiency increased with increase in concentration of the inhibitor. Authors also concluded that the formation of Fe – inhibitor complex may be responsible for corrosion inhibition.

Leticia A.L. Guedes et al. assessed [3] the corrosion inhibition efficiency of the tannins from bark of *Acacia mearnsii* for AA7075 – T₆ aluminium alloy in presence of 0.1 M HCl solution employing electrochemical impedance spectroscopy, scanning electron microscopy and potentiodynamic polarization techniques and observed that inhibition efficacy increased with increase in inhibitor concentration. It was concluded that by forming a layer on the aluminium surface, the tannate compound reduced the metal dissolution reaction.

Hicham Taoui and co-authors investigated [4] the inhibition effect of bark resin of *Schinus molle* on the corrosion of API 5Lx70 pipeline steel in HCl solution using electrochemical impedance spectroscopy and potentiodynamic polarization techniques. It was reported that the resin exhibited about 94% efficiency at 2 gL⁻¹. Probable mechanism

was also proposed by the authors. The anti corrosive property of the bark resin was explained as due to the adsorption of bark resin constituents such as pinicolic acid, isomasticadenoic acid and isomasticadienonalic acid (Fig. 1) on the surface and also due to two types of interactions, such as physisorption and chemisorption. Authors concluded that the bark resin acted as mixed type inhibitor exhibiting geometric blocking effect, and the corrosion was controlled by charge transfer process.

Figure 1. Structure of pinicolic acid, isomasticadenoic acid and isomasticadienonalic acid.

Aprael S.Yaro et al. described [5] apricot juice as a green corrosion inhibitor for mild steel surfaces in presence of 1M phosphoric acid solution at different temperatures. The studies proved that the corrosion rate was influenced by temperature and inhibitor concentration. Adsorption studies indicated that inhibitor was adsorbed on the metal surface. Authors also proved that apricot juice exhibited maximum inhibition efficiency of 75% at 30 °C.

Ahmed A. Farag and co-workers reported [6] that recovery shrimp waste protein acted as a green corrosion inhibitor for carbon steel of in presence of 1M HCl solution utilizing different electrochemical techniques. Authors also showed that the corrosion rate decreases with increase in the inhibitor concentration. Authors stated that the corrosion inhibition is due to the presence of donor atoms in the amino acids included in the protein structure.

Mohammad Tariq Saeed and co-workers demonstrated [7] that corrosion of mild steel can be inhibited by sweet melon peel extract in the presence of 1 M HCl solution with the help of potentiodynamic polarization and weight loss methods. Experiments were conducted with various extract concentrations at different temperatures. With 0.5 g/L concentration of the extract five times lower rate of corrosion was observed at 333 K.

Corrosion rate was directly related to the increase in temperatures from 295 to 333 K even in presence of the extract.

Anees A. Khadan and co-workers investigated [8] the use of *Xanthiumstrumarium* leaves extract for assessing the corrosion inhibition behaviour for low carbon steel in the presence of 1 M HCl solution and found that 94.82% inhibition efficiency at higher level of concentration and temperature. Authors observed that the efficiency increases with increase in temperature and concentration. FTIR studies indicated that the extract contained mixture of compounds such as amides, amines, aromatic and organic acids.

Narasimha Raghavendra and Jathi Iswara Bhat reported [9] red areca nut seed extract containing electron rich polyphenols, flavonoids, alkaloids and tannins as a green sustainable corrosion inhibitor for aluminium in presence of 0.5 M HCl solution utilizing AFM, SEM, electrochemical and weight loss studies. It was observed that protection efficiency is directly proportional to the concentration of the extract and inversely proportional to the solution temperature, and aluminium contact time in the test solution. Author described that the extract reduced the speed of aluminium corrosion by charge transfer process by the adsorption of plant constituents on the metal surface.

Ivan Pradipta et al. investigated [10] corrosion inhibition efficiency of green tea extract, a generous source of natural anti oxidants against steel reinforcing bars (rebars) embedded in mortar and also conducted a comparative study with commercial inorganic calcium nitrite corrosion inhibition at similar concentrations and equal volumes. It was observed that at similar volumes green tea exhibited higher efficiency than inorganic counterpart, attributed to marked increase in rebar polarisation resistance and reduction in iron oxidation rate. With the help of liquid chromatography – tandem mass spectrometry and LCMS studies, authors hypothesized that catechin or (-) epicatechin, (-) epicatechingallate and (-) epigallocatechin gallate are the source for the anti corrosion property of green tea extract as mixed type.

Authors Idouhli et al. evaluated [11] the corrosion inhibitory effect of *Senecioanteuphorbium* extract containing macrocyclic diesters on S300 steel in presence of 1 M HCl solution utilizing electrochemical impedance spectroscopy and potentiodynamic polarisation studies. SEM, energy dispersive X-ray spectroscopy (EDS) and contact angle analysis indicated the adsorption of organic compounds present in the extract on metal surface and the formation of protective film. Authors noted that as the extract concentration increased, there was a significant improvement in the corrosion inhibition potency, reaching a maximum of 91% at 30mg/L.

Rodriguez et al. described [12] *Crataegusmexicana* as a green eco-friendly mixed type corrosion inhibitor for AISI 1018 carbon steel in presence of 0.5 M sulphuric acid.

Authors evaluated inhibitory efficiency of methanolic extract of the leaves of *Cmexicana* at different concentrations from 200 to 500 ppm, with the help of potentio-dynamic polarization curves (PPC), electrochemical impedance spectroscopy (EIS) and weight loss methods. From the results of FTIR spectroscopy the presence of flavonoids in the plant extract was proved.

Saviour Umoren et al. communicated [13] experimental studies related to the corrosion inhibition efficiency of date palm seed extract for mild steel in presence of 1 M HCl as well as 0.5 M sulphuric acid solutions using electrochemical and weight loss methods. Authors proved that the corrosion efficiency increased with increase in extract concentration and decreased with increase in temperature. It was observed that the extract exhibited better corrosion inhibition for steel in presence of HCl solution than in sulphuric acid solution. Maximum effect was noticed in 1 M HCl and 0.5 M sulphuric acid solutions, respectively. Immersion time had also considerably influenced the efficiency. Adsorption of extract components on the metal surface afforded the corrosion inhibition as proposed from the trend of results observed.

Pandian Bothi Raja et al. studied [14] the corrosion inhibition effects of alkaloid extracts of leaves and bark of *Ochrosiaaoppostifolia* and isoreserpiline (Fig. 2), the major alkaloid isolated from the extracts, against mild steel in presence of 1 M HCl solution. The property was evaluated using electro chemical techniques, such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) measurements and scanning electron microscopy (SEM). Isoreserpiline present in the extracts was found to be responsible for the inhibitory effect, as judged from the FT-IR and molecular modelling studies conducted by the authors. The data collected from FT-IR analysis indicated that indole moiety of isoreserpiline was involved in the co-ordination with the MS surface.

Figure 2. Structure of Isoreserpiline.

Nur Izzah Nabilah Haris et al. evaluated [15] oil palm empty fruit bunch extract as green corrosion inhibitor for mild steel in 1 M HCl using weight loss technique. FT-IR and SEM studies indicated the presence of active chemical compounds in the deposited

extracts on metal surface. Mechanism of inhibition was thought to incline more towards physical adsorption. It was considered that the presence of oxygen and nitrogen hetero atoms present in the chemical structures of the active molecules might be contributing towards inhibition apart from the presence of OH, C=C functional groups present in the molecules. Results of the study indicated great potential for the OPETB extract in the corrosion prevention for mild steel in presence of acidic environment.

Rajesh Haldhar et al. [16] investigated Valeriana Willich roots extract as a green and sustainable corrosion inhibitor for mild steel in presence of 0.5 M sulphuric acid solution employing weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization, SEM, AFM, FTIR quantum chemical calculations. Naphthoic acid, Iridoid and analogue are the important components in the extract and facilitate the adsorption on the metal surface. Authors reported maximum inhibition effecting up to 93.47% for mild steel at 500 mgL⁻¹ concentration at 298 K in presence of 0.5 M sulphuric acid solution. Potentiodynamic polarization estimations proved the natural product of mixed type and quantum chemical calculations informed that naphthoic acid was the best corrosion inhibitor.

2.2 Application of organic compounds

Kegui Zhang and coworkers [17] synthesized two novel Schiff bases from renewable sources such as vanilline and amino acids – L-Lysine and L-Arginine by a green method (Fig. 3). Authors investigated the corrosion inhibitory efficiency of these compounds for mild steel immersed in 0.5 ml of 10⁻¹HCl solution and observed that both greatly reduced the corrosion rates. During the study authors utilized various experimental methods such as atomic force microscopy, X-ray photon electron microscopy, potentiodynamic polarization curves and electrochemical impedance spectroscopy.

Figure 3. Structure of compounds of L-Lysine and L-Arginine.

Olga Kaczerewska et al. investigated [18] six dimeric quaternary ammonium salts (gemini surfactants: Fig. 4) for corrosion inhibition property against stainless steel in 3M HCl solution with electrochemical impedance spectroscopy and potentiodynamic

polarization techniques. Authors observed best performance results with almost >95% of IE for surfactants with 12 carbon chain in the hydrophobic tail. Results indicated that adsorption process involved both physisorption and chemisorption.

Figure 4. Structure of dimeric quaternary ammonium salts.

Varvara et al. examined [19] four thiadiazole derivatives (Fig. 5) for their anticorrosive performances against naked and artificially patinated bronze in presence of acidic medium at pH3. The structures of thiadiazole derivatives were investigated by DFT using hybrid B3LYP, 6-31G models and possible inhibition mechanism of the protonated species on the bronze corrosion was proposed. Among the four compounds MMeT was proved to be most promising compound. In addition, in case of MMeT and MAT, it was observed that effectiveness increased with immersion time in acidic solution at pH 3.

Figure 5. Structure of thiadiazole derivatives.

Taha M.A. Eldebss and co-workers [20] synthesized a series of benzimidazole based heterocyclic derivatives embedded with a variety of functional groups (Fig. 6) and studied their copper corrosion inhibition property from elemental sulphur with in non-additive transformer oil following ASTM specified procedures. These compounds were prepared from N-methy-2-bromoacetyl benzimidazoles.

Figure 6. Structure of benzimidazole based heterocyclic derivatives.

Weiwei Zhang and co-authors [21] explained the synergistic inhibition effects of N-(furan-2-ylmethyl)-7-H-purin-6-amine (Fig. 7) and iodide ion on mild steel corrosion in 1 mol/L HCl solution utilizing different techniques like surface analysis, weight loss tests, electrochemical measurements, potentiodynamic polarization experiments and electrochemical impedance spectroscopy. Authors observed that both FYPA and FYPA+KI acted as mixed type and exhibited temperature dependency. Plausible mechanism was proposed. It was also explained that FeI-FYPA+ protective film inhibited anodic dissolution of iron. These studies indicated that as the concentration increased, the corrosion inhibition efficiency increased and further increased in presence of KI.

Figure 7. Structure of N-(furan-2-ylmethyl)-7-H-purin-6-amine.

Eva A.Yaqo et al. demonstrated [22] that an amino triazole derivative 3,5-di(4-hydroxyphenyl)-4-amino-1,2,4-triazole (Fig. 8) exhibited anti corrosive property for carbon steel in presence of kerosene, brine medium. The experiments revealed that it was of a mixed type inhibitor. Authors also examined the antibacterial action of the triazole compound against some types of corrosive bacteria. This amino triazole compound was reportedly achieved maximum of 86.74% efficiency at 100ppm concentration and exhibited temperature dependency. It was observed that efficiency increased with increase in concentration. Thus, the compound showed both anti-corrosive as well as antibacterial activity. Authors also discussed inhibition mechanism.

Figure 8. Structure of an amino triazole derivative 3,5-di(4-hydroxyphenyl)-4-amino-1,2,4-triazole.

Hong Qin Liu and co-workers [23] synthesized some new alkyl hydroxyethylimidazolin salts from 2-alkylhydroxyethyl imidazoline and dimethylcarbonate, initially forming 2-alkylhydroxyethyl imidazolinemethylcarbonate (Fig. 9), which latter reacted with different acids.

Figure 9. Structure of 2-alkylhydroxyethyl imidazolinemethylcarbonate.

Authors observed that the compounds interacted with metals to form a protective layer on the metal surface to block the active sites decreasing the corrosion rates, and that the corrosion efficiency increased with increase in the length of the carbon chain. These exhibited anti corrosive property against mild steel in acid solutions.

Tuan K.A. Hoang et al. [24] developed sustainable gel electrolyte with pyrazole as an additive, which acted as a corrosion inhibitor and dendrite suppressor for aqueous Zn/LiMn₂O₄ battery.

Authors noted that battery in such condition exhibited high cyclability up to 85% capacity retention after 500 charge – discharge cycles at 4°C. It was reported that electrolyte containing 0.2 wt.% pyrazole exhibited superior results with 23% lower corrosion offering lowest absolute value of deposition.

Aiad and co-workers [25] prepared three cationic surfactants based on alginic acid (Fig. 10) and evaluated for corrosion inhibition for mild steel surfaces in presence of 1.0 M solution using different techniques such as electrochemical impedance spectroscopy, polarization and weight loss experiments. Authors observed that the efficiency was directly proportional to the hydrophobic chain length present in the synthesized compounds as well as the concentrations of the alginic cationic surfactants. The Polarization curves suggested that these behaved as mixed type inhibitors.

Figure 10. Structure of cationic surfactants based on alginic acid.

An eco-friendly, one step, multi-component, ultrasound mediated synthesis of three pyrazolo-pyridine derivatives was described by Parul Dohare et al. [26] from hydrazine hydrate, ammonium acetate, β -dicarbonyl compound and appropriate aldehydes in presence of ethanol. Corrosion inhibition efficiency of these compounds was examined for mild steel in 1 M HCl solution with the help of electrochemical impedance spectroscopy, gravimetric and potentiodynamic polarization measurements. The adsorption behaviour and reactivity of these compounds was predicted using molecular dynamics and density functional theory. It was reported that these exhibited better performance (97% IE at 100 mgL^{-1}) than hexamine (90% IE at 100 mgL^{-1}). Among three compounds the one having methoxy substituent exhibited highest efficacy of 97.58% at 100 mgL^{-1} and was ascribed to the parallel adsorption on metal surface. These follow the ranking PP1 > PP2 > PP3 with mixed type inhibition.

Chandrabhan Verma et al. in their interesting communication [27] discussed the adsorption behaviour of glucosamine derived pyrimidine fused heterocyclic compounds (Fig. 11) as environmentally benign corrosion inhibitors for mild steel in presence of 1 M HCl solution. Authors utilized electrochemical, gravimetric, SEM, AFM, EDX

Figure 11. Structure of glucosamine derived pyrimidine fused heterocyclic compounds.

and computational studies in these investigations and noted that the efficiency increased with increase in the concentration of compounds. These compounds were reported to be of mixed type with predominantly cathodic type inhibition. Theoretical studies were conducted using quantum chemical calculations and molecular dynamics simulations. It was concluded that the adsorption of these compounds on the metal surface followed both physisorption and chemisorption. Even though theoretical and experimental studies suggested that the efficiency increased in presence of both electron donating as well as

electron withdrawing functional groups, authors concluded that compounds with electron donating groups exhibited higher protection than the molecules with electron withdrawing substituents.

Bing Lin and Yu Zuo investigated [28] the inhibition efficiencies of some organic carboxylate compounds having various chain lengths of alkylene (Fig. 12) substitution on Q235 steel with the help of surface analysis, electrochemical measurements and quantum chemical calculations. It was observed that as the alkylene chain length increased, the absolute surface charge value increased, and inhibition efficiency also increased. The best inhibitory effect was exhibited by compound having C₁₁ length. Authors examined the effect of acrylic acid, allylacetic acid, 6-heptenoic acid, undecylenic acid and oleic acid. From the results obtained, it was concluded that the adsorption scope of the inhibitor improved with increasing chain length between the C=C bond and the –COO[−] group. Authors suggested that these inhibitors were adsorbed on metal surface by the formation of Fe-OOC-C_x compounds and the presence of C=C bonds enhanced the adsorption process.

Figure 12. Structure of organic carboxylate compounds having various chain lengths of alkylene substitution.

Feng Yang et al. [29] in their interesting research communication described anti corrosive behaviour of a Zinc – rich epoxy coating containing sulfonated polyaniline (SPANi) in 3.5% NaCl solution on Q235 steel employing electrochemical impedance spectroscopy (EIS) and scanning vibrating electrode technique (SVET). Authors reported that Zinc-rich coating with addition of 1.0% wt SPANi enhanced cathodic protection time and barrier performance.

Wei et al. studied [30] anticorrosive property of 4-phenyl pyrimidine (Fig. 13) coating against copper surface in presence of 3 wt% NaCl utilizing electrochemical impedance spectroscopy (EIS) and polarization methods. Authors reported 83.2% inhibition efficiency. Author used different concentrations of 4-PPM for this purpose like 0.05, 0.10; 0.50 and 1 mm and various immersion times 1, 3, 6 and 10 h respectively. It was

concluded that the copper was protected from salt corrosion, by the adsorption of 4PPM molecule on the surface via the N₁ atom in the pyrimidine ring and the formation of uniformly ordered compact layer of 4-PPM molecules.

Figure 13. Structure of 4-phenyl pyrimidine.

Ekemini Akpan and co-workers [31] described corrosion inhibition property of several acridine based thiosemicarbazones (Fig. 14) against mild steel in presence of 1M HCl solution. Corrosion inhibition efficiencies were observed to increase with increase in concentration of each compound. At optimum inhibition concentration the efficiencies are in the order IAB-NF (90.48%) > IAB-ND (87.48%) > IAB-NP (85.28%). Authors reported that these compounds exhibited mixed type behaviour and observed both physisorption and chemisorption mechanisms. Experimental data was supported by both theoretical DFT and Monte Carlo simulation studies.

Figure 14. Structure of acridine based thiosemicarbazones.

Jiyaul Haque et al. [32] synthesized three chitosan Schiff bases (Fig. 15) in an eco-friendly approach under microwave conditions by reacting chitosan and aromatic aldehydes; characterized them spectroscopically and studied their corrosion inhibition behaviour for mild steel in presence of 1 M hydrochloric acid. Authors utilized EIS and PDP techniques for their work. Chitosan Schiff base obtained from 4-hydroxy-3-methoxy

benzaldehyde was reported to exhibit maximum inhibition efficiency of 90.65% at a concentration of 50 ppm. They were described as mixed type inhibitors.

Figure 15. Structure of chitosan Schiff bases.

Xiang Gao et al. investigated [33] the corrosion inhibitory efficiencies of three monoalkyl phosphate esters having various chain lengths, such as mono-n-butyl phosphate ester, mono-n-hexylphosphate ester, mono-n-octylphosphate ester, for iron in presence of 0.5 M sulphuric acid solution by using electrochemical impedance spectroscopy (EIS), and polarization curve methods. Authors observed that these behaved as mixed type inhibitors. Authors reported mono-butyl-phosphate ester displayed lower efficiency when compared to the other two esters, whereas mono-n-hexyl as well as mono-n-octyl phosphate esters exhibited almost similar efficiencies. Authors concluded from X-ray photoelectron spectroscopic (XPS) studies that the three alkyl phosphate esters were adsorbed on the metal surface through the unionized P-OH groups.

Alejandro Ramirez-Estrada et al. [34] developed environmentally benign synthetic zwitterionic compounds derived from β -amino acids prepared from alkylamines such as octylamine, dodecylamine and octadecylamine and acrylic acid under solvent free and ambient conditions (Fig. 16). After characterization, these compounds were evaluated for their anticorrosion efficiency for carbon-steel under CO₂ acidic environments characteristic of oil- field environments with the help of electrochemical techniques such as open circuit potential (OCP), linear polarization potential (LRP), and electrochemical impedance spectroscopy (EIS). These compounds exhibited 60%, 89% and 90% inhibition efficiencies respectively for the compounds obtained from octylamine, dodecylamine and octadecylamine (GZC-8; GZC-12; GZC-18), respectively at a concentration of 25 ppm. Authors observed that these were of mixed type of inhibitors and described that GZC-18 showed best efficiency of 90.14%. Authors claim that this is the first report on the preparation and evaluation of nontoxic zwitterionic corrosion inhibitors as alternative to typical amphiphilic and ionic liquid types and offered

beginning for the GCZ compounds as green corrosion inhibitors for different industries. Authors also conclude that long hydrophobic substitution on an amphiphilic molecule augments corrosion protection when compared to a molecule with smaller hydrophobic substituents. Authors also opined that GZC-12 was the best option with higher efficiency and lower toxicity as observed from the experimental data.

GZC-8: = R = n-Octyl

GZC-12: = R = n-Dodecyl

GZC-18: = R = n-Octadecyl

Figure 16. Structure of zwitterionic compounds derived from β -amino acids prepared from alkylamines such as octylamine, dodecylamine and octadecylamine and acrylic acid.

Nicola Weder and co-authors [35] investigated the adsorption and corrosion inhibition mechanisms of some different symmetrical N,N' -thiourea derivatives (Fig. 17) on aluminium in hydrochloric acid. Authors observed that the corrosion rate measurements indicated cathodic type inhibition by all compounds. Authors selected thiourea, dimethyl thiourea, diethyl thiourea, dipropylthiourea, dibutylthiourea, diphenylthiourea, tetramethylthiourea etc., for their study.

Figure 17. Structure of symmetrical N,N' -thiourea derivatives.

Chandrabhan Verma et al. examined [36] corrosion inhibition capacity of three N-substituted 2-aminopyridine derivatives (Fig. 18) on mild steel surfaces in 1 M HCl solution employing theoretical, chemical, surface, and electrochemical studies. It was reported that the efficiency increased with increase in the concentration of the chemical constituent and reached maximum at $20.20 \times 10^{-5} \text{ molL}^{-1}$ concentration. Inhibition efficiency was observed to be in the order of DMPN > DHPN > DPPN. Authors noted

that these belong to mixed type inhibitors with predominant cathodic inhibitive action. Experimental studies indicated that these molecules were adsorbed on metal surface as protonated species.

Figure 18. Structure of three N-substituted 2-aminopyridine derivatives.

Cano et al. studied [37] Fast green (FG), fuchsine base (FB) and fuchsine acid (FA) (Fig. 19) for copper corrosion inhibition in presence of citric acid solution of concentrations ranging from 0.001 to 1.0 M. Authors observed inhibition efficiency in the order FB > FA > FG.

Figure 19. Structure of Fast green (FG), fuchsine base (FB) and fuchsine acid (FA).

Saad Kaskah et al. [38] investigated anticorrosion properties of N-acyl sacrosine derivatives (Fig. 20) as green corrosion inhibitors for low carbon steel. Authors selected eco-friendly fatty acid N-acyl derivatives of the naturally occurring amino acid sarcosine such as lauroyl, myristoyl and oleoylsarcosine for their study on two low carbon steel variants for the comparison. Both steel variants comply with the standards but differ in the long-term anticorrosion behaviour. Authors utilized electrochemical impedance spectroscopy and potentiodynamic polarization techniques and concluded that the inhibitors belonged to the mixed type. Best results were obtained with oleoylsarcosine (C-18) with 99.6% and 97.4% for the two different steel types followed by myristoyl (C-14) and lauroyl (C-12) sarcosine derivatives. The trend of efficiencies observed is correlated with the chain length of the hydrophobic part. Oleoylsarcosine (C-18) with longest alkyl side chain having additional double bond showed maximum efficiency.

Figure 20. Structure of N-acyl sacrosine derivatives.

Roghayeh Sadeghi Erami and co-workers [39] described anti corrosion properties exhibited by carboxamide ligands (N-(quinolin-8-yl)quinoline-2-carboxamide (Hqcq) and N-(quinolin-7-yl)pyrazine-2-carboxamide (Hqpzc) (Fig. 21) in presence of 1 M HCl solution at 25 °C for mild steel surfaces. Both the compounds were synthesized in an eco-friendly manner using ionic liquid TBAB. Due to uniform layer formation and planar and parallel arrangement on the metal surface Hqcq showed better anti corrosion property. Experimental studies indicated that both the compounds exhibited mixed type of mechanism tending more towards chemisorption process.

Figure 21. Structure of carboxamide ligands (N-(quinolin-8-yl) quinoline-2-carboxamide (Hqcq) and N-(quinolin-7-yl) pyrazine-2-carboxamide (Hqpzc).

Ikenna et al. [40] assessed 2-(2-pyridyl)benzimidazole(PB) (Fig. 22) as a promising green corrosion inhibitor for APIX60 steel for oil-field application, in sweet corrosive environment and observed 2-PB to be more effective in hydrodynamics than in static conditions, where in mass transfer of HCO_3^- species was protonated facilitating the precipitation of Fe_2CO_3 resulting in corrosion resistance. Authors utilized electrochemical techniques such as electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and potentiodynamic polarization (PDP), in their studies. It is suggested that 2-PB get adsorbed on the steel surface with the help of NH-group of benzimidazole skeleton.

Benz-imidazole Skeleton

Figure 22. Structure of 2-(2-pyridyl)benzimidazole(PB).

Dipankar Sukul and coworkers [41] evaluated some newly synthesized quercetin derivatives (Fig. 23) as corrosion inhibitors for mild steel in presence of 1 M HCl solution backed by both experimental and theoretical studies. Quercetin, a poly phenol and a plant derived aglycone form of Rutin, a flavonoid glycoside, exhibits high antioxidant property. Authors prepared 6-((4-(2-hydroxyethyl)piperazine-1-yl)methyl)-quercetin (A), and 6,8-di-((4-(2-hydroxyethyl)piperazine-1-yl)methyl)-quercetin(B) in order to enhance water solubility. A and B are made from paraformaldehyde, 2-piperazinyl ethanol, and quercetindihydrate.

Figure 23. Structure of quercetin derivatives.

Authors utilized electrochemical potentiodynamic polarization, weight loss studies, electrochemical impedance spectroscopy and SEM images. Both compounds exhibited above 90% inhibition efficiency towards corrosion of mild steel in 1 M HCl from ambient to 323 K temperature at 1mM concentration level: and also retarded the rates of both cathodic and anodic reactions by blocking the surface reactive sites.

Yadav and co-workers [42] described the synthesis of two spiroindolinopyrimidine derivatives (1) MPTS (2) CPTS (Fig. 24) following the previously reported experimental procedure and assessed their effect on the corrosion of mild steel in 15% hydrochloric acid. Data suggested that both the compounds behaved as mixed type inhibitors and the surface morphology was analyzed with the help of SEM, XPS, FTIR, AFM and energy dispersion X-ray spectroscopy. Effect of the molecular structure on the inhibition efficiency was studied using quantum chemical calculations with the help of DFT. Molecule MPTS exhibited better performance when compared to CPTS. It was concluded that the corrosion inhibition mechanism was due to the adsorption of spiroindolinopyrimidine molecules on the metal surface. In this research work authors also corroborated experimental results with theoretical studies.

Figure 24. Structure of spiroindolinopyrimidine derivatives (1) MPTS (2) CPTS.

8-Hydroxyquinoline was examined as a new generation corrosion inhibitor by Fatah Chiter et al. [43]. Authors investigated the preference of 8-hydroxyquinoline and its compounds on the Al(III) surface and comprehensive DFT studies were undertaken. Authors assessed the formation of layers of 8-hydroxyquinoline and derivatives as well as the influence of the coverage of Al(III) surface on the adsorption topologies and adsorption energies of organic molecules, charge transfer due to the adsorption process, and the interface dipoles created at the molecule/metal interface. Authors demonstrated that among 8HQ and its derivatives, dehydrogenated 8HQ molecules formed the most stable layer with strongest coupling with the Al(III) surface, with a topology of the molecules tilted on the metallic surface.

Singh and co-workers [44] reported green microwave assisted synthesis of 2-amino-N-(thiophen-2yl)methylene benzohydrazide (ATMBH) (Fig. 25) under solvent free

conditions in presence of montmorillonite clay, an environmentally benign solid acid catalyst, characterized its structure and examined anticorrosion property against mild steel in presence of 0.5 M sulphuric acid utilizing gravimetric and electrochemical methods. Authors described ATMBH to be more effective on cathodic branch of corrosion process, chemical adsorption being more favoured at higher concentrations.

Figure 25. Structure of 2-amino-N-(thiophen-2-yl)methylene benzohydrazide (ATMBH).

Neeraj Kumar Gupta and co-workers [45] synthesized three cysteine based Schiff bases CSB1, CSB2, CSB3 (Fig. 26) and evaluated their corrosion inhibition efficiency for mild steel surfaces in presence of 1 M hydrochloric acid employing different scientific studies. Authors prepared these different title compounds by reacting cysteine and various aldehydes such as benzaldehyde, 4-methoxy benzaldehyde, and 3-methoxy-4- hydroxy benzaldehyde employing known eco-friendly methodologies. These exhibited both physisorption and chemisorption and among all the three compounds CSB3 exhibited better efficiency with 97.3% at 200 ppm concentration. From EIS study results, authors concluded that these compounds inhibited corrosion by increase of the charge transfer resistance between metal-solution interfaces.

Figure 26. Structure of cysteine-based Schiff bases CSB1, CSB2, CSB3.

Chandrabhan Verma and co-authors [46] synthesized three new 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-b]-pyridine-3-carbonitriles (DHPCS) by MCR (Fig. 27) and investigated the anticorrosion properties of the three compounds for mild steel in

presence of 1 M HCl with weight loss method, electrochemical techniques and surface morphology studies (SEM, AFM) supported by theoretical methods (quantum chemical calculations and molecular dynamics studies). Based on the data gathered, authors informed that the inhibition efficiency increased with increasing concentration of inhibitor and concluded that the efficiency of three compounds followed trend DHPC-3 > DHPC-2 > DHPC-1. All these acted as mixed type inhibitors, exhibiting both physisorption and chemisorption. It was considered that the presence of electron withdrawing group was responsible for lowest inhibitive efficiency for DHPC-1. Furthermore, DHPC-3 showed the highest efficiency, as concluded from the observations, due to the presence of electron releasing-OH group at position seven of chromenopyridine ring.

Figure 27. Structure of 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-b]-pyridine-3-carbonitriles (DHPCS).

β -Sitosterol (Fig. 28) was isolated from rice hulls by Maya Krishnan Prabhakaran and co-workers [47] and its corrosion inhibition efficiency was assessed for mild steel surface in presence of 1 M sulphuric acid solution. Authors employed FTIR spectroscopy, weight loss measurements, electrochemical studies and atomic absorption spectroscopy to examine corrosion inhibition behaviour of sitosterol and observed that inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperature. β -Sitosterol exhibited maximum inhibition efficiency of 95% at 500 ppm level. Authors inform that efficiency of β -sitosterol may be due to the relatively flat structure of molecule with hydrophobicity. β -Sitosterol acted as mixed type inhibitor controlling both anodic and cathodic processes.

β -Sitosterol

Figure 28. Structure of β -Sitosterol.

Zheludkevich et al. [48] developed a bi-layer protective coating based on chitosan and examined for application for aluminium alloy 2024, that had wider applications. This new type of corrosion protecting self healing coating consists of a chitosan-based pre-layer coated on the metal surface along with a barrier hybrid layer. The chitosan layer was doped with cerium ions to serve as a pool for corrosion inhibitor. The complex formed by Cerium ion and chitosan functional groups provide for a continuous release of the active agent. Authors demonstrated superior corrosion protection with the Cerium doped biopolymer pre-layer. Chitosan is a linear polysaccharide consisted of units of 2-amino-2-deoxy-D-glucose. It has nice layer forming property with superior adhesion to metallic surfaces and to many organic polymers. It has applications in several fields like pharmaceuticals, biomedicine, cosmetics, biotechnology and in protective coatings. About four types of coatings were studied by authors, an un-doped chitosan film, chitosan film doped with Cerium nitrate, an undoped chitosan film over coated with sol-gel and Cerium containing chitosan layer covered with sol-gel. Chitosan films exhibit excellent adhesion to both metallic surface and the hybrid sol-gel coating. Cerium ions inhibited corrosion forming hydroxide deposits atop the active intermetallic, blocking electrochemical activity, providing superior corrosion protection. Moreover, the released Cerium cations are expected to actively suppress the corrosion process by stabilizing the metal-polymer interface. Authors concluded that the developed self healing coating system can be assumed to be a favourable green solution for corrosion inhibition.

Jiyaul Haque et al. [49] investigated N-methyl-N,N,N-triacetyl ammoniumchloride (Aliquat 336) (Fig. 29) as a novel and green corrosion inhibitor for mild steel in acid chloride medium employing potentiodynamic polarization (PDP), other spectroscopic methods (FTIR, UV-Vis) and also theoretical methods. Aliquat 336 exhibited good efficiency of 94.6%. Authors showed the title compound as a mixed type inhibitor. Aliquat 336 has high hydrophobic character because of the presence of three long

alkylchain substituents and a quaternary N atom and has wider applications as a phase transfer catalyst, metal extracting agent and surfactant.

Aliquat 336

Figure 29. Structure of N-methyl-N,N,N-triacetyl ammonium chloride (Aliquat 336).

Yadav and co-workers [50] synthesized two carbohydrate compounds (Fig. 30) and examined their corrosion inhibition and adsorption characteristics on oil-field N-80 steel in presence of 15% HCl solution using EIS, PZC, Polarization and mass loss procedures. Experimental data was corroborated with DFT and molecular dynamics simulations (MDS). Authors reported 98.3% and 91.5% inhibitor efficiency for BIHT and MIHT respectively at 333 K, in presence of 400 ppm level. It is concluded that BIHT binds stronger on mild steel surface than MIHT due to the presence of two extra benzene rings associated with BIHT structure.

Figure 30. Structure of BIHT and MIHT; carbohydrate compounds.

Conclusion

The last few decades have witnessed substantial growth in finding new organic corrosion inhibitors. The present review was authored purely out of academic interest to familiarize the young science researchers to appraise them about the recent work appearing on green organic corrosion inhibitors, particularly related to organic molecules. The examples covered in this review are chosen from different journals. The authors of this review are highly appreciative of the research articles published for their contributions in the area of

organic corrosion inhibitors. This review is only representative in nature and not intended to be exhaustive. The readers are advised to go through original research communications for detailed information. The figures are drawn simply and selectively in a representative manner.

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