An Up-to-Date Review on Industrially Significant Inhibitors for Corrosion Control of Zinc

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Abstract
Zinc, an important nonferrous metal, is the fourth most used metal in the world. It has innumerable uses in industrial as well as in other segments. The primary utility of zinc is in galvanization and as an anode in the battery. Steel coated with zinc, which is known as galvanized steel, is widely used in industries. Even though zinc protects many metals from undergoing corrosion, by itself, it undergoes corrosion in several acidic, alkaline, and neutral environments. The corrosion behavior of zinc is significant in all industries where it is utilized either directly or indirectly in the form of a sacrificial coating. In-depth analysis of the reported literature indicated that corrosion attenuation of zinc in acidic and alkaline medium was studied by many researchers, and various classes of inhibitors were tried under varying experimental conditions. Most inhibitors can be amalgamated as excellent inhibitors with an inhibition efficiency of 80–90%. Even though this is a subject of intense research, systematic documentation on the same is not available in the literature. This review consolidates research work on corrosion and inhibition studies of zinc and galvanized steel over a period of three decades.

Keywords Corrosion · Zinc · Galvanized steel · Corrosion inhibitors · Nanoparticles · Coatings

1 Introduction
Corrosion is the unavoidable destruction of metals as well as alloys owing to their interaction with surroundings [1]. Even though ferrous materials are known for undergoing corrosion spontaneously in various acidic, alkaline medium [2], corrosion of nonferrous materials is not new. Numerous reports are available in the literature for corrosion of nonferrous materials such as aluminum and its alloys [3], zinc [4], and other materials [5, 6]. Zinc is frequently used for coatings other metals, predominantly steel [7]. Zinc will undergo severe corrosion at pH lower than 6 and above 12. Industrial practices include procedures where metals are being treated with acids during pickling, descaling, etc. Due to these processes, zinc tends to undergo severe corrosion [8, 9]. The corrosion in marine environments is initiated by interaction between metal surfaces and marine aerosols settled down on it [10, 11]. Furthermore, zinc is liable to undergo atmospheric corrosion. Proper corrosion prevention helps to reduce various damages, direct as well as indirect. Thus, material engineers and corrosion scientists intend to lessen the influence of corrosion on all walks of life under multiple situations. Consequently, there would be a decline in economic losses and enhancement of industrial safety, which eventually protects and preserves engineering materials.

Even though researchers have focused on corrosion inhibition studies by adopting various techniques, the utility of corrosion inhibitors has been advocated as the primary tool to retard corrosion rate. Organic inhibitors are heterocyclic compounds containing O, N, S, and P as heteroatoms. These heteroatoms are centers of high electron densities with a lone pair of electrons in them. Through these reactive centers, they quickly form a covalent/coordination bond with metal [12]. Consequently, they tend to form a protecting deposit on the metal surface. It will form a barricade between metal and corrosive which will avoid promoted dissolution of metal and hence material loss [13].

Corrosion inhibitors are practical and flexible means to mitigate corrosion. They are exclusively utilized in innumerable ways in the industrial segments. They are used as the first-line protector in the oil extraction, processing, and chemical industries. These inhibitors minimize the damage of metal, reduce the degree of hydrogen embrittlement,
protect the metal. They reduce corrosion by either controlling anodic or cathodic or both the reaction. A pictorial illustration for the application of inhibitors in pipelines is depicted in Fig. 1.

In industries, every year, many organic compounds were being synthesized and screened for anti-corrosion performance of different engineering materials in various mediums [14–17]. The other methods employed at the industrial level include coatings, cathodic and anodic protection, in addition to the selection of materials [18–21].

As a part of our research work on the studies of corrosion behavior and corrosion inhibition of nonferrous materials [22–27] under static and dynamic conditions [28], we report herein an up-to-date review on corrosion inhibition strategy for zinc under various corrosive mediums.

2 Inhibitors for Corrosion Mitigation of Zinc in Acidic Medium

Zinc is vulnerable to corrosion in an acidic environment. Therefore, pickling [29], descaling [30] are usually done with dilute mineral acids [31]. The accelerated corrosion of zinc results from the predominant cathodic reaction in a highly acidic medium [32]. However, the added inhibitor plays a crucial role by getting adsorbed onto the metal surface, thereby decreasing the speed of hydrogen evolution and protecting the metal surface [7]. Many researchers have comprehensively deliberated the corrosion performance of zinc and inhibition of its corrosion in the acidic environment [33].

HCl is one of the expansively recommended mineral acids for metal pickling [32, 34–36]. Even though the significant role of the acid here is to remove extraneous materials present on the surface of the material, due to its aggressive nature, even though it is dilute, it dissolves the materials to a considerable extent. Hence, to attenuate the metal dissolution, inhibitors are recurrently added to the acidic solutions. The inhibitor’s efficacy depends on its structure, electrolyte composition, and the charge on the metal surface [37, 38]. Diverse categories of organic compounds have been successfully used as inhibitors.

Many researchers have considered the dissolution of zinc in HCl employing different classes of chemical inhibitors. Important among them are: ethoxylated fatty alcohols [39], catholyte containing amino-benzotriazole [40] (Fig. S1), aniline [41], 2-[4-(methylthio) phenyl] acetoxyrazide and 5-[4(methylthio)benzyl]-4H-1,2,4-triazole-3-thiol [42] (Fig. S2), triethylamine, ethanolamine and triethanolamine [43] (Fig. S3), cetrimethyl ammonium bromide (CTAB), bromohexadecyl pyridine and nicotinic acid [9] (Fig. S4), semicarbazide, thiosemicarbazide and diphenylcarbazide [44] (Fig. S5), C_{26}H_{22}N_8O_4, C_{26}H_{22}N_8O_2, C_{28}H_{18}N_8O_2, C_{24}H_{16}Cl_2N_6O_2, C_{23}H_{16}N_10O_6 [45] (Fig. S6).

Some prominent drugs such as ketosulfone [46] (Fig. S7), streptomycin, spectinomycin, and paromomycin [47] (Fig. S8), Seroquel [48] (Fig. S9), and ziprasidone [49] (Fig. S10) containing active functional groups were useful inhibitors for corrosion of zinc in HCl. Their inhibitive capability is exclusively due to the existence of heterocyclic rings, π- and nonbonding electrons.

Sulphuric acid (H_2SO_4) is used as a cleaner for rust, algae, and scale from condensers and cooling towers [50, 51]. A few studies were carried out using diamine N,N′-di (p-methoxybenzyliden) and ethylenediaminedi-N,N′-disalicylidene [52] (Fig. S11), m-substituted aniline- N-salicylidene [53] (Fig. S12), ethoxylated fatty acids [54] ethylamines [50] 4-hydroxy phenyl methylidene-2-(1-phenyl ethylidene) hydrazine carbothioamide (4-HPMHC) [55] as inhibitors in sulfuric acid medium.

Limited studies were accomplished on corrosion inhibition of zinc in nitric acid, sulfamic acid, and phosphoric acid. Nitric acid is strongly oxidizing and hence attacks most metals [56]. Even though phosphoric acid is quite mild, it is reported to corrode zinc significantly [57]. Sulfamic acid is a strong acid used as a cleaning agent to remove rust, algae, and hard water scale from cooling towers and condensers [58]. Inhibitors like organic phosphonium and ammonium compounds (Fig. S13) were tried and tested as antirrogressive agents for corrosion of zinc in 1.0 M H_3PO_4 [57]. In addition, isomers of toluidines in sulfamic acid and HNO_3 [58, 59] (Fig. S14) and ethylamine were tried for corrosion hindrance of zinc in HNO_3 [60]. The inhibitors mentioned above have shown good inhibition efficiency.

2.1 Mechanistic Aspects of Acid Corrosion of Zinc

Metal dissolution in acid is an electrochemical process. At the anode, zinc dissolves, giving corresponding ions [58, 59].
Zn $\rightarrow$ Zn$^{2+}$ + 2e$^-$

The reaction taking place in the cathodic region in aerated acidic chloride solution is

$\text{H}^+ + e^- \rightarrow \text{H}_{\text{ads}}$

$\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$

or

$4 \text{H}^+ + \text{O}_2 + 4e^- \rightarrow 2\text{H}_2\text{O}$

The results of various inhibitors reported in the acid medium are tabulated in Table 1.

Careful observation of Table 1 clearly shows that researchers adopted both non-electrochemical and electrochemical methods for corrosion rate measurements. The non-electrochemical method, popularly known as the classical method, mainly involves weight loss techniques [58–60]. On the other hand, potentiodynamic polarization (PDP) measurements and electrochemical impedance spectroscopy (EIS) techniques are extensively applied at laboratory levels. A detailed procedure for these is available in the literature [49, 50, 57].

The potentiodynamic polarization method suggests the type and behavior of the inhibitor. Based on the shift in corrosion potential ($E_{\text{corr}}$) after the inhibition, it is possible to predict whether the inhibitor acts as an anodic inhibitor, cathodic inhibitor, or both. Regarding the literature [61], if the alteration in corrosion potential ($E_{\text{corr}}$) is beyond $\pm$ 85 mV, the inhibitor can be treated explicitly either as anodic or cathodic. If not, it can be viewed as a mixed inhibitor. From Table 1, it can be seen that almost 80% of the inhibitors act as mixed inhibitors. This means added inhibitors are capable of bringing down both anodic and cathodic reactions.

Adsorption isotherm provides information regarding the mode of adsorption of inhibitors onto the metal surface. In addition, it helps evaluate thermodynamic parameters related to adsorption [62]. Langmuir, Frumkin, Bockris-Swinkel, and Temkin were significant isotherms tested and tried to fit experimental data. Linear correlation coefficient ($R^2$) values, close to unity, were taken to measure best fitment [63] (Fig. S15).

Adsorption of the inhibitor can take place either due to physisorption and chemisorption. Physical adsorption encompasses the electrostatic force of attraction between metal and inhibitor. Chemical adsorption is a consequence of the covalent/coordination bond between metal and inhibitor. The schematic representation of adsorption of inhibitor through physisorption and chemisorption is represented in Fig. 2.

From the above Table 1, it is evident that all the inhibitors showed moderate to good efficiency of about more than 85%, with a few exceptions.

When studies were done under identical conditions [42] among 2-[4-(methylthio) phenyl] acetohydrazide and 5-[4(methylthio)benzyl]-4-h-1,2,4-triazole-3-thiol, the latter turned out to be a very good inhibitor. This is because triazole derivatives are expected to have better adsorption capacity than hydrazide derivatives due to two nitrogen and one sulfur atom.

Inhibition effectiveness of aliphatic amines could be due to the nitrogen atom of the amino group ($-\text{NH}_2$) [43]. The relatively greater efficiency of ethanolamine is because of the hydroxyl group, which enhances electron concentration on the nitrogen atom, which resulted in better efficacy. To some extent, poor inhibition efficiency is witnessed with triethanolamine. With the increased number of ethanol groups around the nitrogen atom, steric factor arises, which may be responsible for lower inhibition efficiency. The high efficiency of triethylamine may be endorsed to the $-\text{C}_3\text{H}_7$ group, which enriches the electron charge density of the amino ($-\text{NH}_2$) group, and liable for increased efficacy.

Corrosion inhibiting capacity of semicarbazide was not as much of thiosemicarbazide and diphenyl carbazide [44]. Diphenylcarbazide demonstrations improved efficiency due to the presence of aryl group and then comes thiosemicarbazide and semicarbazide. The efficiency of the inhibitor depends on molecular size and charge density on the active sites, and it increases with an increase in both [64]. Further, aryl groups are more protective than alkyl groups. So diphenylcarbazide tops the series. Among thiosemicarbazide and semicarbazide, thiosemicarbazide is a better inhibitor due to the presence of sulfur atom, which has more tendency for adsorption than oxygen atom [64].

Among the compounds studied by Fouda et al. [45] compound A with the molecular formula $\text{C}_{26}\text{H}_{22}\text{N}_5\text{O}_4$ exhibited maximum efficiency of 91%. This could be attributed to the presence of an electron-donating p-OCH$_3$ with Hammett constant ($\sigma_p^{\text{CH}_3} = -0.27$), which is negative. This will upsurge the electron charge density of the atom. However, the least protection efficiency of compound $\text{C}_{24}\text{H}_{10}\text{N}_5\text{O}_6$ could be due to the presence of electrons with drawing p-NO$_2$ groups, with a positive Hammett constant ($\sigma_p^{\text{NO}_2} = +0.78$).

Maximum efficiency of 99% was observed for diamine $\text{N},\text{N'}$-di(p-methoxybenzylidene) and ethylenediamine $\text{N},\text{N'}$-disalicylidene [52] m-substituted aniline-$\text{N}$-salicylidenes [53] owing to the occurrence of electronegative atoms ($\text{N}$ and $\text{O}$), the unsaturated bonds, and the aromatic ring.
Table 1  Inhibitors for corrosion mitigation of zinc in acid medium

| Inhibitor                                         | Method                  | Medium                        | Mode of adsorption | Type of inhibitor | Maximum I.E (%) | Ref   |
|--------------------------------------------------|-------------------------|-------------------------------|--------------------|-------------------|-----------------|-------|
| Ethoxylated fatty alcohols                        | Weight loss, PDP        | 0.5 M HCl                     | Temkin             | Mixed             | 88              | [39]  |
| Catholyte containing aminobenzotriazole           | Weight loss, PDP        | 0.2, 0.4, 0.6 M HCl           | Temkin             | Mixed             | 68              | [40]  |
| Aniline                                           | Weight loss, PDP        | 0.01, 0.05, 0.10              | 0.15 M HCl         | Langmuir          | 94              | [41]  |
| 2-[4-(methylthio)phenyl] acetoxydrazide (HYD); 5-[4(methylthio)benzyl]-4 H-1,2,4-triazole-3-thiol (TRD) | Weight loss, PDP, EIS   | 0.1 M HCl                     | –                  | Mixed             | TRD-95 HYD-71   | [42]  |
| Triethylamine, triethanolamine ethanolamine       | Weight loss, PDP        | 0.01, 0.025, 0.05 M HCl       | –                  | Mixed             | 96              | [43]  |
| Cetyltrimethyl ammonium bromide (CTAB); bromohexadecyl pyridine, and nicotinic acid | Weight loss, PDP        | 0.5 M HCl                     | –                  | Mixed             | 66, 97          | [9]   |
| Semicarbazide, thiosemicarbazide diphenylcarbazide | Weight loss, PDP        | 2 M HCl                       | Bockris-Swinkel    | Mixed             | 30, 32, 40      | [44]  |
| C_{26}H_{22}N_{4}O_{2}                            | EIS, EFM, PDP, weight loss | 0.5 M HCl                     | Langmuir           | Mixed             | 96, 94, 91      | [45]  |
| C_{26}H_{22}N_{2}O_{2}                            |                          |                               |                    |                   | 78, 68          |       |
| C_{24}H_{18}N_{8}O_{2}                            |                          |                               |                    |                   |                 |       |
| C_{24}H_{16}N_{4}O_{2}                            |                          |                               |                    |                   |                 |       |
| C_{24}H_{16}N_{10}O_{6}                           |                          |                               |                    |                   |                 |       |
| Ketosulone                                        | PDP, EIS                | 0.1 M HCl                     | Langmuir           | Mixed             | 59              | [46]  |
| Streptomycin spectinomycin paromomycin            | PDP, EIS, weight loss   | 1 M HCl                       | Temkin             | Mixed             | 91, 89, 93      | [47]  |
| Seroquel                                          | PDP, EIS, weight loss   | 0.1 M HCl                     | Temkin             | Mixed             | 82              | [48]  |
| Ziprasidone                                       | PDP, EIS, weight loss   | 0.1 M HCl 0.05 M HSO_{4}      | –                  | Mixed             | 87, 84          | [49]  |
| Ethylenediamine N,N’-dibenzylidene; ethylenediamine N,N’-dis(p-methoxybenzylidene); ethylenediamine N,N’-disalicylidene | Weight loss             | 0.25 M 0.5 M H_{2}SO_{4}      | –                  | Cathodic          | 99              | [52]  |
|   m-substituted aniline-N-salicylamides            | Weight loss, galvanostatic polarisation | 0.25 M 0.5 M H_{2}SO_{4}      | Langmuir           | Mixed             | 99              | [53]  |
| Ethoxylated fatty acids                           | PDP, weight loss        | 1.0 M HCl 1.0 M HSO_{4}       | Frumkin and Flory-Huggins | Anodic, mixed    | 80, 85          | [54]  |
| Ethylamine                                        | PDP, weight loss, EIS   | 0.1, 0.3, 0.5 M H_{2}SO_{4}   | Langmuir           | Mixed             | 92              | [50]  |
| 4-hydroxy phenyl methylidene-2-(1-phenyl ethyldiene) hydrazine carbothioamide (4-HPMHC) | Weight loss             | 0.01, 0.02, 0.03, 0.04, 0.05 M H_{2}SO_{4} | Langmuir           | Mixed             | 86              | [55]  |
| Organic phosphonium and ammonium compounds        | PDP, EIS                | 1 M H_{3}PO_{4}               | Frumkin and Langmuir | Mixed             | 92              | [57]  |
| Isomers of toluidines                             | Weight loss, galvanostatic polarisation | 0.1 M, 0.5 M, 1 M NH_{4}SO_{4}H | Langmuir           | Mixed             | 71              | [58]  |
| Isomers of toluidines                             | Weight loss, PDP        | 0.15 M, HNO_{3}               | Langmuir           | Mixed             | 88              | [59]  |
3 Inhibitors for Corrosion Mitigation of Zinc in Alkaline Medium

Mercury is expected to attenuate corrosion of zinc in alkaline medium significantly. However, environmental protocols motivate researchers to look for environmentally benign inhibitors. However, recommending a new class of compounds for zinc corrosion in alkaline storage batteries is a severe problem, and it is under investigation. Organic compounds like polyethylene glycol (PEG) and polyoxyethylene alkyl phosphate alkyl phosphate ester acid (GAFAC RA600) [65], dicarboxylic acid (HCO$_2$–CH$_2$–(OCH$_2$CH$_2$)–CH$_2$–CO$_2$H), modified polyethylene glycol (PEG) [66], surfactants and polyethylene glycols (PEGs PEG200, PEG400) and a surface-active substance of trade name Brij 30 containing ethylene oxide groups as main components C$_{12}$H$_{25}$O–[CH$_2$–CH$_2$–O–]$_n$–H) and ethoxylated polyflouro alcohol (FPEA) [67], dodecyl trimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (HTAB) [68] (Fig. S16) have been studied.

3.1 Mechanistic Aspects of Alkaline Corrosion of Zinc

Anodic reaction:
$$\text{Zn} + \text{OH}^- \rightarrow \text{ZnOH} + \text{e}^-$$

$$\text{ZnOH} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_3^- + \text{e}^-$$

Zn(OH)$_3^-$ + OH$^- \rightleftharpoons$ Zn(OH)$_4^{2-}$

Cathodic reaction:
$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$

Inhibitors used in the alkaline medium are recorded in Table 2.

The maximum inhibition efficiency was observed for PEG400 and (FPEA) [67]. From the surface studies, it was seen that PEG400 strongly adsorbed onto the zinc surface, and there was almost no presence of zinc oxide formed. However, the number of inhibitors tried, tested, and reported for their anticorrosive property in alkaline medium is relatively less. This is because zinc undergoes severe corrosion in a highly alkaline medium; electrochemical measurement for the corrosion is very challenging in such a situation.

4 Inhibitors for Corrosion Mitigation of Zinc in Near-Neutral Medium

The corrosion in marine environments is determined using chloride media. Therefore, 3.5% NaCl solutions are often used to stimulate laboratory conditions and carry out corrosion studies.

Manov et al. [69] explored the corrosion activities of zinc with 2-hydrazone-3-bornan-emethylenedithiol disodium salt (Fig. S17) with chelating groups as inhibitors at pH 6. (mixture of 0.2 M Na$_2$SO$_4$ and 0.2 M NaCl). Inhibitor principally intimidated cathodic reaction. It is due to the chelation
between zinc and organic molecules, which formed a protective organometallic layer on zinc. Another study was carried out in an aqueous chloride-sulfate medium [70] using Benzaldehyde thiosemicarbazone (BTSC) (Fig. S18) as the inhibitor. Due to highly electronegative nitrogen and sulfur atoms, a strong adherent layer was formed on the metal surface. It was ascertained by surface morphology studies by SEM, EDX, and FT-IR.

Aramaki [71–73] studied zinc’s corrosion in 0.5 M NaCl using various anionic and cationic inhibitors. Maximum efficiency was obtained for using cationic inhibitors [73]. X-ray photoelectron spectra of zinc treated with a solution having Ce³⁺ shown that dense protective deposit is devoid of chloride ions. Assaf et al. [74] deliberate the pitting corrosion behavior of zinc in NaCl, NaBr, and NaI. Passivity was developed due to the formation of a protecting barrier of ZnO at the anodic area. The aggressiveness of halide ions towards the stability of the passive film decreased in the order: Cl⁻ > Br⁻ > I⁻. The corrosion of zinc was enhanced with an increase in the halide ion concentration and temperature. Hinton et al. [75] considered corrosion of zinc and zinc-coated steel in tap water containing small concentrations of cerous chloride. The protecting film was developed by exposing zinc surfaces to cerous chloride solution for a prolonged time or by quenching hot zinc or zinc-coated surfaces into cerous chloride solution. Inhibitors used in the near-neutral medium are listed in Table 3.

Almost a inhibitors showed excellent inhibition efficiency; among them, Ce³⁺ [73] showed maximum inhibition efficiency. This is because of the direct interaction between hydrated Ce³⁺ with hydroxide of the solution resulting in the formation of cerium-rich oxide and hydroxide layer.

### 5 Inhibitors Patented for Corrosion Mitigation of Zinc

Charkoudian et al. [76] patented chloride double salt containing mercuric ions and quaternary ions (Fig. 3) as a corrosion inhibitor in a galvanic cell having zinc anode.

Harvey et al. [77] patented corrosion inhibitor for zinc-containing 10 gL⁻¹ chromic acid solution in water. Busch et al. [78] patented a corrosion inhibitor for the corrosion control of zinc in open evaporative cooling water circulation systems. The inhibitor was a mixture of various compounds like 2-phosphonobutane-1,2,4-tricarboxylic acid (C₇H₁₂O₇P) (Fig. 4a), phosphono-hydroxyacetic acid (C₂H₅O₆P) (Fig. 4b), and sodium diethyldithiocarbamate.

### Table 2 Inhibitors for corrosion mitigation of zinc in alkaline medium

| Inhibitor                                             | Method                               | Medium                  | Maximum I.E (%) | Reference |
|-------------------------------------------------------|--------------------------------------|-------------------------|-----------------|-----------|
| Polyethylene glycol, polyoxyethen alkyl phosphate ester acid | Linear polarization potentiodynamic potentiostatic | 8.5 M KOH              | –               | [65]      |
| Dicarboxylic acid modified polyethylene glycol        | Linear polarization potentiodynamic potentiostatic | 8.5 M KOH              | –               | [66]      |
| PEG200, PEG400, and a surface-active substance Brij 30 and ethoxylated polyfluoro alcohol (FPEA) | Potentiodynamic, volumetric, gravimetric | 7 M KOH | 81            | [67]      |
| DTAB, TTAB, HTAB                                      | Anodic and cathodic polarization resistance Potentiodynamic method | 2 M KOH | 66 75 80       | [68]      |

### Table 3 Inhibitors for corrosion mitigation of zinc in the near-neutral medium

| Inhibitor                                                  | Method                             | Medium                  | Maximum I.E (%) | Reference |
|------------------------------------------------------------|------------------------------------|-------------------------|-----------------|-----------|
| 2-Hydrazono-3-bornanemethylenedithiol disodium salt        | EIS, polarisation measurements     | 0.2 M Na₂SO₄ + 0.2 M NaCl, pH 6 | 90              | [69]      |
| Benzaldehyde thiosemicarbazone (BTSC)                     | Galvanostatic polarisation         | Aqueous chloride-sulfate | 87              | [70]      |
| Ce(NO₃)₃·6H₂O                                              | PDP                                | 0.5 M NaCl              | 91              | [71]      |
| Na₃MoO₄·2H₂O, Na₃PO₄·12H₂O, Na₂B₄O₇·10H₂O                 | PDP                                | 0.5 M NaCl              | 90              | [72]      |
| Al³⁺, La³⁺, Ce³⁺, Ce⁴⁺                                    | PDP                                | 0.5 M NaCl              | 93              | [73]      |
| –                                                         | PDP, Cyclic voltammetry            | NaCl, NaBr, NaI         | –               | [74]      |
| CeCl₃·7H₂O                                                | Weight loss, PDP                   | Tap water or 0.1 M NaCl | –               | [75]      |
(NaC₅H₁₀S₂N) (Fig. 4c). The amalgamation of these compounds was found to constrain the formation of white rust on galvanized steel panels to the extent of 95% in solution with pH ranging from 7.5 to 10.0.

6 Experimental Techniques

The majority of literature specified that corrosion and inhibition studies are accomplished employing both classical and electrochemical approaches. Weight loss is one of the most commonly adopted and most reliable methods under classical techniques. It gives highly reproducible results and is still being used by many researchers. However, this method is time-consuming [63]. It will not provide much information regarding the nature of the corrosion inhibition process. Nowadays, researchers prefer fast electrochemical techniques. The potentiodynamic polarization method (PDP), (Fig S19a), which is quite fast, gives a lot of information regarding corrosion current density, corrosion potential, etc. All these electrochemical parameters are beneficial in arriving at the nature and mechanism of corrosion inhibition. The electrochemical impedance spectroscopy (EIS) method helps understand the mechanistic aspects of the corrosion and inhibition process [79] (Fig. S19b). It provides detailed information on the various resistance parameters that play a decisive role in the corrosion and inhibition process. From the carefully done experimental observation, it is possible to prove that inhibition efficiency evaluated from all three methods will agree with one another with less than 2% deviation.

Careful analysis of published papers related to corrosion inhibition of zinc in various mediums gives the information that surface morphology was studied by SEM (Fig. S20), elemental composition by EDX, and topography was studied by AFM [80]. Surface morphology studies demonstrated the deposition of inhibitors on the surface of the metal, thereby forming a physical barricade between metal and corrosive. The surface has become extraordinarily even after adding the inhibitor. EDX studies were done to understand the elemental composition on the metal surface. In almost all cases, there was a rise in the % composition of elements, which are accountable for barrier film formation. This reaffirms the adsorption of inhibitors on the surface of the metal. However, this can be further studied and supplemented by spectroscopic techniques and quantum chemical calculations.

7 Corrosion Inhibition Studies of Galvanized Steel

Coating iron or steel with zinc is known as galvanization. In galvanized articles, zinc protects the underlying metal by the sacrificial anode method. Zinc, being less noble, will undergo corrosion, thereby protecting the base metal. Hot-dip galvanization, thermal spraying, and electrodeposition are primary practices implemented for coating [81]. Galvanized steel pipes have widespread industrial applications. Galvanized steel wires are used in fencing to support wall projections, locking down windows, as a construction material, in telecommunication cables, earth wires, and suspension bridges. Galvanized steel sheets are used in building frames, handrails, street furniture, support beams, nails, nuts and bolts, piping, playground equipment, and automobiles. Galvanized steel bars are used in architectural building features, concrete reinforcement, coastal and marine structures, and transport infrastructures. In industrial sectors, it is used in conveyor castings, chains, supports, storage racks and shelves, electrical conduits, equipment hooks, equipment supports, farm implements, conveyor casing, conveyors, high-speed freezing equipment, cooling towers, condensers [82].

Atmospheric corrosion of galvanized steel structures commences when the Zn surface becomes damp with rain, mist, or dew [83]. According to the report available in the USA, atmospheric corrosion of zinc is more severe in seawater [84]. Reinforced concrete is an important construction
material. Hot-dip galvanized reinforcement dramatically diminishes the problem of steel corrosion and concrete spalling. Thus it provides a cost-effective and robust impact on the toughness of the concrete [85].

Even though galvanized steels are comparatively corrosion-resistant, at certain conditions and the medium, they undergo corrosion. An overview of the corrosion pattern seen in galvanized steel is given below.

Al-Saade et al. [86] considered the corrosion of galvanized steel in solutions of pH 2–4 and 8–10; by adding a minimal concentration (0.05–1 M) sodium chloride at 25–55 °C. In a pure acid medium, corrosion products of zinc were freely soluble in water. In strong alkaline solutions, water-soluble products were formed. This accelerated the corrosion process, not only by destroying the corroded protective layer at galvanized steel surface but also by exposing steel that has to be protected. At high NaCl concentration, the corrosion rate of zinc declined drastically, at elevated temperatures, specifically in an alkaline medium, because after zinc, the steel that was exposed remained cathodically protected by zinc.

Suzumura et al. [87] studied the corrosion of galvanized steel wires in a humid environment composed of sodium chloride. Corrosion rate increased remarkably with the rise in salt concentration, particularly at elevated temperatures. Further, it was witnessed that this article did not undergo corrosion at a humidity level lower than 60%.

Macias et al. [88] studied the behavior of galvanized corrugated reinforcing bars, which were designed to feign aqueous environments in concrete pores. A white, dusty corrosion product was perceived in the presence of 0.001–1.5 M KOH and NaOH. In addition, hydrogen evolution was observed pH greater than the threshold level of 12.8 ± 0.1.

Macias et al. [89] studied corrosion of galvanized bars in the pH range of 11.1–12.6 using calcium hydroxide solutions. Corrosion kinetics were influenced by solution pH and corrosion products Ca(3Zn(OH)2)2·2H2O. Restricted corrosion was detected at pH < 11.5.

Kartonakis et al. [90] explored corrosion resistance of HDG steel panels in sodium chloride solution in the presence of six different inhibitors. In a pH range of 5.8–6.3, Ce(NO3)3 exhibited the best corrosion protection, and Ca3(PO4)2 had no positive impact.

Wanich et al. [91] used 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU) as inhibitor for galvanized steel in 1.0 M HCl, at 30 °C and 40 °C. Inhibiting efficiency of DBU was up to 88% at 30 °C.

Zhu et al. [92] studied the corrosion performance of AA 2024-T3, and hot-dip galvanized steel (HDG) in 0.6 M sodium chloride solution. Bis-[3-(triethoxysilyl)propyl] tetrasulfide (bis-sulfur silane), bis-[trimethoxysilylpropyl] amine (bis-amino silane), and their mixture were tried as inhibitors. Hydrophilic bis-amino silane did not exhibit any positive impact on metal dissolution prevention. Hydrophobic bis-sulfur silane accomplished just fine on AA 2024-T3 but futile on HDG. A mixture of bis-sulfur/bis-amino (ratio of 3/1) prominently improved the corrosion tendency of both AA 2024-T3 and HDG.

Coelho et al. [93] deliberated on corrosion opposition of hot-dipped galvanized steel in 0.05 M NaCl. Efficacy of Na2MoO4 was estimated on HDG substrate, mechanically scratched material. SVET was utilized to examine localized corrosion on scratched HDG samples.

8 Coating Studies on Galvanized Steel

As discussed in the previous section, galvanized articles are vulnerable to undergo atmospheric corrosion, and they can be upgraded by smearing. To avoid corrosion and enrich coating adhesions, galvanized steel sheets should be shielded with a film by surface treatment. This is known as coated galvanized steel. This methodology conglomerates benefits of inorganic and organic components. The organic component offers flexibility, diminishes defectiveness, and advances the compatibility with polymer coatings. Simultaneously, the inorganic part is liable for greater adhesion to the metal surface. Moreover, coatings can be carried out at lower temperatures [94].

Acid rain is a mix of H2SO4, HCl, and HNO3, which freely react with Ca(OH)2 forming an equivalent amount of hydrated salts. Because of their greater solubility, they infiltrate the inner pores of the concrete. After the evaporation of rainwater, these salts solidify and impart stress on the metallic structure leading to complete damage [95]. According to reports, United States alone spends more than five billion dollars [96] to rectify the destruction of concrete structures triggered by acid rain.

Zin et al. [97] considered corrosion of galvanized steel in artificial acid rain, with a mix of zinc phosphate/molybdate and calcium ion exchange silica. They turned out to have substantial synergetic anti-corrosion influence compared to the pigments used alone.

Barry et al. [98] studied the corrosion activity of pure zinc, 5%Al-Zn, 55%Al-Zn film specimens in simulated acid rain. Galvanized steels displayed sacrificial corrosion hindrance for steels. Alloying of zinc and application of inorganic silicon sealer amplified anticorrosive performance. Pokhmsuryki et al. [99] studied the inhibition activity of pigments containing phosphate and calcium as a substitute for toxic chromate pigments on zinc metal. The corrosion studies were carried out in acid rain. The pigment mix formed phosphate film on metal and delayed the course of corrosion progression.
Gonzalez et al. [100] smeared epoxy polyamide primer on galvanized steel. Corrosion thickness was in the range of 100, 200, and 500 μm. Corrosion assessments were accomplished by exposing painted coupons to a 3.0% NaCl solution in a horizontal flat cell. The thinnest primer film could not afford sufficient protection for the metal, and metal underwent corrosion. However, the effectiveness of the protection of primer increased with its thickness.

Foremost strategies for corrosion mitigation by coating techniques avoid the electrolyte or air from reaching the metal surface for progressive corrosion reaction. Therefore, most of the work is devoted to replacing harmful chromate coating with safe, non-toxic, environment-friendly replacements, and various such coating formulations are in progress [101].

9 Coating Studies on Zinc and Galvanised Steel with Nanoparticles

Anticorrosive properties of the coatings on the galvanized steel could be upgraded by including nanoparticles in the coating. Nanostructured materials maintain exceptional mechanical, electronic, and physicochemical properties because they have a high effective surface area. These properties have urged to prepare coatings of more excellent wear and tear resistance [102, 103].

Montemor et al. [104] studied corrosion of hot-dip galvanized steel pretreated with microparticles of SiO2. Bis-1,2-[triethoxysilyl]ethane silane or bis-[triethoxysilyl]propyl tetrasulfide were used for pretreatment. Results showed that the pretreated silane films embodied with silica particles extended maximum corrosion protection.

Montemor et al. [105] explored electrochemical performance of galvanized steel pretreated with bis-[triethoxysilyl]propyl tetrasulfide silane (BTESPT) solutions, incorporated with SiO2 or CeO2 nanoparticles activated by cerium ions. Silanes formed a hybrid compact and homogeneous surface film, which became deferment for corrosion initiation. In addition to this, the existence of nanoparticles reinforced the silane films’ barrier properties and brought down corrosion action. CeO2 nanoparticles were more prominent than SiO2 nanoparticles.

Motte et al. [106] reported that Silane sol–gel based films could replace customary chromate pre-treatments. Montmorillonite clay was reformed to get Ce(III) montmorillonite clay (Ce-MMT). Quantity of amalgamated Ce(III) is considered by XRF studies. X-ray diffraction disclosed that the Ce(III) was situated in interlayer regions. The impact of ionic strength and nature of counterion on the kinetics of Ce(III) release was explored in NaCl and ZnCl2 solutions.

Zand and co-workers [107] examined morphological and electrochemical aspects of hot-dip galvanized steel, which was previously treated with 3-glycidoxypropyl trimethoxysilane and bisphenol-A impregnated with cerium ion-activated CeO2 nanoparticles. Results showed the development of a reasonably smooth, nanostructured surface with a small heterogeneity on coating. In addition, the presence of the nanoparticles was reported to reinforce barrier properties of the silane films, reducing corrosion activity.

Neha et al. [108] deliberate on the corrosion diminishing capability of coriander seeds extract by integrating zinc oxide nanoparticles for zinc corrosion in 0.5 M HCl. Examination of polarization records showed that both inhibitors acted as mixed-type. The incorporation of nanoparticles has enhanced the barrier properties of silane coatings due to crack-free films. In addition, nanoparticles enhanced corrosion protection of a sol–gel hybrid coating.

10 Summary and Conclusions

In this review article, an account of different chemical inhibitors used to alleviate deterioration of zinc in acid, alkaline, and near neural medium is provided. A detailed study of coating techniques is also given. Most inhibitors can be consolidated as excellent inhibitors with an inhibition efficiency of 80–90%. More inhibitors are reported for acid corrosion than corrosion in alkaline and near-neutral medium. Still, there is more scope to explore the corrosion behavior of zinc in an alkaline medium and introduce innovative class of inhibitors. Some of the inhibitors can be tried for industrial applications. Simultaneously, a few advanced experimental techniques are needed to understand the adsorption tendency of the inhibitor. UV–Vis, FT-IR, AAS, Raman spectroscopy, and X-ray diffraction would provide value-added information to affirm the adsorption of inhibitor onto metal surfaces, which is very much lacking in the reported literature. Furthermore, an insight into computational modelings such as DFT studies, Mulliken charge distribution, and Monte-Carlo Simulation could bring value-added information on the mechanistic aspect of corrosion inhibition in a more realistic way.

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Declaration
Conflict of interest On behalf co-author, the corresponding author claims no conflict of interest.

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