Corrosion Inhibitors as Building Evidence for Mild Steel: A Review

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Abstract

Mild steel is the most common type of metal used in large industries due to its acceptable material properties and low cost. However, a growing concern of its use has been limited as a result of its low resistance to corrosion especially in acidic and alkaline environments. The use of corrosion inhibitors has been encouraged by various researchers as a means slow down the corrosion rate and thus reduce monetary losses to industrial vessels, surfaces and equipment. This paper presents the types of inhibitors employed by different researchers on various mediums. It also seek to consider the limitation processes caused by some factors such as temperature of the media and concentration of the inhibitors and the media. Although the use of green inhibitors has been greatly encouraged due to its low cost but the combination of it with other kinds of inhibitors can prove to boost its effectiveness in corrosion inhibition process. Other organic materials such as animal discharge, and biomaterial should also be considered in future research works. These will further provide more literature to corrosion inhibition of mild steel which in essence promotes the life span of the metal.

Keywords: Mild steel, corrosion, organic inhibitors, Hydrochloric acid, sodium hydroxide.

1.0 Introduction

In various industries, mild steel has been used extensively as a building material owing to its cost effectiveness, and high mechanical strength [1, 2]. Although, through electrochemical and chemical reactions it has been very reactive with the environmental constituents and hence, component metal loss arises as a result of corrosion. Corrosion occurs as a result of cross section losses, having lower ductility, ultimate strength and yield strength. It decreases the life span of structures resulting into structural vulnerability leading to structural failure [1]. Various efforts have been previously carried out to reduce unfavorable reactions mostly through frequently occurring industrial developments such as acid pickling, acid descaling, and acid cleaning etc. of which the utilization of corrosion inhibitors is one of the best methods [3]. Globally, corrosion problems mostly occurs in industries as a result of service and environmental conditions. Corrosion might not have immediate negative effect on the material but it affect the physical appearance, mechanical behavior and strength resulting into significant operational
complications [4]. In industries, acidic solutions are largely used for acidizing, de-scaling, chemical cleaning and acid pickling for steel, the most frequently used is hydrochloric acid. Naturally, these occur in corrosive environment resulting into intense corrosion complications experienced in industrial processes. Acid corrosion inhibitors are applied extensively to minimize or prevent loss of material associated with the acid [5].

Mild steel is frequently used as a raw material for construction of pipelines, buildings and bridges [6], its pre-mature failure and deterioration has resulted into a gross expenditure of several billions of dollars globally [7]. Since mild steel is an essential part of infrastructural facilities which includes pipelines, port facilities and bridges, these cost expenditure include replacement, maintenance and loss of productivity. The use of paint coatings has been applied to create a protective barrier. The use of pigments inhibiting corrosion is an essential constituent in paints. Over time, these pigments percolate from the coatings thereby inhibiting the concealed metal substrate, which breaks particularly in paint coating [8]. The most efficient pigment inhibiting corrosion used for different alloys and metals, e.g. mild steel, has compounds of metal chromates in its oxidation state (Cr\(^{\text{VI}}\)) [9] for example strontium chromate. Chromate compounds behaves in a method of either reducing or blocking both cathodic and anodic rate of reaction. In addition, (Cr\(^{\text{VI}}\)) has been reported as an occupational carcinogen related to sinus, naser and lung cancer [10]. In recent decades, various alternative inhibitors have been considered as substitutes for chromates, including metallic ions (rare earth metals and zinc), oxyanions (phosphates, molybdates and nitrates) and organic compounds (carboxylates). All have demonstrated some extent of inhibition effectiveness [8].

Mild steel corrosion by atmospheric conditions is a broad topic that have been researched by different authors. Various researchers have reviewed the corrosion process [11 – 15]. A huge quantity of these information is obtainable on mild steel by atmospheric corrosion at mid and short term [16]. Various studies have been conducted on the use of organic corrosion inhibitors, it has frequently been applied in various control measures such as its effectiveness to impede corrosion of mild steel in seawater [17], [18]. Usually, the use of inhibitors as a preventive mechanism against corrosion is principally attributed to inhibitor molecular adsorption which result to surface modification of the mild steel and formation of subsequent protective layer [19-21]. Several kinds of inhibitors has been utilized as an effective means of inhibiting corrosion in various electrolytic media for mild steels. These media include sea water, hydrochloric and sulfuric acid concentrations. This manuscript reviews corrosion inhibitors as building evidence for Mild Steel

2.0 Inhibition efficiency in fresh/sea water

Globally, the decomposition of exposed infrastructure to aggressive marine environment has progressively received attention. Careful observation and study of these materials have been carried out by structural engineers and naval architects in order to determine the rate at which structural material such as steel losses its strength, thus, resulting to infrastructural loss of material. Loss of material occurring from short term exposures is essential since protective measures are not totally effective. It can be concluded that modelling and understanding of these medium is required in order to determine a suitable inhibitor [22]. Natural seawater comprise of
several medium of corrosion such as microorganisms, organic acids, hydrogen carbonate ions, carbonate and sulfate ions, hence, result into several problems such as corrosion [23 – 27]. As it can be noted, corrosion results into notable reduction in the efficiency of the cooling systems, but it result into rapid degeneration of matter leading to significant economic waste and safety complications [28 – 31].

Organic inhibitors has been mostly considered to be an effective corrosion inhibitor used to control and inhibition of mild steel corrosion in seawater [18], [32]. Usually, protection by corrosion inhibitors are frequently ascribed to alteration of mild steel surface by the adherence of the inhibitor molecules followed by protective layer formation [19 – 21]. An ecofriendly polymeric material naturally extracted from leaves or seeds have stimulate high interest and attention at a low cost. Various researchers have made use of natural products, ecofriendly and green which include cassava starches [33], lignin polymer [34], and aqueous extracts of fruits [21] as inhibitors to reduce the rate at which several steels and non-ferrous metals corrode. These results show that naturally occurring products demonstrate better protective capability of aluminum, copper and mild steel. Also, studies have reported the application of synthetic polymers on various metals [16], [32], [35].

Various parameters affecting the efficiency of corrosion inhibitors include hydrodynamic flow conditions, pH, temperature and concentration of the inhibitor [36]. Corrosion inhibition may occur positively as a result of hydrodynamic flow, since it enhances the admission of inhibitor unto the metal surface [37 – 39]. Although the efficiency of the inhibitor may decrease due to the absence of protective film formed or removed as a result of localized erosion corrosion [40], [41]. In order to determine the rate at which oxygen depolarize, the effect of variations in water temperature is essential and in essence, the rate at which corrosion loss takes place. This has been considered in field [42] and laboratory studies [43], as a based on fundamental considerations [44]. Various studies such as Mercer and Lumbard [43] have performed a careful study on temperature effects noting that at 70 – 80 °C, corrosion rate occurs early as the water temperature is increased after which it reduces. The latter result is ascribed to notable amount of oxygen soluble in high temperature of water. Early corrosion loss is in agreement with Arrhenius behavior, but this is not identical in various kinds of waters [45]. Influence of temperature on water has been demonstrated to be essential evaluation of corrosion loss in steel as a result of its exposure to immersion conditions of actual seawater and also in fresh water and brackish immersion in steel [46], for different variations of water temperatures natural environmental exposures are about 30 °C [47].

3.0 Inhibition Efficiency
Exposure of a metal’s stability to the environment greatly determines its stability; hence, inhibition performs differently in different environment. This section highlights the efficiency of inhibition in different environments.

3.1 Inhibition efficiency in NaCl
Corrosion of steel has been investigated by various studies, one of the most frequently used method in salty solutions is surfactants, the efficiency of various kinds of surfactant has been reported. Although, corrosion taking place in marine environments can be determined by various
factors, the major role is performed by the chloride media [48]. Therefore, NaCl solutions of about 0.35-0.85 M have been used oftentimes to stimulate laboratory conditions, these are usually more hostile toward the use of steel in contrast to natural seawaters [49]. Mixed inhibitor of CTAB (cetyltrimethylammonium) and (SDS) sodium dodecyl sulfate bromide has been used in 3.5% NaCl solution as a corrosion inhibitor on mild steel [50]. The inhibitor decreases the rate of cathodic and anodic reaction. Increase in the surfactants concentration (to about the concentration of the critical micelle) result to a rise in the inhibition effects. Also, another study used mixed corrosion inhibitor of sodium gluconate (SG) and CTAB in 3.0% NaCl solution on galvanized steel, resulting into a reduction in the cathodic reaction while the rise in the mixture occurs due to the inhibition efficiency [51], [52]. Farahmand et al. [50] investigated the effect of coating with molybdenum and SDS (sodium dodecyl sulfate) inhibitor on mild steel in 3.5% NaCl solution. The best efficiency was noticed at SDS of 0.8 mM and molybdenum of 75 mm thickness. Two rare-earth (RE) carbonates complexes of 3-(4-methylbenzoyl)-propanoate (mbp) (RE (mbp)); RE = La, Y) compounds were examined and compared with lanthanum 4-hydroxycinnamate (La (4-OHcin)) in solutions of 0.01 M NaCl, AS1020 mild steel. Electrochemical analysis reveal that a high performance of the Y (mbp)3 was observed as the corrosion inhibitor, this is a function of the rise in surface film covering the layer with high resistance to corrosion essentially after 24 hours [53]. Nam et al. [54] observed the corrosion inhibition of cerium hydroxycinnamate compounds on mild steel in 0.6 M NaCl solution. It was noted that less corrosion attack occurs on the surface of the mild steel exposed to the inhibitor in contrast to the surface where the inhibitor is not applied. This is as a result of a protective film caused by the action of the cerium hydroxycinnamate compounds. The result indicate that cerium hydroxycinnamate compounds reduces the rate of electrochemical corrosion in 0.6 M NaCl solution, and also minimize protective and magnitude of the CPE double layer, promote the charge and protective resistances. Other studies have also reported the use of various method of protection of mild steel in NaCl solutions [54 – 61].

3.2 Inhibition efficiency in chloride solutions

Various factors influences Cl\(^-\) and SO\(_4^{2-}\) concentration on the environment. One of the most broadly used metallic material in the environment is the mild steel, significant problems arises as a result of the corrosion of these result into water circulating in pipes, storage tanks and pipes supplying water among others., several researchers have study the corrosion behavior [46], [62], [63]. The rate of corrosion of mild steel can be increased by the availability of compound containing SO\(_4^{2-}\) and Cl\(^-\) [64 – 66]. An immerge quantity of chlorine compounds such as Cl\(_2\), Ca(OCl)\(_2\), NaOCl etc. are used in the treatment of waste water and for bleaching of industrial and domestic materials. These compounds are broadly utilized to purify water for swimming pool and drinking purposes, and to check odors and bacteria presence in food industry [67], [68]. Large amounts of chlorine are used in laundry services (washing and bleaching of clothes). Chlorine compounds are classified as poison and it has a negative impact on system circulation of water in pipe lines and other exposed metallic equipment’s in the environment, Cl\(^-\) and OCl\(^-\) are produced from aqueous dissociation of these compounds [69]. Various other literatures have successfully carried out corrosion inhibition of chloride solutions on mild steel [70].
3.3 Inhibition efficiency in HCl

Occurrence of mild steel corrosion inhibition processes specifically in acidic media has essentially been studied based on the use of acid solution in industrial applications. For example, various corrosive conditions occurs from refinery process of crude oil. In most cases, refinery corrosion is induced by an attack on the equipment’s surface by strong acids [71]. Other areas where these is applied include petrochemical processes, oil recovery using oil-well acid, acid descaling, industrial cleaning, acid pickling [72]. Hydrochloric acid is one of the most extensively used acidic agents. Mild steel exposure to corrosive environment results in its vulnerability to various kinds of corrosion techniques; hence, corrosion inhibitors are used to suppress the inevitable dissolution of metals [73]. Corrosion inhibitors are frequently applied in acidic solutions for cleaning surfaces of steel and iron in order to preserve against corrosion damage [74], [75]. Concerning the inhibitor strength of adsorption, definite factors are notably considered which are; the inhibitor structure, the electrolyte composition, the metal surface charge and nature [76], [77]. Different types of organic compounds has been effectively used as corrosion inhibitors [78 – 81]. However, most of these inhibitors are very toxic to the environment as well as to humans, hence this has promoted the use of inhibitors that are naturally synthesized [82]. Organic compounds that are mostly efficient often contain heteroatoms which are; oxygen, sulfur and nitrogen in a conjugated system [83 – 87]. The inhibitors acts on the boundary between the aqueous corrosive solution and the metal, their influence through adsorption on the surface of the metal results in alteration of the electrochemical process techniques [88]. Centers of reaction that ensures the stabilization of this process of adsorption is referred to as polar functional groups [89], this assist in reducing the vulnerability of a metal surface to corrosion [86], [90]. Sequel to this, the service life span of a metal is increased [88].

Various products that occur naturally has several compounds that are naturally biodegradable. Mild steel dissolution in 1 M and 2 M HCl in various plant extracts of Papaya, Datura stramonium, Cassia occidentalis and Poinciana pulcherrima seeds have been studied by Zucchi and Omar [91]. The use of green inhibitors including extracts from various parts of plants have been reportedly carried out these includes; Rosa canina fruit [92], Elaeis guineensis [93], henna extract (Lawsonia inermis) [73], Murraya koenigii leaves [94], Turmeric (Curcuma longa L) [95], Griffonia simplicifolia [96]; Longan seed and peel [97], Lychee fruit waste [98], Amino acids modified konjac glucomannan [99], Plantago ovata Polysaccharide [100], Griffio leaf [101], Musa paradisica peal [21], Xanthium strumarium leaves [102], Hunteria umbellata seed husk [103], Urtica dioica leaves [104], Spermidine [105], Mangifera indica (mango) leaves [106], Sunflower seed hull [107], Pism sativum peel [108], Glycyrrhiza glabra leaves [109], bamboo leaf [110], watermelon waste products [111], Capsicum annuum fruit paste [112], oil palm (Elaeis guineensis) fronds lignin [113], Glycine max, Cuscuta reflexa and Spirogyra extracts [114], Rosmarinus officinalis [115], Lemon Balm extract [116], watermelon rind extract [117], Neolamarckia cadamba alkaloids [118], Justicia gendarussa [119] Punica granatum [77].

Other inhibitors such as aminated hydroxyl ethyl cellulose [120], xanthan gum and synergistic surfactant [121], Irbesartan drug molecules [122], Analgin [123], Ampicillin [124], expired asthalin drug [125], ondansetron hydrochloride drug [126], Tryptamine [127], Quinazoline
Schiff base compounds [128], poly(vinyl alcohol-cysteine) [129], perimidine derivatives [130], 1,3,5-tris(4-aminophenoxy)benzene [131], tetrahydropyridines [132], 4-6-diamo-no-2-pyrimidinethiol [133], 4-(((5-ethyl-1,3,4-thiadiazol-2-yl) imino) methyl) phenol [134], 4-((2,3-dichlorobenzylidene) amino)-3-methyl-1H-1, 2, 4-triazole-5(4H)-thione [135], 2-((thiazole-2-ylmimo)methyl) phenol [4], 4-((thiophene-2-ylmethylen)amino)benzamide [136], 1,3,5-tris(4-aminophenoxy)benzene [131], Ascorbic acid [88], 6-substituted 3-chloropyridazine derivatives [137], benzaldehyde thiosemicarbazone derivatives [138], 2-(substituted phenyl) benzimidazole derivatives [139], cosmetic additive cocamidopropylamine oxide (CAO) [140], alkyl imidazolium ionic liquids comprised of tetrafluoroborate anion [141], 5-(Phenylthio)-3H-pyrrole-4-carbonitriles [142], tetra-n-butyl ammonium methioninate [143] among others have also reported corrosion inhibition for mild steels in HCl solutions. Recently, the efficiency of Calf Thymus Gland DNA inhibitor was used on stainless steel and best performance was obtained at 10°C and 20 mg/L [144].

3.4 Inhibition efficiency in H$_2$SO$_4$

Since mild steel and its alloys have been used extensively in various applications such as oil and gas, petroleum, engineering, automobile and construction industries due to their cost effectiveness and outstanding mechanical properties [72]. These industries uses sulfuric and hydrochloric acid for descaling and cleaning process. But, the mild steel erodes when exposed to hostile acidic environments, hence the use of inhibitors have been proposed to reduce the corrosion rate. A major essential product used is sulphuric acid (H$_2$SO$_4$), principally in surface coating, passivation, storage batteries and fuel cells production. The application of corrosion inhibitors form an economical method of reducing the rate of corrosion, thereby protect surface of metals against corrosion and ultimately safeguard industrial equipment’s in the hostile environment [145].

Several studies have explored the use of eco-friendly inhibitors that are biodegradable and nontoxic such as plant extracts [146], [147]. In order to evade synthetic corrosion inhibitors devastating effect, the use of natural inhibitors such as plant extract is encouraged [148], [149]. Extracts of Murraya koenigii leaves [94], Cryptostegia grandiflora [150], watermelon rind extract [117], Sida cordifolia [151], Cuscuta reflexa [152], Saraca ashoka [153], Lannea coromandelica leaf [154], Aster koraiensis leaf [155], Tagetes erecta (Marigold flower) [156], Armoracia rusticana [157], Myristica fragrans [158], Ficus religiosa [159], Hunteria umbellata seed husk [140], Spermidine [105], bamboo leaf [110], Punica granatum [77], Caffeic acid [160], Ascorbic acid [77], have been investigated to determine their effectiveness on mild steel in sulfuric acid solution.

Other studies carried out with sulphuric acid as the environmental media include; expired asthalin drug [125], urispas drug [145], Irbesartan drug molecules [122], substituted 1,3,4-oxadiazoles [147], diamine derivatives [148], benzodiazepines [161], 4-(2-amino-3-methylphenyl)iminomethyl)benzaldehyde [162], 1,4-di [1'-methylene-3'-methyl imidazolium bromide]- benzene [163], polyacrylamide-grafted copolymer of Okra mucilage [164], Acetyl thiourea chitosan polymer [165], mixed inhibition of Chloride ion and 1,5-Diaminonaphthalene
(1,5DNA) compound [166], imidazolium-based ionic liquids [167]; 4-hydroxy-3-methoxybenzaldehyde and hexadecyltrimethylammoniumbromide [168].

4 Inhibition efficiency on other acidic media (such as Acetic, phosphoric and HNO₃)

Numerous researchers have considered the use of other media in corrosion inhibition. Report on corrosion techniques carried out in pipelines for oil and gas transmission in the presence of acetic acid have been documented [169]. Corrosion of X65 mild steel by CO₂ in acetic acid medium has been studied by Gulbrandsen and Bilkova [170]. The corrosion rate mixed behavior was reported by these authors at high and low temperatures as the acetic acid concentration increases. They observed that at higher concentration of acetic acids the rate of corrosion reduces at 25 °C, this was in contrast to their observations at 80 °C. This observations justifies the consequence of acetic acid inhibition on anodic reaction. It was stated that the union of retarding anodic reaction and increasing the rate of cathodic reaction, occurs as a consequence of reduction by direct acetic acid, causing mixed behavior. Corrosion of X65 mild steel in atmospheric CO₂ and N₂ in acetic acid by controlling the pH was studied by George and Nesic [171]. It was observed that at a low pH of 4, the corrosion rate notably rises in the presence or absence of CO₂, when acetic acid is increased to 100 ppm. While at higher concentration of acetic acid to about 1000 ppm, there was no significant increase in the rate of corrosion. It was also deduced that at 100 ppm acetic acid, with temperature rise from 40 °C to 60 °C, has a consequential effect on rise in the rate of corrosion. It was confirmed that in the presence of acetic acid, the rate at which corrosion increases is as a result of direct reduction of acetic acid during the process of corrosion. This was corroborated by Okafor et al. [172], which reported that higher rate of corrosion was observed as the concentration of acetic acid increases. Singh and Mukherjee, [173] also study the use of acetic acid as a corrosion medium. More studies are required in this area using mild steel.

Phosphoric acid produced from hemihydrate wet process result to serious problems in the corrosion of containers. An appropriate method required for protection against corrosion is the use of inhibitors that can withstand extreme metal dissolution [174]. Various organic compounds such as nitrogen, sulphur and oxygen has been effectively used as inhibitors [175], [147], [176 – 178]. Inhibitors such as Polyethylenimine and polyvinylpyrrolidone [179], 2-Mercaptobenzimidazole [175] and food additives [180] has been used for corrosion prevention of mild steel in phosphoric acid media. Although, limited studies appears to have been carried out on the inhibition of mild steel in phosphoric acid media. But among the few study carried out for instance by Wang, [175] it was reported that 2-Mercaptobenzimidazole is a very effective inhibitor when applied to mild steel immersed in phosphoric solutions over a wide range of concentration. It reduces both the cathodic and anodic processes involved corrosion reactions. Gunasekaran and Chauhan [174] report that as the plant extract (Zenthoxylum alatum) concentration increases in different concentrations of phosphoric acid medium (80, 50 and 20%) the mild steel inhibition efficiency also increases. It was stated that there was a higher performance of the inhibitor in phosphoric acid concentration of 88% as compared to that of 20 and 50%. Moreover, apricot juice was used on mild steel immersed in phosphoric acids, the highest inhibition efficiency was noted at 75% at 30 °C [181].
Nitric acid, $\text{HNO}_3$, functions as an oxidizing and acid agent. Palaniappan et al. [182] reported the use of 1 M $\text{HNO}_3$ as an aqueous medium to determine the inhibition effect of mild steel using phosphonium salts. It was observed that the derivatives were great inhibitors, and the efficiency of inhibition increases in a sequence of ($\text{BnPh}_3\text{PBr} > \text{BuPh}_3\text{PBr} > \text{EtPh}_3\text{PBr} > \text{MePh}_3\text{PBr}$) derivatives of phosphonium bromide. Other studies that have carried out corrosion prevention in nitric media but using other materials such as stainless steel include Nagano et al. [183], Tcharkhchtchi-Gillard et al. [184] and Kasparova et al. [185].

5. Conclusion

From previous published literatures, it can be concluded that most of these studies focus on acidic environments namely; $\text{HCl}$ and $\text{H}_2\text{SO}_4$, it is worthy of note that sea water and saline or simulated sea water has also been considered. But less studies has been carried out on acetic, phosphoric and nitric acids which should be considered. Although, various plant extracts has been used as inhibitors especially for mild steel in sea water, $\text{HCl}$ and $\text{H}_2\text{SO}_4$ solutions, these should also be carried out on acetic, phosphoric and nitric acids. Moreover, the use of animal extracts such as DNA, genetically stimulated mucus, and bone tissues should also be carried out. In addition, the use of chitosan as a corrosion inhibitor is limited, therefore more study should consider its use and its primary component (chitin), as an inhibitor. Binary inhibitors should also be dwelled upon in order to get an optimum range of inhibition. Finally, it is necessary to note that the number of years a particular inhibitor is active on a surface should be considered.

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