Development of Sustainable Inhibitors for Corrosion Control

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Abstract: Metal degradation due to corrosion is a major challenge in most industries, and its control and prevention has to maintain a balance between efficiency and cost-effectiveness. The rising concern over environmental damage has greatly influenced this domain, as corrosion prevention should comply with the waste regulations of different regions. In this respect, a fundamental question is which modern synthetic materials are more viable from the point of view of their effectiveness. Therefore, this paper is aims to provide an advanced and holistic review of corrosion prevention and control methods. Corrosion prevention techniques have become extensive; however, the literature indicates that polymer coatings, nano-composite coatings, and encapsulation techniques consistently provide the most efficient and feasible outcomes. Therefore, this review article examined the phenomenon of corrosion inhibition mainly from the perspective of these three techniques. Moreover, this research utilized secondary qualitative methods to obtain data and information on comparative techniques. It is found that due to the rapid development of novel materials, corrosion inhibition techniques need to be developed on scales that are more general, so that they could be applied to varying environments. The self-healing coatings are generally based on epoxy-resins incorporated with synthetic compounds such as inhibitor ions, amino-acids, or carboxylic acids. These coatings have become more widespread, especially due to bans on several traditional prevention materials such as compounds of chromium (VI). However, self-healing coatings are comparatively more costly than other techniques because of their method of synthesis and long-term durability. Therefore, although self-healing nanomaterial-based coatings are viable options for limited usage, their utilization in large and complex facilities is limited due to the costs involved. Amino acids and other biological macro-molecules provide another option to attain environmental sustainability and long durability, especially due to their origins being most of naturally occurring compounds such as lignin, cellulose, and proteins.

Keywords: corrosion prevention; synthesized inhibitors; amines; encapsulated inhibitors; naturally occurring materials; environment

1. Introduction

Corrosion is the cause of significant damage to society as it deteriorates structural innovations and engineering materials. In the United States alone, it is estimated that costs incurred due to corrosion exceed USD 500 billion each year [1]. Meanwhile, a study conducted by NACE International projects that the global cost of corrosion is estimated at USD 2.5 trillion, i.e., 3.4% of global GDP in 2013 [2]. This study aims to present a review of recent developments in the synthesis of corrosion prevention materials and strategies. The constant corrosive deterioration of material degrades various material properties [3]. Corrosion manifests itself as a failure of systems and leads to an unsightly appearance. It occurs in almost all materials in their operating environments [4]. Moreover, the costs of contending with corrosion are also very high, with an expenditure of USD 276 billion
annually [5]. In this respect, this review is intended to examine the effectiveness of corrosion prevention materials under different environmental conditions and in applicable metals.

Deterioration due to corrosion is known as an unavoidable fact of nature [6], which has led to a lack of interest in the most essential investigation of different aspects of corrosion and basic preventive measures. Despite the deficiencies in the corrosion protection techniques, such techniques have been pursued more as remedial maintenance rather than as an aspect of material and environmental design, which would result in the prevention of corrosion and work against it [7]. Therefore, this paper analyses the standard prevention techniques and provides an in-depth view of the contemporary studies on corrosion prevention materials. However, since the domain of corrosion prevention is extremely broad, this article mainly covers advancements in environmentally sustainable coating and encapsulation methods.

2. Frequently Utilized Corrosion Control Methods

The term corrosion control is used in construction and manufacturing industries when the materials in use are in constant exposure to chemicals or seawater. Although various types of chemical inhibitors are applied to impede the rate of corrosion, their applicability is often limited due to their own degradation rates, lack of flexibility against different types of corroding elements, and operational and maintenance costs [8]. The foremost criteria for using any corrosion control technique is the balance between durability and cost. A patent has been filed related to a technique of introducing corrosion inhibitors in small amounts in the water stream of industrial facilities in primary and secondary dosages [9]. Moreover, in order to reduce the cost of replacing piping systems of HVAC, industrial water supply, municipal water supply with traces of chloride and other salts present, petroleum refineries, etc., [10] invented a mechanism for spraying barrier coatings inside pipes of diameters ranging from 3/8” up to approximately 6”, which is the standard range of ASME/ANSI pipes and fittings. However, mechanical techniques are limited in their effectiveness since their prevention efficiency is dependent upon efficiency of the coating materials.

In order to achieve a feasible balance between durability and cost, the following techniques are used separately or in combination with one another:

(a) Surface coatings
(b) Chemical inhibitors
(c) Modified material of construction
(d) Alteration in equipment design

Figure 1 shows the classification of surface coatings. In large industrial complexes such as petroleum refineries, the coating of all major and auxiliary equipment is often a tedious and costly process; therefore, the operators instead use construction materials (metals and polymers) which are inherently corrosion-resistant. Certain mixtures of steel with metals such as Mn, Cu, Si, Ni, Cr, and P result in weathering steels due to their ferrite-pearlitic microstructures, which are resistant to usual atmospheric exposure [11].

![Figure 1. Classification of surface coatings.](image-url)
Metallic coating is carried out through methods such as electroplating, whereas non-metallic coatings comprise the coating of polymers, organic solvents, organic oils, inorganic pigments, lacquers, etc. [12].

Corrosion inhibitors are a special class of synthetic materials that are usually dissolved in a fluid medium whose exposure causes corrosion, to hinder the electrochemical corrosion at surface metals. Figure 2 shows the classification of corrosion inhibitors. Inhibitors function through absorption on the metal surface to form protective layers, combining with corrosion products to form a film that impedes further corrosion, or directly forming a visible coating on the surface. However, most of the synthetic organic inhibitors tend to pollute the ecosystem and create a need for developing and exploring highly effective and eco-friendly inhibitors based on natural extracts, biomacromolecules, oral drugs, food spices, etc. [13,14]. Corrosion inhibitors are classified as follows:

![Figure 2. Classification of corrosion inhibitors, Adapted from [15].](image)

Among the inorganic class, cathodic inhibitors are compounds that hinder the cathodic reaction in corrosion cells such as ZnSO₄, Ca (HCO₃)₂, MnSO₄, etc., as they form hydroxides through the transfer of OH⁻ ions. On the other hand, compounds such as Na₂SO₃ act as oxygen scavengers and react with oxygen present in the surroundings to form neutral products. This technique is increasingly being utilized in petroleum refineries’ wastewater infrastructure to protect mild steel and catalyst membranes [16]. Anodic inhibitors such as Na₂SiO₃ and Na₃PO₄ are compounds that inhibit the anodic side of cell reaction and form Fe³⁺-charged films or iron silicate and iron carbonate which isolate the anodic sites of corrosion cells, thus stopping the transfer of electrons [17].

3. Corrosion of Modern Materials

The extent of the damage from corrosion is a function of the time since the start of the corrosion process, the type of materials, and the concentration of the corroding substance. It also depends upon the preventive methods adopted on the material such as coatings, etc. [18]. In this respect, materials development plays a major role in controlling the extent of corrosion. Therefore, modern material synthesis is designed with consideration for its effectiveness against natural corrosion [19]. Koch identified that corrosion can have a costly and detrimental impact on the critical industry sectors, which has led researchers and scientists to study the costs of corrosion for many decades [20]. Furthermore, an in-depth and detailed comparison of corrosion costs in different industries and sectors provides the opportunity to identify the common problems and issues which might be appropriate for corrosion control. The identification of corrosion prevention and control strategies also allows the mitigation of increased cost of countering corrosion and developing awareness regarding the magnitude of corrosion issues [21]. In this respect, synthetic materials such as alloys and superalloys are manipulated on the basis of their composition, structural properties, and surface characteristics. For this purpose, corrosion-resistant design is adopted either on the basis of data-driven approaches supported by computer simulations and/or the utilization of first-principles models of standard theory, through which further improvement is gained in an interactive manner [1]. However, it is also shown that the utilization of simulation-gained data
is not always conducive to be applicable in real life [22]. This is attributable to the systemic limitations of such simulations, since the viability of the data obtained from simulations is dependent upon the viability of the initial data provided by the investigator [23,24]. Moreover, it is also shown that the availability of the environment is a key issue in this regard. This is because the material to be tested should exhibit neutral/passive behavior in its local chemical environment, which cannot be completely ascertained through simulations [25]. Furthermore, this difficulty could be attributable to the thermodynamics and kinetics of the corrosion process, which is a function of fluid flow conditions—primary environmental variables as well as metallic surface properties at a particular point in time. Therefore, materials development which address such issues is crucial, and thus corrosion-resistant materials have become the focus of research.

However, rapid development in materials science has led to complex materials which could not be protected through normal techniques. In fact, corrosion prevention and control depends on the protection of specific materials, environmental concerns, humidity, exposure to industrial and saltwater environments, and the type of product being processed or transported [26]. A study discussed that the prevention strategies of corrosion control are often based on post-corrosion processes, which raises the costs of combating the phenomenon [27]. Therefore, a holistic analysis of novel corrosion prevention strategies that focuses on synthetic chemicals is essential.

4. Corrosion Prevention through Coatings and Encapsulation

In order to achieve efficacious corrosion prevention, it is theorized that techniques which are “smart”, i.e., automated for corrosion prevention according to the type of variables involved, could achieve better results than traditional methods of material development [28]. Moreover, the option of tackling corrosion through resistant-material synthesis is limited because of the costs involved and the pace of the development of applicable materials. It is shown that developing materials that are intrinsically corrosion resistant such as superalloys usually incurs higher capital costs compared to secondary methods, such as synthetic coatings [29]. Figure 3 shows the example of tube Stub diaphragm valve, in which three cases; 1. Untreated 304 Stainless steel, 2. Dursan-coated 304 stainless steel, and 3. Superalloy C276 were tested [30]. The results show that though superalloy achieves the best performance, coating developed by Dursan is more economically viable.

![Figure 3. Costs of Materials for a tube stub diaphragm valve [30].](image)

Therefore, investigation is diverted towards secondary approaches to the issue, which focus on coatings and other external protection techniques. This would allow the current materials to continue manufacturing, alongside a parallel field of coating development. In this respect, coatings and encapsulation techniques have become a major area of investigation in the last two decades, focusing on pH-sensitive synthetic coatings and capsules to be applied on standard materials to be protected. However, this option is also limited because pH sensitivity introduces unique issues such as the identification of allowable pH range,
which is complex in cases of continuously changing environment [31]. Moreover, modern coatings face the limitation of environmental sustainability because reliance on environmentally hazardous substances would lead to disastrous repercussions in future, especially in the scenarios where the materials are in direct contact with the natural environment, such as the marine environment [32].

5. Contemporary Materials Development for Sustainable Corrosion Inhibition

With the exponential research and development in polymer science, nanomaterials, alloy technology, and biomaterials, several techniques and materials have been developed to prevent against various kinds of corrosions. Inhibitors have been proven as prominent methods for corrosion protection in various environments [33,34]. Conducting polymers are being intensely investigated as a sustainable and cost-effective method to prevent corrosion. The performance of polyaniline–epoxy coatings on mild steel has been studied [35]. Analysis through SEM confirms the incorporation of polyaniline and silicone particles into the epoxy polymer to form homogeneously micro-structured IPN, as shown in Figure 4.

![Figure 4](image-url)

Figure 4. (a) Micrograph of resin (b) Micrograph of resin combined with hardener [35].

However, studies indicate that over-reliance on polymer-based products is not sustainable, especially from the perspective of application in environments that are in direct contact with extreme conditions such as high pressure and the marine environment [36]. Therefore, in the sustainable organic domain, a wide range of coatings of polyaniline/coconut oil polyesteramide composites are available. Although polyesters are highly prone to degradation, their complex combinations with polyamides lead to alkyl chains of varying lengths of polyesteramides (PEAs). Such PEAs are thermoplastic in nature and can be applied to various surface coatings. Coatings of coconut oil-based conducting blend of polyaniline (PANI) and oil of coconut-based mixtures of conducting polymers with esteramide urethane (CPEAU) have been shown by [37] to exhibit lasting durability on mild steels, as shown in Table 1.

| Sample     | H₂O (15 Days) Before Aging | After Aging | 5% NaOH (15 Days) Before Aging | After Aging | 5% HCl (15 Days) Before Aging | After Aging | 5% NaCl (15 Days) Before Aging | After Aging |
|------------|---------------------------|------------|--------------------------------|------------|-------------------------------|------------|-------------------------------|------------|
| CPEAU      | a                         | -          | f                              | -          | e                            | -          | f                            | -          |
| 2-PANI/CPEAU | a                         | b          | c                              | e          | b                            | c          | d                            | e          |
| 4-PANI/CPEAU | a                         | a          | c                              | e          | a                            | c          | c                            | d          |
| 8-PANI/CPEAU | a                         | a          | b                              | e          | a                            | b          | c                            | c          |

a = the film remains intact and unaffected (slight loss in gloss observed after 10 days). b = the film remains unaffected for 8 days (shows loss in gloss after 8 days). c = the film remains intact for 5 days (shows slight dissolution and discoloration after 5 days). d = the film remains unaffected for 3 days (shows discoloration after 3 days and dissolution after 8 days). e = the film remains intact and unaffected for 2 days (shows dissolution and loss in gloss after 2 days) and f = film completely removed within 2 h.
Furthermore, the corrosion rate performance of the aforementioned combination of coatings with respect to loading of mixture of alkyd are also presented [37] (Figure 5).

Figure 5. Corrosion rate of PANI/alkyd and PNA/alkyd in (a) HCl, (b) NaOH and (c) NaCl [37].

The minimum observed corrosion rates in 5% HCl, 5% NaOH, and 3.5% NaCl were 0.35 mpy, 0.25 mpy, and 0.023 mpy respectively. The PNA/alkyd combination exhibited the lowest corrosion rate. The lowest corrosion rate was observed for 2.5-PNA/alkyd coatings as 0.35 mpy in 5% HCl, 0.13 mpy in 3.5% NaCl, and 0.13 mpy in 5% NaOH. The decreased rate of corrosion with increments in the CP loading can be attributed to effective cross-linking of CP particles with alkyd, thus covering micropores of surface materials. However, while the PANI coatings with the blend of organic oils exhibit positive performance, coatings which could be observed through an indicator or from the naked eye are more desirable, since the detection of corrosion is a sensitive domain in some industries, such as water treatment and pharmaceuticals. Therefore, corrosion indicating agents are being studied to be incorporated directly into the coating formula which will activate in the early occurrence of corrosion [38].

Moreover, another strategy of durable corrosion prevention coating are anti-fouling reagents. Anti-fouling coatings are traditionally designed through organic matrices abundant in nature and containing biocides to prevent the growth of microbes on surfaces such as pipes and ship hulls. Antifouling agents such as tributylin oxide are toxic for other organisms when released uncontrolled, and thus present an environmental hazard. Hence the techniques to encapsulate the biocides in particles of protective coatings. Mesoporous
silica nanoparticles sulfide ion-controlled release mechanism have been shown by [39] to envelop corrosion inhibitors such as hydroxyquinoline and benzalkonium chloride in capsules. A study highlighted the development of active materials encompassed in surface protective coatings (nano-containers) which not only provide controlled release of corrosion inhibitors, but also provide self-healing ability to the paint mixture when added in 5–10 wt% concentrations [40].

In recent advancement to control the release of copper under the action of seawater as an antifouling agent, capsule-shaped splats containing polyimide-copper layers have been prepared [41]. The polyimide structure depicted a hollow structure with a tiny hole of 1–5 μm over its surface, and an inner pore of 10–15 μm. The release of copper after 1000 h exposure to the testing synthetic seawater, containing up to 30 wt% Cu have been found to show remarkable performance. On the other hand, the performance of organic biocides encapsulated in polylactic acid nanoparticles is has also been shown, especially in long-term applications in environments that limit the direct use of metal nanoparticles [42]. Figure 6 Shows the bacterial removal ratios with respect to surface energy analysis. It also shows adherence on bacteria Bacillus sp. over the layer of polyimide-Cu coatings.

![Figure 6](image_url)

Figure 6. Analysis of the adhered bacteria on the coatings, (a): bacterial removal ratio versus surface energy of the polyimide-Cu coatings; Depiction by SEM images of the morphology of the adhered Bacillus sp. bacteria on the polyimide−10 wt% Cu coating (b), the polyimide−20 wt% Cu coating (c), and the polyimide−30 wt% Cu coating (d) [41].

The combination of micro-hollow polyimide capsule and Cu nano-particles results in the reduction of surface energy, which in turn causes less charge. It is observed that for the coatings containing 20 wt% Cu and 30 wt% Cu, the extent of bacteria in testing petri dishes was reported to be almost indicating the elimination of bacteria due to action of copper ions.
which acted as an obstacle in oxygen circulation and food intake pathways [41,43]. Twelve-hour exposure resulted in almost 100% extermination of bacteria and other microbes.

In a progression to the above mentioned technique, the utilization of bio-polymeric microsphere to envelop benzotriazole (BTA) has been demonstrated [44]. Carboxymethyl-cellulose (CMC-Na), augmented with sodium mixture was spray-dried to encapsulate BTA. The observation of release mechanism and timing of BTA revealed that the material under encapsulation of CMC-Na could be stimulated by pH, thermal, and mechanical action. As shown in Figure 7, the release of BTA stabilized after the initial rise in release rate after contact with water. This may be attributable to hydrophilicity.

Figure 7. Release profile of CMC-Na encapsulated BTA [44].

The performance of the CMC-encapsulated BTA microsphere on steel is shown in Figure 8. EIS studies of the material indicate that the BTA acts as an inhibitor under both conditions (with or without encapsulation), and encapsulation certainly increases the effective action time of epoxy resins.

Figure 8. Photographs of carbon steel after 48 h of dip in NaCl sol. (a) Control material (b) CMC laden carbon steel (c) BTA free sample (d) CMC encapsulated BTA-MS [44].
With regard to BTA encapsulation, the envelopment of graphene oxide (GO) in mesoporous silica, and benzotriazole-loaded nanoreservoir is also tested as shown in Figure 9 [45]. The resultant nanoreservoirs were investigated particularly in the pH factor inducing the release of BTA from nanostructures. The release rate of benzotriazole increased with an increase in the aqueous medium pH. The initial stage experienced an increment in the release rate, somewhat similar to the study of [44]. After that, the highest concentration of release was recorded to be 6 mg/(L·g nanocontainer) at around 300 min, close to 95%. The results showed that these techniques can effectively protect the corrosion inhibitor and improve efficiency. However, the cost comparisons differ due to the availability of raw materials for the synthesis.

![Figure 9](image_url)

**Figure 9.** Release rate and concentration of BTA, and the release of kinetic models for BTA from mSiO$_2$/GO nanoreservoir at different pH values [45].

Table 2 Provides a holistic view on recent developments in encapsulated corrosion inhibitors for controlled release rates, enhanced self-healing, and environmental sustainability.

| Material                  | Encapsulation Material                                                                 | Corrosion Inhibitor | Performance                                                                 | Reference |
|---------------------------|----------------------------------------------------------------------------------------|---------------------|-----------------------------------------------------------------------------|-----------|
| Carbon Steel              | Biopolymeric microspheres, carboxymethylcellulose (CMC-Na)                              | Benzotriazole       | BTA enhanced the coating performance on surface metal                       | [44]      |
| Q235 steel                | Halloysite nanotubes with CaMoO$_4$                                                    | Na$_2$MoO$_4$       | Highest performance could be attained by 10 wt% Ca$^{2+}$ treated          | [46]      |
| N/A; General study        | Mesoporous silica; benzotriazole-loaded nanoreservoir                                  | Graphene oxide      | Increased IE with self-healing properties                                    | [45]      |
| 2024–T3 aluminum alloy    | poly(lactic acid) (PLA) nanoparticles combined in polyurethane/polyisiloxane hybrid coating | 2-mercaptopbenzothiazole | 200 times improvement in corrosion induction time                           | [47]      |
| Coatings of oil wells     | Polymer particles (Styrene)                                                             | Various inhibitors  | Improvement in release timing                                               | [48]      |
| Steel                     | synthesized titania nanotubes                                                          | Epoxy monomer and dodecylamine | Improvement in release rates and self-healing due to polymer               | [49]      |
| AZ31 magnesium alloy      | Acid-modified halloysite nanotubes                                                     | Praseodymium ions   | Substantially lowered corrosion rates                                       | [50]      |
Table 2. Cont.

| Material               | Encapsulation Material                     | Corrosion Inhibitor         | Performance                                                                 | Reference |
|------------------------|--------------------------------------------|------------------------------|------------------------------------------------------------------------------|-----------|
| N/A; General study     | Lignin microspheres                        | Benzotriazole                | pH responsive behavior with improved self-healing                            | [51]      |
| Low alloy steel        | Porous polystyrene                         | Benzotriazole                | Long term improvement of protection                                           | [52]      |
| Steel                  | Feldspar nano-container                    | Zinc cations                | Improvement of 83% in charge transfer resistance and improved self-healing    | [53]      |
| Mild steel             | Nettle-loaded nanocontainers with Zinc Acetate | Silane                       | Enhancement of synergetic inhibition effects                                 | [54]      |
| Mild steel             | Zinc Molybdate                             | Myristic acid, Polyaniline layer, benzotriazole layer and polycrylic acid | Successful use in multifunctional coatings                                  | [55]      |

With the rise of awareness about environment and sustainability, the science of corrosion prevention has also been impacted with modern developments of biodegradable, sustainable, and benign inhibitors and protective coatings. As a widely available, biodegradable and low-cost material, Chitosan has been shown to prepare an epoxy/chitosan slurry of application in cement oil wells by [56]. The results highlight the properties, including the protective features of the material and its potential as an environment-friendly strategy for oil wells.

The applicability of CTS doped with Ce$^{3+}$ metal cation for the prevention of corrosion in aluminum alloys has been shown by [57]. However, the CTS is limited in its application because of the ion-exchange mechanisms, which impede its function in surfaces with less luster compared to aluminum. In this respect, the encapsulation of chitosan in other preventive materials could enhance their applicability, without obstructing prevention efficiency. Meanwhile, a study of a chitosan-based nanocapsule of silica containing benzotriazole is presented in [58]. The highest efficiency of around 90% at pH 7.0 was reported by the capsule prepared through sol-emulsion-gel method. Whereas at pH 9.0, 65% efficiency was shown by capsules synthesized with the help of layer-by-layer deposition, and it exhibited the best efficiency of 90% at pH 3.0. Therefore, in combination, the particles delivered benzotriazole in the range of pH from 3 to 9.

Amino acids such as methionine, cysteine, and alanine have been investigated to indicate better corrosion prevention efficiency. The complex molecules have also been shown to effectively protect Cu and Ni surfaces against corrosion. Also demonstrated to be effective is the preparation of three artificially synthesized amino acids-derived inhibitors, i.e., 2-(3-(carboxymethyl)-1H-imidazol-3-ium-1-yl)acetate (AIZ-1), 2-(3-(1-carboxyethyl)-1H-imidazol-3-ium-1-yl) propanoate (AIZ-2), and 2-(3-(1-carboxy-2-phenylethyl)-1H-imidazol-3-ium-1-yl)-3-phenylpropanoate (AIZ-3) through the condensation process carried out on glyoxal, formaldehyde, and amino acids [59]. Figure 10 reveals that AIZ-3 exhibits maximum inhibition efficiency (IE) of 96.08% at a concentration as low as 0.55 mM (200 ppm). The results of a potentio-dynamic study reveal that AIZ-1 is a cathodic inhibitor while AIZ-2 and AIZ-3 act as mixed type inhibitors.

Figure 11 shows that rising temperature leads to decrement in IE especially from 308 K to 338 K. The authors, and another study [60], attribute this decrement to the detachment of AIZ molecules from the metal surface due to a rise in temperatures.

From the analysis of Figure 7, the activation energy data obtained from an Arrhenius plot, it is deduced that in the studied molecules in 1 M HCl, inhibition efficiency increases with increasing concentration, in the presence of AIZs. At 0.55 mM concentration, the maximum efficiencies shown by three studied inhibitors were 90%, 93.4%, and 96% for AIZ-1, AIZ-2, and AIZ-3 respectively.
The performance analysis of biogenic amino acid methionine-based corrosion inhibitors of mild steel in acidic media is presented in another study [61]. The researchers used N, N-Diallyl methionine ethyl ester hydrochloride that had gone through alternating copolymerization with SO₂ via the Butler cyclopolymerization protocol in dimethyl sulfoxide (DMSO) to give water-soluble cycloterpolymer 6 with a 1:1 molar ratio of sulfide and sulfoxide groups. The resulting complexes were found to be mixed-type inhibitors, and it is shown that the maximum corrosion inhibition efficiency of copolymer compounds 6–8 was 92%, 97%, and 95%, respectively at a polymer concentration of 175 µM. The performance of other recently developed amino-acid based corrosion inhibitors is provided in Table 3.

Figure 10. Effect of temperature on inhibition efficiency [59].

Figure 11. Arrhenius plots for the corrosion rate of mild steel versus the temperature in 1 M HCl [59].
Table 3. Recent developments in amino acid-based corrosion inhibitors.

| Material          | Inhibitor                                      | Technique                                      | Medium                          | Results Obtained                                                                 | References |
|-------------------|------------------------------------------------|-----------------------------------------------|---------------------------------|---------------------------------------------------------------------------------|------------|
| Carbon steel      | Leucine, Alanine, glutamic acid, Methionine    | Optical microscopic method                     | Hydrocyanic acid                | Good inhibition efficiency but glutamic acid cannot be absorbed on surface       | [34]       |
| Carbon steel      | L-glutamic acid-Zn²⁺                           | Weight loss and electrochemical               | Well-water of varying pH        | IE = 90% at pH = 6.7, and IE = 33% at pH = 3.1                                | [62]       |
| Iron              | Serine, Glutamic acid, Ornithine Lysine Aspartic acid, Alanine Valine Asparagine, Glutamine, Threonine, Methionine, Cysteine, Cystine Glycine Leucine Arginine, Asparagine, Glutamine, Threonine | Chemical measurements                      | HCl, 1 M                        | Highest efficiencies shown by Methionine, cysteine and cystine                   | [63]       |
| Carbon Steel      | Glutamic acid-Zn²⁺                             | AFM analysis, electrochemical methods         | Sea water                       | IE = 87%                                                                        | [64]       |
| Copper            | Aspartic and glutamic acid                     | Molecular dynamics simulations                | Cu surface                      | Glutamic acid shows better performance than aspartic acid                       | [65]       |
| Copper surface    | Glutamine, Leucine Methionine Threonine, Acid aspartic Acid Glutamic Alanine Asparagine | Electrochemical methods and quantum chemical computations | HNO₃; 1 M                       | Highest IE shown by Methionine (80.38%)                                        | [66]       |
| Copper            | Cysteine glutamic acid, glycine and their derivative glutathione | Density functional theory                    | N/A                             | Glutathione exhibited highest IE of above 90% in all simulations                | [67]       |
| Tin               | Threonine, Asparagine and Glutamine            | Electrochemical impedance spectroscopy and potentiodynamic polarization | NaCl Solution, 2 wt.%           | Highest efficiency was shown by Asparagine and Glutamine at pH 2 and 5 respectively | [68]       |
| Stainless Steel AISI309S | L-methionine                                      | Tafel polarization, electrochemical noise methods, and electrochemical impedance spectroscopy | H₂SO₄; 1 M                       | 97% and 95%                                                                    | [69]       |
| Nickel            | Cysteine                                       | Polarization and electrochemical impedance spectroscopy | H₂SO₄; 0.5 M                   | Poor inhibitive efficiency                                                      | [70]       |
| Mg alloy          | Montmorillonite nanoparticles with amino acids | Electrochemical impedance spectroscopy        | Varying proportions of amino acids with MMT | Highest efficiency shown by 0.5 wt.% methionine                                | [71]       |

6. Comparative Analysis of Corrosion Prevention Methods

Corrosion prevention methods have drastically improved with the development in materials and chemical sciences [72]. With the rise in awareness of the requirements of environmental protection, corrosion prevention and control methods not only compete in the domains of cost and durable performance, but also in their impact on the environment [73]. Due to this, research has almost entirely shifted towards the utilization of naturally occurring and cheap materials for protective coating and the controlled release of inhibitor ions. In order to achieve a feasible balance between long-term durability and cost effectiveness, novel self-healing coatings are being developed.

The self-healing coatings are generally based on epoxy-resins incorporated with synthetic compounds such as inhibitor ions, amino acids, carboxylic acids, etc. These coatings have become more widespread especially due to bans on several traditional preventive materials such as compounds of chromium (VI) [74]. However, self-healing coatings are comparatively more costly than other techniques because of their method of synthesis and long-term durability. Therefore, although self-healing nanomaterial-based coatings are viable options for limited usage, their utilization in large and complex facilities is limited due to the relatively high costs [75].

Amino acids and other biological macro-molecules provide another option to attain environmental sustainability and long durability, especially due to their basis in naturally occurring compounds such as lignin, cellulose, proteins, etc. [34]. Amino acids have been proven to be environment-friendly options and are used for various industrial cleaning
purposes [76]. However, their full-scale implementation is halted by their corrosive nature at higher temperatures. In order to prevent this outcome and further enhance the control over release rates, techniques of encapsulation are being developed. The encapsulation materials range from common hydrogels and nanoparticles to polymeric and organic microspheres [77,78]. Commonly utilized inhibitors in such encapsulations are mercaptobenzothiazoles, mercaptobenzoxazoles, and benzotriazoles [79,80]; however, the complexity in their synthesis, the lack of a general description of their functioning, and higher costs limit their use compared to traditional options such as paints and varnishes.

7. Conclusions

This paper reviews recent progress made in the development of polymer-based, nanocomposite-based, amino acid-based materials, and encapsulation techniques, which are not only environment-friendly but also exhibit long-term applicability. In this regard, amines derived from glutamic acid, aspartic acid, and complex amines such as methionine, aniline, and glutamine are a focus of intense research. However, a prominent limitation on the wide usage of amines is their synthesis cost and instability at higher temperatures, which often makes them corrosive for industrial-scale application. The paper also discussed alternate strategies to improve the durability of inhibitors by encapsulating them in synthetic macromolecules. Lastly, in this regard, the recent research in the development and experimental performance of polymer macromolecules, nano-spheres and nanotubes, and derivatives of graphene is analyzed. In terms of overall performance, nanotubes-based encapsulations provide the greatest range of applicability.

Henceforth, further research is needed on their viability. This review also revealed that the feasibility of encapsulation techniques is dependent upon the suitability of encapsulating materials, which is a function of the size of the capsule and their ion-exchange mechanism with the surface. Furthermore, the lattice structure of the metal surface also plays the part of providing sufficient space for the capsule to reside, which determines the lifetime of encapsulated materials on the metal surface. In conclusion, although the current pace of progress is yielding a wide range of corrosion inhibitors, their general applicability in a variety of situations is yet to be analyzed.

8. Recommendations and Future Implications

The analysis of current progress in the domain of sustainable, cost-effective corrosion inhibitors reveals a rapid pace of material development which is often not matched with equally rapid industrial-scale implementation. The extremely corrosive environment in process industries often disrupts the performance of inhibitors [81]. This aspect hinders more wide-ranging applicability of corrosion inhibitors. Moreover, the abundant use of high concentration acids such as HCl and H$_2$SO$_4$ in petroleum and process industries limits the usage of mild polymeric inhibitors [82,83]. Furthermore, complex inhibitors often pose the challenge of their after-life disposal, which frequently affects marine life [84]. Easy applicability of corrosion inhibitors mandates their easy availability which, in turn, lowers their costs. This introduces the complication of identifying specific inhibitors for specific applications, which is uneconomical for the majority of industries [15,85]. Moreover, alloys with unique metals such as lanthanides developed for aerospace engineering present another domain of corrosion inhibitor materials [86,87]. In this respect, corrosion inhibitors are to be synthesized which could resist high vacuum environments, and also provide protection from intense solar radiation. Improvement in such kinds of inhibitors could also be beneficial for on-land usage, since many regions experience intense heat and solar flux on an annual basis, which is problematic for technologies like solar cells, solar panels, and modern windmills.

The literature indicates that inhibition strategies are mainly a function of industrial applicability, which is dependent upon industrial needs. Therefore, development in corrosion prevention has to be in line with materials development, especially in the domains of steel and aluminum alloys. Amine-based inhibitors have the potential to occupy this
domain because of their range of functions and applicability [8], however their instability at high temperatures is a research direction that should be further developed. Further studies regarding amine salts is a possible area of future development [88]. Research in this domain could encompass the actions of imidazolines and other sweet corrosion inhibitors, as described by [89]. Furthermore, the synthesis of inhibitors that could perform in both acidic and alkaline environments without major disruptions in operations is another avenue for future research on environment-friendly strategies. From this current study, future researchers could develop a comparative analysis between amine-based, encapsulation-based, and nanotube/GO-derived corrosion inhibitors which would provide the groundwork for further development in each of these fields.

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