



REVIEW ARTICLE

A comprehensive review on the nature and synthetic organic compounds as corrosion inhibitors

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Abstract

Although corrosion is an inevitable part of daily life, it is always kept under control due to its technical, financial, and aesthetic significance. Erosion is a gradual phenomenon stimulated by anxiety about energy. Defense against corrosive environments on metals is inhibition. One of the most common and financially viable methods of preventing corrosion in metallic materials is the use of corrosion inhibitors (CIs). One of the five ways to prevent material corrosion, along with material selection, design, cathodic protection, and coating, is to use organic CIs. Particles with an unoccupied orbit on a metal substrate depend on adsorption values on the steel surface through the interactions of heteroatoms (N, O₂, P, S), heterocyclic and aromatic rings, and conjugated double bonds. Through these interactions, molecules are attracted to the metal surface, where they bind and form an inhibitory barrier. This reduces the metal's corrosion rates as well as improves inhibition effectiveness. This review included a presentation of the CI compound's history before moving on to a discussion of how inhibition efficiency is affected by structure, substitution, heteroatoms, and molecular chain length. Weight loss (WL), electrochemical impedance spectroscopy (EIS), and dynamic active polarization techniques are used in a comparative investigation of the inhibitory performance of corrosion-inhibited compounds. Adsorption isothermal concepts and blocking processes. This paper discusses corrosion processes and scaling, various experimental corrosion techniques, the relationship between anticorrosion structure and effectiveness, and the process of novel inhibitors.

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1. Introduction

The main way through which metals corrode is corrosion. Many aspects of our lives are being eroded [1, 2]. Most of us personally understand the importance of wear. The appearance of corrosion cracks in the structure of relatively modern cars has caused a large number of people to sag [3]. Rusting of steel, outdoor home and garden equipment is a typical occurrence.

Everyone has seen the strains that hot food on cooking equipment can cause or the acidic tasting cans of food with a metallic flavor after leaving them open for too long. It is generally accepted that rust is the cause of these consequences [4]. The clearest example of corrosion is the appearance of cracks in certain areas of the Taj Mahal, which were caused by steel supports implanted inside that were highly rusted and corroded, causing cracks in the stone [5]. However, other types

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of materials including ceramics, plastics, and rubber are also subject to wear on a regular basis. Since almost all surrounding areas are corroded to some extent, it contributes significantly to mineral stress and has a significant financial impact on society [6]. As in Fig. 1, corrosion is a serious problem in constructions and buildings.



Figure 1: The problem of corrosion in the constructions.

The term corrosion is defined chemically as the process of decomposition of a particular substance as a result of its interaction with its surrounding environment, whether liquid or gaseous. The factors that accelerate this process are heat, acids and salts [7]. The danger of corrosion lies in the damage to metal surfaces as a result of oxidation of atoms or part of the atoms present on the metal surfaces [8]. Corrosion has types, including regular corrosion, which is the most familiar type as a result of electromechanical interactions in wet or watery environmental conditions, for example, and it spreads evenly over time [9]. Although when talking about corrosion, only metal comes to mind, nonmetals including the polymeric compounds, ceramic rubber materials, concrete used in construction, etc. are also susceptible to the corrosion process when exposing them to the corrosive environment [10]. After discussing the factors that lead to the acceleration of the corrosion process, the investigation leads to researching the factors that lead to this process. Where the researchers found that the difference between the potential energies of the corroding metals and the products from this process is the main factor that drives the corrosion process. Therefore, if researchers need to extract certain materials from minerals that occur spontaneously in nature, they must apply this difference between energies. This is followed by the return of materials to its original state when exposed to its surroundings environments. It is interesting that each material needs diverse energy, energy storage capacity, and energy dissipated during wear. Minerals are thermodynamically unstable and have a smaller temporary lifetime in the metallic state, the more energy required to extract the mineral. As a result, corrosion is sometimes described as the opposite of extractive metallurgy [7, 11]. As mentioned above, the electromechanical dissolution process is the base of corrosion forms: the localized corrosion and homogeneous corrosion. The oxidation process, rubbing,

molten salt are common forms of corrosion which can easily be explained rather than using electrochemistry [7]. In both aqueous and atmospheric conditions, a few electrochemical principles (Fig. 2) should always regulate the process of corrosion attack.

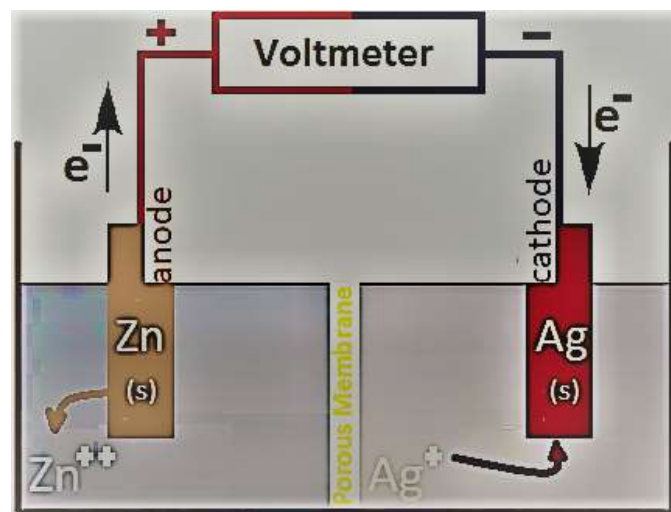


Figure 2: The electrochemical cell and its principle of working.

A solution that can conduct ions will allow electrons to move from one area of the metallic substrate to another. This is a result of the metal's amazing tendency to electrochemically react with gases molecules like O_2 , water molecules (H_2O), and other chemicals in aqueous environmental conditions. In electrochemical corrosion (ECC), there is an anode and a cathode. The corroded metal surface is the anode and the electron consumption area resulting from the corrosive reactions represents the cathode [12]. The International Organization for Standardization (ISO) defines metal corrosion as “a physical-chemical contact between a material and its environment that leads to modifications in the properties of the metal and can lead to significant damage to the component of the material, the surrounding environment, or the technical system, of which it is a part” [13]. This is the most visible and undesirable type of corrosion. Total corrosion costs are estimated at US\$2.5 trillion, or 3.4% of global GDP, and include “engineering, construction or production, maintenance, repair and rehabilitation expenses related to corrosion, and Costs of replacing structures that have become practically useless due to corrosion” [14]. (2013). Application of modern technologies to control corrosion. Present corrosion prevention techniques and methods, which include the use of organic CIs, could reduce corrosion expenses by 15–35% [14]. Corrosion costs vary by industry sector, although they are often higher in the chemical and automotive industries. Transportation-related direct corrosion costs in China in 2014 totaled 268.72 billion RMB, or 23.97% of all corrosion expenses [15]. There is no way to totally stop corrosion, which occurs everywhere. Some innovative approaches will only slow this process. Furthermore, the system to predict of rising corrosion expenses is environmental problem, global warming,

and climate change. Even just a 2°C rise in the global temperature can result in an up to 15% rise in corrosion potential [16]. In order to assess their impact on the effectiveness of corrosion inhibition, recent studies have examined the carbon steel ability as an anticorrosion in a corrosive media employing organic molecules. These molecules' abundance of heteroatoms, benzoic rings, and double bonds make it easier for them to stick to the surface of metals. Due to their benefits to the environment and human health, ionic liquids, biomolecules obtained from nature, and ecofriendly heterocyclic compounds have all been regarded as protective coatings. The review you're reading now compiles particular studies on CIs in hydrochloric acid (HCl). Furthermore, we have supplied the outcomes for each molecule. As a result, a thorough discussion of the various kinds of organic CIs is provided.

2. Corrosion inhibitors (CIs)

When applied in modest amounts to the metallic surroundings, a CI is reducing, inhibiting, and regulating corrosions. The initial defense line versus corrosion in the chemical and oil industries is thought to be CIs [17]. CIs are looked afterwards to provide temporary protection for metals during storage and transportation as well as localized prevention to stop corrosion that may have been caused by buildup of small amounts of an aggressive phase. When available in modest concentrations, an efficient CI should have the intended effect, be cost-effective,

and be friendly with the corrosive environment [18]. CIs work by (i) creating an absorbable coating on the steel surfaces, and (ii) creating a corrosion product, such as the iron sulphide (FeS), which serves as a corrosion product. The three main mechanisms by which CIs work are (i) the formation of an adsorbed film on the metal surface, (ii) the production of corrosion products; like a passivating FeS, and (iii) Producing a solid precipitate that acts as a protector against the undesired compounds [19].

The classification of film-forming inhibitors goes into anode, cathode or mixed inhibitor types basing on which electrochemical reaction is being inhibited [20]. Anodic inhibitors, also referred to as passivation inhibitors, reduce the rate of anodic reactions by forming low solubility deposition in nearly neutral conditions, such as hydroxides, oxides, or salts. Contrarily, cathodic inhibitors work by lowering the rate of cathodic or reduction reactions by forming a barrier on cathodic sites that protects them from oxygen in alkaline settings and hydrogen in acidic conditions. Mixed inhibitors work by creating an adsorptive coating on the metal surface, which affects both the cathodic and anodic reaction sites. The majority of organic inhibitors—about 80%—fit into this group. The inhibitors can be classified as either organic or inorganic depending on their chemical makeup [21]. Organic and inorganic inhibitors can be further divided into neutralizing, scavenging, barrier or film-forming, and other unspecified inhibitors based on their chemical compositions and mechanisms of action [22].

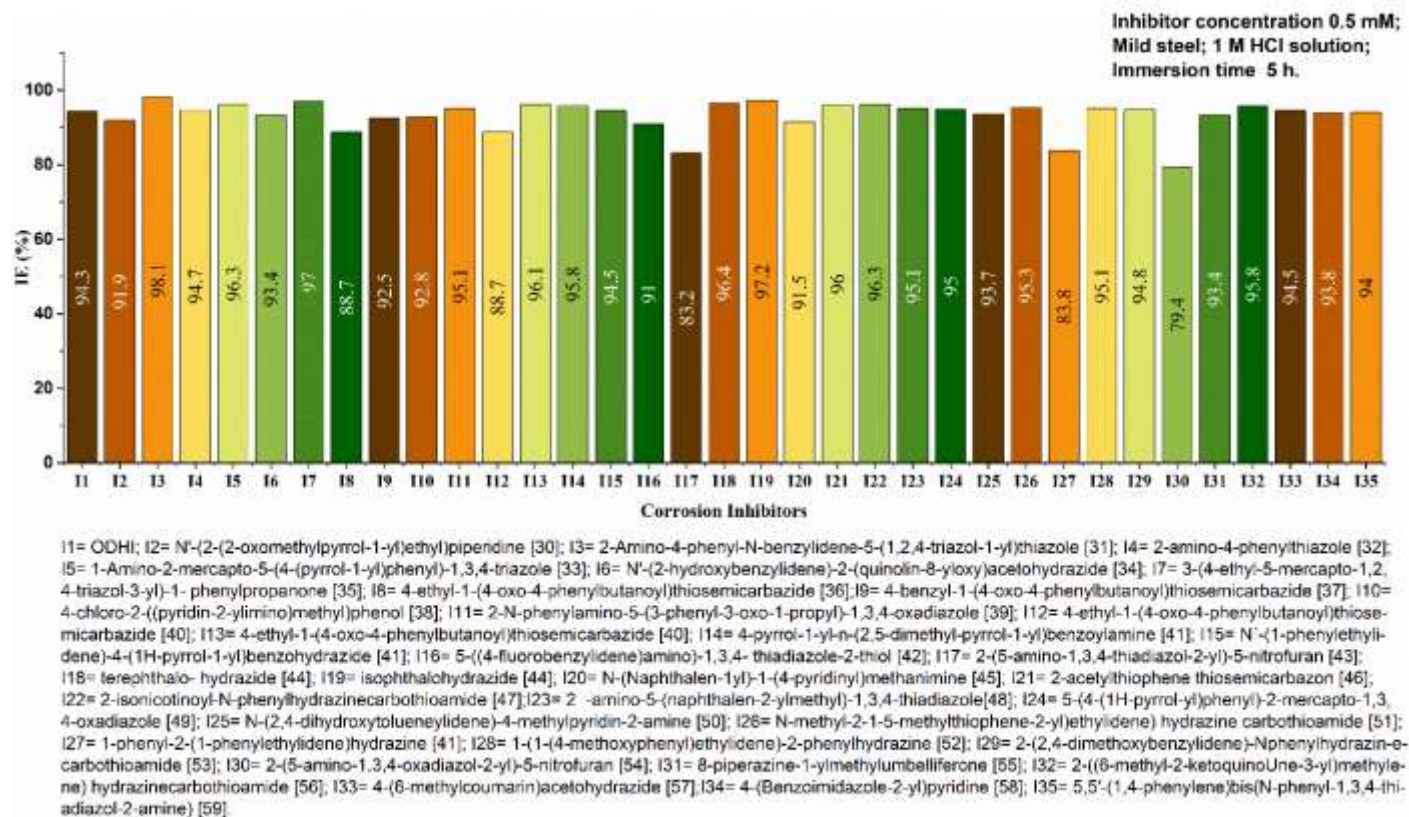


Figure 3: Comparison of selected synthesized CIs.

2.1 Organic inhibitors

Basing on the chemical compounds structures and composition, organic inhibitors works as an anode, cathode or mixed inhibitor type. Such inhibitors are working by creating a coating film over the surfaces of the used metals. Interaction forces such as orbital absorption, chemisorption, and electrostatic absorption help create this protective envelope and stop corrosive species from attacking the material [23]. This absorption often covers only one molecular thin film and does not reach the metal core [24]. The adsorption process is controlled by physicochemical characteristics like the presence of functional groups, the existence of aromatic groups, the steric factors, orbital nature, electron density in donor atom, donor electron, and electronic structure of molecules [25, 26]. The effectiveness of an organic inhibitor in preventing corrosion depends on its adsorption capacity and the mechanical, structural, and chemical properties of the adsorption layers developed in a given environment [27]. An effective organic inhibitor usually has a hydrophobic moiety that will repel aqueous corrosive species away from the metal surface and polar functional groups containing S, O, or N atoms in the molecule. However, the polar head is believed to be responsible for creating the adsorption layer [28]. The chemical families of pyridines, fatty amides, imidazolines, and 1,3-azoles are examples of organic inhibitors [29]. A comparison of the inhibitory efficacy of synthesized published inhibitors is presented in Fig. 3.

2.2 Inorganic inhibitors

Inhibitors that use an inorganic component as the active ingredient are known as inorganic inhibitors. One of the simplest ways to increase the passivity of a metal is to add electro sensitive metal ions to the corrosion environment. To be able to discharge the protecting metal ion onto the metallic surfaces, the protecting metal ion must have an oxidation potential higher than that of the protecting metal and possibly higher than that required to discharge protons. The deposition of a protective metal on the corrosion-prone metal surface removes cathodic depolarization by reducing overvoltage and the consequent creation of adherent deposits. Palladium (Pd), platinum (Pt), iridium (Ir), rhodium (Rh), mercury (Hg), and rhenium are a few of the metals used for this (Re). Several inorganic anions, including chromates, molybdate, silicates, phosphate, and nitrates as well, protect metallic surfaces through passivation by incorporating themselves into the oxide layer [29]. When selecting an inhibitor for a particular disease, issues such as toxicity, availability, cost, and environmental friendliness should be given top priority. It is very worrying because traditional CIs released into the environment are hazardous, biodegradable and bio accumulative. Commercial CIs have potentially dangerous effects on the environment, despite the fact that this is not yet fully understood [61]. Inorganic inhibitors, such as arsenates, phosphates, chromates, and dichromate, has a promising inhibitory efficacy as well as proving intolerable due to the long-term risks to the human

health. Similarly, the risk of environmental pollution resulting from organic inhibitors directs researchers to exploit environmentally friendly materials and to stay away from toxic substances that would negatively affect the environment [26]. Fig. 4, represents the classification of inorganic inhibitors.

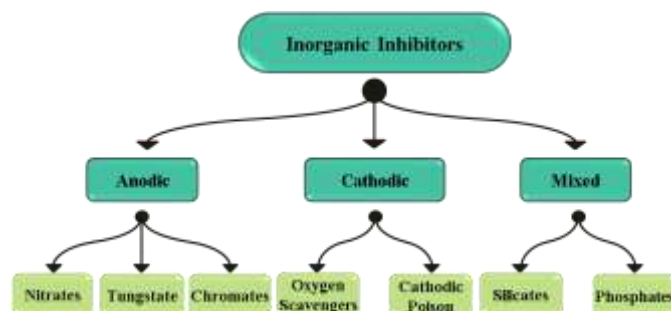


Figure 4: The of inorganic inhibitors classification.

2.3 Green corrosion inhibitors

Due to environmental concerns, CIs are frequently employed to preserve the metallic surfaces and machinery. Such Inhibitors are required to have acceptable characteristics, non-toxicity property, and ecofriendly. The cost and negative effects of commercial organic and inorganic inhibitors have greatly increased the knowledge of corrosion mitigation. Therefore, there is a growing demand for affordable, accessible, ecologically acceptable, environmentally friendly and renewable green CIs among corrosion engineers and technicians. Below, a brief discussion among the many types of these inhibitors is provided. Al-Amiery, evaluated the Citrus aurantium Leaves corrosion inhibition properties (Fig. 5) and used it as CI for steel in 1 M HCl [62].



Figure 5: Image of Citrus aurantium Leaves.

2.4 Plant extracts

Gum Arabic (GA) was tested for its ability to inhibit corrosion of mild steel in 0.1 M H₂SO₄ at various temperatures, in both the presence and absence of halide ions. At a maximum

temperature of 60 °C, 0.05 M KCl, 0.05 M KBr, 0.05 M KI and GA (0.5 g/L) alone gave an IE of 27.7, 32.2, 53.6 and 37.9%, respectively. GA mixed with each of these halide solutions independently showed improved efficiencies of 38.7, 47.1 and 59.1%, respectively, at the same temperature and using the same procedure. Organic cations and halide anions interact as ionic pairs, which have a greater surface coverage and, ultimately, an improved synergistic protection [63]. At 40 °C, the IE of GA on pure aluminum plate type AA1060 was rated at 98.5%. According to the measurements made using the hydrogen evolution method and thermogravimetric method, GA (0.5 g/L) showed an IE of 74.2 and 75.9%, respectively [64]. Using dynamic effective polarization (PP) and electrochemical impedance spectroscopy (EIS) methods, Buchweishaija and Mhinzi examined the IE of mucilage secretions from *Acacia seyal* var. *Sial* gum and acacia from *Sial* Far. *Sial* on mild steel in chlorinated drinking water. The maximum IE of 98.5% was observed in mucilaginous secretions at a concentration of 1000 ppm at 30 °C. However, at a higher temperature of 80 °C and a concentration of 600 ppm, the acacia gum showed an IE of 96.8%.

3. Adverse economic and social effects of corrosion

Corrosion effectively affects machines and buildings, and these applications are directly used by humans, in addition to its impact on the minerals and the resulting alloys. In machines, for example, small parts of the metals that make up these machines erode, but their effect will be very clear after the passage of time if they are not treated or replaced with new parts. These operations are expensive because of the huge facilities and factories that operate on a daily basis and need permanent maintenance. In the following, we review some of the effects of corrosion in the factories and the environment:

- A failure at a nuclear power facility, such as a nuclear reactor during the decontamination process, led to the shutdown.
- Replacement of equipment due to corrosion, which is expensive.
- Preventive maintenance at a high cost
- Loss of efficiency.
- Product leakage from rusty containers.
- Health issues, such as lead contamination of drinking water, which may be caused by corrosion. Safety procedures against fire and explosion risks or the release of toxic substances.

4. Forms of corrosion

Consistent corrosion, also known as general corrosion, galvanic corrosion, intergranular corrosion, intergranular corrosion, selective leaching, corrosion, stress corrosion, corrosion fatigue, and fret corrosion are just a few of the many corrosion manifestations that can occur [66]. They are divided into two main categories to aid in the understanding between corrosion and design engineers. They are shown in a schematic

diagram (Fig. 6).

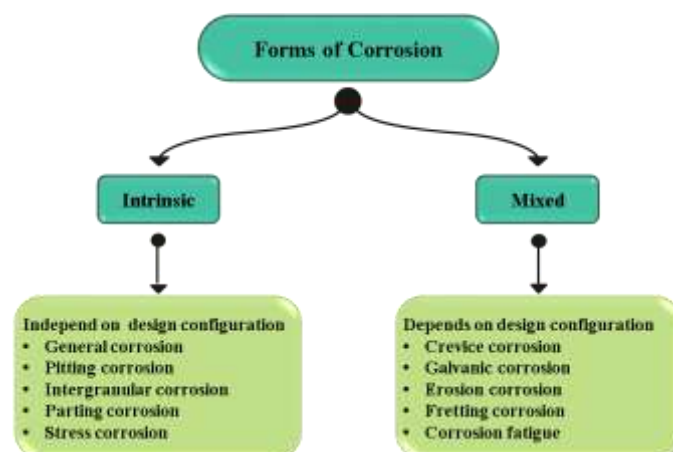


Figure 6: The intrinsic and extrinsic forms of corrosion.

5. Techniques for corrosion measurement

5.1 Weight loss (WL) measurement

WL technique is the most straightforward, reliable, and time-tested method for determining wear losses in machinery and other structures. A sample of the metal or alloy being tested is weighed, immersed in a corrosive solution for a predetermined period of time, and then withdrawn from the corrosive medium. After all corrosion products have been removed, the metal sample is weighed again. Equations (1) to (3) can be used to calculate corrosion rate, surface coverage (θ), and corrosion prevention efficiency (%):

$$\text{Corrosion rate} \left(\frac{\text{mm}}{\text{year}} \right) = 8.76 \times 1000 \frac{m_i - m_f}{S \rho t} \quad (1)$$

$$\theta = \frac{C_{R0} - C_R}{C_{R0}} \quad (2)$$

$$IE\% = \frac{C_{R0} - C_R}{C_{R0}} \times 100 \quad (3)$$

Where t is the amount of time in hours that the sample was immersed, m_i is the weight of the metal sample in grams before immersion, m_f is the weight of the mineral sample in grams after immersion, S is the total area of metal in cm^2 that was exposed to a corrosive solution, ρ is the density of the metal sample in g/cm^3 , and C_{R0} and C_R represent the corrosion rates (in mmpy) without and with the inhibitor, respectively [67]. Al-Amiery, used WL techniques to determine the inhibition efficiency of new CI as in Fig. 7 [68].

5.2 Polarization measurements

ECC monitoring tests can be used to determine the corrosion rate and corrosion prevention mechanism because corrosion is an electrochemical process [68]. The basis of polarization techniques is to change the current or potential in a sample

under study and to record the resulting change of potential or current. Either a direct current (DC) source or an alternating current (AC) source can make this easier. Below, some important and common strategies are briefly explained. Al-Amiery, used the polarization techniques to determine the inhibition efficiency of new CI as in Fig. 8 [68].

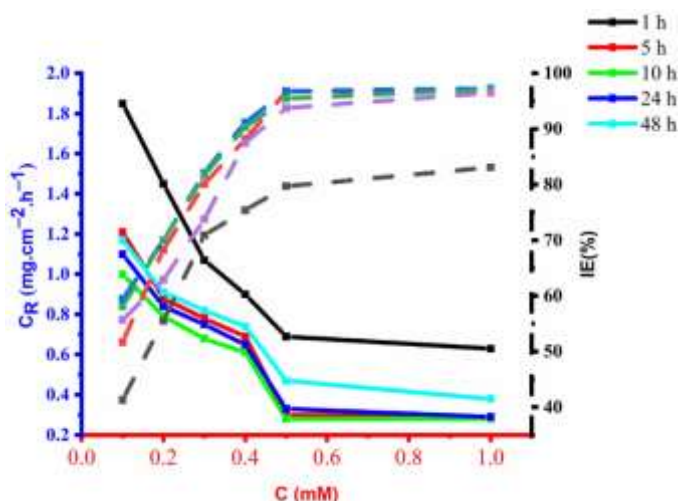


Figure 7: The weight loss measurements for determining the inhibition efficiency.

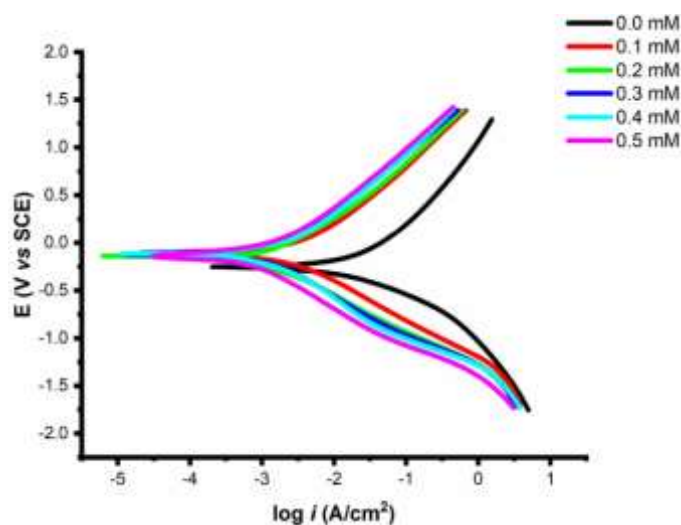


Figure 8: The polarization measurements for determining the inhibition efficiency.

5.3 Tafel extrapolation

The anodic and cathodic reactions in the electrochemical cell are depicted by a Tafel curve, which is a schematic diagram of current and voltage. In this procedure, the working electrode voltage was set over a predetermined frequency range, and the response was recorded at the resulting current. The arcing line is used to indicate the total current produced by the simultaneous anodic and cathodic reactions. The point that is an estimate of the corrosion current (i_{corr}) and the corrosion potential is generated by the intersection of the linear parts of

the logarithmic tafel plot (E_{corr}). This i_{corr} makes it easy to determine the corrosion rate using equation (4) and the corrosion inhibition efficiency (%) using equation (5):

$$C_R = \frac{i_{corr} \times K \times EW}{\rho \times A} \quad (4)$$

$$IE\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (5)$$

where K is a corrosion rate constant, EW is mass equivalent, ρ is metal density, A is the immersed coupon area, i_{corr}^0 and i_{corr} are the corrosion currents in absence and presence CI, respectively.

5.4 Linear polarization resistance (LPR)

The most widely used electrochemical method is the linear polarization impedance (LPR) method because it is non-destructive [69], has a rapid application, and can be used in field testing with a portable device [70]. The basic idea behind LPR is to disrupt the corrosion equilibrium on the surface of a metal sample by applying a modest DC perturbed electrical pulse. With reference to the reference cell half, the homeostasis response to this perturbation is measured [72]. The slope E/i of the potential current density curve at free corrosion potential is recognized as the polarization resistance (R_p) of the material. Using the Stern–Gehry approximation, the polarization resistance can be related to the corrosion current (EC), where is anodic (B_a) and cathodic (B_C). The slopes of the tafel can be obtained experimentally from the real polarization plots.

5.5 Electrochemical impedance spectroscopy (EIS)

The evaluation of coatings in corrosion research makes extensive use of a very powerful electrochemical technique denoted by EIS. This method provides useful information regarding the corrosion protection provided by an inhibitor. In this method, the system under investigation is subjected to an AC voltage (in the case of active EIS) or current (in the case of galvanic EIS) to elicit a response as AC current (voltage) or voltage (current) as AC. frequency function. With the help of a potentiostat-galvanostat and a frequency response analyzer (FRA), this procedure can be performed in a 2- or 3-electrode system [73]. The system is typically subjected to AC voltages applied at frequencies from 100 kHz to 10 MHz, with typical disturbances of 5 to 10 mV. The electrochemical cell containing the metallic sample, the adsorbed inhibitors, and the electrolyte medium is represented by an equivalent circuit based on the Nyquist diagram form generated from the experiment. This equivalent circuit contains data for solution resistance R_s , charge transfer resistance R_{ct} , and double layer capacitance C_{dl} . Better protection against corrosion is indicated by a higher R_{ct} value and decreasing C_{dl} values with higher inhibitor concentrations. [74]. Al-Amiery, used the EIS techniques to determine the inhibition efficiency of new CI as in Fig. 9 [68].

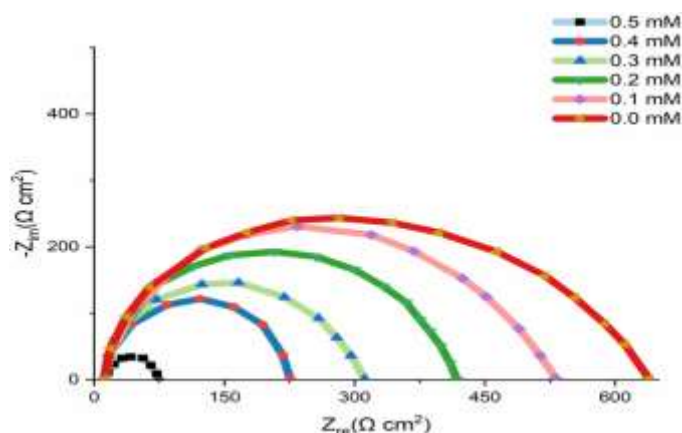
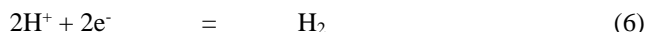


Figure 9: The EIS techniques for determining the inhibition efficiency.

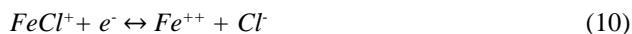
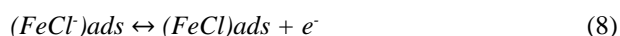
6. Mechanism of corrosion

The main causes of corrosion are chemical and electrochemical reactions. Chemical corrosion occurs in non-conductive liquids and dry gases that are devoid of current or electron flow. The oxide layer produced by oxidation in air is the primary result of chemical corrosion [75]. Due to redox reactions and varying voltages on the surface of the corroded metal, ECC occurs in solution between metallic materials and electrolytes. The anode is the part of the metal where oxidation and ionization occur. Figure 10 depicts an ECC scheme.

Equation (6) describes the mechanism of cathodic reaction.



The mechanism of anodic reaction in absence of inhibitor (Equation (7-10)):



The mechanism of anodic reaction in presence of inhibitor (Equation (11-16)):

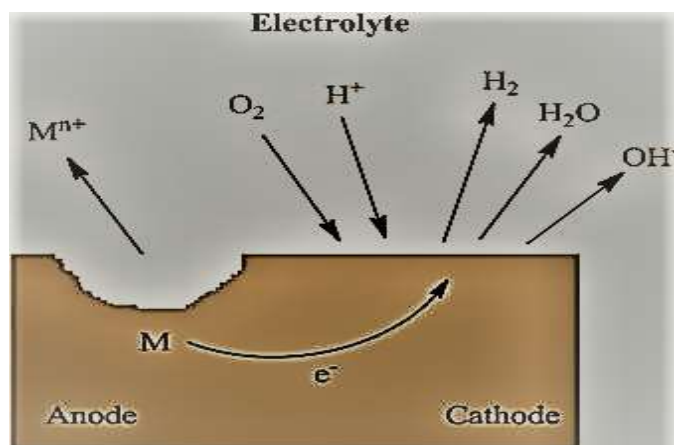
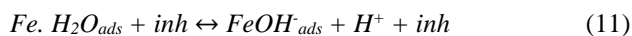


Figure 10. Electrochemical Scheme for corrosion process.

Biocorrosion, also known as microbial-induced corrosion (MIC), is another type of corrosion that is characterized by the breakdown of mineral materials caused by microbial consortia [76]. On the metal surface, microbes create a biofilm that provides an excellent habitat for their growth [77]. Exopolysaccharides, protein, and sometimes extracellular nucleic acids make up the extracellular matrix of biofilms, the aggregations of multicellular bacteria [78]. It is very difficult to remove biofilms from any environment. They are resistant to most antibiotics [79]. The main culprits of bioerosion are sulfate-reducing bacteria (SRB) and sulfate-oxidizing bacteria, both of which produce extensive biofilms [79]. Corrosion is a word used to describe the gradual removal of the parent material from a solid surface as a result of a mechanical interaction between the surface and a liquid, a multi-component liquid, or the collision of liquid or solid particles [80]. Corrosion – Corrosion is a process that involves both corrosion and corrosion simultaneously [81]. One of the best examples for the suggested mechanism process for an organic CI for metallic substrate in corrosive media was reported by Al-Amiry [68], as in Fig. 11.

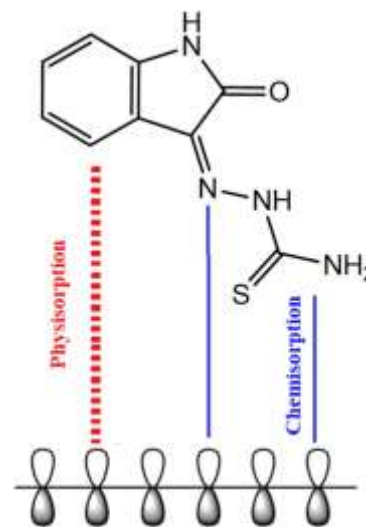


Figure 11. Example for suggested mechanism by an organic inhibitor

7. Adsorption

Adsorption isotherms can be used to study the interaction of inhibitors and metallic surfaces using thermodynamic factors and adsorption models. To understand how electrochemical organic reactions work (Table 1).

Table 1: Lists several types of adsorption isotherms.

Adsorption Isothermal	Models	Curves
Freundlich	$\log\theta = \log K + \frac{1}{n} \log C$	$\log\theta$ vs $\log C$
Langmuir	$\frac{c}{\theta} = \frac{1}{K_{ads}} K_{ads} + C$	$\frac{\theta}{1-\theta}$ vs $\log C$
Temkin	$K_{ads} \cdot C = e^{\theta}$	θ vs $\log C$
Frumkin	$K \cdot C = \frac{\theta}{1-\theta} e^{\frac{\theta}{1-\theta}}$	θ vs $\log C$

Using an alternate adsorption procedure with H₂O adsorbed molecules over the metals surfaces, the organic matter can be adsorbed there [82]. WL measurements were used to produce surface coverage values with and without inhibitor doses, which were then used to evaluate the type of adsorption process and explain the optimal isotherms [83]. The most popular models—Freundlich, Langmuir, Temkin, and Frumkin—were used to examine the surfaces coverage values for several CI doses in 1 M HCl media. These models are shown in Table 2 [84]. The type and number of active sites on the surface of a metal, the charge density, the molecular size of the inhibitor, how the metal interacts with the inhibitor, and the formation of metal complexes all influence the effectiveness of the inhibitor. The following are some of the parameters evaluated to understand the adsorption behavior of particles on a metal surface:

- The increased adsorption capacity of the particles on the metal surface is reflected in the increase in the value of the adsorption constant of K_{ads} [84].
- The strong and spontaneous adsorption of particles on carbon steel can be demonstrated by the relatively high and negative adsorption free energy ΔG_{ads}° , which represents high corrosion inhibition efficiency [84].
- Electrostatic interactions (physical adsorption) between charged particles and charged metal surfaces are indicated by standard negative ΔG_{ads}° free energy values of less than 20 kJ/mol. The coordinated covalent bond is created by charge sharing or transfer of inhibitor molecules to the metal surface (chemisorption) when the value is negative or greater than 40 kJ/mol [82-86].

8. Conclusions

Here, the key points of reviews on CIs are collected and addressed.

These conclusions were reached:

- Finding environmentally friendly CIs is crucial, and current research is more heavily weighted in favour of sustainable solutions.
- There is a dearth of literature on green concrete CIs in which researchers can focus their efforts.

- The proposed mechanism of corrosion inhibition for both synthetic and environmentally friendly CIs is still up for debate.

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