PROTECTION OF METALS FROM CORROSION BY ORGANIC, IN ORGANIC AND ECO- FRIENDLY INHIBITORS: A REVIEW

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ABSTRACT

Globally, corrosion has caused financial losses and environmental damage to infrastructure in all industrial sectors. To address this essential concern, researchers have developed unique and useful corrosion mitigation solutions. For corrosion issues, inhibitors are best. Compounds that hinder, decrease, or produce a thin coating on metal surfaces defend against corrosion in diverse situations. An overview of natural and manufactured organic corrosion inhibitors, their categories, active functional groups, and effectiveness estimates. As well as organic corrosion inhibitor adsorption equations and processes, prior investigations on natural and manufactured organic inhibitors are covered. Corrosion kinetics simulation reveals organic inhibitors' corrosion-reducing effects. A detailed overview of organic corrosion inhibitors is provided in this study to promote their broader usage in corrosion prevention. Dynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), and weight loss are statistic methods for corrosion rate calculation. A long-term research resource in corrosion control, this paper gives a complete methodology overview that permits innovation and increased preventative performance.

Keywords: Metals, corrosion inhibitors, types of inhibitors, performance evaluation of inhibitors, corrosion mechanism

NOMENCLATURE

icorr	corrosion current
d	density
EW	equivalent weight
Ecorr	corrosion potential
bc	cathodic Tafel slope
ba	anodic Tafel slope
PDP	Potentiodynamic polarization
EIS	Electrochemical impedance spectroscopy
CPE	constant phase element

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INTRODUCTION

Corrosion has long been defined as the failure of a metallic or non-metallic material resulting from exposure to structurally destructive agents. For metals, corrosion is an electrochemical process, while for ceramics or concrete, it is a purely chemical decomposition process. To mitigate its effects and reduce its rates, the scientific community has found inhibitors to be the ideal solution to address corrosion issues (Yebra et al., 2004). Specialists have divided these inhibitors into different types, including natural and synthetic. The latter are characterized by their harmful uses, unlike the natural ones, which have benign uses. From this perspective, replacing inhibitors manufactured from environmentally harmful materials with safe and environmentally friendly compounds is a major goal of modern scientific research. When metallic components are exposed to corrosive conditions, the harmful effects of chemically manufactured materials on artificial joints become apparent, ultimately leading to their damage and deterioration, in addition to serious health consequences. This results in huge financial losses and serious operational risks to the work environment and equipment (Al-Rawajfeh et al., 2024).Chemical or electrochemical reactions with the environment cause corrosion of metals and their alloys, weakening their mechanical integrity . Corrosion results in partial or complete disintegration of the metal. It is an oxidation-reduction process that occurs between two electrodes, one of which emits electrons and the other attracts electrons, in the presence of an active medium. This can be achieved through the dissolution of oxygen and moisture on the metal surface (Ogunleye et al., 2021). It is worth noting that corrosion occurs depending on several variables, including temperature, pressure, surface contaminants, and the influence of acidic or basic fluid components, in addition to salt. Oxides, sulfides, and hydroxides are common forms of these components. Carbon steel is inexpensive compared to other metals and is therefore widely used in the manufacture of pipes (above and below ground) in the oil and gas industries and others (Shatab et al., 2023). As a result, steel may corrode in basic or acidic environments, such as saltwater rich in basic ions or loaded with carbon dioxide, chloride, and active sulfur ions in petroleum media. Other compounds that can cause corrosion include hydrofluoric acid, acetic acid, hydrochloric acid, and hydro sulfuric acid, which can render pipes dangerous and unusable. With the rapid advancement of technology, corrosion has become a global problem that calls for an environmentally friendly solution. It has been estimated that 3% of global GDP, or one-third of the world's steel production, is lost annually to corrosion(Iannuzzi & Frankel, 2022). Consequently, companies have developed a range of corrosion control strategies, including coatings, inhibitors, and cathodic protection, to halt these losses. This is despite the additional costs faced by industrial machinery and metal pipes used in industries when they fail. Some examples of these strategies include voltage modification, surface coating, structural design optimization, material selection, environmental modification, and the use of corrosion inhibitors as effective preventive measures (Shwetha et al., 2024).Corrosion inhibitors have been considered the most serious solution to addressing corrosion issues due to their unique advantages, such as rapid reaction time, high performance efficiency, ease of use, reasonable or low costs, and the possibility of using them without requiring changes to machine design and process (Serdaroğlu & Kaya, 2021). Inhibitors employ mechanisms that prevent the metal from contacting corrosive materials or by removing it from the corrosive environment. This is achieved by forming a barrier layer that blocks corrosive electrons from reaching the metal.

In general, corrosion inhibitors are divided into two categories: organic and inorganic(Ahmed et al., 2024). For example, phosphates, chromates, rumates, dichromates, and nitrites are examples of inorganic inhibitors. In contrast, organic compounds such as silicates, alkaloids, flavonoids, heteroatoms, tannins, and nitrogen-based compounds found in plant flowers, seeds, leaves, roots, and stems, as well as soil components such as sand or industrial waste, can naturally suppress corrosion. In brief, organic inhibitors include synthetically sourced materials, while inorganic inhibitors include naturally occurring organic compounds that are synthesized by industry. Therefore, organic inhibitors contain one or more polar groups such as oxygen, nitrogen, phosphorus, and sulfur atoms, and are therefore more likely to form coordination bonds with vacant pathways due to their high electron density and availability of free electron pairs. According to a review of previously published literature, most metals are thermodynamically unstable under changing conditions(Q. Zhang et al., 2023). Considering the ongoing industrial development and the introduction of modern technologies and techniques into the scientific community, all of which are directed towards safe use to preserve the environment and public health, researchers have found it necessary to create green corrosion inhibitors as an alternative to traditional inhibitors, which are known for their high costs and negative health effects. In this regard, researchers have discovered that many natural and biodegradable materials are suitable as environmentally friendly and highly efficient corrosion inhibitors(Q. Wang et al., 2022). These natural materials fall under the category of plant, animal, and mineral extracts, being rich in polar molecules and containing nitrogen and oxygen, in addition to functional groups consisting of aliphatic or homogeneous and heterogeneous aromatic cyclic chains.

In contrast, inorganic chemicals have undeniable advantages in corrosion prevention, but they have disadvantages that largely outweigh their advantages(Palou et al., 2014). In the twentieth and twenty-first centuries, specialists and companies operating in the chemical industry, supported by major corporations and governments, have pioneered a scientific exploration that has become a modern trend known as nanotechnology. This science has found widespread industrial applications, making it more mature in all scientific disciplines, especially in sustainable protection against corrosion attacks. This paper addresses current issues related to corrosion describing its mechanism, causes, and resulting damage as well as the factors contributing to its manifestation and the mechanism of using inhibitors that prevent it or mitigate its destructive effects. The paper also addresses the function of environmentally friendly inhibitors derived from safe, natural sources, organic and inorganic inhibitors, and procedures for testing or evaluating corrosion inhibitors. The paper provides a brief overview of the effectiveness of inhibitors in combating corrosion problems. By bridging the gap between theory and practice, this study helps researchers and practitioners make informed judgments, develop practical methods for preventing corrosion, and pave the way for a future where appropriate inhibitors protect materials and structures from the harmful effects of corrosion.

Progress and Limitations in Corrosion Inhibitors

Development of organic inhibitors, including compounds with heteroatoms like nitrogen and sulfur, has improved their capacity to adsorb to metal surfaces and create a protective coating. In acidic and basic conditions, aromatic chemicals and polymer derivatives boost protection(Bahlakeh et al., 2017).

Limitations: Organic inhibitors may decompose in severe settings and include harmful substances in their formulation, which may harm the environment. Their efficiency depends on concentration and temperature, which may restrict their industrial usage.

Advanced Inorganic Inhibitors: Compounds like phosphates and chromates affect the chemical environment around metals to minimize corrosion. Improved nanoscale metal oxide chemical adsorption methods safeguard against hostile conditions (Mandal et al., 2020).

Limitations: Chromates, which are poisonous and harmful to public health, are restricted in the environment. Inorganic chemicals may also impact metal physical characteristics, needing careful investigation before commercial usage (Mandal et al., 2020).

As sustainability becomes more important: nanocomposite-based inhibitors like nano silica provide good protection without harming the environment. Safe and sustainable corrosion reduction using plant extracts and bio composites is also promising.

Limitations: Despite their environmental advantages, environmentally friendly inhibitors may be expensive compared to traditional inhibitors and need stability improvements in demanding industrial conditions to be effective(Bastidas et al., 2021).

Impacts on inhibitor performance, issues, and advice

Inhibitor efficiency depends on chemical composition, metal surface adsorption, and corrosive medium parameters like pH and temperature. These factors affect inhibitors' corrosion-preventing electrochemical barrier. For good protection, inhibitor concentration and injection strategy are critical due to inhomogeneous distribution(Goni et al., 2021).

Since chromates are hazardous, sustainable, and eco-friendly inhibitors are needed. Nanocomposites like nano silica improve adsorption and protection without damaging the environment. In hostile environments like acidic and alkaline systems, inhibitor stability needs surface chemistry and inhibitor-metal interactions study. Finally, good inhibitors must balance performance, cost, and environmental impact. Adsorption mechanisms and chemical reactions research will increase inhibitor efficiency, industrial process sustainability, and metal equipment and structural corrosion(Quraishi et al., 2020).

CATEGORIES OF CORROSION INHIBITOR

Organic Inhibitors

Organic corrosion inhibitors exhibit many functions and applications via their anodic, cathodic, and adsorptive characteristics, or a combination thereof in different manners. To elucidate their processes and functions, we enumerate the main categories of organic inhibitors as follows(Sheetal et al., 2023).

Phosphate-based corrosion inhibitors

Phosphates, classified as organic corrosion inhibitors, are extensively used in water systems to mitigate corrosion rates. They are fundamental inhibitors, suitable for amphoteric or alkaline environments, including water. These inhibitors create complexes with metal cations, rendering them exceedingly stable and resilient even under extreme circumstances due to their robust carbon-phosphorus bonds. Several of these categories are listed below(Kuznetsov, 2015).

- $C_2H_8O_7P_2$, $C_3H_{12}NO_9P_3$, $C_4H_{11}NO_4PS$, $C_3H_{12}NO_9P_3$, $C_6H_{20}N_2O_{12}P_4$, $C_{10}H_{28}N_2O_{12}P$,
- $C_7H_{11}O_9P$, $C_2H_5O_6P$ (Chen et al., 2022). Figure 1(a) illustrates their chemically modified structures, demonstrating that they are compounds that physically associate with cellular phosphate complexes, consisting of regulatory proteins and catalytic subunits, to restrict phosphate activity and modulate certain biological functions. These inhibitors regulate phosphoproteins in both spatial and temporal dimensions, hence governing standard cellular functions. Numerous human illnesses may be linked to abnormalities in the expression and function of phosphate inhibitors(Boughoues et al., 2020).

Heterocyclic corrosion inhibitors

Numerous heterocyclic compounds have a significant capacity to suppress or retard metal corrosion owing to their crystalline properties, since they include one or more heteroatoms inside their chemical ring structure (P, S, N, or O). Consequently, they interact more readily with ferrous ions since these atoms constitute their structure and possess little electronegativity. This produces stable, insoluble compounds that, upon adsorption to the metal surface, may inhibit or diminish corrosion rates(Ituen et al., 2017). A general guideline indicates that compounds containing heterocyclic atoms exhibit enhanced inhibitory performance, since atoms with reduced electronegativity facilitate more charge transfer and efficacy(Umoren & Solomon, 2015). Figure 1(b) illustrates the molecular structures of the heterocyclic compounds evaluated as corrosion inhibitors for API X52 steel pipe samples submerged in 1 M aqueous sulfuric acid solutions.

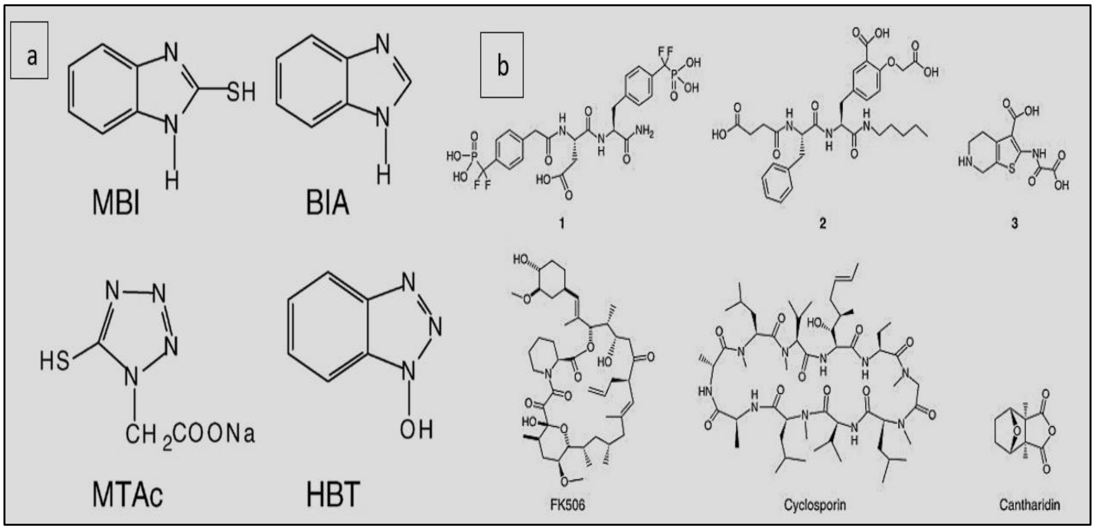

Fig.1. Structural structures of organic inhibitors a: Heterocyclic organic inhibitors, b: Organophosphorus inhibitors.

Summary of organic inhibitors

The high activity of phosphoric acids makes them effective corrosion inhibitors. They can adsorb to specific surfaces and form insoluble, protective barrier layers on metal surfaces capable of resisting corrosion in often basic media, increasing the activation energy and reducing the active surface area of the target metal. These inhibitors are characterized by their efficiency, ease of use, low toxicity, and low cost. These organic inhibitors are resistant to deposits and corrosion and provide strong protection over a wide range of applications. While they have advantages, they also have disadvantages. The most significant potential disadvantage is the potential for localized corrosion, in addition to reduced performance in areas with stagnant electrolytes and the presence of hydrogen sulfide. Furthermore, phosphonate inhibitors may degrade because of oxidizing biocides. Studies have shown that inhibitors with unpaired electrons and heteroatoms (N, P, O, and S) are essential for chemical or physical adsorption to form a barrier that protects certain metal surfaces. Table 1 shows the main properties of some common organic corrosion inhibitors along with their characteristics(Chauhan et al., 2021).

Table 1. provides examples of some studies on organic inhibitors, along with their properties, nature of adsorption, working media, and efficiency.

Inhibitor	Environment	Nature of adsorption	IE%	IE%	Ref.
Phosphonate anion (PHOS)	Mild steel/SCW	Langmuir/anodic inhibitor	88%	88%	(Popoola, 2019)

Pyridine	Mild steel/1 M HCl	Langmuir/mixed type inhibitor	46%	46%	(Quraishi et al., 2021)
Quinoline	Mild steel/1 M HCl	Langmuir/mixed type inhibitor	64%	64%	(Vukasovich & Farr, 1986)
1,10-Phenanthroline	Mild steel/1 M HCl	Langmuir/mixed type inhibitor	80.4%	80.4%	(Gill, 1993)
3-Pyridylaldoxime (3POH)	Mild steel/1 M HCl	Langmuir/mixed type inhibitor	94%	94%	(Robertson, 1951)
1-Benzylimidazole	Carbon steel/1 M HCl	Langmuir/mixed type inhibitor	82.0%	82.0%	(Ma et al., 2022)
Benzotriazole (BZT)	Carbon steel/2 M HCl	Chemisorption/mixed type inhibitor	78.1%	78.1%	(Al-Amiery, Yousif, et al., 2023)
5-Methyl-1H-benzotriazole (5MBZT)	Carbon steel/2 M HCl	Chemisorption/mixed type inhibitor	91.8%	91.8%	(Rauta et al., 2025)
3-Amino-5-methylthio-1H-1,2,4-triazole (3AMT)	Carbon steel (C38)/1 M HCl	Langmuir/mixed type inhibitor	95%	95%	(X. Wang et al., 2024)
Allyl-6-nitro-1H-indazole	Carbon steel (C38)/1 M HCl	Langmuir/mixed type inhibitor	97.5%	97.5%	(Umoren et al., 2022)
2-Amino-5-chloropyridine	Mild steel/1 M HCl	Langmuir/mixed type inhibitor	93.7%	93.7%	(Aslam et al., 2022)
Imidazole-4-methylimine thiourea (MIT)	Mild steel/1 M HCl	Langmuir/mixed type inhibitor	93.7%	93.7%	(Figueira et al., 2015)

Inorganic inhibitors

Inorganic corrosion inhibitors work by reducing or stopping the anodic and/or cathodic activity of the corrosion cell. This is accomplished by depositing a thin layer on the metal surface, which removes oxygen and forms a protective oxide layer. Typical examples of inorganic inhibitors are nitrites, silicates, phosphates, chromates, molybdates, and other salts such as zinc, calcium, and magnesium. Table 2 lists six common inorganic corrosion inhibitors, along with their basic properties and levels of effectiveness in corrosive media(Aydinsoy et al., 2024).

Nitrite Inhibitors

Nitrite, a commonly used inorganic inhibitor, has received significant scientific attention due to its strong inhibitory effects and low cost. Nitrite inhibitors often reduce corrosion current density, which also contributes to improved corrosion performance(Al-Amiery, Isahak, et al., 2023).

Molybdate Inhibitors

The low toxicity and environmental friendliness of molybdate ions have led to extensive research into their use as a corrosion inhibitor for a variety of metals and alloys under adverse conditions. The mechanism by which molybdate inhibits the corrosion of carbon steel under neutral conditions was discovered in 1955, after its inhibitory effect was first studied in 1953. Since then, extensive research has been conducted into the use of molybdate as a potent corrosion inhibitor for steel(A. A. Alamiery et al., 2021). Since molybdate is an anodic oxidation inhibitor, it requires ambient oxygen to form a protective oxide layer on iron alloys. The chemical reaction at the anode ($FeO/Fe^{2+} + 2e-$) produces ferrous ions. These ferrous ions react with molybdate ions to form an inactive molybdate-iron complex. This complex is oxidized in the presence of dissolved oxygen to form a thin, insoluble molybdate-ferric complex, which subsequently combines with ferric oxide to improve corrosion resistance(Hossain et al., 2021).

Silicate Inhibitors

Alkali silicates are a type of inorganic inhibitor. They are harmless, non-toxic, insoluble in water due to their hydrophobic properties, and have a long shelf life. They are not suitable for use in agriculture. Their use in combating corrosion has recently become increasingly popular, especially after nanotechnology treatment, which has enhanced their ability to combat corrosion more effectively. Their ability to create a protective silicate layer, which is an iron oxide layer in the form of g-Fe2O3, or in the order Fe2O3/FeO/Fe2O, formed by water displacement at the interface between steel and the surrounding solution, effectively protects the metal surface from the harmful effects of the corrosive environment(Ashrafi-Shahri et al., 2019).

Tungstate Inhibitors

Tungstate has shown promising performance as a corrosion inhibitor in various industries due to its ease of use and integration into numerous corrosion control techniques, such as immersion, spraying, and dipping. Thanks to its distinctive properties, it is a good choice for preventing the corrosion of various metals, including copper, nickel, aluminum, and steel, in a variety of environments. Furthermore, tungstate operates effectively in both acidic and alkaline environments.

Its excellent chemical stability allows it to withstand degradation and maintain its protective properties in highly corrosive environments. Tungstate is particularly useful in industries where corrosive chemicals change, regardless of pH(Sanni et al., 2018).

Summary of inorganic inhibitors

Inorganic inhibitors are essential for protecting metals in harsh environments. Their non-volatility, chemical and thermal stability, and corrosion resistance make them superior to organic inhibitors in some applications. Understanding how these inhibitors affect the cathodic and anodic polarization branches is essential to predicting their effectiveness in stopping corrosion. Because they can alter the reactions in each branch of the corrosion process, inhibitors are effective tools for metal protection.

Inorganic inhibitors come in three main types: anodic, cathodic, and mixed. However, the need for high concentrations and environmental concerns limits their use. Furthermore, there is a significant risk that the use of anodic inhibitors at low concentrations will lead to corrosion, especially pitting. The selection and application of inorganic corrosion inhibitors requires comprehensive analysis and evaluation considering these factors. Table 2 (Emmanuel, 2024) shows the characteristics of some typical examples of inorganic corrosion inhibitors.

Table 2. List of types of inorganic inhibitors with an evaluation of their efficiencies according to specialized studies.

Inhibitor	Environment	Nature of adsorption	IE%	Ref.
Zn^{2+}	Carbon steel/sea water	N.A., cathodic inhibitor	83.3%	(Chigondo & Chigondo, 2016)
Sodium silicate	Carbon steel/simulated cooling water	Langmuir, anodic inhibitor	74.0%	(Ali et al., 2008)
Sodium phosphate	Carbon steel/simulated cooling water	N.A., anodic inhibitor	95%	(Madlangbayan et al., 2021)
Silicate-phosphate	Carbon steel/ simulated cooling water	-	62.3%	(Namus et al., 2024)
Sodium vanadate	N80 steel/concentrated $K_3P_2O_7$ solution	N.A., anodic inhibitor	99.85%	(Zeng & Qin, 2012)
Sodium nitrite	Carbon steel/5 mM chloride	N.A., anodic inhibitor	90%	(Ali et al., 2008)
Sodium nitrite	Carbon steel/simulated primary cooling water	N.A., anodic inhibitor	N.A.	(B. Zhang et al., 2015)
Sodium nitrite	Carbon steel/simulated primary cooling water	N.A., anodic inhibitor	N.A.	(Namus et al., 2024)
Sodium nitrite	Carbon steel/250 NaCl	N.A., anodic inhibitor	99.061%	(B. Zhang et al., 2015)
Sodium nitrite	Carbon steel	N.A., anodic inhibitor	N.A.	(Zeng & Qin, 2012)

Eco- Friendly Corrosion Inhibitors

Recently, both synthetic organic corrosion inhibitors (SOCIs) and conventional inorganic corrosion inhibitors (TICIs) have been subject to strict environmental regulations. They pose a risk to ecosystems or human health, accumulate in the environment, are non-biodegradable, and are costly and difficult to remove. Therefore, organic green corrosion inhibitors (OGCIs) must replace them due to these environmental issues. Environmentally friendly corrosion inhibitors have recently been recognized as a leading class of corrosion inhibitors that could be developed over the coming years to address various corrosion challenges, as the scientific community has focused on developing effective, environmentally friendly, and economically viable corrosion inhibitors (B. Zhang et al., 2015). Environmentally friendly inhibitors are classified according to technology and source (extraction or manufacturing) (inorganic or organic), respectively. When introduced in small quantities into a corrosive medium, these inhibitors prevent corrosion or limit the effects of its causes. This is achieved by forming a single-molecule absorbent surface that prevents the metal and corrosive materials from direct contact with the target metal surface. These compounds are natural organic compounds that can prevent metallic materials (steel of all kinds) and inorganic materials (concrete) from corrosion in corrosive environments. Being environmentally friendly, most of their sources are natural, and may include medicinal plants, aromatic herbs, and natural spices, animals and animal bones, or soil components (sand) (Namus et al., 2024). Figure 2 illustrates several sources of environmentally friendly inhibitors. The most important functional groups of natural extracts that are critical to the corrosion inhibition process are listed in Table 3. Table 4 illustrates the most important previous research on environmentally safe natural corrosion inhibitors (B. Zhang et al., 2015).

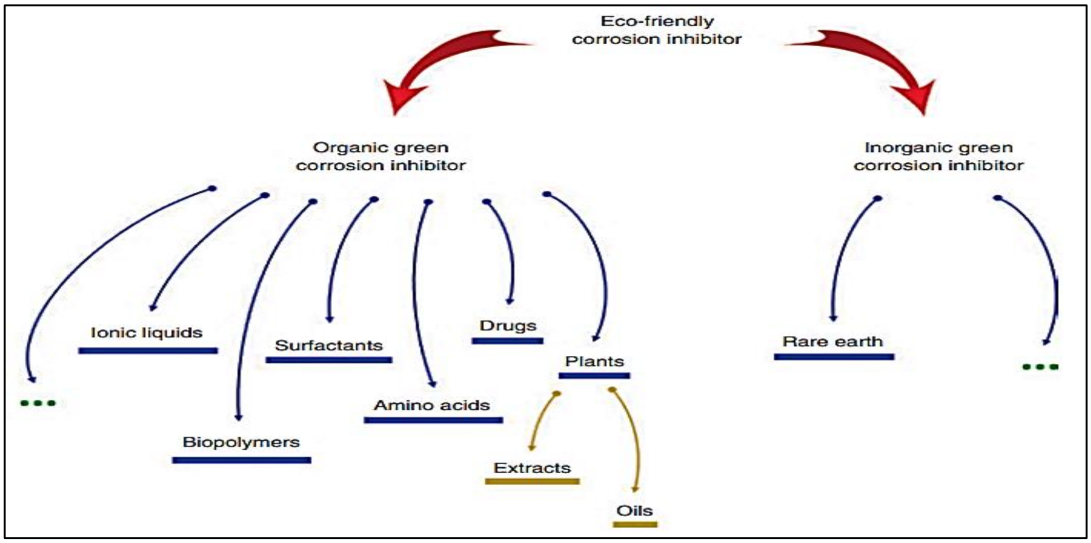

Fig.2. Sources of environmentally friendly materials (B. Zhang et al., 2015).

Table 3. Some functional groups of environmentally friendly natural extracts (inhibitors) (Chigondo & Chigondo, 2016)

Functional group	Name	Functional group	Name
-OH	Hydroxy	-NH2	Amino
-C-N-C-	Amine	-SH	Thiol
$-NO_2$	Nitro	-C≡C-	-yne
$-CONH_2$	Amide	-S=O	Sulfoxide
-COOH	Carboxy	-NH	Imino
-S-	Sulfide	-N=N-N-	Triazole
-C=S-	Thio	-C-O-C-	Epoxy
-P=O	Phosphonium	-P-	Phospho
-Se-	Seleno	-As-	Arsano

Table 4. Summary of some previous studies on environmentally friendly inhibitors from natural sources, their role in inhibition, and their components.

Eco-friendly source	Functional groups and compounds	Corrosion inhibitory roles
G. biloba leaf extracts	Flavonoids and terpenoids; phenol groups and aromatic rings	Terpenes, the interactions of donor-acceptor between O and aromatic ring p-electrons and surface iron empty d-orbitals are the basis for quercetin adsorption on mild steel surfaces. Flavonoids: oxidation to benzoquinone by O2 dissolved in the solution prevents oxygen-adsorption corrosion (Marzorati et al., 2018)
Rothmannia longiflora extract	Monomethyl fumarate, 4-oxonicotinamide-1-(1-β-Dribofuranoside), and D-mannitol	The protonation of the aromatic ring and hydroxyl group causes molecules to be adsorbed on the mild steel surface. An electron-releasing group is connected to the aromatic rings (π-electrons) of constituent molecules. Moreover, the enhanced capacity of π-electrons to form bonds with empty d-orbitals in Fe (Singh Raman et al., 2022).
Extract of Ficus asperifolia	Saponins, alkaloids, tannins, anthraquinones, flavonoids, reducing sugars, n-hexane, ethyl acetate, and butanol	The presence of heteroatoms or rich bonds in the chemical structures made it easier to donate electrons. As a result, complexes that prevent corrosion on the material surface formed more readily(Guo et al., 2024).
Tobacco extract	Polyphenols, terpenes, alkaloids, alcohols, carboxylic acids, and	electrochemical activity that inhibits metal corrosion because of a fused benzene ring structure with a charge dislocation characteristic (Singh Raman et al., 2022).

	nitrogen-containing compounds	
Guar gum	Polysaccharides, mainly sugars galactose and mannose	Short-side branches of a linear chain generated by 1,4-linked mannose residues subsequently formed complexes on the metal surface to prevent corrosion(Singh Raman et al., 2022).

Valuable data has been provided for the development of sustainable corrosion inhibitors, contributing to the global progress towards environmentally friendly corrosion control technologies while simultaneously competing with the effectiveness of conventional inhibitors. Furthermore, advances in nanotechnology have enabled the development of new methods for corrosion inhibition. Nanoparticles and nanocomposites are examples of nanomaterial-based inhibitors that have demonstrated remarkable corrosion inhibition capabilities without any environmental impact. The production and application of nano inhibitors have been the subject of recent research, highlighting their potential to revolutionize corrosion control(Singh Raman et al., 2022). As a result, the scientific community has identified a variety of environmentally friendly corrosion inhibitors, including self-healing and smart corrosion inhibitors; each of which helps prevent corrosion by releasing its protective molecules in a controlled manner onto the metal surface, and improves corrosion protection by reacting to environmental changes, such as changes in pH, humidity, and temperature. These inhibitors can also change their structure or properties in response to environmental changes. Table 5 shows the most popular patents related to the production of green inhibitors using nanotechnology.

Table 5. The most important recent patents in the field of creating environmentally friendly materials.

No	Patent Name	Type of Inhibitor	Application
1	Environmentally Friendly Composite Corrosion and Scale Inhibitor for Circulating Cooling Water Systems	A green, phosphorus-free, biodegradable corrosion and scale inhibitor.	This inhibitor addresses important issues including corrosion, deposits, and pollution and is specially made for recirculating industrial cooling water systems (Wilson, 2016).
2	Eco-Friendly Low-Phosphate Composite for Corrosion and Scale Prevention in	An ecologically safe, low-phosphate, biodegradable corrosion, and scaling inhibitor.	This damper is specially made to be used in industries like water cooling and HVAC, chemical production, and power generating. This green damper lessens its impact on the environment while improving operating dependability(Ning et al., 2024).

	Circulating Cooling Water Systems		
3	Innovative Corrosion Inhibitor Compositions and Methods Using Natural Components	urine or compounds generated from urine as a natural, bio-based corrosion inhibitor.	This patent is particularly relevant to industries that rely on metal containers exposed to corrosive environments, such as oil and gas extraction, water treatment, and industrial fluid systems (Wilson, 2016).
4	Amino Acid-Based Corrosion Inhibiting Compositions for Aqueous Systems	A corrosion inhibitor based on polymers that uses tin compounds and amino acids.	These fittings are perfect for use in water-related industrial operations, such as cooling water systems, boilers, and other water-exposed metal infrastructure (Ning et al., 2024).
5	Construction Method for a Corrosion Inhibition Functional Super-Hydrophobic Self-Healing Anti-Corrosion Coating	a covering made of polydimethylsiloxane and layered double hydroxide (LDH) that is very hydrophobic, self-healing and inhibits corrosion.	This coating was created especially for use on components made of magnesium alloy used in the automotive, aerospace, and marine sectors, which are environments that are prone to corrosion. Super-hydrophobicity, self-healing qualities, and corrosion inhibition work together to offer durable defense against environmental deterioration(Wilson, 2016)..
6	Self-Healing Agent Formulations Containing Liquid Corrosion Inhibitors	Microencapsulation is used in a self-healing corrosion inhibitor system to restore damage.	The formulations of self-healing agents are perfect for use in coatings and materials exposed to hostile conditions where mechanical damage and corrosion are frequent occurrences. This technology may be used in sectors including infrastructure, automotive, and aircraft, where long-term protection and lower maintenance costs are essential(Ning et al., 2024).
7	Preparation Method for a Magnetic Gradient Self-Healing Corrosion-Inhibiting Coating	a coating that uses magnetic nanoparticles and external magnetic fields to prevent corrosion and cure itself.	This coating is perfect for usage in settings including the maritime, automotive, and infrastructure industries where improved corrosion protection is necessary. A more customized reaction to environmental circumstances is made possible by the enhanced control over corrosion inhibition offered by the

			magnetic gradient distribution(Gomri et al., 2022).

Hybrid Corrosion Inhibitors (Organic and Inorganic)

Hybrid corrosion inhibitors are advanced blends of organic and inorganic materials used to improve the corrosion resistance of metals under harsh conditions. These inhibitors combine the chemical and electrochemical properties of organic materials, including polymers and cyclic molecules, with the structural stability and layer-forming ability of inorganic compounds, including silicates and metal oxides. The inorganic components enhance stability by redistributing electron density, reducing the likelihood of unwanted redox reactions. These inhibitors have been used in numerous industrial applications, including the protection of steel pipelines in the petroleum sector by integrating organic polymers with nano-silica to enhance corrosion resistance in acidic conditions. Enhancing the effectiveness of smart coatings using organic corrosion inhibitors using metal oxide compounds to build layers resistant to electrochemical degradation. Formulating sustainable alternatives to reduce reliance on hazardous organic materials by integrating natural extracts with inorganic elements such as graphite or titanium oxide(Gomri et al., 2022).

Mechanisms of action of hybrid chemical and electrochemical inhibitors

Hybrid inhibitors operate in several ways, including:

1. Adsorption on the metal surface - Organic chemicals interact with the surface via covalent or non-covalent interactions, including electrostatic forces or hydrogen bonds. Inorganic components, such as nano silica, enhance the mechanical and thermal integrity of the protective layer.
2. Formation of a double protective layer - Inorganic components, such as metal oxides or nanoparticles, are responsible for forming mechanically stable layers. Organic materials, including polymers and indole derivatives, enhance the layer's ability to inhibit the transfer of electrons and ions, reducing the electrochemical activity of corrosion.
3. Electron Effect on Metal Surfaces: Some organic compounds contain electron-donating functional groups, such as aniline or imidazole, which exhibit strong affinity for electrochemically active spots on the metal surface(Aljamali et al., 2021).

Benefits of hybrid inhibitors compared to conventional inhibitors

1. Enhanced thermal and chemical flexibility of the protective layer.
2. Reducing material toxicity by decreasing concentrations of hazardous organic compounds.
3. Enhancing effectiveness under harsh conditions, such as highly acidic conditions.

4. The ability to alter metal surface properties by regulating the ratio of organic to inorganic components (Al-Sultani & Abdulsada, 2013).

Research and development challenges

Despite the numerous benefits of these inhibitors, there are still issues that require further development, such as:

1. Regulating the adsorption rate of organic molecules to enhance efficiency.
2. Enhancing structural homogeneity between organic and inorganic compounds.
3. Reducing production costs through the development of environmentally friendly manufacturing techniques(Al-Sultani & Abdulsada, 2013).

Corrosion Inhibition mechanisms of organic, inorganic, and eco-Friendly inhibitors

Through a variety of methods, corrosion inhibitor mechanisms are generally divided into three main processes (Figure 3) (Al-Sultani & Abdulsada, 2013), which work to impede or halt the corrosion process. First, they work by forming a thin, film-like passivation layer on the target surface(Peng et al., 2021).

Passivation processes

The passivation process prevents a metal from interacting with its environment by forming a protective layer on its surface. This thin layer typically consists of an oxide, hydroxide, or other corrosion-resistant material. Chromates, phosphates, and molybdates are a few examples of corrosion inhibitors widely used to assist in passivation. However, many of these traditional inhibitors pose risks to human health and the environment. Sustainable alternatives to traditional passivation inhibitors include the use of organic compounds such as amino acids, polyphenols, and carboxylic acids, as well as non-toxic metals such as zinc and aluminum (Jaddoa et al., 2025,S Hussein et al., 2023).

Film formation process

Film inhibitors protect the metal surface from corrosion by forming a protective layer. The formation of these coatings may result from the physical adsorption of the inhibitor onto the metal surface, as well as from chemical interactions between the inhibitor and the metal surface. Examples of sustainable film inhibitors include chitosan, cellulose, and natural and synthetic polymers such as polyvinyl alcohol and polyurethane. On metal surfaces, these polymers provide durable coatings that ultimately prevent corrosion(A. Alamiery et al., 2022).

Adsorption process

Adsorption inhibitors prevent corrosion by adhering to the metal surface and forming a barrier. These inhibitors typically contain functional groups such as amino, carboxyl, or hydroxyl groups that can interact with the metal surface. Natural materials such as tannins and lignin, as well as synthetic materials such as thiourea, imidazole, and benzotriazole, are examples of sustainable adsorption inhibitors. In addition to being non-toxic and environmentally safe, these inhibitors provide effective corrosion prevention(Betti et al., 2022).

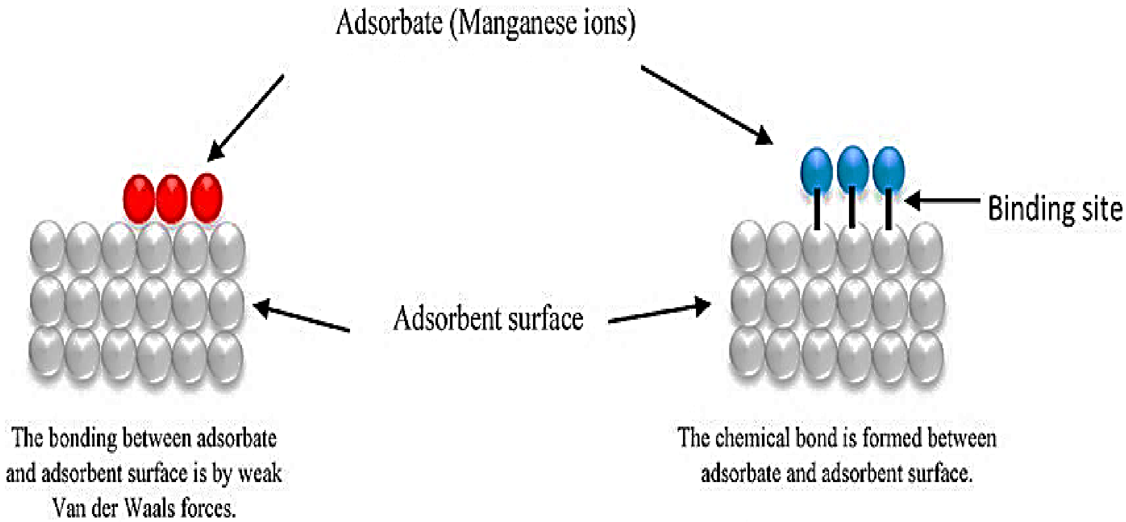

Fig. 3. Chemical and physical adsorption mechanisms of inhibitors a: physical adsorption, b: chemical adsorption(Al-Amiery, Isahak, et al., 2023)

Evaluation of Corrosion Inhibitors

Potentiodynamic polarization method

Tafel curves, sometimes known as Potentiodynamic polarization (PDP) diagrams, are an essential and important tool for analyzing inhibition processes and estimating corrosion rates using voltage and current data. These diagrams provide an efficient and reliable method for studying corrosion, allowing the calculation of cathodic reduction and anodic oxidation rates. The equivalent current density can be calculated by extending the linear segments of these curves to their intersections. The anodic Tafel slope (ba), cathodic Tafel slope (bc), corrosion potential (Ecorr), and corrosion current density (icorr) are important parameters that can be determined using the Tafel extrapolation technique(Al-Amiery, Isahak, et al., 2023). These factors help understand the characteristics of the corrosion process and assist in studying inhibition strategies using organic, inorganic, and environmentally friendly inhibitors. The presence of a corrosion inhibitor alters the polarization behavior of a metal electrode. The polarization curves resulting from efficient inhibitor action show a shift towards more positive (less active) potentials than those from inefficient inhibitor action, and the current values appear lower. This modification indicates a lower corrosion rate and better protection effectiveness(Yang et al., 2021). Equation 1 illustrates the Tafel law for representing the corrosion rate and how variables depend on each other when calculating the corrosion rate. Two important variables are the change in equivalent weight and the current density. Figure 4 shows the Tafel curves plotted for evaluating an environmentally friendly corrosion inhibitor based on nano-silica extracted from natural sand, both with and without varying amounts of inhibitor concentration in an acidic 1M HCl medium(Walczak et al., 2019).

CR (mpy) = (0.13×EW×icorr)/d 1

Where: icorr is the corrosion current, d is density (μA/cm^2) and EW is the equivalent weight (gm/mol).

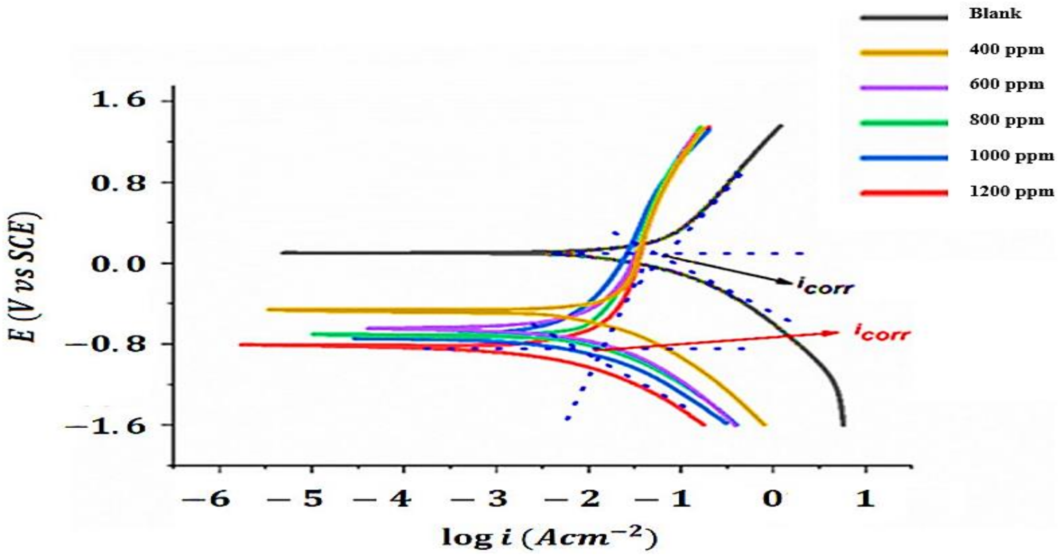

Fig.4. Tafel curves for testing a corrosion inhibitor based on using nano silica from natural sand in 1M HCl medium(Yang et al., 2021).

Analysis of the tafel curve

The Tafel curve is constructed with polarization data. An alternating electrical potential is supplied to a metallic specimen in an electrochemical environment, and the resultant current is then measured. Plotting the correlation between the potential difference and the logarithm of the current density elucidates the behavior of the anode and cathode, hence enhancing the comprehension of the reaction process.

1. Cathodic region: Denotes the reaction occurring during the reduction of ions, exemplified by the reduction of oxygen or hydrogen.
2. Anodic region: Represents the reaction responsible for the metal's oxidation, which is the principal factor in the corrosion process.
3. The intersection of the two curves: Ecorr, denoting the voltage at which typical corrosion transpires, and icorr, indicating the corrosion rate.

The significance of the tafel curve in corrosion research

The Tafel curve is used to assess the efficacy of inhibitors. The comparison of icorr before and after the addition of the inhibitor helps ascertain its efficacy in reducing the corrosion rate. It is used to ascertain the response mechanism, whether cathodic or anodic control, hence aiding in the selection of suitable protective techniques. In short, the polarization method is the most professional way to evaluate the inhibitory factor(Liu et al., 2019).

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful non-destructive technique for determining the impedance of a metal in the presence of a corrosion inhibitor. Using this technique, the impedance of a metal inhibitor system is determined by measuring the current response generated by applying a small sinusoidal voltage to the metal surface. By measuring the complex impedance of the system, EIS provides comprehensive insights into the corrosion process, including the effects of different inhibitors, corrosion rates and processes, and interactions between inhibitor molecules and the metal surface. This technique can be applied in both basic and acidic environments. The effectiveness of inhibitors can be tracked over time and can identify potential defects in protective coatings. In addition to its use in the design of corrosion-resistant materials and coatings, EIS is widely used in corrosion studies and inhibitor development. As a result, electrochemical impedance spectroscopy (EIS) is a flexible and successful approach for investigating and inhibiting corrosion in metallic systems. An electrolyte solution coupled with a constant phase element (CPE) and an RCT, which simulates a metal substrate, adsorbed inhibitors, and electrolyte solution, is used to demonstrate a typical EIS measurement. Figure 4b shows the evaluation of a corrosion inhibitor based on nano silica extracted from natural sand, which was prepared in the laboratories of the Department of Chemical Engineering, University of Babylon, using EIS technique(Silvestru et al., 2021). Figure 5. illustrate Nyquist plot and electrochemical impedance curves of the natural sand-derived nano-silica inhibitor.

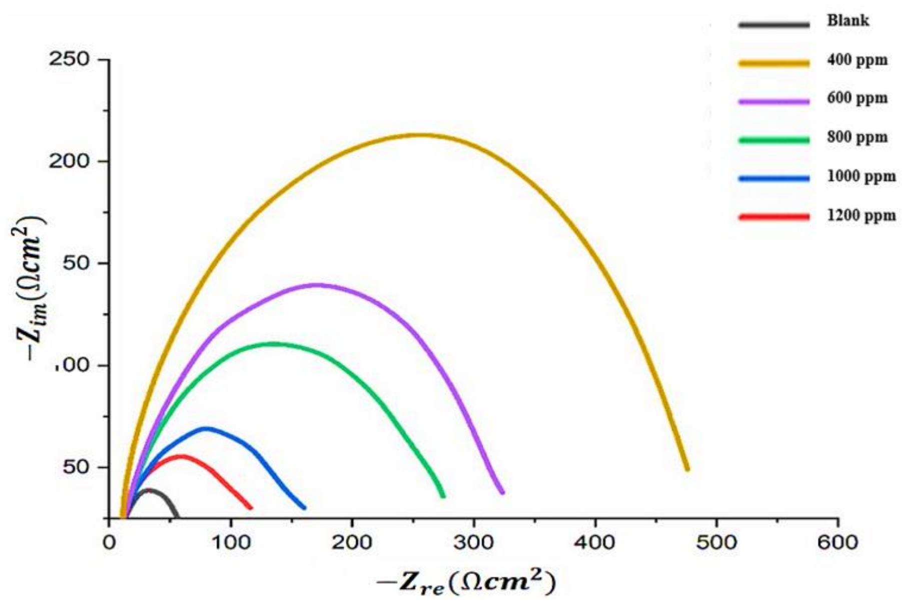

Fig. 5. Nyquist plot, electrochemical impedance curves of the natural nano-silica inhibitor(rehackova et al., 2021).

The Nyquist plot is a crucial instrument in electrochemical impedance spectroscopy (EIS). It is used to comprehend the corrosion characteristics and electrical qualities of materials. The horizontal axis represents the real component of electrical resistivity, while the vertical axis denotes the imaginary component. Data are presented as semicircular curves or curves with defined slopes.

Interpretation of the curve

1. General Shape of the Curve - The Nyquist curve often manifests as a semicircle in most systems subject to corrosion or featuring corrosion-resistant coatings. An increased radius of the circle correlates with elevated polar resistance signifying enhanced corrosion resistance performance(Silvestru et al., 2021).
2. Impact of Concentration on the Curve
3. The Nyquist curves seen in the picture you provided vary with differing additive concentrations.
4. the raising the concentration results in an expansion of the circle's radius, signifying enhanced corrosion resistance of the material.
5. At the maximum concentration (400 ppm), the polar resistance exceeds that of lower concentrations, suggesting that this substance may serve as an efficient corrosion inhibitor.
6. Examination of Resistance and Surface Interactions
7. Surface resistance (Rs) is ascertained at the juncture where the curve contacts the horizontal axis.
8. Polar resistance (Rct) is derived from the diameter of the semicircle and indicates the material's capacity to withstand the electrochemical reactions that cause corrosion.
9. The introduction of nanoparticles or corrosion inhibitors alters this behavior, enhancing surface stability.

The significance of the nyquist curve in scientific inquiry

- It aids in comprehending corrosion behavior in various situations, including acidic and alkaline conditions.
- It is used in the formulation of intelligent corrosion-resistant materials, including polymeric coatings and nano inhibitors.
- It offers insights into the electrochemical processes at the surface, enabling researchers to formulate precise mathematical models for response analysis.

Weight Loss

The effectiveness of corrosion inhibitors under various conditions is typically evaluated using weight loss (WL) methods. Unlike more sophisticated techniques such as dynamic polarization and EIS, weight loss analysis is a simple and cost-effective method that provides a gravimetric assessment of the corrosion rate as well as a realistic simulation of corrosion conditions in each application. A key part of the weight loss approach involves exposing metal samples to a corrosive environment under controlled conditions for a specified period. The traditional procedure for preparing and analyzing a metal sample involves several steps. The sample is first sanded with sandpaper to prepare it for testing. Acetone is then used to remove any remaining residue after drying and cleaning it with double-distilled water. A scale with a sensitivity of ±0.0001 g is used to estimate the sample weight for measurements before and after immersion. The proposed technique involves immersing the metal sample in a variety of test solutions for a specified period at a predetermined temperature. This technique uses inhibitors of varying concentrations. The sample is cleaned, dried, and weighed again after the experiment. To ensure accuracy, it is recommended to conduct tests three times, considering the average values. Equation (2) is used to calculate the corrosion rate (CR) for each condition by comparing the sample weight before and after immersion(Alkadir Aziz et al., 2021).

$$\text{Corrosion rate (CR)} = (534 \times \Delta W)/ (d \times A \times t) \qquad 2$$

Where: A is the sample surface area (in^2), T is the exposure time (hours), d is the sample density (gm/cm^3), ΔW is the weight loss rate (gm), and CR is the corrosion rate per year (mpy)(A. Alamiery, 2021).

Summary of Corrosion Inhibitor Evaluation Techniques

Corrosion detection and monitoring is critical in many industrial sectors to prevent infrastructure damage, equipment downtime, and address existing corrosion challenges. Electrochemical polarization, resistivity, and weight loss are examples of electrochemical techniques that provide a rapid and non-destructive method for measuring corrosion and evaluating inhibitor effectiveness. Problems such as corrosion byproducts and surface roughness can reduce the effectiveness of these techniques. Atomic fluorescence microscopy and scanning electron microscopy (SEM) are two additional examples that provide high-resolution images for examining corrosion rates and surface topography. Spectroscopic methods, such as XPS and infrared spectroscopy, support the identification, evaluation, and characterization of inhibitors, providing comprehensive information about the molecular structure and chemical changes on material surfaces. Computational studies using DFT and MD models, which also predict the thermodynamics and kinetics of corrosion processes, can provide a better understanding of the atomic-level interactions between inhibitors and metal surfaces. Integrating electrochemical, microscopic, spectroscopic, and computational methodologies from various fields enables researchers and engineers to gain a comprehensive understanding of corrosion processes. This multidisciplinary approach facilitates the optimization of inhibitor formulations, careful material selection, and the development of more effective corrosion prevention solutions.

CONCLUSIONS

This review provides a comprehensive understanding of corrosion and its resistance using both organic and inorganic inhibitors, as well as environmentally friendly corrosion inhibitors. It covers several analytical techniques, such as electrochemical induction, current impedance, and weight-loss techniques, as well as case studies and research on corrosion inhibition, highlighting the growing trend toward using environmentally friendly inhibitors instead of synthetic ones. The study enhances our general knowledge of corrosion and inhibitor-based corrosion resistance. There are still certain gaps to be filled, such as improving existing corrosion inhibitors and attempting to reduce their adverse environmental effects; establishing concepts for synergistic inhibition mechanisms using complex inhibitors; guiding the development of more effective corrosion mitigation technologies using fundamental knowledge gained from elucidating the complex relationships between inhibitors and their impact on the development of protection and the interaction between anodic and cathodic processes; creating multilayer inhibitors using the concept of synergistic inhibition to form multilayer inhibitory structures on metal surfaces; searching for environmentally friendly corrosion inhibitors as alternatives to traditional inhibitors that have harmful effects; and creating fast-acting, multifunctional, and intelligent inhibitors that not only stop corrosion but also address other surface-related issues such as corrosion resistance and self-healing.

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