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Development of corrosion inhibitors and nanocontainers for self-healing epoxy coatings: A review

Joghee Manivannan[1] and **Kalaiselvan Shanmugam**[2*]

[1]Department of Chemistry, V.S.B. College of Engineering Technical Campus, Coimbatore, Tamil Nadu, India

[2]Department of Chemistry, Rathinam Technical Campus, Coimbatore, Tamil Nadu, India

Abstract

Self-healing coatings are composed of anti-corrosive polymers that can recover from any damage caused to the coating film and regain their original performance. One of the methods for preparing self-healing coatings is by incorporating a healing agent stored in nanocontainers. When there is damage to the coating film, the nanocontainer ruptures due to the mechanical impact. It releases the healing agents, which form a protective film via polymerization over the damaged part, thereby protecting against corrosion. The second method for preparing self-healing coatings involves the embedment of corrosion inhibitors (healing agent) into a nanocontainer. Upon damage, the inhibitor is released into the exposed part of the film and retards corrosion reactions occurring at the defective part of the metal surface. The two components responsible for the self-healing functions are the nanocontainers and the corrosion inhibitors (polymerizable material). This article provides a detailed report on the development of several types of corrosion inhibitors and nanocontainers, their properties, and applications as self-healing coating materials, including their advantages and limitations.

Keywords: Epoxy resin; Corrosion inhibitors; Nano materials; Polymerization; Biomaterials

***Corresponding author:**
Kalaiselvan Shanmugam
(kalaiselvan.sh@rathinam.in)

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1. Introduction

Paints and organic coatings have become a key method for protecting against corrosion in equipment, machinery, and large metal structures across various fields. The binder is the major ingredient of paint, and there is a wide range of synthetic resins available for the coating industry. Modern synthetic resins comprise polymers with a wide range of molecular weights, including alkyd, amino, vinyl, acrylics, epoxies, polyurethanes, silicones, nitrocellulose, and chlorinated rubbers. Epoxy resins are one of the important classes of synthetic resins that provide high chemical and corrosion resistance. The epoxy resin is widely used as a coating material due to its easy conversion into high molecular weight products upon reacting with a curing agent through its terminal epoxy or hydroxyl groups (or both). There is a wide variety of curing agents available, and the choice of curing agent depends on the end-application requirement. The coating protects metal structures against corrosion, but the coating surface can be damaged externally, making them susceptible to corrosion due to the easy permeation of water, oxygen, and other ions through these damaged sites. Recently, coating systems with the capability to repair damage internally and recover their coating properties have been developed.[1] These self-healing coating systems utilize self-healing materials that respond to external damage and retard corrosion.[2-4]

There are types of self-healing coatings commonly reported. The first type of self-healing coating involves microcapsules (loaded with polymerizable components) dispersed in the coating film. The polymerizable components are released when the coating film is damaged, and this disrupted region is healed through polymerization reactions.[5-7] The second type of self-healing coatings involves loading micro/nanocontainers with corrosion inhibitors, which are released to the damaged region in a controlled manner, protecting the surface.[8-10] This self-healing action of coatings with nanocapsules occurs through various methods, for example, controlled release of inhibitor by desorption, pH-controlled release, ion exchange, and mechanical rupture.[11] The mechanism of self-repair in coatings by external stimuli is displayed in Figure 1.

This review covers some of the important classes of corrosion inhibitors and nanocontainers used to carry the inhibitors. The important factors considered for choosing the inhibitors are based on the compatibility of the material with the coating matrix, its ability to be encapsulated, and its inhibitor efficiency. In contrast, the factors considered for nanocontainers are the type of inhibitor used, the healing mechanism, and the ability to release the inhibitor in a controlled manner when triggered by specific stimuli. The investigations on these inhibitors and nanocontainers presented in this review were selected based on the intrinsic advantages these self-healing materials have over similar functional materials. The inhibition mechanism and effectiveness of each type of corrosion inhibitors and nanocontainers to function as self-healing coatings for repairing damaged coating films are also discussed.

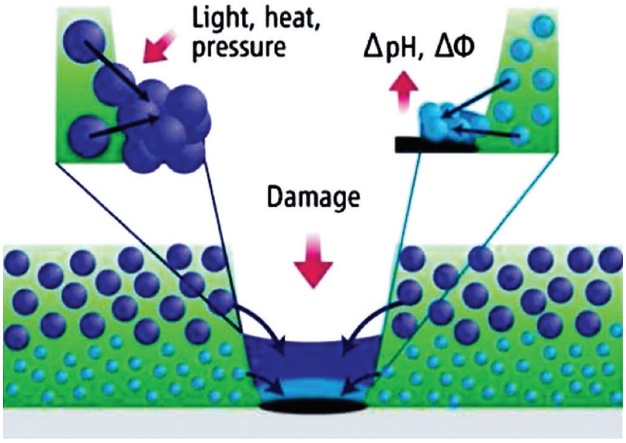

Figure 1. Self-healing mechanism. Reproduced with permission from ref.[1]

2. Nanocontainers

2.1. Inorganic nanocontainers

Nanocontainers are used to encapsulate inhibitors, protecting them and enabling controlled release into the damaged part of the coating. Inorganic nanocontainers are preferred due to their environmental friendliness; in contrast, polymeric nanoparticles generally possess lower mechanical stability. Hence, research focus has shifted to the use of inorganic nanoparticles. Various inorganic nanoparticles have been used as nanocontainers for self-healing coatings, including nanoparticles, nanotubes, and nanomaterials with porous nanostructures.

2.1.1. Mesoporous silica

The commonly used mesoporous inorganic materials for nanocontainers include mesoporous TiO_2, ZrO_2, and silica. Among these materials, mesoporous silica particles are not reactive with the corrosion inhibitors, stable under ultraviolet light, and have a large pore volume and surface area to incorporate a higher quantity of inhibitor.[12] It is reported that the inhibitor-loaded silica nanoparticle could be modified with octyl group functionalization to enhance its dispersibility in oil-based coatings.[13] However, corrosion inhibitor encapsulated in mesoporous silica nanocontainers could be released prematurely, necessitating the development of novel nanocontainers with controlled pore opening/closing at a molecular level. This could be achieved by functionalizing silica nanoparticles with organic substances (e.g., en-triacetate, ethylenediamine).[14] Mesoporous silica nanocontainers functionalized with organic groups have been reported to be excellent anti-corrosive containers for encapsulating inhibitors.

2.1.2. Halloysite nanotubes

Halloysite nanotubes are potential inorganic nanocontainers that are natural and inexpensive. These are 2:1 layered aluminosilicates with hollow tubular structures. The inner halloysite lumen has an inhibitor loading capacity of up to 20 wt%, depending on the origin of halloysite. The loading capacity can be increased by 2–3 times when the alumina within halloysite lumen is etched with sulfuric acid.[15] The dispersion of inhibitor-loaded halloysite nanotubes requires intensive mixing to avoid aggregating the nanocontainers. Shchukin and Mohwald[16] reported that halloysite nanotubes containing inhibitors were covered by a layer-by-layer assembly of polyelectrolyte cell, which facilitates precise controlled release of inhibitors.

Several other inorganic nano clay containers have been studied, such as Kaolin, montmorillonite, bentonite, and graphene oxide.[17] The key characteristics assessed are eco-friendliness and safety concerns, and these are primarily dependent on particle size and chemical composition. The biosafety of several nanocontainers is presented in Table 1. The presented order suggests that halloysite nanotubes are the safest among all inorganic nano clay nanocontainers.

2.2. Nanocontainers with layer-by-layer assembled shell

The layer-by-layer assembly method is a new approach where oppositely charged molecules are adsorbed on a flat surface. The technique allows for proper control over the film thickness of the multilayer and composition. The technique has been applied first to silica nanoparticles by coating with layers of polyethylene imine and polystyrene sulfonate, and the corrosion inhibitor is entrapped within the polyelectrolyte multilayer; pH changes during corrosion initiate the release of the entrapped inhibitor.[18]

The layer-by-layer assembly technique for self-healing assembly has been further modified with the formation of core-shell-type containers with core oil and polyelectrolyte shell. It has been observed that the layer-by-layer coated emulsion improved stability toward droplet aggression, and the interfacial layer improved its resistance to rupture.[19,20] The prospect of customizing the functionality of the shell is the major advantage of the layer-by-layer assembly approach. However, the approach is challenged by the poor mechanical strength of the shell, making it difficult to maintain the integrity of the dried coating films.

Table 1. Biosafety ranking of nanocontainers

Safety number	Nanocontainers	Origin/type	Biocompatibility
1	Halloysite	Aluminosilicate nanotube	Generally good and safest
2	Kaolin	Aluminosilicate (Kaolinite)	Moderate to good
3	Montmorillonite	Smectite clay (layered)	Good biocompatibility
4	Silica (amorphous)	Non-crystalline silicon oxide	Generally good (amorphous)
5	Bentonite	Mostly montmorillonite-based	Similar to Montmorillonite
6	Graphene oxide (GO)	Carbon-based 2D nanomaterial	Variable (dependent on oxidation and size)

Note: Safety numbers are presented as follows: 1 represents the highest safety; 6 represents the lowest safety.

2.3. Nanocontainers with polymer shell

Nanocontainers with an organic shell (polymer shell) are prepared by oil-water emulsion polymerization. Though these shell structures are not as controlled as the layer-by-layer assembled shells, they have better mechanical strength. These nanocontainers are responsive to local pH changes. A research study revealed that a polymer shell nanocontainer made from urea formaldehyde and encapsulated with linseed oil effectively healed a damaged site on an epoxy coating.[21] Linseed oil from the organic shell was released and formed a protective film on the damaged part of the film.

A bilayer nanocapsule made with a hydrophilic inner shell and a hydrophobic outer shell could load amine-type corrosion inhibitors.[22] The amine released from the nanocapsules as a self-healing coating enhanced the corrosion resistance of the coating film.

The organic polymer shell nanocontainer forms an effective self-healing material for water-borne coatings to protect steel and aluminum alloys. However, it has limited applications to oil-based coatings due to the dissolution of these shells in organic solvents. Thus, both organic and inorganic nanocontainers are developed for the encapsulation of various corrosion inhibitors for self-healing anticorrosion coatings.

3. Inhibitors

Metal corrosion develops due to a disruption in the protective coating layer and propagates faster from the damaged part. Considerable investigations have been carried out to arrest corrosion at the damage site through self-healing with corrosion inhibitors (organic or inorganic) encapsulated in micro/nanocontainers. These inhibitors retard the reaction between metals and the environment by either adsorption of the molecules onto the metal surface or by altering the anodic or cathodic reaction. The performance of several common organic inhibitors in different corrosive media is described below.

3.1. Organic corrosion inhibitors

Organic compounds contain oxygen, nitrogen, and sulfur atoms and act as corrosion inhibitors due to their higher basicity and electron density. These atoms become the active centres for adsorption on the defective surface, and their efficiency follows the order: Oxygen < nitrogen < sulfur < phosphorus atoms. The lone pair electrons and p-electrons in inhibitors are involved in electron transfer to the metal surface, forming coordinate covalent bonds.

Heterocyclic compounds with sulfur and nitrogen having various substituents form effective corrosion inhibitors. The physicochemical properties and chemical structure of the inhibitor compound (e.g., electron density at the donor atom, p-orbital character, the functional group) and electron structure of the molecule determine the efficiency of the inhibitor. Replacing a hydrogen atom in the carbon in the ring with a functional group (-NO_2, -CHO, or -COO) would enhance its inhibition.[23] The nature of the binding between metal and organic inhibitor molecules determines the corrosion inhibition performance of the protective layer formed. Therefore, more active sites in the heterocyclic parts provide a stronger inhibitor-adsorption shield through chelation on the metal surface.[24] At the point of attachment, the electron density increases, consequently decelerating anodic or cathodic reactions. The electrons are absorbed by the cathode, regulating the anodic oxidation or corrosion.

The derivatives of thiophene, hydrazine, and pyrrole effectively inhibit metal corrosion in acidic solutions. However, these inhibitors are relatively toxic, thereby limiting their application as anticorrosive coatings and primers. Organic compounds containing heteroatoms in the conjugated system are an alternative to the above inhibitors (Table 2).

Synthetic organic inhibitors are widely studied for their inhibition efficiency, including 8-hydroxyquinoline, benzotriazole, 2-mercaptobenzothiazole (MBT), mercaptobenzoimidazole, and polyaniline. MBT and mercaptobenzoimidazole have reportedly improved corrosion resistance when incorporated into montmorillonite nanoparticles.[22,25] MBT and mercaptobenzoimidazole form a thin protective layer on the damaged metal surface during the self-healing process. Benzotriazole, as a corrosion inhibitor, is adsorbed on the metal surface and provides anodic inhibition.[26] 8-Hydroxyquinoline, a chelating agent, acts as a cathodic inhibitor for aluminum in neutral chloride solution by forming poorly soluble chelate complexes.[27]

Table 2. Types of organic corrosion inhibitors

Type of inhibitors	Examples
Nitrogen-containing compounds	Amines, pyridine derivatives, quaternary ammonium salts, triazole derivatives, Schiff base, amino acids, and indazole
Nitrogen- and sulfur-containing compounds	Imidazole derivatives, thiadiazole derivatives, and thiazole derivatives
Nitrogen- and oxygen-containing compounds	Oxazole derivatives, phthalimides, and plant extracts/natural
Sulfur-containing compounds	Thiourea derivatives and sulfonates

3.2. Important organic corrosion inhibitors

3.2.1. Indole-3 butyric acid (IBA)

Various corrosion inhibitors provide improved corrosion resistance, as they are more ductile with less stress tension. These inhibitors are classified according to their inhibition mechanism and composition.[28] The inhibitive and healing efficiency are determined using the scanning vibrating electrode technique and electrochemical impedance spectroscopy (EIS). Hang *et al.*[29] studied clay modified with IBA and observed enhanced corrosion resistance due to increased inhibitive action of IBA at the carbon steel surface by the enhanced barrier properties. Therefore, the self-healing property of the IBA-modified clay improves protection against corrosion. This has been confirmed by polarization curves, whereby IBA acts as an anodic inhibitor for carbon steel; local electrochemical impedance measurements on a scratched sample were in agreement with the findings.

3.2.2. Polyaniline

In general, larger molecules with a bulky structure cover more area on the electrode surface. In addition, they possess chemisorptive properties, as they contain nitrogen atoms in the polymer chain. These nitrogen atoms provide a reactive site for chemisorption, which further enhances the inhibition. Due to their stability and lower cost, these conducting polymers are widely investigated. The presence of large pi-electron clouds and quaternary nitrogen atoms confers inhibitive properties.[30,31] In its conductive state, polyaniline displaces the electroactive interface from its usual location and retards corrosion. The mechanism of corrosion inhibition of polyaniline begins with iron being oxidized, along with simultaneous electron release. Metal dissolution due to the initiation of corrosion causes a cathodic shift of the potential, which induces the reduction of polyaniline and transfer of the stored positive charge in its oxidized form to the defect site. This action forms a passive layer of metal oxide, which retards the propagation of corrosion.[32]

Han *et al.*[33] investigated the self-healing anti-corrosion properties of polyaniline/epoxy copolymer-urea-formaldehyde microcapsule coatings on rusty steel sheets. The polyaniline/epoxy copolymer, as a core material, at the ratio of 0.05:1 (wt.%), exhibited the highest electrochemical resistance to corrosion. The microcapsule (15 wt.%) within the coating provided excellent corrosion resistance due to the self-healing action. It was inferred that the polyaniline/epoxy copolymer-containing microcapsule system acts as an effective anticorrosion coating and could be applied directly onto rusty steel surfaces.

3.2.3. 8-Hydroxyquinoline

Various studies have been conducted on the application of quinoline derivatives as corrosion inhibitors in acidic media.[34] Among these, 8-hydroxyquinoline has been reported as an outstanding complexing agent.[35,36] 8-Hydroxyquinoline is a good bidentate-complexing agent, which can form four and six covalent complexes with many metal ions. Based on this, 8-hydroxyquinoline has been used specifically for metal corrosion protection. Recent studies have revealed that 8-hydroxyquinoline is a mixed-type inhibitor of aluminum corrosion and forms complexes with copper and aluminum.[37] The inhibition process is formed by this complex formation with dissolved metals, enabling barrier film formation to retard further corrosion.

8-Hydroxyquinoline functions as an effective corrosion inhibitor for high-strength pipeline steel in 15% HCl solution.[36] It forms a protective surface film through adsorption by acting as a mixed-type inhibitor. The inhibitive efficiency increases with increasing concentrations of 8-hydroxyquinoline and is further enhanced upon the addition of potassium iodide (KI). The heteroatoms present in hydroquinone complexes with iron ions, forming a protective film.

3.2.4. Benzotriazole

Benzotriazole is a renowned corrosion inhibitor that forms a protective layer on metal surfaces through covalent and coordinate bonds. It is also used in combination with other corrosion inhibitors to enhance inhibition efficiency.

The corrosion inhibition efficiency of benzotriazole on carbon steel used as reinforcement in concrete has been studied.[38] To imitate marine environments, the effect of benzotriazole (1.5 wt.%) on the corrosion resistance of carbon steel of a matured concrete, along with the addition of 3.5 wt.% NaCl solution was studied. The investigation was carried out using potentiodynamic polarization tests and EIS. Compared to the nitrites used for inhibiting corrosion of reinforcement steel in concrete, benzotriazole addition displayed better inhibitor efficiency; hence, benzotriazole can be a desirable and attractive alternative to nitrites.

In one study, 1,2,3-benzotriazole was incorporated into an acrylic coating that was applied onto cold-rolled mild steel in an acidic medium (H_2SO_4 solution); further testing of the organic corrosion inhibitor revealed that there was no corrosion progression on the coated film even after 30 days of exposure of the coated substrate.[39] The study was conducted with different concentrations of benzotriazole, and 0.1 wt.% benzotriazole in acrylic coating reported the best corrosion protection.

3.2.5. Mercaptobenzothiazol

Several studies have been conducted to investigate the efficiency of corrosion inhibition of 2-MBT on various metals, including copper, aluminum alloy, and carbon steel. The studies have indicated that the heterocyclic compound 2-MBT is a good corrosion inhibitor on these metals.[40,41]

Copper-based alloys (primarily Cu-Ni) find extensive use across various fields of applications in industries. The performance of 2-MBT and its inhibition efficiency on Cu-Ni alloys in a corrosive environment (with 3 wt.% NaCl solution) was evaluated using weight loss methods, potentiodynamic polarization, and EIS. It was observed that MBT enhances the corrosion resistance of copper-based alloys; at 80 ppm, the maximum inhibition was approximately 92%. Furthermore, 2-MBT functioned as a mixed-type inhibitor. The nitrogen and exocyclic sulfur atoms of 2-MBT are adsorbed on the metal surface, forming a thin film that inhibits corrosion.[42]

Another study evaluated the inhibitive efficiency of 2-MBT in 5% HCl solution on aluminum and aluminum–titanium alloys.[43] EIS and Tafel polarization were employed to assess varying concentrations of 2-MBT and temperatures. It was found that 2-MBT exhibited good anticorrosive properties on aluminum and aluminum–titanium alloys. As the concentration of 2-MBT increased, inhibition efficiency enhanced as well. Conversely, inhibition efficiency decreased with increasing temperature.

3.2.6. Mercaptobenzimidazole

Benzimidazole, a heterocyclic compound, and its derivatives are regarded as good corrosion inhibitors for many metals and their corresponding alloys, even in highly corrosive environments (both acidic and basic media) and salt solutions.[44] Benzimidazole and its derivatives behaved as mixed-type inhibitors, with the inhibitive effect more evident towards cathodic reactions over anodic reactions.

The inhibition efficiency of imidazolium-based inhibitors on mild steel in H_2SO_4 was studied recently.[45] The corrosion inhibition performance indicated that the molecular modification of benzimidazole led to enhanced corrosion inhibition. Theoretical molecular modelling methods have helped develop potential corrosion inhibitors. The mechanism for the corrosion protection of benzimidazole and its derivatives is attributed to the presence of pi-electrons on the planar-fused moiety and non-bonding lone pair electrons on the heteroatoms.

Obot *et al.*[46] studied the corrosion inhibition performance of 2-mercaptobenzimidazole on iron, copper, and aluminum surfaces. The study revealed higher inhibitor efficiency of 2-mercaptobenzimidazole (MBI) on steel compared to aluminum and copper. EIS measurements indicated that benzimidazoles are readily adsorbed, and the thin layer formed on the metal surface provides a physical barrier, which inhibits charge transfer reactions at the metal-solution interface. Benzimidazole derivatives are regarded as mixed-type inhibitors, exhibiting better inhibitive effect on cathodic reactions over anodic reactions. Furthermore, adsorption of the inhibitors on the metal surface to protect the metals was also confirmed by scanning electron microscopy images. The study also reported that benzimidazoles exhibit high inhibition efficiencies of up to 99% in concentrated HCl or H_2SO_4 solutions at different temperatures.[47] The inhibiting properties observed at different temperatures presented a marginal decrease in inhibition efficiency with increasing temperature.

However, the disadvantages of using synthetic organic inhibitors have limited their scope of application, necessitating the development of cost-effective, non-toxic products or natural green inhibitors.

3.3. Green inhibitors

Due to changes in environmental laws and the awareness of environmental issues, the research focus has shifted from conventional corrosion inhibitors towards environmentally friendly green inhibitors. These natural products contain a range of active substances that can bind to organic compounds, subsequently adhering to metal surfaces and forming a film layer to protect against corrosive elements. As natural extracts contain abundant active elements, a wide range of corrosion inhibitors can be produced from these extracts. For instance, natural extracts containing a mix of phytochemicals and functional groups have an affinity to adsorb onto metal surfaces. These natural extracts are non-toxic and biodegradable, making them the preferred option as corrosion inhibitors in organic coatings.[48]

A handful of studies have investigated the inhibition effect of naturally occurring materials in both acidic and alkaline conditions. The extract of *Delonix regia* was found to inhibit metal corrosion in HCl solutions. In addition, higher concentrations of the inhibitor are associated with enhanced inhibition efficiency. However, inhibition efficiency decreases with longer exposure time when tested on aluminum in HCl solutions.[49] Rosemary leaves (*Rosmarinus officinalis*) have been studied as corrosion inhibitors on aluminum-magnesium alloys in a 3% NaCl solution; the presence of flavonoids in the extract enhanced the passivating film properties of the steel.[50]

El-Etre[51] studied the corrosion inhibition property of natural honey on carbon steel and reported that natural honey exhibited a remarkable corrosion inhibition in high saline water. Although the inhibition efficiency increased with increasing natural honey concentration, the inhibition efficiency decreased over time due to fungal growth in the medium. He investigated the corrosion inhibition efficiency of *Opuntia* extract on aluminum; the efficiency of inhibition increased with increasing concentration of the extract.[52] A separate study assessed the corrosion inhibition efficiency of khillah seed extract on SX 316 steel in HCl solution; the inhibition mechanism is attributed to the formation of insoluble complexes from the interaction of iron cations with khellin.[53]

Ebenso *et al.*[54,55] investigated the corrosion inhibition of aluminum and mild steel using ethanolic extracts of African bush pepper, *Carica papaya* leaves, and neem leaves (*Azadirachta indica*). The concentration and temperature of the extracts have a direct correlation with inhibitor efficiency; *C. papaya* exhibited maximum inhibition at 30°C, whereas *A. indica*'s performance peaked at 40°C.[56] Zucchi and Omar[57] observed reduced corrosion in steel using various plant extracts, with an efficiency of 88–96% in 1 N HCl and a marginally lower efficiency in 2 N HCl. It was reported that the protein content of these plants is hydrolyzed into products with inhibitory properties. Another study investigated the corrosion inhibition capacity of honey and *R. officinalis*[58]; the inhibitive effect of these compounds increased when zinc was polarized by the addition of salts, such as NaCl and Na_2SO_4. Likewise, the electronegativity of halide ions enhances inhibition efficiency, suggesting a significant role in the surface adsorption process.[59] In another study, guar gum, a polysaccharide compound, has been used as a corrosion inhibitor for carbon steel,[60] reportedly enhancing the efficiency of corrosion inhibition. The inhibitive property of guar gum is attributed to its horizontal adsorption on the steel surface, and it follows the Langmuir adsorption isotherm. Okafor *et al.*[61,62] studied the extracts of onion (*Allium sativum*), *C. papaya*, *Garcinia kola*, and *Phyllanthus amarus* for their corrosion inhibition efficiency; the results suggest that these extracts served as good corrosion inhibitors through chemical adsorption on the metal surface.

A large number of studies have been carried out using the extracts of natural honey, jojoba oil, Artemisia oil, *Telfaria occidentalis*, *Ocimum viridis*, *A. indica*, *Sanseviera trifasciata*, and rosemary for their anti-corrosion properties.[63-69] The results indicate that these extracts inhibit the corrosion process in both acidic and basic solutions; inhibition efficiency increased with increasing concentrations of these extracts. Similarly, the inhibition efficiency of *Musa* peel and *Punica granatum* extract was evaluated.[70,71]; the inhibition efficiency of *P. granatum* extract increased with increasing concentration but decreased with increasing temperature and time. Nonetheless, most of these studies are limited to steel, and only a few studies have used aluminum and copper.

The corrosion inhibition efficiency of natural plant extracts has been tested mostly in mildly acidic or basic solutions at varying concentrations. Hence, natural plant products have great potential to serve as a corrosion-inhibiting material, effective in preventing metal corrosion and comparable to organic inhibitors. Although natural plant extracts are environmentally safe, inexpensive, and derived primarily from renewable sources, further research is warranted to study the inhibition efficiency of plant extracts under varying conditions, their compatibility with different coating systems, and their effectiveness in different substrates.

3.4. Drugs as green corrosion inhibitors

In the virtual screening method, results from corrosion studies of drugs have indicated that the substructures of drugs share many similarities with general corrosion inhibitors.[72] Five- and six-membered rings of heterocyclic and carbocyclic systems are commonly found in drug structures, and most of these compounds are aromatic. Hence, heterocycles and substituted benzene rings, such as furans, thiophenes, pyridines, isoxazoles, and imidazole, commonly occur in drug structures. The effectiveness of a corrosion inhibitor depends on its molecular structure, chemical composition, and binding affinity to the metal surface. Owing to their high molecular weight, compounds containing heteroatoms (O, S, or N) with lone-pair electrons and aromatic rings can enhance adsorption onto the metal surface, particularly at damaged sites to prevent corrosion.[73]

There is great potential for further exploration, as these compounds are environmentally friendly. Over the past two decades, several research investigations have been carried out on the use of a wide range of drugs as corrosion inhibitors. The drugs investigated so far are predominantly hydrophilic and biodegradable. However, since the transformation products of some drugs may be highly hazardous to the environment, more studies are required before any drug can be considered truly eco-friendly when evaluating its suitability as a green corrosion inhibitor.

4. Conclusion

In this review, we discussed some of the most important classes of organic corrosion inhibitors and highlighted their observed improvements in corrosion resistance. Most organic inhibitors investigated have been found to adsorb onto metal surfaces, forming a protective barrier coating. The availability of non-bonding electrons and pi-electrons in the inhibitor molecules facilitates electron transfer from the inhibitor to the metal, and the efficiency of inhibition depends on the stability of the chelate formed. Among these compounds, triazoles and benzotriazoles are particularly known for their strong adsorption and protective film formation on metal surfaces.

The importance of green inhibitors of plant origin has been reviewed, as they are derived from renewable resources and are biodegradable. The inhibition efficiency of plant-based green inhibitors, along with their effectiveness under increasing extract concentration, elevated temperature, and different environments (acidic and alkaline conditions), has been reported. Green inhibitors containing compounds such as tannins, flavonoids, and alkaloids adsorb onto the metal surface and form a protective layer.

This review also focused on studies of some of the most essential classes of nanocontainers, their effectiveness as smart containers, and the advantages and limitations associated with their practical applications. Mesoporous silica and halloysite clays are among the most widely studied inorganic nanocontainers, owing to their superior performance in self-healing coatings and their biosafety.

The self-healing coatings developed to date are capable of repairing only minor damages, such as abrasion or puncture, on the substrate. Future research could look into developing intelligent healing mechanisms capable of repairing more complex damage. In addition to self-healing, future research should also focus on incorporating antimicrobial functions in nanocontainers to broaden their industrial applications. Currently, most nanocontainers are based on single-stimulus-responsive materials; however, multi-stimulus-responsive nanocontainers may be developed to further enhance self-healing performance.

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Conflict of interest

The authors declare they have no competing interests.

Author contributions

Conceptualization: Joghee Manivannan
Writing–original draft: Joghee Manivannan
Writing–review & editing: Kalaiselvan Shanmugam

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