Review

A Comprehensive Overview on Corrosion in RCC and Its Prevention Using Various Green Corrosion Inhibitors

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Abstract: Reinforced cement concrete (RCC) is a versatile material that deteriorates over time due to corrosion when exposed to any surrounding aggressive environment. In order to avoid this ramification, many researchers have carried out different work to find the most feasible way to reduce corrosion. To tackle this at the initial stage itself, one such convenient method is through the application of inhibitors. These inhibitors have most applications in their use as an admixture. This review paper mainly focuses on the inhibitor and its types, the drawbacks of inorganic, commercial organic, and hybrid inhibitors, and application to RCC, and also provides detailed information on green corrosion inhibitors (GCI). In recent years, widespread attention has been paid towards the utilization of different natural plant components/parts in concrete structures. This review paper consolidates the work done by various researchers using different GCIs with the main focus on plant extracts as an additive to concrete or RCC specimens which will be significant to sustainable progress in the field of corrosion.

Keywords: corrosion; reinforced cement concrete; green corrosion inhibitor; plant extracts

1. Introduction

Construction materials such as metals and alloys are extensively used in the field of engineering. These materials, if not properly protected, are often exposed to the neighbouring environment, leading to gradual degradation over a period of time. This aspect of degradation or disintegration of metals and alloys is termed corrosion [1]. Some of the properties such as chemical composition and the process of electrochemical reactions tend to affect a particular metal with a higher corrosion rate when compared to other metals. The general definition of corrosion is a natural occurrence in which a metal reacts with an external environment chemically or electrochemically, leading to the alteration of metal from its unstable state to a chemically noble form. It is an unwanted aspect which ruins the favourable properties of metal. It is also referred to as an oxidation process which results in loss of metal.

Some of the outcomes of corrosion in different metals are rust development on the iron's surface and green film emergence on the surface of copper. The factors influencing the corrosion rate in metals are the nature of the metal, temperature, salt medium in the environment, carbon dioxide gas present in the air, and acids existing in the atmosphere [2].

Corrosion is an indefinite and expensive issue which is generally very hard to eliminate wholly [3]. Metal and alloy structures can corrode leading to severe destructions, resulting in financial penalties in the form of recover, restoration, production losses, safety, and environmental pollution. It causes serious degradation issues to the environment by affecting numerous sectors such as civil, chemical, mechanical, metallurgical, medical, and engineering, with implications for safety, preservation, and economy [4]. In the field of civil engineering, concrete is a mandatory material utilised for any cost-efficient construction. The tensile strength and durability factor is compromised in concrete and, to tackle it,

steel reinforced bars are added. However, the occurrence of corrosion in steel affects the durability of reinforced concrete structures in the long run. It is an unappealing and apparent fact that must be averted. Thus, researchers have brought forth Green Corrosion Inhibitors as one of the means to reduce the corrosion phenomenon and bring about the maximum resource efficiency of the materials used during construction.

This paper helps to gain a better understanding of the need to shift towards the sustainable GCI. The objective of the paper is to showcase the research undertaken to minimise or to delay the corrosion process occurring in RCC structures through the application of different GCIs. This paper aims to provide complete knowledge on plant extracts—the parameters required for its extraction, the extraction process, application on steel or concrete, and the different tests that can be performed to determine its efficiency and effectiveness.

2. Reinforced Cement Concrete

Concrete is an extensive and cost-effective material which is used in the civil construction industries [5,6]. Following water, concrete is the planet's second most utilized material and, based on the demand it generates, it will be continuously employed in the near future as well. Concrete has an excellent crushing strength, but it lacks tensile and elastic strengths, which is often compensated for by adding steel to the concrete matrix in order to retain its durability [7]. The compressive strength and durability of the concrete is inversely proportional to the pore sizes and number of pores present in it. Steel reinforcement bars are adaptable, dependable, acceptable, and an everlasting material. Because of this, they are often used in the construction and other infrastructural sectors. They are normally embedded in concrete to carry the heavy load [8]. This integration of steel and concrete is designated as reinforced cement concrete (RCC), and normally enriches the attributes of ingredients physically, mechanically, and chemically [9]. In civil and hydraulic engineering, reinforced cement concrete structures are regularly utilised structural components [10]. Reinforced Concrete is a heterogeneous material, and thus provides assurance in terms of its long-lasting nature, authenticity, practicality, and cost-effectiveness, making it one of the most widely used materials in the construction field all over the globe [11–13].

3. Corrosion in RCC

The main complication of RCC structures with regards to durability is the occurrence of steel corrosion. Nevertheless, infrastructures built with RCC material, such as bridges and buildings are degrading prematurely due to their exposure to extreme environmental conditions [14]. The renowned Pamban bridge located in the coastal side of Tamil Nadu is the best practical example which is requiring periodic maintenance against corrosion. This bridge is located in what is considered as the second principle eroding environment—the coastal region. The 2017 data estimated that approximately 105 million rupees was utilized to repair around 27 bridge girders that had been corroded due to the salt exposure [8].

Corrosion of reinforcement bars has become a serious concern in several RCC structures, due to unwarranted loss of serviceability and reliability, which has a negative impact on the structures' effectiveness, leading to considerable financial losses all around the globe [15]. Early or abrupt structural collapse can be detrimental with not just millions of dollars squandered every year—3.4% of global GDP or \$3 trillion per year [6], but also in regards to loss of time and lives [15,16]. The cost of new building has been found to be significantly lower than the repair works due to the RCC structure's lack of durability [11]. Reinforcement bars to a certain extent can be protected from corrosion when embedded inside the alkaline environment (pH = 12–14) of concrete generated by the cement paste. This is because cement paste in concrete additionally forms a thick film surrounding the steel to prevent corrosion. However, it can be damaged based on the porous and heterogeneous nature of concrete in RCC, creating pathway for substances such as carbon dioxide, chloride ions, and water to enter inside the concrete, thereby decreasing its durability. [12,17]. RCC structures can deteriorate owing to three variety of factors. The first is physical causes—cracking due to frequent freezing and thawing cycles or thermal

discrepancy between cement and aggregates. Second is the chemical cause—acid attacks, alkali-aggregate reaction, leaching, seawater and sulphate attacks. This is followed by mechanical abrasion, impacts, and erosions.

Chloride, carbon dioxide, and sulphur are the most important causes in the loss of alkalinity in concrete. As a result of this reaction, the pH of the concrete pore solution near the rebar surface tends to decrease, exposing RCC structures to corrosion damage [7]. The second most important factor affecting steel rebar corrosion is the action of freezing and thawing occurring in cycles. As a result of this phenomenon, cracks evolve in concrete, forming a path for the corrosion-causing ions to penetrate inside the concrete, thereby attacking steel. Chloride ions present in the surrounding environment enter the reinforced concrete through its pore spaces and when the concentration of these chloride ions surpasses the threshold value, it does not influence the concrete directly, but instead it penetrates via the pores of the concrete thereby affecting the passivation film of steel reinforcement bar leading to the initiation of corrosion. Expansive stresses are generated in concrete when the volume of rust formed on steel reinforcement bar exceeds the volume of reinforcement bar itself, leading to the fracture and spalling of concrete, thus minimizing the prolonged durability of RCC structures [11]. Some of the possible ways in which the chloride ions can penetrate the concrete is during its blending operation where the materials like superplasticizers, water, and aggregates which are frequently adopted in making concrete specimens are contaminated with the chloride ions. Another possible source can be during the construction of marine structures wherein the sea water is used for making concrete [12]. The reinforced cement concrete corrosion process is focused broadly on the de-passivation of formerly passivated reinforcement [18], the passivation will sustain when high alkalinity of pH 12–14 is maintained as long as possible inside the concrete. Alkalinity is reduced when chloride ions enter into the concrete, reducing the pH level below 10 and leading to damage of the passivation layer causing corrosion in steel reinforcement bars [12] which ultimately results in a loss of serviceability, durability, soundness, safety issues and financial costs to people [7]. When CO_2 interacts with concrete in its porous form, it results in the formation of carbonic acid. The carbonic acid formation results in lower pH levels leading to depassivation of the steel rebars, hence giving way to corrosive action on the metal. This corrosive reaction is termed carbonation corrosion [8]. Apart from carbonation corrosion, the sulphurous compounds arise in the form of acidic rain in the industrial setting and the existence of microbial agents in the sewage which produce biogenic sulphuric acid; all are responsible for attacking concrete hydrated products resulting in gypsum and ettringite formation. These two are detrimental compounds as they result in expansion of concrete, causing cracks, integrity deformation, and further exposure to acidic attack [13].

4. Methods of Corrosion Inhibition

Due to the obvious significance of reinforced concrete in today's world, a lot of research work is being done to find the best ways to reduce the detrimental corrosion effects in concrete [19]. The rapid decline of structural integrity necessitates expensive repair and rehabilitation to avoid catastrophic failure of the structural steel-reinforced concrete, posing major dangers to human life and property devastation [20]. Based on comprehensive study, it is found that corrosion is highly accountable for the decrease in the ultimate strength, strain, and cross-sectional area of steel rebar. As a result, the continuous degradation of such mechanical properties might have a serious impact on the prolonged safety and reliability of RC structures. Various protection strategies have been introduced to address these limitations, enabling the corrosion process to be slowed, delayed, or stopped [21]. Preventing these problems, as well as the fact that steel-reinforced concrete remains a popular structural material due to its adaptability and cost-effectiveness, necessitates a crucial search for appropriate steel-rebar corrosion-protection measures [20,22]. The various steel reinforcement corrosion protection methods practiced by different authors over the years includes the use of admixtures such as pulverised fly ash, ground granulated blast furnace

slag and Rice Husk Ash, painting the outer concrete surface, cathodic protection, improving metallurgy by adding chromium and copper, membrane type coatings, encapsulation of fibre reinforced polymers, use of coating on the reinforcement, re-alkalization of carbonated concrete, epoxy coatings, proper storage and stacking of reinforcing steel, altering water-cement ratio, electrochemical chloride extraction, use of stainless steel, galvanised steel bars, adding hydrophobic layers with asphalt overlay, use of fibreglass, penetrating sealant, use of silica fumes as additives and anodic protection technique [1,8,9,23–27]. It is critical to control concrete corrosion using traditional ways, and therefore there is a need to develop unique strategies and techniques to combat this dangerous problem [4]. Although a wide range of corrosion prevention strategies have been developed and studied, no clear optimal method has been identified before [23]. By lowering metal impurity concentration, employing a variety of modification techniques, and introducing proper alloying elements, a good level of corrosion protection has been obtained [28].

5. Drawbacks of Some Corrosion Prevention Methods

1. Admixtures in concrete (Fly ash, Metakaolin, GGBS, Natural Zeolite, Silica fumes etc.)—showcases poor workability, greater level of absorption of surface.
2. Stainless Steel Reinforcement—Costly method which adds 10% extra cost to the overall project cost.
3. Epoxy Coated Rebars—Chances of chemical attack can occur if there improper bonding between steel and concrete.
4. Cathodic protection—Employing impressed current system is extremely costly in terms of its installation, operation and to maintain.
5. Water-proofing membranes and sealers (barriers)—Throughout the life span of the structure, it is necessary to maintain and reapply the material.
6. Galvanizing steel rebars—The substantial amount of zinc lost due to the initial high corrosion rate may not be sufficient to provide adequate long-term protection to the underlying steel.
7. The surface protection method—Needs appropriate professional expertise for suitable design, construction, and workmanship for adequate performance and for preventing improper or faulty waterproofing, a contravention of which have created plenty of harm to building structures in most places.
8. Anodic protection—Restricts the current capacity depending on the mass of the electrode, a lack of performance in a high-resistivity environment, greater weight on the protected surface, routine replacement of the anode, elevated noise levels from the anode and current output are uncontrollable.
9. Fibreglass usage—Moisture-related problems, mould concerns, coverage, and air exchange problems.
10. Fibre Reinforced Polymer—Exposure to rain, random and improper orientation of this material could result in poor quality concrete. In addition, it is 10 to 15% costlier than non-reinforced concrete.

According to the results of various studies performed in anticorrosion material applications [4] from the numerous corrosion control and prevention techniques [29], it is found that the most significant, financial, feasible [28], convenient [10,30], and viable technique [25] used to decrease or slow down [31,32] the corrosion rate of metal is via the addition of inhibitors [33]. This happens to be one of the most efficient and suitable ways to improve corrosion resistance properties [26]. Corrosion inhibitors are booming in popularity because of various benefits such as ease of application in resisting concrete rebar corrosion in severe environments [20], fairly low costs, high effectiveness [34], and work force savings, thus making it one of the most efficient methods in reducing the corrosion impacts in reinforced concrete [35]. Some of the remarkable properties of corrosion inhibitors include adaptability, durability, sustainability, and affordability [36]. Corrosion inhibitors added to steel reinforced concrete components have proven to be an effective method

in both enhancing stability and through chemical surface protection, thereby completely refining the steel in terms of serviceability [37].

6. Inhibitors Definition

Inhibitors are substances that are added in parts per million concentrations to reduce or prevent steel rebar corrosion. The level of inhibition is based on the nature of the metallic specimen to be adopted and the type of exposure medium [33]. They reduce the corrosion action on the vulnerable material by performing as a barrier, or by materialising an adsorbed film or by decelerating the cathodic or anodic processes, or a combination of both, thus improving the durability of RCC structures [12,38]. Therefore, the application of inhibitors in reinforced concrete structure is an effective approach in regulating the corrosion to reasonable levels [39]. It is not sufficient to perform only the anticorrosion tests in order to study the binding strength of reinforced concrete and inhibitor, but also requires various mechanical tests which needs to be performed [40]. Inhibitors are typically admixed in low permeability concrete specimens [41]. An effective corrosion inhibitor is the one which shows better adsorption potential on the metal surface, thus providing a tight adherent coating film which can be accomplished either through the process of physisorption or chemisorption, or by both [3,42]. These inhibitors also have their application in RCC as shown below in Figure 1 [27].
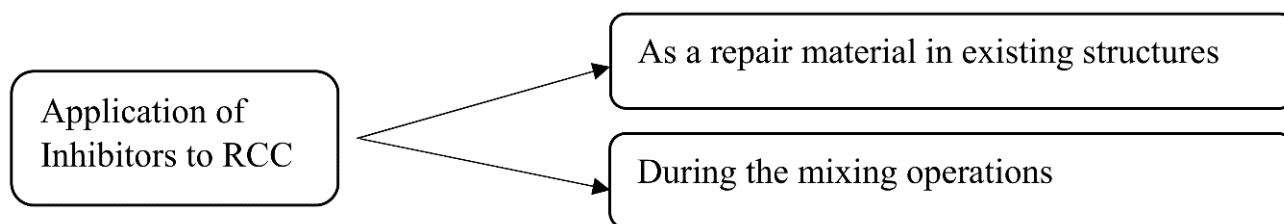
Figure 1. Inhibitors Application to Reinforced Cement Concrete.

Factors affecting the choice of suitable Inhibitor selection:
1. The form of chemicals used in the industry;
2. Concentration of the inhibitor molecules;
3. Category of metals to be adopted;
4. Temperature.

Factors affecting the inhibitors adsorption capacity [43]:
1. Characteristics, properties, composition and reaction of metal surface;
2. Chemical structure of inhibitor; and
3. Kind of aggressive mediums.

Properties of corrosion Inhibitors [3]:
1. Significant adsorption on the metal surface;
2. Altering the anodic or cathodic reactions or both;
3. Reducing the dispersion rate of reactants on the steel surface; and
4. Lowering the electrical resistance of metal surface.

$$\text{Inhibitor Concentration on metal} \propto \frac{1}{\text{Corrosion Rate}}$$

It is highly necessary to maintain an appropriate level of inhibitor concentration on the metallic surface in order to cover the metal completely, otherwise there will be localised corrosion at the unprotected sites [44]. The classification of corrosion inhibitors can be seen below in Figure 2.
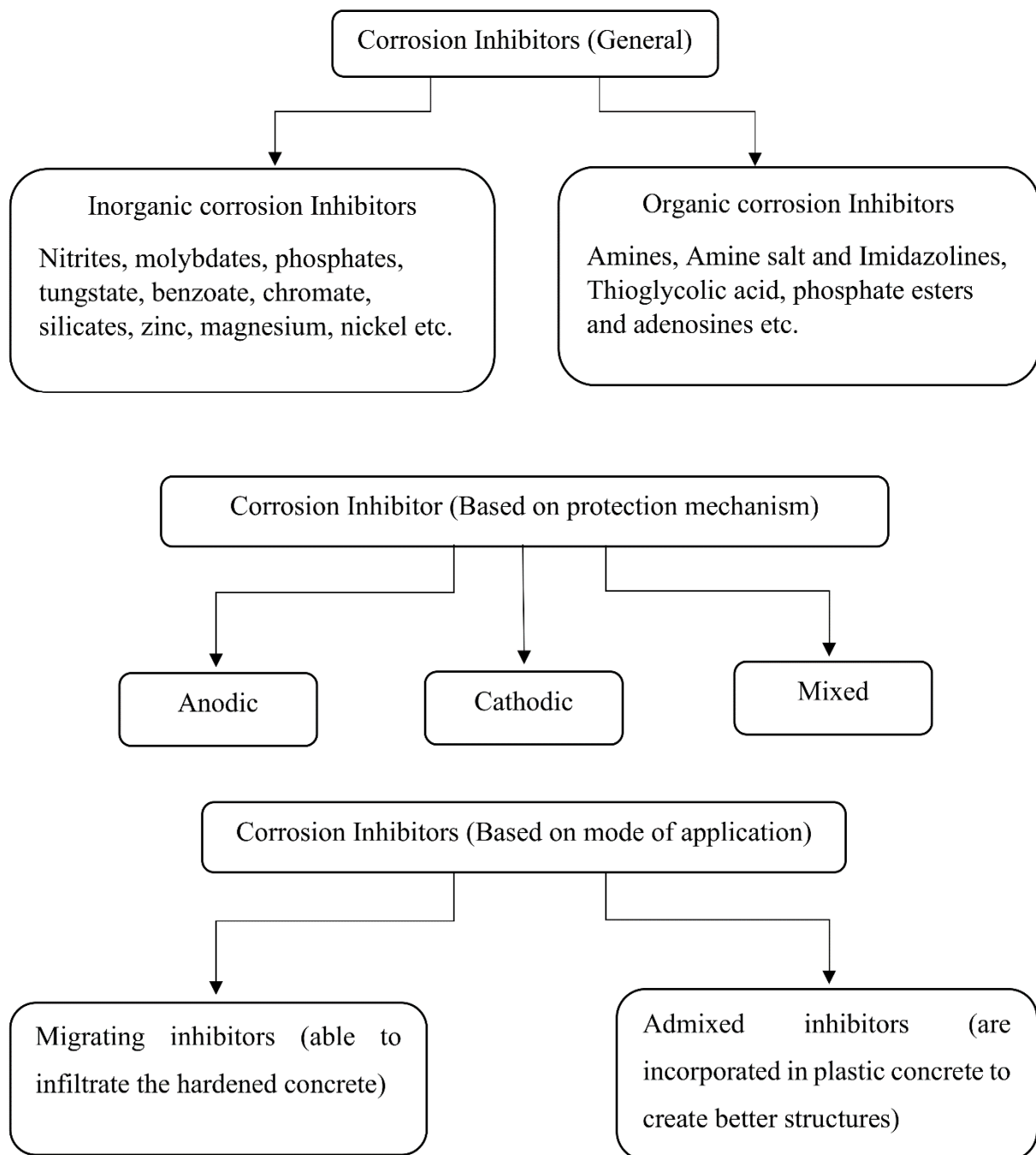
Figure 2. Classification of Corrosion Inhibitors.

In order to mitigate corrosion in new concrete structures, inorganic inhibitors are added to the mixing water at the initial stage. Sodium nitrite, calcium nitrite, and other nitrites were the most well-known and sought-after inorganic-based corrosion inhibitors in the previous century. Calcium Nitrite was shown to be the most effective RCC corrosion inhibitor when compared to its alternatives.

Even with their effectiveness, the bulk of the inorganic corrosion inhibitors such as nitrites, tungstate, benzoate, molybdates phosphates, chromate and silicates, continue to be banned around the world on account of their high biological toxicity and carcinogenicity. One such toxic inhibitor is nitrites which have been found to delay the setting time, and lowering the strength of concrete thus affecting the overall performance of the structure. Similarly, chromate anti corrosive properties, although beneficial, are limited as they are shown to have water polluting and carcinogenic properties. Overall, inorganic corrosion

inhibitors have been shown to be non-biodegradable, noxious, uneconomical along with damaging multiple human organs such as liver and kidneys due to prolonged exposure [21].

Organic Inhibitors are unusually the effective mixed class of inhibitors which exhibits both anodic and cathodic operations in a simultaneous manner because of the existence of hetero atoms such as Oxygen, Nitrogen, Sulphur, Phosphorous, conjugated double bonds [45] and aromatic rings in it. These hetero atoms perform as an active core material for the physical and chemical adsorption process to occur on the surface of steel, possessing a high electron density [16]. Through the transport of lone pair of electrons from the atoms of the inhibitor to the stable metal surface, these molecules present in the inhibitor form a stronger link with the steel concrete interface, thus obstructing the active corrosion site [46], hence preventing the entry of destructive species which are accountable for the depassivation of rebar [16] such as CO_2, SO_4^-, Cl^-, and moisture content on the surface of steel [47].

Some of other parameters influencing the performance of corrosion inhibitors are:

1. Chemical composition of functional groups;
2. The existence of pi-bonds;
3. The electronic characteristics of the molecule; and
4. Non-bonding p-orbitals [48].

The mechanism of organic corrosion inhibitor relies on its chemical constituents. When these inhibitors are admixed to a solution, they are adsorbed strongly on the metal's surface and embedded in concrete, thus displacing water molecules and destructive agents such as chloride ions from its surface. The drawbacks of both organic and hybrid inhibitors are detailed below in Figure 3.
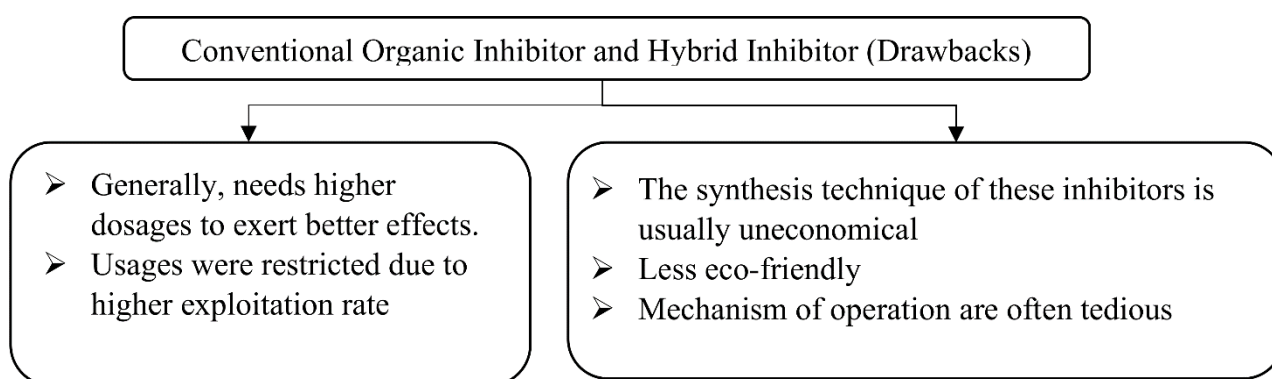
Conventional Organic Inhibitor and Hybrid Inhibitor (Drawbacks)

➢ Generally, needs higher dosages to exert better effects.
➢ Usages were restricted due to higher exploitation rate

➢ The synthesis technique of these inhibitors is usually uneconomical
➢ Less eco-friendly
➢ Mechanism of operation are often tedious

Figure 3. Drawbacks of Conventional Organic Inhibitor and Hybrid Inhibitors.

7. Green Corrosion Inhibitors

Human life expectancy and environmental consciousness have both substantially developed along with the advancement of society [49]. The majority of corrosion inhibitors used by several researchers over the years are synthetic chemicals which are found to be costly and harmful to the environment. Accordingly, there is a requirement for an inhibitor which can be highly protective to the environment. As a result, there has been an increasing demand in recent years for the hunt for inhibitors which are proven to be economical [48], less harmful and biodegradable when compared with the conventional inhibitors. Thus, the environmentally friendly corrosion inhibitors are gaining a lot of popularity from researchers all over the globe [50]. During this stage, scientists started to target completely the "green" botanic corrosion inhibitors leading to the increased demand in the field of Science and Technology [51]. Recently, various research has been carried out by several authors using the green corrosion inhibitor as an admixture in RCC to test its efficiency experimentally in order to increase the mean service life of structures. The efficiency of inhibitor is based on the characteristics of its chemical ingredients [47]. It also showed an improved consistency in producing the results. Owing to the accessibility

and much better inhibitive characteristics, the green corrosion inhibitors can be taken as an effective alternative to the prevalent conventional organic inhibitors. These are the compounds which are going to be used more prominently in the upcoming years [52]. The two subcategories of green corrosion inhibitors are classified in Figure 4.
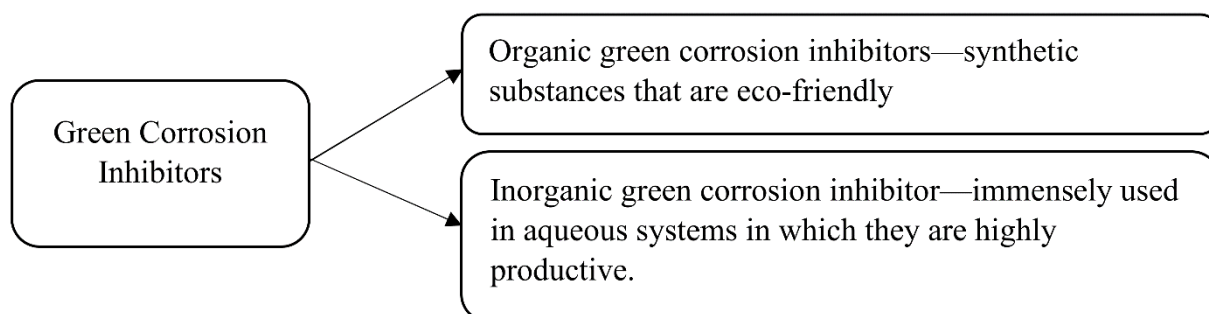
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┌──────────────┐         ┌─────────────────────────────────────────────┐
│ Green        │ ──────▶ │ Organic green corrosion inhibitors—synthetic │
│ Corrosion    │         │ substances that are eco-friendly             │
│ Inhibitors   │         └─────────────────────────────────────────────┘
│              │ ──────▶ ┌─────────────────────────────────────────────┐
└──────────────┘         │ Inorganic green corrosion inhibitor—immensely used │
                         │ in aqueous systems in which they are highly  │
                         │ productive.                                  │
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Figure 4. Classification of green corrosion inhibitors.

Inorganic green inhibitor initiates the formation of adsorption layers that tend to be brittle, thereby revealing the surface of the metal vulnerable to pitting and crevice corrosion attacks. In contrast, organic green inhibitor, when weighed upon with inorganic corrosion inhibitors, tend to passivate the surface of the metal consistently and yield the maximum possible protection against the destructive medium [52].

There are many varieties of green corrosion inhibitors that are gaining traction such as biopolymers, surface active agent, pharmaceutical compounds, chitosan, honey, yeast, plant extracts, and amino acids, etc., to reduce the corrosion in reinforced concrete structures because of their easy availability, eco-friendly, biodegradability, low toxicity, and renewable properties. When these eco based inhibitors are added as an admixture to the mixing water in the reinforced concrete specimen, the organic compounds present in these inhibitor sources are adsorbed on the surface of metal, forming a passivation layer that protects the active area from the action of corrosion [48,50]. Figure 5 shows the various types of green corrosion inhibitors that are obtainable.

It is exceedingly practical and affordable to obtain or collect the ingredients that are necessary for inhibition from natural plants along with their waste materials due to the presence of phytochemicals which are able to strongly bind on the surface of metal. The extraction of green corrosion inhibitor from natural plants has become a popular subject in the anticorrosion industry. Owing to the accessibility and much better inhibitive characteristics, the green corrosion inhibitors can be adopted as an effective alternative to the prevalent conventional organic inhibitors [46].

In order to hinder scale development and microbial corrosion, plant substances have the ability to remove oxygen as well as several types of reactive oxygen from a biological environment. The occurrence of heterocyclic compounds such as sulphur, oxygen, or nitrogen atoms, aromatic rings, pi-electrons and specifically its polar functionalities all aid to this performance. The reaction centre that initiates the adsorption method is commonly represented by the polar function [53]. Plant extracts can be classified as green and sustainable materials to be used as eco inhibitors for metals and alloy mixtures in aggressive mediums such as HCl, H_2SO_4, H_3PO_4, and HNO_3 due to their diverse natural origins, as well as their environmental-friendly isolation [51].

Through the action of photosynthesis, plants transform radiation energy absorbed from sunlight into useful organic compounds such as carbohydrates. These plants are the natural producers of the following raw materials namely fruits, vegetables, oils, woods, and dyes which have a wide variety of regular use in our daily lives. Through the phenomenon of photosynthesis, plants possess an ability to absorb the following contaminants such as the harmful CO_2 gas, toxic minerals, etc., hence purifying the area around it [51].
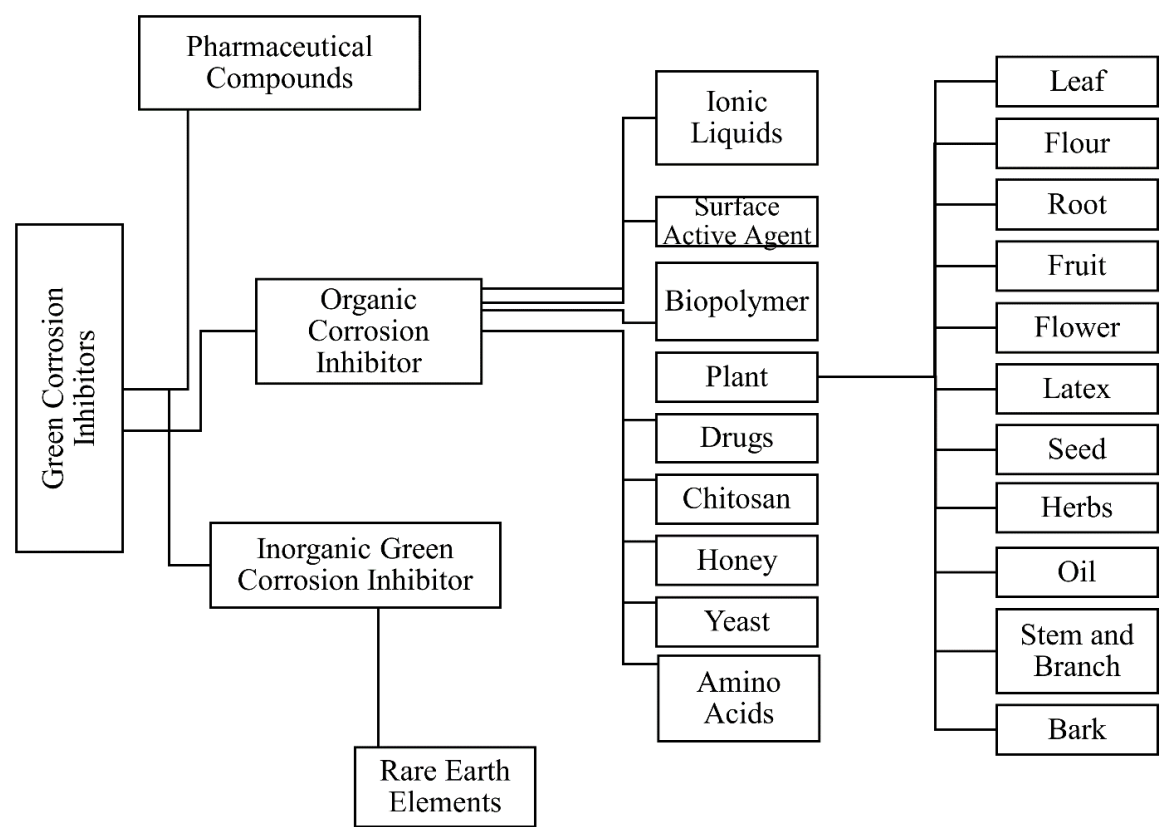
Figure 5. Flowchart of various Green Corrosion Inhibitors.

The green inhibitor components are obtained from their respective plant sources primarily through the process of extraction. This is a tedious process due to the presence of different polarities of the chemical compounds from the same plant source. The nature of the extraction solvent to that of the organic compound is the most significant factor that might influence the extraction outcome [53]. The plant extraction parameters that need to be noted is listed in Figure 6.

Figure 6. Parameters considered during the preparation of plant extract [51].

To recognise the distinctive property of water retention, plant extracts such as tannins, sugars and starch are employed as curing members in the form of bio admixtures added to concrete as they impact its characteristics in a positive manner [5,54].

8. Plant Extract Preparation

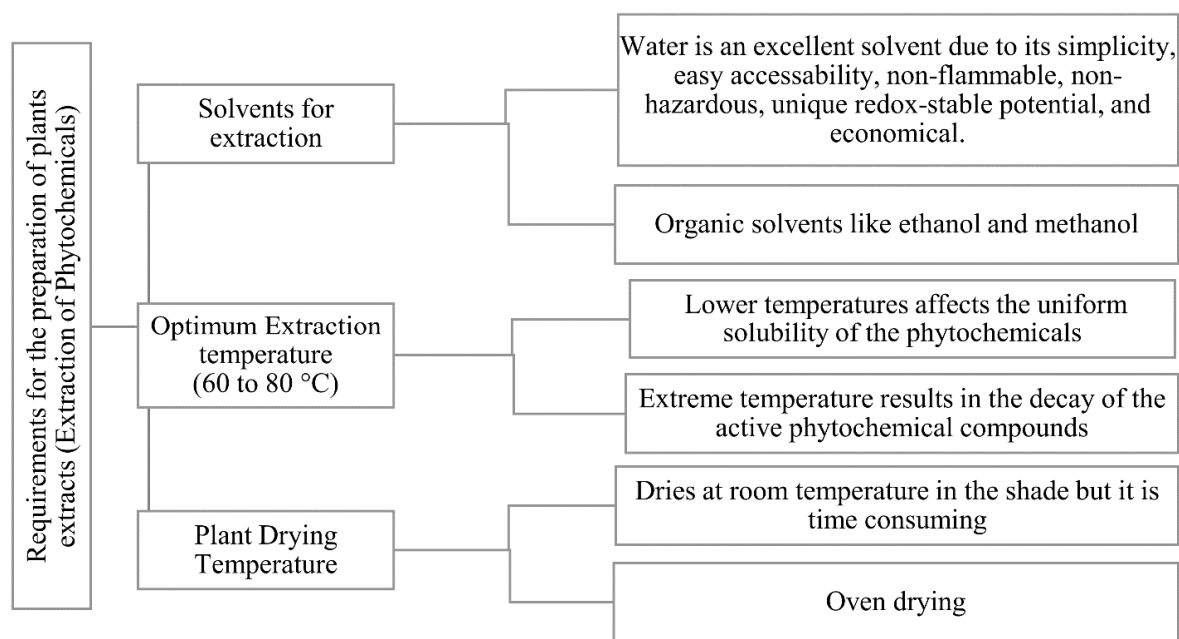When the plant or its different parts such as leaf, stem, roots, flowers, etc., are added to a particular medium such as the solvent, it forms an extract solution containing the active phytochemicals in it. These phytochemical compounds deliver the important properties present in plants which can be utilised for various purposes. Depending upon the different Phytochemicals present in the plant and along with its concentration level, it can be advantageous. The methodology adopted to obtain the extract solution from a solvent depends upon its polarity. Some of the important roles of a plant extract is that they function as an anti-inflammatory, antifouling, antioxidant, antiviral, self-healing, and as an antimicrobial agent. Plant extracts can be added as an admixture to concrete as an inhibitor in a combined form, i.e., with a greater number of extracts to obtain a synergising result [55,56]. Figure 7 shows the extraction process of obtaining the phytochemicals.
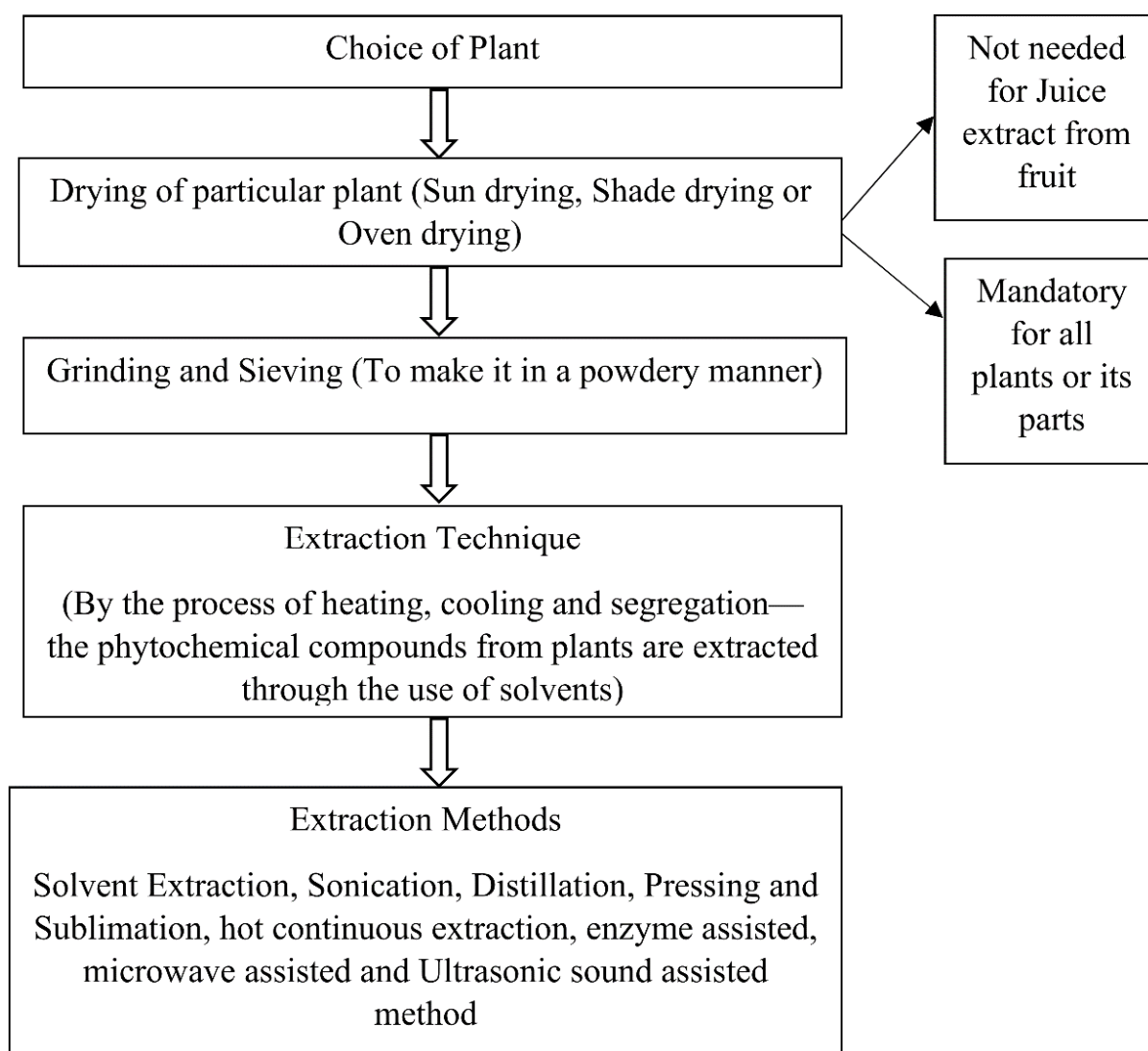

Figure 7. Schematic diagram of extraction procedure of phytochemicals.

From the above-listed approaches, solvent extraction is the most commonly practised technique used for extracting active chemicals from plants or its parts. The solvent is used to perforate into the plant tissue, which then absorbs the required phytochemical compound and is then extracted. This process is known as solvent extraction. For the required extract of phytochemicals, multiple solvents such as ethanol, methanol, distilled water, acetone, ether, chloroform, di-chloro methanol, n-propanol, n-butanol, and hexane might be used as an extraction medium for different varieties of plants. Alternatively, effective extracting agents in the form of compressed liquids such as supercritical fluids, subcritical water, and pressurised fluids have also been utilised. Supercritical fluids are a newer family of alternative solvents that enable for the selective extraction of phytochemicals from plants at moderate temperatures, along with the shortest processing time possible.

The most often and extensively used solvents by different researchers for extracting a greater number of phytochemicals are ethyl alcohol, methyl alcohol and distilled water. For better yield of extracts, mixing alcohols such as methanol/ethanol with distilled water is highly preferable. The phytochemical present in a particular plant part can be derived using any of the above solvents. If a particular phytochemical turns out to be negative through a particular solvent medium, then it is necessary to examine whether it is present through other solvent mediums.

Some of the most commonly present phytochemicals in different parts of the plants are, alkaloids, tannins, terpenoids, steroids, flavonoids, saponins, anthraquinones, glycosides, phenols, carbohydrates, amino acids, proteins, starch, coumarins, cyanins, ascorbic acid, phytosterols, monosaccharides, and reducing sugars. The presence and absence of these above-mentioned phytochemicals varies from plant to plant also within the plant parts.

Factors influencing the properties of plant extract through solvent extraction methods are:

1. Solvent to solid ratio;
2. Multiple solvents having diverse polarities;
3. Extraction Temperature and extraction time;
4. Physical characteristics and chemical composition of plants [52].

Figure 8 below details the various tests to determine the active phytochemical compounds, functional groups and to determine inhibitor efficiency.

Through weight loss or gravimetric tests, the presence or absence of an inhibitor when the metal or steel is immersed in different acid/alkali/salt mediums for a specific timeframe at variable temperatures, the weight loss value, the rate of corrosion, the values inhibition efficiency and surface coverage can be computed [57–68]. Gasometric method was carried out using gasometric assembly in order to assess corrosion through the volume of hydrogen gas liberated as a by-product of cathodic reaction at specific time intervals from a corroding metal in an aqueous medium containing inhibitor concentration [65]. The disintegration reaction liberates hydrogen gas. The volume of H_2 gas emitted was used to calculate hydrogen evolution rate that can be associated to a mild steel corrosion rate. The corrosion rate, surface coverage values, and inhibitor efficiency can all be computed from the hydrogen evolution rate [69]. The greater the volume of gas released, the sooner the corrosion will occur [70]. The gasometric technique is more accurate than the gravimetric technique [71,72].

The most commonly conducted electrochemical measurements by most of the researchers are Potentiodynamic polarization using Tafel extrapolation [73–75], EIS [76–79] and Linear polarization resistance technique [80–82]. The advantages of these procedures are that they are quick to perform and are efficient. The electrochemical measurements are usually performed using an Electrochemical workstation or potentiostat/galvanostat setup consisting of three electrode arrangement in which the platinum acts as a counter electrode, saturated calomel electrode as the reference electrode, and steel specimen or reinforced concrete specimen as the working electrode. The corrosion current value can be calculated using the variation in the applied potentials. In Potentiodynamic polarisation, the reference electrode monitors and governs the system's voltage, while the counter electrode gauges

and regulates the current. The voltage values enforced in the Potentiodynamic polarisation test are normally from below the open circuit potential to extending between -0.25 and $+0.25$ V of the higher potential ranges. In Electrochemical Impedance Spectroscopy (EIS), a small potential of about 5–50 mV of AC voltage was applied, over frequencies ranging from 100 kHz to 10 mHz. Nyquist and bode graphs depict the results of EIS analysis. The voltage range used in Linear Polarization Resistance is between 10 and 20 mV. While performing these electrochemical tests, it is necessary to perform Open Circuit Potential test on a metal substrate in order to attain a stable current reading thus examining the stability of the cell system. The major advantage of these electrochemical methods is that the results in the form of corrosion current/rate, inhibition efficiency, and surface coverage can be obtained very quickly within a short period of time by means of a computer setup with an inbuilt software program, mainly the Nova software which will be usually provided by the company along with the electrochemical cell setup with three electrodes during purchase. When compared to standard methods, these electrochemical tests save time and produce equal inhibitory efficiency. All of these electrochemical experiments were carried out with and without an inhibitor in the form of an aqueous solution added to the corrosive medium with respect to the substrate (steel/RCC) or as a coating directly applied to the steel substrate.

The different surface analysis tests were also done on the steel substrate in order to examine the surface morphology (shape, size, texture) of each specimen in the presence and absence of green corrosion inhibitor. The list of diverse tests on surface analysis carried out by researchers are: scanning electron microscope (SEM) [72,83–87], Atomic Force Microscopy (AFM) [72,73,88,89], X-ray diffraction analysis (XRD) [86,90], Energy dispersive spectroscopy (EDS) [91], Optical Microscopy [92], Raman spectroscopy [87], Energy dispersive X-ray analysis (EDX) [84,93], Contact angle measurement [72], Grazing Incidence X-ray Diffraction (GIXRD), Transmission electron microscope (TEM) [94], Trinocular metallurgical microscopy [70], X-ray photoelectron spectroscopy (XPS) and Electron probe micro-analyser (EPMA) [95]. From the above-mentioned surface analysis tests, the most commonly performed tests are SEM and AFM. These SEM and AFM tests are performed on steel substrates in order to determine the surface smoothness or roughness or texture of the metal in the presence and absence of inhibitor. In SEM, if the surface texture is smooth, it indicates that the inhibitor molecules are well adsorbed on the steel surface and thereby protecting the areas/spots from the corrosive medium. However, if the surface is rough, in case of no inhibitor application, this indicates that the corrosive medium has attacked the steel's surface, leading to damage. AFM tests give the results in the form of three-dimensional images, whereas the SEM test provides results only in two-dimensional form. The main difference between SEM and AFM is that the SEM can measure the chemical composition of surface of the steel while the AFM can measure the various physical properties of the surface of steel. SEM test can only be conducted in a vacuum environment while the AFM image tests can be performed in vacuum, air, and liquid.

Adsorption isotherms are crucial for analysing the mechanism of corrosion inhibition [96]. They provide precise information about the interaction between green corrosion inhibitor molecules and the metal surface [97]. The surface coverage values obtained from conventional or electrochemical methods for determining inhibition efficacy on a substrate vs. the concentration of the inhibitor in the aqueous medium can be represented using adsorption isotherm models [53].

Tests to determine the Inhibitor Efficiency

Standard

Electrochemical analysis

1. Weight Loss Method
2. Gasometric Method

1. Electrochemical Impedance Spectroscopy (EIS)
2. Linear Polarisation Resistance (LPR)
3. Potentiodynamic Polarization (Tafel Plots)
4. Electrochemical Noise Analysis
5. Electrochemical Frequency Modulation
6. Cyclic Voltammetry

Tests to determine the active phytochemical compounds

Liquid chromatography-mass spectrometry (LC-MS)

Thin layer chromatography (TLC)

High Performance Liquid Chromatography (HPLC)

Gas chromatography-mass spectroscopy (GC-MS)

Tests to determine the functional groups present in plant components

Fourier-transform infrared spectroscopy (FTIR)

UV–Visible spectroscopy

Attenuated Total Reflectance-FTIR

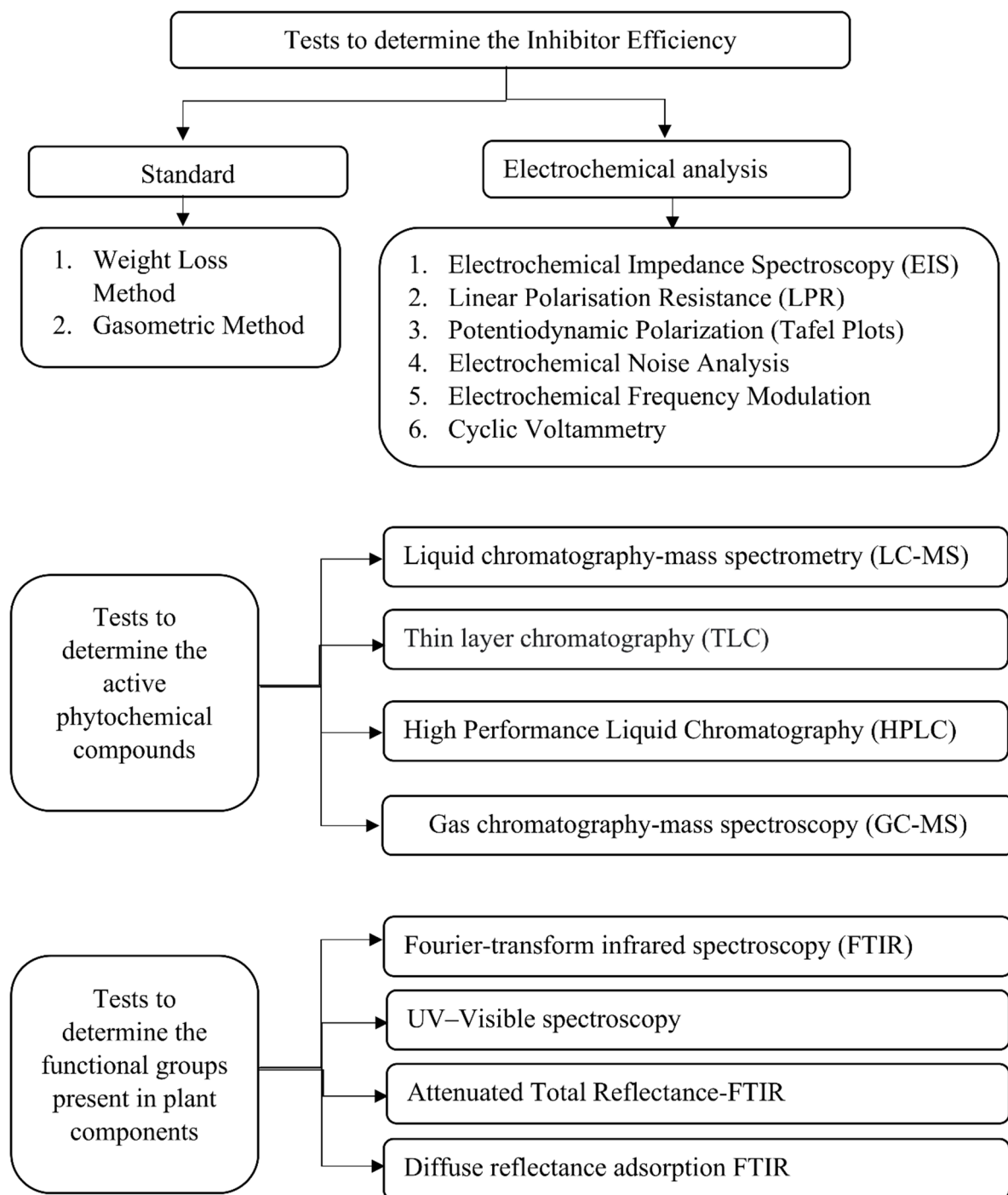Diffuse reflectance adsorption FTIR

Figure 8. Tests to conduct to determine the active phytochemical compounds, functional groups in plant components and tests to determine inhibitor efficiency.

Surface coverage estimates are helpful in gauging of inhibitor features and are useful for fitting experimental data to adsorption isotherms, which provides precise perspective about the inhibition mechanism [98].

The variable parameters of the studied isotherms were calculated using linear regression analysis. In order to outline the goodness-of-fit of the experimental data to the proposed models, the correlation coefficient was calculated [99].

Langmuir, Freundlich, Temkin and Frumkin, Flory-Huggins, El-Awardy, and Bockris-Swinkels are by far the most commonly plotted adsorption isotherm models [98–101]. The model that best fits the experimental values is the most acceptable. The Langmuir isotherm is the model that best fits for plant extracts as corrosion inhibitors on metals in most circumstances (highest regression coefficient) [55].

Evaluation of thermodynamic/kinetic variables for inhibitor adsorption on substrate, such as Gibbs free energy of adsorption (ΔG^o_{ads}), enthalpy of adsorption (ΔH^o_{ads}), entropy of adsorption (ΔS^o_{ads}), and apparent activation energy (E_a), can also provide good data about the corrosion inhibition mechanism. These variables are calculated by mathematical formulae depending on different temperatures (Absolute temperature). The standard equilibrium constant of the adsorption-desorption process (K_{ads}) can be computed by applying the most appropriate isotherm model, as previously described. The K_{ads} values would then be used to compute the standard Gibbs free energy of adsorption (ΔG^0_{ads}) and the enthalpy of adsorption (ΔH^o_{ads}) using the van't Hoff equation. The parameters obtained from Gibbs free energy of adsorption and enthalpy of adsorption (ΔH^o_{ads}) can be used to compute the entropy of adsorption (ΔS^o_{ads}). The value of activation energy (E_a) can be measured by comparing corrosion rates with various inhibitor concentrations at various temperatures. The activation energy for the corrosion response is derived using the Arrhenius equation.

The (ΔG^0_{ads}) values are always used to distinguish whether the adsorption process is physisorption, chemisorption, or mixed adsorption. The negative data obtained for any of the above types of adsorptions indicate that the adsorption process actually occurred spontaneously, resulting in the emergence of a stable protective green inhibitor layer. The value of activation energy in relation to temperature being increased or decreased could also correlate to whether the inhibitory mechanism is linked to physisorption or chemisorption. If the input of the conventional Gibbs free energy of adsorption is not viable to compute, this estimate of activation energy is usually worked out.

The enthalpy of adsorption (ΔH^o_{ads}) values is used to determine whether the adsorption process is exothermic, i.e., physisorption for the negative value acquired, or endothermic, i.e., chemisorption for the positive value attained. The values of entropy of adsorption (ΔS^o_{ads}), if positive, specifies the substitution process, which can be ascribed to the increase in the solvent entropy and more positive water desorption entropy. A positive result implies an orderly configuration of inhibitor molecules on the substrate's surface, while a negative result suggests that the activation complex represents association steps and as such the process was spontaneous and feasible.

The values of heat of adsorption (Q_{ads}), if negative, portrays that the adsorption process is exothermic wherein the negative value shows that there is an adsorption in which inhibition efficiency decreases with rise in temperature. The values of heat of adsorption (Q_{ads}), if positive, shows that the adsorption process is endothermic, which showcases the adsorption, and that the inhibition efficiency increases with rise in temperature [4,55,96,97,99–107].

Computational techniques are increasingly being used in the study of finding compounds responsible for corrosion inhibition potential based on their geometry, electronic structure, and binding property on the metal surface. These studies help to lower the experimental costs for testing many compounds with the goal of synthesising those that show promise for corrosion inhibition. In particular, density functional theory-based quantum chemical calculations and molecular dynamics along with Monte Carlo simulations have been developed as new techniques to depict the efficacy of a number of compounds analysed as corrosion inhibitors [108]. Since each plant extract has a number of compounds (phytochemicals), the newer and greener computational tools should be used to establish their relative effectiveness against the metallic surface. These techniques are environmentally friendly since they use software simulations to anticipate chemical reactivity and

adsorption mechanisms of chemical compounds at metal such as steel-electrolyte interface. The horizontal or vertical orientations of inhibitors compounds at interfaces can be established using molecular dynamics along with Monte Carlo simulations [51]. The calculations above are frequently used to investigate the link between inhibitor molecular characteristics and corrosion inhibition efficiency. The cause of incorporating the use of DFT-based quantum chemical and molecular dynamic simulations is to find which compounds are responsible for observed corrosion inhibition in a given mixture of organic compounds of a specific plant extract when adsorbed on a substrate material, particularly steel [109].

Quantum chemical estimates is a type of theoretic chemistry concept used to elucidate corrosion inhibition mechanisms. The total energy and distribution of the highest occupied molecular orbital and lowest unoccupied molecular orbital, absolute electronegativity values, and the proportion of electrons transferring from inhibitors to the substrate can all be determined using this approach. Many scientists prefer to use quantum chemical calculations to highlight and explain the independent molecular interactions of active organic compounds of green inhibitor with a metallic substrate because it allows researchers to analyse the structural reactivity of the various chemicals present in a plant extract [108,109].

9. Mechanism of Green Corrosion Inhibitors

The green corrosion Inhibitor (natural plant extracts) inhibition mechanism is being studied profoundly by various researchers in order to examine their effectiveness. The inhibition mechanism of plant extracts on the surface of metal occurs through a process termed adsorption [55,110]. The three types of adsorption mechanism can be seen in Figure 9.

Three Adsorption Mechanisms

Physisorption (Physical Interaction)—Electrostatic force of attraction between the inhibitor molecules (Nitrogen, Oxygen, Sulphur, double bonds, triple bonds, aromatic rings) and metal surface

Chemisorption (Chemical Interaction)—Chemical bond formation due to the electron transfer from inhibitor molecules to the surface of metal

Physisorption + Chemisorption = Mixed type Adsorption (or) Comprehensive Adsorption

Mixed Type Adsorption—They influence or inhibit Anodic and Cathodic reactions as a result furnishes the best protection measures.
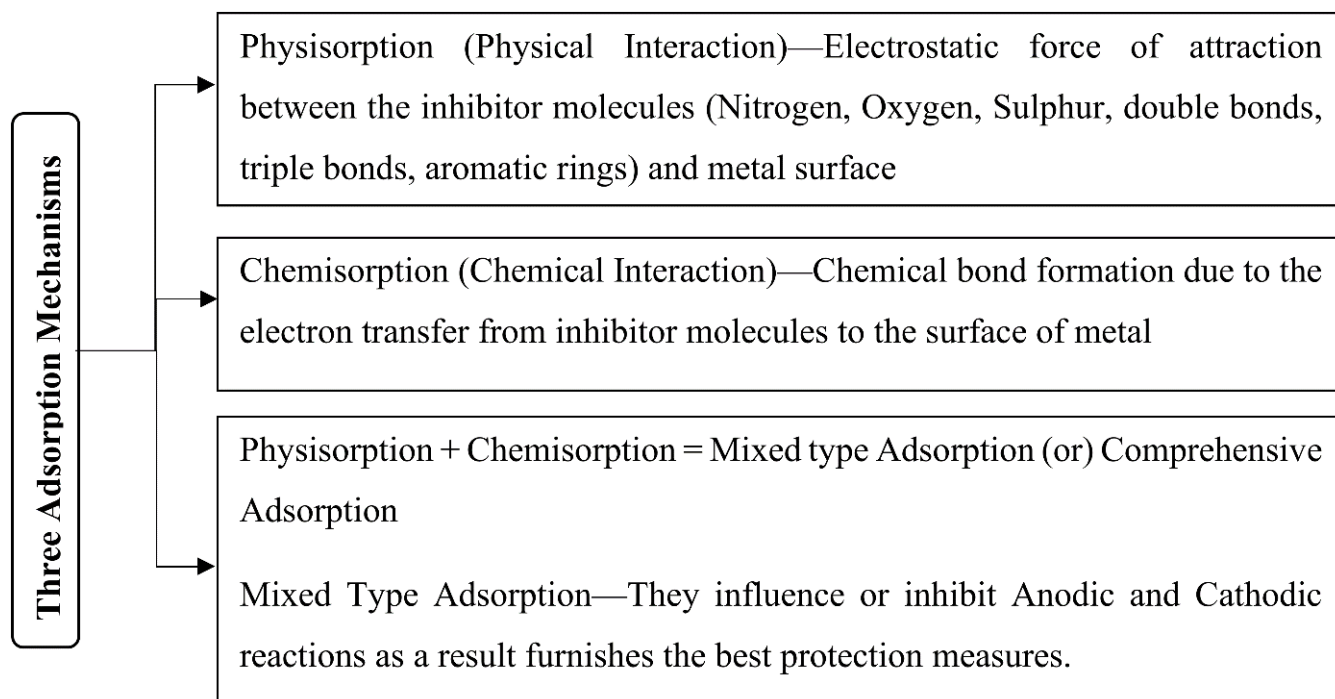
Figure 9. Mechanisms of Adsorption.

It is necessary to comprehend the Inhibition mechanism to improve the efficiency of green corrosion inhibitors.

Among the plant part varieties, the leaf is the one which contains the richest source of active phytochemical compounds that are produced by the process of photosynthesis.

Concise overview of green corrosion inhibitors in RCC is showcased in Figure 10.
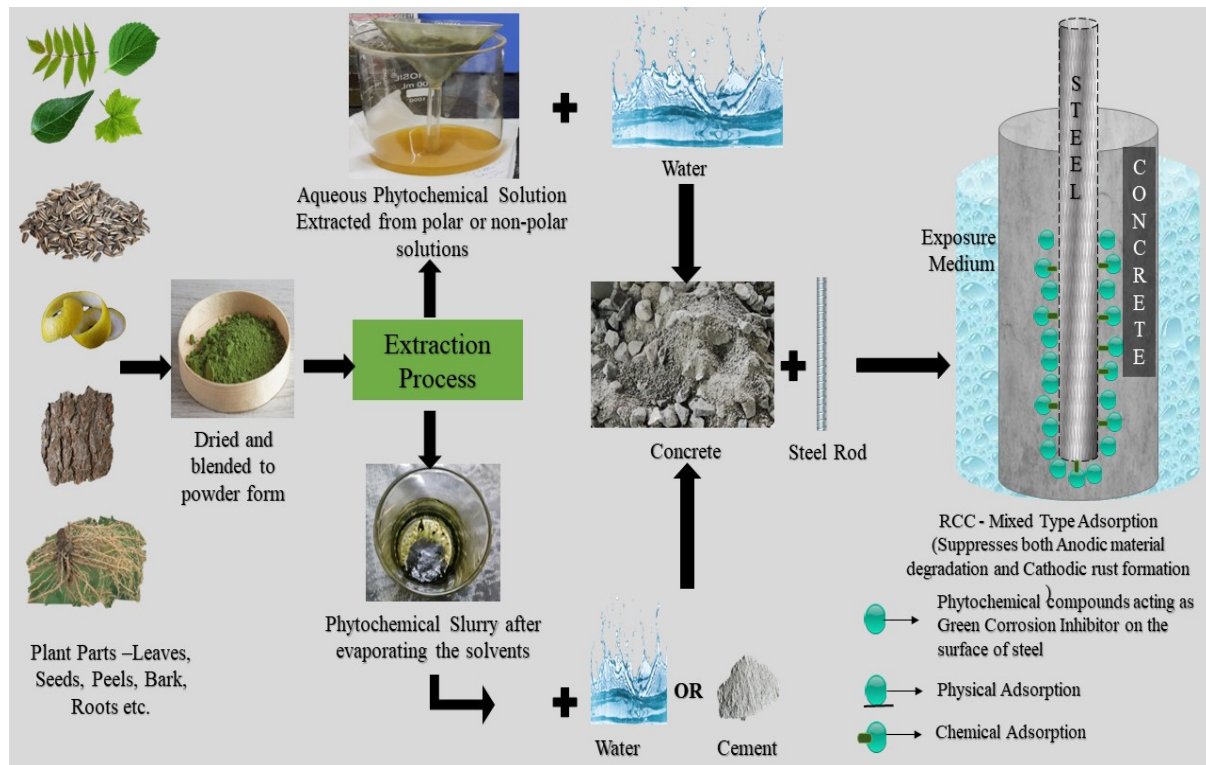
Figure 10. Concise overview of green corrosion inhibitors in RCC.

10. Selection of Inhibitor

One of the important criteria for selection of inhibitors is its Biological Oxygen Demand which should measure at least 60% for it to be considered as an effective green inhibitor. Another essentiality is that it should be non-toxic when measured using the LC 50 or EC 50 scale [17]. When it comes to natural inhibitors, the most difficult aspect is usually selecting and isolating the active molecules with the highest inhibitory potential [48].

Tables 1–7 are designed to illustrate a general comparative overview of the various GCIs used by different researchers. The tables showcase the different solvents used for the extraction, concentrations added, type of corrosive medium added to the substrate (concrete or steel), the optimum concentration of the GCI required to achieve high mechanical strength, and inhibition efficiency.

TABLE—List of Various Green Corrosion Inhibitors Used by Different Researchers with its main Focus on Strength Test Results, Corrosion Rate and Inhibition Efficiency.

Table 1. HYSD/Ribbed/Deformed Steel.

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
1.	*Azadirachta indica* (Neem) and Aloe-Vera	M 25 grade concrete w/c—0.5 Mix ratio—1: 1.53:3.15	Water	Inhibitors are added in 2% by weight of cement	-	NaCl	3.5%	Accelerated Corrosion test, Weight Loss Measurement, Compressive and Split Tensile Strength test	1. CST (28days)—Concrete with GCI < Control concrete—but within permissible limits 2. STST (28days)—Concrete with Neem (5.18% ↑) and Concrete with Aloe Vera (8% ↓) when compared to conventional concrete	WLM— I.E (%)—Neem > Aloe Vera C.R—Neem < Aloe Vera	[1]
2.	*Vitex negundo* (Chinese chaste tree) leaves and *Catharanthus roseus* (Madagascar periwinkle) leaves	w/c ratio—0.45 Mix ratio—1:2:3	Methanol	500, 1000, 2000, 4000 ppm of each plant extracts or water proofing agents	Alkaloids, saponins, flavonoids, glycosides and tannins	-	-	Open circuit corrosion potential (OCCP), Half-cell corrosion potential (HCP)	-	@ 500 and 1000 ppm, HCP I.E (%)—Vitex Negundo > Catharanthus Roseus	[7]
3.	*Anthocleista djalonensis* (Cabbage Tree)	w/c ratio—0.499 Mix ratio—1:2.96:3.68	Methanol (CH$_3$OH)	Concrete admixed with *A. djalonensis* in the following weight percentages (0.0000%, 0.0833%, 0.1667%, 0.2500%, 0.3333%, 0.4167%) relative to cement weight	Alkaloids, flavonoids, saponins, phlobatannins and tannins	H$_2$SO$_4$	0.5 M	Half-cell potential and linear polarisation resistance (LPR) test	-	@ 0.4167% Conc., LPR— Correlation prediction model (η = 96.23 ± 1.16%) Experimental model (η = 89.84 ± 2.46%)	[13]
4.	*Eucalyptus tereticornis* (Eucalyptus leaves-EL)	f$^1_{ck}$ = 48 and 42 MPa w/c ratios—0.38 and 0.47	Distilled Water	EL powder was used as coating on the steel rebar, mixed with distilled water at different percentages (0%, 20%, 30% and 40% by weight of distilled water)	-	NaCl	3%	Accelerated Corrosion Test, Ultrasonic Pulse Velocity (UPV), Half-cell potential, Flexural test and Pull-out test	1. FST—Specimen containing 40% EL → only less flexure cracks without any failure on the concrete specimen	@30% and 40% Conc. HCP—less corrosion	[15]

Table 1. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
5.	*Rhizophora mangle* L. Bark-Extract (Red Mangrove)	w/c ratio—0.499 Mix ratio—1:2.96:3.68	Methanol (CH₃OH)	Conc. of *R. mangle* L. bark-extract admixture in concrete ranged from 0% in the normal control specimens, through increments of 0.0833% up to 0.4167% relative to the weight of cement	Rich in tannins	NaCl	3.5%	Corrosion-rate, corrosion-current, andcorrosion-potential (Electrochemical techniques) and Analyses of Experimental Data through Applied Statistical Probability Distribution Models and Goodness-of-Fit Studies	-	@0.4667 Conc., LPR—99.08 ± 0.11% (experimental) 97.89 ± 0.24% (correlation)	[20]
6.	*Euphorbia tirucalli* (Indian Tree Spurge)	w/c ratio—0.65 mix ratio—1:2:4	The extract was directly purchased from the local government	The viscous resin of *Euphorbia tirucalli* was coated to the rebar directly of different thickness.	Alkaloids, flavonoids, tannins, and terpenoids	Sodium chloride (NaCl)	5%	Flexural Beam Test, Corrosion Test, Ultimate Tensile Strength and Yield Strength	a. Corroded samples → ↓ in diameter of the reinforcement bar b. Coated samples → ↑ in diameter due to the thickness of the resin film on rebar	*Euphorbia tirucalli* as coating in RCC—Corrosion resistance	[111]
7.	*Daniellia oliveri* (African copaiba balsam tree) exudates/re-sin	w/c ratio—0.65 Mix ratio—1:2:4	Exudates are obtained from Local Government	The exudates/resin is coated directly to reinforcing steel of different thicknesses, embedded in concrete slabs	Alkaloids, phenol, tannin, saponin and steroids	Sodium chloride (NaCl)	5%	Accelerated Corrosion Test, Half-Cell Potential Measurement, Resistivity of concrete test and Tensile Strength of reinforcement test	Coated specimens → higher failure loads applications with respect to corroded specimens	*Daniellia oliveri* as coating in RC—Corrosion resistance	[112]

Table 1. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
8.	*Anthocleista djalonensis* (Cabbage Tree)	-	Methanol (CH$_3$OH) & Isopropyl alcohol (C$_3$H$_8$O)	Concrete was admixed with *A djalonensis* in the following weight percentages (0.0000%, 0.0833%, 0.1667%, 0.2500%, 0.3333%, 0.4167%) relative to the weight of cement	Alkaloids, tannins, phlobatannins, saponins and flavonoids	NaCl	3.5%	Half-cell potential and Linear polarisation resistance (LPR)	-	@0.4167% Conc. LPR— η exp = 97.43 ± 1.20%, η pred = 94.80 ± 3.39%	[113]
9.	Reed Leaves Extract (RLE)	M-20 grade w/c—0.45 (CST) and 0.55 (PP) Mix ratio—1:1.5:3 & 1:3	Boiling water	Reed Leaves extract of 0.001, 0.01, 0.1 and 0.5 % (Relative to % Cement)	Alkaloids and flavonoids	NaCl	3.5%	Linear polarization resistance, Potentiodynamic polarization, Cyclic polarization, Photographic examination, Impressed voltage, and Compressive strength tests	1. CST (28 days)—Specimen with 0.5% RLE → ↑ in strength by blockage of pores	@0.5% Conc., PP—76.98% (180 days of Curing)	[114]

WLM—Weight Loss Method; PP—Potentiodynamic Polarization; EIS—Electrochemical Impedance Spectroscopy; LPR—Linear Polarization Resistance; EFM—Electrochemical Frequency Modulation; GM—Gasometric Method; HCP—Half Cell Potential; CST—Compressive Strength Test, STST—Split Tensile Strength Test; FST—Flexural Strength Test; →—showed/displayed/exhibited; ↑—increases; ↓—decreases; @—at; <—less than; >—greater than; K—Temperature in Kelvin; °C—Temperature in Degree Celsius.

Table 2. Carbon Steel/Steel mentioned in general.

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
1.	*Citrus sinensis* (sweet orange)	-	Ethanol, Dimethyl Formamide, Distilled water	50, 100, 150, 200, 250 and 300 ppm	-	H_2SO_4	0.5 M	Weight loss (ML) method, Potentiodynamic polarization (PP), Electrochemical impedance spectroscopy (EIS) and Electrochemical frequency modulation (EFM)	-	@ 300 ppm Conc., WLM—96.1% PP—88.1% EIS—80.2% EFM—80%	[2]
2.	*Cedrela odorata* Linnaeus (Spanish Cedar)	w/c ratio—0.55 and 0.60 Mix ratio—1:2:2	-	Exudate percentage in the mixture by weight of cement (0.3, 0.5, 0.7, and 0.9%)	-	Saline solution	3.53%	Chloride penetration test (CPT) and Probability of steel corrosion	-	@0.7% Conc. and w/c ratio—0.55, CPT → less corrosion	[6]
3.	*Zingiber officinale* (Ginger extract) and kelp extract (Algal Sea weeds)	w/c ratio—0.6 cement-to-sand ratio—1:3	Distilled Water, 0.1 mol/L NaOH	Added as an admixture 0.5%, 1%, 2% and 4% by mass of binder	Phenols	NaCl	8 wt.%	Open circuit potential (OCP), Linear polarization resistance (LPR), Electrochemical impendence spectroscopy (EIS), X-ray photoelectron spectroscopy analysis (XPS), Molecular dynamics simulations, Quantum mechanics, Flowability, Compressive and Flexural strength	1. CST—1% Ginger (2.2% ↑ in strength), 0.5%, 2% and 4% ↓ in strength when compared to conventional concrete 2. FST—1 % Ginger—Minor ↑ in strength	@ 2% Conc., LPR AND EIS—Less C.R and High I. E	[10]
4.	Rice Husk Ash (RHA)	Control sample strength = 29.80 N/mm² w/c ratio—0.45 Mix ratio—1:2.2:4.3	-	Weight of cement is replaced by 5%, 10%, 15%, 20% of Rice Husk Ash	-	NaCl	5%	Compressive strength, Carbonation depth, Half-cell potential, Electrochemical Test	1. CST—Strength ↑ up to 15% replacement of RHA in cement, strength ↓ at 15–20% replacement	@20% Conc., PP—85.04%	[11]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
5.	*Citrullus lanatus* (Watermelon rind extract)	Control sample strength = 50 N/mm² w/c ratio—0.43 Mix ratio—1:1.35:2.59	1 M HCl	Cement was replaced with watermelon rind extract by 2%, 4%, 6% and 8% by weight of cement	Alkaloids, flavonoids, phenol and saponin	NaCl	5%	Compressive Strength, Relative Dynamic Modulus of Elasticity, Chloride Content, Rapid Chloride Permeability Test Results, Half-cell potential for steel bar after exposure to different freeze–thaw cycles.	1. CST—Concrete with 2% *Citrullus lanatus* showed highest strength, decreased when added > 2%	@8% Conc., HCP—lowest steel corrosion	[12]
6.	*Pseudomonas aeruginosa* Commercial Rhamnolipids (RL)	Simulated concrete pore solution—0.027 M $Ca(OH)_2$ + 0.5 M NaCl (3 wt.%)	Distilled water	Four aqueous solutions with RLs Conc. (g/L) of 0.1, 1, 5 and 0 (Blank -H_2O)	-	NaCl	0.5 M	Open circuit potential, Potentiodynamic polarisation curves, Linear polarisation resistance measurements, SEM micrographs, Electrochemical impedance spectroscopy	-	@1 g/L Conc., PP—99%	[18]
7.	Silver nanoparticle (AgNPs) doped *Elaeis guineensis*—EG (palm oil) leaf extracts (EG/AgNPs)	$f^1_{ck} \geq 28$ MPa w/c ratio—0.55 Mix ratio—1:1.8:2.7	Ethanol	Green EG/AgNPs inhibitor (5%) was added to the cement on weight basis	Tannins, alkaloids, flavonoids, coumarins, saponins, terpenoids.	weekly wet and dry cycles in natural seawater in a lab curing tank for 365 days	-	Linear polarization resistance (LPR), Potentiodynamic polarisation, Half-cell potential (HCP), Electrical resistivity, Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Thermal gravimetric analysis (TGA), Atomic force microscopy (AFM) Analyses and Transmission electron microscopy (TEM)	1. CST—5% EG/AgNPs inhibitor → greater compressive strength than the control specimens. 2. EG/AgNPs inhibitor strength was greater at early ages (7, 28, and 90 days) than at later ages.	@5% Conc. for 365 days, PP—94.72 LPR—94.74	[21]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
8.	*Ricinus communis* (Castor Oil Plant)	Control Strength = 101.6 MPa w/c ratio—0.31 Mix ratio—1:1.54:1.76	Methanol	The powdered inhibitor (*R. communis* extract) was dissolved in water in desired Conc. (25, 50, 75 and 100 ppm), which was used to prepare concrete specimens	-	NaCl	3.5%	Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization study (PDS), atomic force microscopy (AFM), Temkin adsorption isotherm, Density functional theory (DFT) analysis, Compressive strength, and Split Tensile Strength tests	1. CST and STST (30 days and 120 days)—The specimen with inhibitor Conc. of 75 ppm → the highest strength, strength ↓ at 100 ppm Conc	@100 ppm for 120 days EIS—87% PP—79%	[23]
9.	Exudates/resin extract of *Lannea coromandelica* (The Indian Ash Tree)	w/c ratio—0.65 Mix Ratio—1:2:4	-	The extracts are layered or coated to the steel rebars of different thicknesses	-	Sodium Chloride (NaCl)	5%	Accelerated Corrosion Test, Half-Cell Potential Measurement, Test for measuring the resistivity of concrete and Tensile Strength of reinforcement	1. Tensile strength of reinforcement The coated samples recorded higher failure load over corroded samples	HCP— C.R—Coated sample < Uncoated Sample	[27]
10.	*Prosopis juliflora* (Mesquite) extract	w/c ratio—0.51 Mix ratio—1:1.72:3.44	Methanol	(100 ppm)	Alkaloids, polyphenol, flavonoids	NaCl	3.5%	Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization study (PDS) and atomic force microscopy (AFM) and Density functional theory (DFT) calculations.	-	@ 100 ppm EAS—86% (120 days) PP—91% (120 days)	[30]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
11.	*Cymbopogon citratus* (Lemon Grass)	w/c ratio—0.499 Mix ratio—1:2.96:3.68	CH₃OH (methanol)	Different Conc. of *Cymbopogon citratus* leaf-extract ranged from 0.00% in increment of 0.083% up to 0.4167% relative to cement proportion for the concrete casting	-	NaCl and Distilled water environment, tagged blank (H₂O)	3.5%	Electrochemical methods (corrosion-potential, corrosion-current and Corrosion-rate) and Compressive strength test.	CST—1. 0.0833% Lemon grass leaf-extract + concrete → utmost compressive-strength improvement	@0.0833% Conc., LPR—99.35%	[35]
12.	*Azadirachta indica* (Neem) leaf extract	f¹ck = 28 MPa w/c—0.65 Mix ratio—1:2.32:4.60	Distilled water	10 L/m³ of the neem leaf extract was added as an additive to the concrete specimen	Large amounts of alkaloids, saponins, tannins and terpenoids	AgNO₃	0.1 N	Half-cell potential, Compressive strength test & chloride ion penetration	CST— 1. 7 days strength—Neem < Control and Commercial inhibitors (Sika CNI and DCI) 2. 28 days strength—Neem = Control < Commercial inhibitors	@182 days, HCP—Corrosion Potential of Neem leaf extract—5%	[37]
13.	*Pinus resinosa* (Conifer Cone)	Synthetic concrete pore solutions (SCPS)—dissolving 8.33 g NaOH, 3.36g KOH and 2 g CaO in 1 L distilled water	Ethanol	Dosage of inhibitors (mg/L) 250, 500, 1000 and 1500	Flavonoids, and glycosides	Chloride	30,000 mg.L⁻¹	Electrochemical impedance spectroscopy (EIS)	-	@1000 m/L EIS— (i) SCPS with 30,000 mg/L of chloride—78.67% (ii) SCPS without chloride—61.46%	[38]
14.	*Phyllanthus muellerianus*	w/c ratio—0.5	Methanol (CH₃OH)	Admixture of 2 g, 4 g and 6 g of Phyllanthus muellerianus in concrete specimens	Tannins, phlobatanins, saponins, flavonoids, terpenoids and alkaloids	NaCl	3.5%	Linear polarization resistance (LPR) and compressive strength test	1. CST—4 g *P. muellerianus* leaf-extract admixture + RCC → the optimum compressive strength improvement	@6 g Conc., LPR—93–96%	[40]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
15.	*Crataegus* (Aubepine) and *Corchorus olitorius* (Molokhia) extract	w/c ratio—0.48 Mix ratio—1:2.48:2.84	Double distilled water	Extract Conc. (g/L)—0.25, 0.5, 1.0, 1.5, 2.0, 2.5	Flavonoids	1. S1 solution = saturated Ca (OH)$_2$ solution + NaOH + KOH 2. S2 solution = S1 + KCl (mol/L) + NaCl (g/L)	Ca(OH)$_2$ (mol/L)—Saturation NaOH (mol/L)—0.001 KOH (mol/L)—0.001 NaCl (g/L)—35 KCl (mol/L)—0.006	Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization techniques, Energy-dispersive X-ray (EDAX) analysis technique and Scanning electron microscopy (SEM)	-	a. @2.5 g/L Molokhia Conc., PP—92.66% EIS—92.147% b. @1 g/L Aubepine extract PP—94.97% EIS—93.99%	[42]
16.	L-arginine (LA)—natural occurring amino acid found in plant seeds and fish	Simulated concrete pore (SP) solution—NaOH, KOH and CaO in distilled water using magnetic stirrer	Obtained from naturally occurring amino acids	Conc. of LA (M)—0, 0.0574, 0.115, 0.172 in SP + 0.17 M NaCl corrosive medium.	-	NaCl	0.17 M	Potentiodynamic polarization, Open circuit potential (OCP), Electrochemical impedance spectroscopy (EIS), Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy	-	@0.115M Conc., PP—95.94% (144 h)	[50]
17.	*Spincea oleracea* (Spinach) and *Calotropis gigantea* (Crown Flower)	M20 grade fly ash-based concrete w/c ratio—0.53 Mix ratio—1:1.49:3.48	Water	30% of fly ash is replaced for cement, dosage of *S. oleracea* at 0.6%, *C. gigantea* at 0.24% and polyethylene glycol at 0.3% by weight of binders.	Phenolic compounds	-	-	UV–visible, FT-IR studies, XRD, SEM, Compressive strength, and Bond strength	1. CST (3, 7, 14, 21, 28 and 56 days)—*Spincea oleracea* > Polyethylene glycol, *Calotropis gigantea* and conventional concrete	-	[54]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
18.	*Camellia sinensis* (Green tea)	Control sample strength = 14.64 ± 1.31 w/c ratio—0.54 Cement to sand ratio—2.58	Hot water	(1) Dosage of Green Tea at equal volume—Volume of inhibitor—40.14, 30.11, 24.10, 20.08 (L/m^3) (2) Dosage of Green Tea at similar Conc.—Weight of Inhibitor 48.97, 36.73, 29.40, 24.50 (kg/m^3)	Polyphenols, alkaloids and volatile compounds	Sodium chloride (NaCl) solution	3.5%	Accelerated corrosion, Linear polarization resistance (LPR), Compressive strength test, Liquid chromatography mass spectrometry and Liquid chromatography-tandem mass spectrometry tests.	CST—1. At similar concentration of CI and GT—At higher Conc. GT strength > CI 2. At equal volume of CI and GT—Greater volume of GT → higher compressive strength compared to Conventional specimens	LPR— a. Similar Conc.,—51–70% b. Equal volume—75–80%	[115]
19.	*Morinda citrifolia* (Noni) leaf	M-15 grade of concrete w/c ratio—0.45 mix ratio—1:2:4	Methanol	Noni leaf extract—an admixture in concrete *Morinda citrifolia*—0.08, 0.17, 0.25, 0.33, and 0.42% (volume of extract to weight of cement)	Ascorbic acid, Flavonoids and coumarins	NaCl solution	3%	Compressive strength test, Chloride penetration resistance test and Weight/mass loss method	1. CST—(28 days)—The Noni leaf of 0.42% → the highest compressive strength	@0.42% Conc., WLM—59%	[116]
20.	*Spincea oleracea* (Spinach) extract	OPC strength (90 days) = 1060 Kg/cm^2	Double distilled water	OPC is replaced by Fly ash in 10, 25 and 50% by mass of cement Conc. of Spinach extract in (mg/L) are 0, 50, 100, 200, 400 and 600 ppm	Carbohydrates, quinone, phytosterol, glycosides, proteins flavonoids and terpenoids	Sodium chloride solution	5%	X-ray fluorescence (XRF), XRD, SEM, Consistency and setting time test, Compressive-strength test, Differential thermal analysis and Potentiodynamic polarization test	CST (till 90 days)— 1. Specimen with low fly ash → the highest strength. 2. Specimen with 10% Fly ash + SP—highest strength	@600 ppm Conc., along with 10% fly ash PP—82% (1 h @ 298 K)	[117]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
21.	*Disporopsis pernyi* (Evergreen Solomon's seal) leaves extract (DPLE)	Control sample strength (28 days) = 80 N/mm² w/c ratio—0.5	DI water	The cement replacement was done with metakaolin and micro silica (MS) 0, 10, 50 and 100 mg/L of DPLE in 3.5 wt% NaCl solution	-	NaCl Solution	3.5 wt.%	Electrochemical impedance spectroscopy technique, polarization measurement, water absorption test and compressive strength	1. CST—(1day, 1 week, 2 weeks and 4 weeks)—sample MS15M15 (70 wt.% cement, 15 wt.% metakaolin and 15 wt.% micro silica → the highest strength at all ages when compared to other specimens	@1000 mg/L Conc. PP—87.6%	[118]
22.	*Portulaca quadrifida* (PQ) (Chicken weed) leaves	-	Ethanol	100, 200, 300, 400 and 500 ppm of PQ extract are immersed in well water containing Zn^{2+} ions	-	Well water with and without Zn^{2+} ions	-	Weight-loss study, SEM, EDX, AFM, Potentiodynamic polarization study and the Electrochemical impedance studies	-	@500 ppm of PQ & 300 ppm of Zn^{2+} WLM—92% (303 K)	[119]
23.	*Camellia sinensis* (Green tea) extract	w/c ratio—0.54 Cement to sand ratio—2.58	Hot water	Volume of inhibitor (L/m³ concrete)—40.14, 30.11, 24.10, 20.08	Flavan-3-ols, caffeoylquinic acids, flavanols, and theaflavins	Sodium chloride (NaCl)	3.5%	Impressed current and cyclic wetting-drying, and corrosion development was measured with linear polarization resistance	-	Equal volume—Green Tea → 75–80%	[120]
24.	*Zingiber officinale* (Ginger) extract and Kelp extract inhibited separately	The saturated Ca (OH)₂ solution—used as the Simulated Concrete Pore solution	Distilled water	The Simulated Concrete Pore solution (SCP) is incorporated with 1%, 2% and 3% ginger extract also the SCP solution is incorporated with 1% and 2% kelp extract.	-	NaCl	Different concentrations	Potentiodynamic polarization (PDP), Linear polarization (LP), Electrochemical impedance spectroscopy (EIS), Liquid chromatography-Mass spectrometry (LC MS), attenuated total reflection Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy	-	@2% Conc., high ↓ in chloride induced corrosion	[121]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
25.	Green *Bambusa arundinacea* (Common Bamboo) Leaves extract	Control Sample strength = 42 MPaw/c ratio—0.45 Mix ratio—1:1.2:2	Ethanol	Inhibitor addition was 2% by weight of cement	-	MgCl$_2$	Chloride concentration = 0.94%	Compressive strength test, Durability permeability using Initial surface absorption test (ISAT) and Field emission scanning electron microscopy (FESEM)) for 360 days exposure	1. CST (180 & 360 days)—Concrete + 2% inhibitor → highest strength	-	[122]
26.	*Rhizophora mangle* L. Leaf-Extract (Red Mangrove)	w/c ratio—0.499	Methanol	Conc. of extract from 0% in increments of 0.0833% up to 0.4167% relative to the weight of cement	-	H$_2$SO$_4$	0.5 M	Half-cell potential, Linear Polarization resistance and Compressive strength test	1. CST (28days)—0.25% *Rhizophora mangle* L. leaf extract → optimum compressive strength surpassed control sample	@0.1667% Conc., LPR—76.32 ± 4.44%	[123]
27.	*Phyllanthus muellerianus*	-	Water	The variations of *Phyllanthus muellerianus* admixed during casting of fresh concrete are in the Conc. of 1.67, 3.33 and 6.67 g/L	Tannins, Saponins, Alkaloids, Steroids, Terpenoids, Glycosides, Phlobatannins and Flavonoids	H$_2$SO$_4$	0.5 M	Atomic Absorption Spectroscopy/Fourier Transform Infra-Red Spectroscopy, Total corrosion test	-	Concrete + Phyllanthus muellerianus → less corrosion as compared to sample	[124]
28.	*Taraxacum officinale* (Common Dandelion) extract (TOE)	-	Aqueous/Ethanol solution	TOE concentration (mg L^{-1})—100, 200, 300 and 400 mg/L	Polyphenols, lactones, phenyl-propanoids, triterpenoid saponins, polysaccharides, amino-acids and flavonoids	Sea water	-	High Performance Liquid Chromatograph (HPLC), mass loss test, Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization, UV spectra, FT-IR, and SEM	-	@400 mg/L Conc., WLM—94.3% (298 K for 7 days) WLM—90.9% (328K) EIS—90.4% (298 K for 30 min) PP—88.2% (298 K for 30 min)	[125]

Table 2. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
29.	Green ionic liquid compound, Isostearyl ethylimidonium ethosulfate (Quaternium-32)	Control sample strength (28days) = 46.97 MPa w/c ratio—0.45 Cement sand ratio—1: 1.5	Green ionic liquid inhibitor was bought from a company	Inhibitor Conc. (μmol L^{-1})—5, 10, 15 and 20	-	1. Simulated concrete pore solution at pH 12—saturated Ca $(OH)_2$ solution) + NaCl + $NaHCO_3$ powder.2. NaCl solution at pH 7	Calcium hydroxide solution (0.013 M), 3.5 wt.% NaCl	Open circuit potential, EIS, atomic force microscope and scanning electron microscope coupled with an energy dispersive x-ray unit, Compression and Flexure strength tests	1. CST (2, 7, 14, 21, and 28 days)—Mortar samples + 20 μmol/L of Quaternium-32 $\rightarrow$ more strength (up to 14 days) when compared to blank samples and then the strength starts to decrease slowly for 28 days. 2. FST (2, 7, 14, 21, and 28 days)—Mortar samples + 20 μmol/L of Quaternium-32 $\rightarrow$ more strength (up to 21 days) when compared to blank samples and then the strength constant 28 days	@20 μmol L^{-1} Conc., EIS—93.4% (20 °C, pH—12)	[126]

Table 3. Mild Steel (A).

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
1.	*Rosa damascena* (Damask Rose) leaves	Simulated concrete pore solution of 0.5 M Ca(OH)$_2$, 0.1 M NaOH, 0.5 M KOH	0.5 M H$_2$SO$_4$ & Ethanol	Conc.—2, 6 and 12 *v/v*%	Tannins, alkaloids, phenols and saponins	NaCl (coastal environment)	0.5 M	Gas chromatography-Mass spectroscopy analysis (GC–MS), Fourier transform infrared spectroscopy (FT-IR) analysis, Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization techniques and Scanning Electron Microscopy	-	@12 *v/v*%, PP—81.6% EIS—81.9%	[8]
2.	*Areca catechu* (Betel-Nut Palm) leaves, *Acacia longifolia* (Golden Wattle), *Melastoma malabathricum* (rhododendron), *Elaeis guineensis* (Palm Kernel oil) and *Cocos nucifera* (Coconut Palm)	f$^1_{ck}$ = 30 N/mm^2 (28 days) Concrete Mixes—OPC, MN5C, CI2C, GI2C	Ethanol	(1) 0, 2, 4, 6 and 8% (*v/v*)—Weight loss test (2) The inhibitor Conc. for strength tests is 1, 2, 3, 4, 5 and 6% by cement weight	Alkaloids, tannins, flavones, and triterpenes	HCl	1 M	Weight Loss Method, Nitrogen content analysis, Slump, Fresh density and air content, Water absorption, Modulus of elasticity, Initial surface absorption, Tensile and Flexural strength test and Compressive strength	1. CST—GI2C batch (17% ↑ @28 days and 22.5% ↑ @365 days) when compared to Contaminated Samples 2. STST—GI2C batch (10.2% ↑ @28 days and 10.63% ↑ @365 days) when compared to Contaminated Samples 3. FST—GI2C batch (10.57% ↑ @28 days and 5.33% ↑ @365 days) when compared to Contaminated Samples	@8 *v/v*%, WLM—73.78%	[9]
3.	*Vernonia amygdalina* extract -VA (Bitter Leaf)	Control sample strength = 18 MPa w/c ratio—0.44 mix ratio of 1:2:4	Ethanol	Inhibitor test Conc. of 25, 50, 75, and 100% were prepared by diluting with distilled water	Saponin and tannin	H$_2$SO$_4$	0.2 M	Potential and pH measurements, Compressive strengths, and Weight loss measurements	1. CST—Concrete with 25% VA extract → highest strength	@50% Conc., WLM—60.68%	[19]

Table 3. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
4.	Waste *Platanus acerifolia* (London Plane Tree) leaves (PAL)	The saturated limewater—Simulated concrete pore (SCP) solution	NaOH, aqueous solution and Ethanol	The SCP solution -the blank system, added with 3% extract 1#, extract 2#, and extract 3#, SCP solutionwith 1, 3 and 5% extract 4#.	Massive flavonoid compounds	NaCl	0.01 mol/L per day for a 10-day period to detect chloride ion penetration	Ultrasonic-assisted alkali-pre-treated ethyl extraction method, Ultra-performance liquid chromatography-mass spectrometry (UPLC-MS), X-ray photo electron spectroscopy (XPS), Quantum mechanics, molecular dynamics simulations, Linear polarization (LP) and Electrochemical impedance spectroscopy test	-	EIS—99.652 LPR—98.44	[22]
5.	Sugarcane (bagasse)	w/c ratio—0.5 Mix ratio—1:1.5:3	-	The weight of cement is replaced with the Conc. Of bagasse in percentages such as 0, 8, 11, 14, and 17%	-	Exposed to air and water.	RC samples are partially and totally soaked in water	Electrochemical polarization technique was conducted using a computer program to measure the Corrosion Potential, Polarization measurements, Corrosion Current and Electrical Resistance of Concrete	-	CR— a. Samples exposed to air> partially immersed in water> totally immersed in water. b. phosphatized steel > oxidized steel > cleaned steel.	[25]
6.	*Thymus mastichina* (Marjoram) & *Illicium verum* (Star Anise)—(TMAV) oil extracts	-	Oil Extracts were obtained on commercial basis	Volumetric Conc. of 1, 2, 3, 4 and 5% of TMAV Conc. per 200 mL of the acid electrolytes electrolyte	Phenols	H_2SO_4 and HCl solution	0.5 M	Weight loss analysis, Potentiodynamic polarization, Open circuit potential measurement, ATR-FTIR spectroscopy, Optical microscopy, and Macroscopic characterization	-	@5% Conc. a. 1 M H_2SO_4 PP—80.85% WLM—81.24% (480 h) b. 1 M HCl PP—70.43% WLM—68.33% (480 h)	[29]

Table 3. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests conducted	Strength Test	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.				
7.	*Origanum vulgare* L (Oregano) and *Ilex paraguariensis* (Yerba Mate)	Control sample strength = 34.7 MPa	Demineralized water	The Liquid form (LQ) was used directly as mixing water and the vacuum freeze-dried-FD form was first diluted in demineralized water	Phenolic compounds	NaCl	3.5%	Setting-time, flexural, compression strength and XRD technique	1. CST—Specimens + Oregano (OR) extract → higher strength when compared to Yerba Mate (YM) extract in both aqueous and vacuum freeze-dried form (lyophilized)	-	[39]
8.	*Areca catechu* (palm oil tree)	f^{1}ck = 30 MPa	Ethanol	Addition of 2% bio-friendly *Areca catechu* per cement weight	Flavonoids, terpenes, alkaloids and tannins	NaCl and MgSO$_4$	5%	Compressive strength, Weight loss and Field emission scanning electron microscopy (FESEM)	1. CST—Concrete contaminated with MgSO$_4$ and NaCl + 2% *Areca catechu* → highest strength	WLM—Areca Catechu ↓ CR of contaminated concrete	[41]

Table 4. Mild Steel (B).

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
1.	*Areca catechu* (palm oil tree) leaf Extract	$f^1ck = 30$ MPa	Ethanol	1. MN5C—the batch contaminated with 5% ($MgSO_4$) and NaCl 2. CI2C—the contaminated batch added with 2% ($NaNO_2$) 3. GI2C—The contaminated batch containing 2% *Areca catechu* extract by the weight of cement	Saponins, tannins, flavonoids, and alkaloids	$MgSO_4$ and Sodium chloride (NaCl)	5%	Electrochemical impedance spectroscopy (EIS), Linear polarization resistance, weight loss test, Ultrasonic pulse velocity	Areca Catechu—↓ CR of contaminated concrete	[45]
2.	(*Olea europaea* L.) Olive leaf extract	-	Methanol, ethyl acetate, dichloromethane and hexane	NaOH (0.1 M) + NaCl (0.5 M) in the absence and presence of different organic extracts from *Olea europaea* L.	Polyphenols and flavonoids	The solution of corrosion test was NaOH + NaCl with pH around 13	NaOH—0.1 MNaCl—0.5 M	Polarization curves, Electrochemical impedance spectroscopy, Mott-Schottky analyses and Gas chromatography mass spectrometry (GC–MS) analysis	For methanol extract PP—91.9%	[53]
3.	*Davidian involucrata* (handkerchief tree) Leaves (DILE)	Concrete pore solution of 0.2 M NaOH, 0.5 M KOH and 0.3 M $Ca(OH)_2$ with 13 pH containing 3.5 wt.% $CaCl_2$	DI water	0, 10, 50 and 100 mg/L of DILE at 15, 25 and 35 C	-	NaOH, KOH, Ca (OH)₂ and $CaCl_2$	NaOH—0.2 M, KOH—0.5 M, $Ca(OH)_2$—0.3 M, $CaCl_2$—3.5 wt.%	Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization, FESEM	@100 mg/L Conc., EIS—80.3% (18 h at 25 °C) PP—96% (18 h at 25 °C)	[127]
4.	*Sinapis arvensis* (Seed Mustard) extract (SASE)	-	Deionized water	800, 600, 400 and 200 ppm of *Sinapis arvensis* Mustard seed extract	-	Sodium chloride	3.5%	FE-SEM, EDS, GIXRD, AFM, FT-IR test, UV—Visible analysis, Electro chemical impedance spectroscopy (EIS) and Tafel-polarization tests	@SASE: ZN—200:600 ppm PP—88% EIS—85%	[128]

Table 4. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
5.	*Nicotiana tabacum* (Tobacco) Extract	Self-Compacting Concrete	Ethanol	0, 0.25, 0.5 and 0.75 g of the extract in 1 N NaCl solution	Alkaloids and terpenoids	NaCl	1 N	Weight loss method and accelerated electrochemical test	0.75 g of extract—WLM—12.5%	[129]
6.	Oil coating containing—*Elettaria cardamomum* (Cardamom), *Syzygium aromaticum* (Clove), *Myristica fragrans* (Nutmeg), Indian Sambrani, *Chrysopogon zizanioides* (vetiver), *Cinnamomum camphora* (Camphor) and *Santalum album* (sandalwood oil)	-	Water	Oil extract coated mild steel	-	NaCl Solution	3.5 wt.%	Weight loss method, Electrochemical studies such as Polarization study and AC impedance spectra, Surface analysis by FTIR spectra, Scanning Electron Microscopic studies (SEM) and Contact angle measurement	WLM—99% (1 day period)	[130]
7.	Leaf and Bark Extracts of *Acacia tortilis*—ATL and ATB (Umbrella Thorn)	-	Aqueous ethanol	ATL and ATB Inhibitor Concentration C (g/L)—0.25, 0.5, 1.0 and 1.50.	Alkaloids, saponins, glycosides, flavonoids, tannins, triterpenes and anthraquinones	Uninhibited and inhibited seawater	-	Potentiodynamic polarization curves, Electrochemical impedance spectroscopy and Mass loss measurements	@1.5 g/L Conc. WLM—88.7% (298 K) PP—81.7% EIS—87.5%	[131]
8.	Maize gluten meal extract (MGME)	Synthetic concrete pore solution: 0.6 mol/L KOH + 0.2 mol/L NaOH + saturated CaOH solution with 3 wt.% NaCl	Ethanol	Five different MGME Conc.— 0, 0.25, 0.5, 1.0, and 2.0 g/L	Protein, amino acids	Sodium chloride	3.0 wt.%	Electrochemical impedance spectroscopy (EIS), Tafel polarization curve, SEM-EDS, ATR-FTIR and surface structure analysis	@2 g/L Conc., EIS—88.10% PP—86.86%	[132]

Table 4. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
9.	Maize gluten meal extract (MGME)	Synthetic concrete pore solution: 0.6 mol/L KOH + 0.2 mol/L NaOH + saturated CaOH$_2$ solution with 3 wt.% NaCl	Water, Acetone, Ethanol, acid, and alkalis	The synthetic concrete pore solution with Conc. of MGME is 1.0 g/L	-	NaCl	3 wt.%	Electrochemical Impedance Spectroscopy (EIS), Polarization measurement, High performance liquid chromatography, X-ray Photoelectron Spectroscopy method, Quantum chemical computations and molecular dynamics simulations	@1 g/L Conc., EIS—86.02% PP—80.27%	[133]
10.	Thyme leaves extract	-	Double-distilled water	Inhibitor Conc.—200, 400, 600, 800, 1000 and 1200 mg/L	Phenols	HCl	2 M	Weight loss method, cyclic sweep linear polarization resistance (LPR), Electro chemical impedance spectroscopy (EIS), and Fourier transform infrared spectroscopy	a. @1000 ppm Conc., WLM—84% PP—75.6% b. @≤400 mg/L Conc., LPR—80% c. @400 ppm Conc., EIS—78% (25 °C)	[134]
11.	*Ficus hispida* (Hairy Fig) leaves extract (FHLE)	-	Absolute ethanol	Conc. Of FHLE is 50, 100, 150, 200 and 250 ppm	Alkaloids	HCl	1 M	Weight loss measurement, Potentiodynamic polarization, Electrochemical impedance spectroscopy (EIS) techniques, Gas Chromatography–Mass Spectrometry (GC–MS), Diffuse reflectance Fourier transform infrared spectroscopy, Scanning electron microscopy, Energy-dispersive X-ray (EDX), and X-ray diffraction studies.	@250 ppm Conc., PP—95.71% EIS—90.29%	[135]

Table 4. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
12.	*Hyptis suaveolens* (Pig Nut) leaves	-	Water and ethanol	Inhibitor test solutions were prepared in the Conc. Range 50–250 mg/L	Tannins, saponins, alkaloids, flavonoids and glycosides	H_2SO_4	1 M	Mass loss measurement, Potentiodynamic polarization, Electrochemical impedance spectroscopy measurements, FT-IR, XRD and SEM	@250 mg/L Conc., WLM—76% (308 K)PP—95% EIS—93.3%	[136]
13.	Leaves (L.V) and stem (S.T) extracts of *Sida acuta* (Common Wireweed)	-	Absolute ethanol	L.V(leaves extract)—0.5, 0.4, 0.3, 0.2 and 0.1 g/L Stem extract (ST)—0.5, 0.4, 0.3, 0.2 and 0.1 g/L	Saponins, flavonoids, tannins, alkaloids, organic acid and anthraquinones in the leaves Tannins, alkaloids, and anthraquinones only present in the stem extract	H_2SO_4	1 M	Chemical (weight loss and hydrogen evolution), Spectroscopic (AAS, FTIR and UV-V)	@0.5 g/L Conc., WLM—85% (30 °C) GM—80% (30 °C)	[137]
14.	*Piper betle* (Betel) leaves extracts (BLE)	-	Water	Conc.—50, 100, 200 and 400 mg/L	-	HCl	1 M	Fourier infrared spectrum research, OCP analysis, EIS test, Potentiodynamic polarization, Adsorption isotherm model, Analysis of corrosion kinetics, SEM analysis, AFM analysis, Quantum chemistry research and Molecular dynamics simulation.	@400 mg/L Conc., EIS—95.4% (308 K) PP—94.7% (308 K)	[138]

Table 4. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
15.	*Phyllanthus amarus* leaf extract (PAE)	-	Ethanol	Conc. Of PAE—1, 2, 3, 4 (*v/v*%)	-	HCl	1 M	Potentiodynamic polarization, Electrochemical impedance spectroscopy, Weight loss studies, and Computational studies	@4 *v/v*% WLM—94% (24 h & 303 K) EIS—95.76% (2 h & 303 K) PP—95.34% (2 h & 308 K)	[139]
16.	Orange Peel Extract	-	-	Concentration (g/L)—1,2,3,4 and 5	Terpenoids, flavonoids, saponins, tannins, and phenols	HCl	1 M	GC-MS analysis, Potentiodynamic polarization measurements, and Electrochemical impedance analysis	@2 g/LConc., PP—93% EIS—99%	[140]
17.	Cysteine based silver-gold nanocomposite (Cys/Ag-Au NCz) and *Punica granatum* (Pomegranate seeds)	-	Double distilled water and Ethanol	Inhibitor concentrate-ion (ppm)—30, 50, 100, 150, 200 and 300 ppm	-	HCl	1 M	Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Ultraviolet-visible spectroscopy (UV-Vis), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDAX), Thermogravimetric analysis (TGA) and Transmission electron microscopy (TEM), Weight Loss, Potentiodynamic polarization, Open circuit potential and Electrochemical impedance spectroscopy	@300 ppm Conc., WLM—95.08% (303 K for 6 h) PP—94.01% (303 K) ES—96.01% (303 K)	[141]

Table 4. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
18.	*Turbinaria ornata* (Tropical Brown Algae) (TO)	-	Methanol, Diethyl ether and chloroform (Soaking and Soxhlet extraction)	1. 5, 10, 15, 20, 25 and 30 g/L for Weight Loss test. 2. 5, 10, 15, 20 and 25 g/L for PP and EIS tests	Phenolics, Terpenoids, steroids, Alkaloids and Tannins.	Conc. HCl	37% or 12 M	Metal leaching analysis, Potentiodynamic polarization and Electrochemical Impedance spectroscopy, FT-IR, GC-MS, Identification of marine bio filming bacteria using phylogenetic analysis, antimicrobial activity, Antibacterial activity study, SEM, In-situ detection of biofouling using phytagel, Mortality bioassay of Artemia marina and Antifouling bioassay against Balanus Amphitrite	a. @30 g/L Conc., WLM—99.3% (20 & 30 min, methanol extract) b. @25 g/L Conc., PP—90.5% (30 min, methanol extract) EIS—94.5% (30 min, methanol extract)	[142]
19.	Laurhydrazide N′-propan-3-one (LHP)	-	This inhibitor was purchased from a company	Concentrations: 92, 185, 277, and 370 μmol/L	-	HCl	5 M	Open circuit potential, Potentiodynamic polarization and Electrochemical Impedance spectroscopy, scanning electron microscopy (SEM) coupled with an energy-dispersive X-ray spectroscopy (EDX) unit, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS), kinetics and thermodynamic parameters study and Density functional study	@370 μmol/L Conc., PP—94% (30 min exposure, 20 °C) EIS—92.8% (30 min, 20 °C)	[143]

Table 4. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/ Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
			Solvent	Conc.		Medium	Conc.			
20.	*Vitis vinifera* (Grape seed) extract (GSE)	-	This inhibitor was purchased from a company	Conc.—0, 100, 200 and 300 ppm	Flavonoids and phenolics	HCl	1 M	Electrochemical impedance spectroscopy, Potentiodynamic polarization, and electrochemical noise technique, water droplet contact angle, field-emission scanning electron microscopy coupled with energy dispersive spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and atomic force microscopy	@300 ppm Conc., EIS—91.93% (3 h @ 25 °C) PP—96% (25 °C)	[144]
21.	*Eriobotrya japonica* Lindl. (Loquat) leaves extract	-	0.5 M H_2SO_4	Conc.—5, 10, 25, 50 and 100 (%*v*/*v*)	Anthraquinones, amino acids and glycosides	H_2SO_4	0.5 M	Weight loss, open circuit potential (OCP), Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and scanning electron microscope	@100% *v*/*v* Conc., PP—96.3% (298K) EIS—94.3% (298K) WLM—96.2% (298 K for 4 h)	[145]
22.	*Posidonia oceanica* (Mediterranean Tapeweed leaves)	-	Ethanol & Isopropanol	Conc.—100, 300, 500, 700 and 1000 ppm	Alkaloids and Tannins	HCl	1M	Weight reduction, open circuit potential, Potentiodynamic polarization and SEM	@1000 ppm Conc., WLM – 79% (293K)	[146]

Table 5. No usage of steel.

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Ref.
			Solvent	Conc.		Medium	Conc.			
1.	*Citrus sinensis* (Orange) peel extracts	Control Sample strength—30 MPa (Oxydtron) and 37.5 MPa (Mapei Dynamon SR 31)	-	Inhibitor was added to the concrete mix with Conc. of 1% and 3% by weight of cement	-	-	-	Compressive strength test	CST—1. Concrete without GCI + Mapei Dynamon SR 31 → highest strength. 2. Concrete with 3% GCI + Oxydtron → highest strength.	[34]
2.	*Solanum torvum* (Turkey Berries) Leaves	M25 grade of concrete w/c ratio—0.50 Mix ratio—1:1.53:3.15	Water	0%, 0.5%, 1.5%, 2% and 2.5% by weight of cement is added as the green inhibitors	Tannins and alkaloids	-	-	Cube Compression Test, Split Tensile and Flexural Strength of Concrete	1. CST, STST and FST—Concrete + 1.5% Turkey Berries) Leaves → highest strength compared to other % additions	[36]
3.	*Cedrela odorata* Linnaeus (Spanish Cedar) extract	w/c ratio—0.55 and 0.60 Mix ratio—1:2:2	Water	Dosages of cedar extract by weight of cement added in the mixing water of 0.0, 0.3, 0. 5, 0.7 and 0.9%	-	-	-	Workability and compressive strength of concrete	1. CST—Sample + 0.7% *Cedrela odorata* Linnaeus → highest strength	[49]
4.	*Colocasia esculenta* (Taro)	-	-	The fresh extract from the stem and the leaf part of the Colocasia plant were added in percentages of 1, 2, 3, 4, and 5% by weight of cement	Alkaloids, glycosides, terpenoids, saponins, phenols, flavones, and anthocyanins	-	-	Setting time of cement, Marsh cone flow study, Mini slump cone study and Fourier transform -Infrared spectroscopy (FT-IR)	-	[147]

Table 5. *Cont.*

S. No	Natural Green Corrosion Inhibitors	Concrete Details	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Strength Test	Ref.
			Solvent	Conc.		Medium	Conc.			
5.	*Amazonian Açaí* (Palm) Leaves	w/c ratio—1:3 (*w/w*), 1:2.5 (*w/w*), fibre/cement ratio—1:20 (*w/w*) and fibre/cement ratio—1:100	Water	Fibre/sol. proportion of 20:1 (g/L) and fibre/sol. proportion of 10:1 (g/L)	Phenol	NaOH	1 & 5%	Scanning electron microscopy, X-ray diffraction, and thermogravimetry	-	[148]
6.	*Coffea* (Caffeine molecule)	Control sample strength (28 days) = 57.9 MPa	Caffeine supplied by Sigma Aldrich as an inhibitor	0, 25, 50 and 75 ppm of caffeine was added as an additive to the mixing water to prepare cement paste and mortar specimens	-	-	-	X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT–IR), Differential thermal (DTA), Thermal gravity (TGA), Scanning electron microscopy (SEM) and Compressive strength	1. CST (28 days)—Mortar + 75 ppm caffeine → more strength than other Conc.	[149]
7.	*Azadirachta indica* (Neem) leaves and *Curcuma* (turmeric tubers)—Biopolymers	M30 grade concrete w/c ratio—0.45 mix ratio—1:1.36:2.58	Ethanol	Partial replacement of biopolymer in the concrete specimen in both powder as well as in extraction forms in the proportion of 0.25, 0.5, 0.75 and 1%.	Phytochemicals present in Turmeric are Phenols, Flavonoids, Tannins, Alkaloids, Terpenoids and Steroids Phytochemicals present in Neem are Flavonoids, Tannins, Alkaloids, Terpenoids, and Steroids	Sodium Chloride and Sodium Hydroxide	3% NaCl and 0.3% of NaOH	Specific Gravity test, Phytochemical analysis, Compressive strength test, Split tensile test, and Rapid Chloride penetration test	1. CST (28days)— a. Specimen + 0.25% Turmeric → highest strength in powder form b. Specimen + 0.25% Neem → highest strength in extraction form 2. STST—Specimen + 0.25% Neem → highest strength in extraction form	[150]

Table 6. Iron.

S. No	Natural Green Corrosion Inhibitors	Extract Properties		Phyto-Chemicals	Corrosive Medium		Characterization/Tests Conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
		Solvent	Conc.		Medium	Conc.			
1.	*Satureja montana* L. (Winter Savory)—(SM)	Water	The Conc. of the *Satureja montana* L. extract was 2.0 g/L. 1 mL *Satureja montana* L was added in 50 mL NaCl solution	Phenols	Sodium chloride solution	0.1 mol/L	Potentiodynamic polarization, EIS study, Cyclic voltammetry (CV) and atomic absorption spectrometry	@2 g/L Conc. PP—57% CV—52.56%	[33]
2.	*Allium cepa* (Onion)	Water	*Allium cepa* Conc. (g/L)—0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4	Flavonoid	Industrial Chill Waste-water System	-	Weight loss technique	@0.6 g/L Conc., WLM—92%	[151]

Table 7. Copper.

S. No	Natural Green Corrosion Inhibitors	Extract Properties		Corrosive Medium		Characterization/ Tests conducted	Highest Inhibitor Efficiency (I.E)/Corrosion Rate (C.R)	Ref.
		Solvent	Conc.	Medium	Conc.			
1.	Ibuprofen	Expired ibuprofen syrup is used which is purchased at a local pharmacy	Conc. of amount of ibuprofen in the synthetic acid rain solution is 5×10^{-3} M, 1×10^{-2} M, 1×10^{-3} M and 5×10^{-4} M	Synthetic acid rain = Na_2SO_4, $NaHCO_3$, and $NaNO_3$ and H_2SO_4 solution	Na_2SO_4 (0.2 g/L), $NaHCO_3$ (0.2 g/L), $NaNO_3$ (0.2 g/L)	Open circuit potential, Potentiodynamic polarization, Cyclic voltammetry, Electrochemical impedance spectroscopy, scanning electron microscopy with energy dispersive spectroscopy and Quantum chemical calculations	@1×10^{-2} M Conc., WLM—96.25% EIS—97.3% PP—97.2%	[152]

11. Conclusions

This research investigates the damage occurring on structural materials such as RCC and steel in the form of corrosion when exposed to external factors. To hinder this phenomenon, the use of inhibitors has become the norm and it has been seen that they have remarkable properties in terms of adaptability, durability, sustainability, and affordability. However, with time, research has paved the way for a highly green and eco-friendly approach to reduce corrosion in a sustainable manner by using green corrosion inhibitors as its economical, less harmful and biodegradable compared to their counterparts such as the disadvantages of traditional organic, hybrid, and inorganic inhibitors. Studies showed that it was practical and affordable to collect the ingredients that are necessary for inhibition from natural plants as they contained the phytochemicals. The active compounds of the phytochemicals get easily adsorbed on the surface of steel in RCC, thus obstructing the active corrosion spot and thereby preventing the entry of destructive species which can lead to degradation of RCC structures. The paper categorically details the advantages of using natural plant extracts, types of plants and its parts, parameters to be considered to extract the plant phytochemicals, methods of extraction and techniques, and tests to determine the inhibitor efficiency and corrosion rate on steel. Although major research works have been carried in the industrial sector by using different plant extracts as an admixture to the corrosive media to reduce steel rebar corrosion, there is a lack of research work in using these natural plant extracts as an admixture to the concrete or as a replacement to the materials present in the concrete or as a coating to steel in the civil construction field to reduce the damage of RCC. There is limited research on green corrosion inhibitor that has the potential to determine which phytochemical compound is responsible for the inhibition process by the means of software analysis using quantum chemical calculations and molecular dynamic simulation methods to clearly understand the adsorption mechanism of plant extract on the surface of the substrate (steel). The outcome of this paper aims to provide a comprehensive and streamlined data set that can be used to gain a better knowledge of how practically and efficiently each plant extract acts as a green corrosion inhibitor. It can also be used to make insightful observations about how the use of different plants and their parts perform as a green corrosion inhibitor in concrete or steel.

Author Contributions: J.A.E.S. established the framework, data collection, drafted and edited the manuscript; G.M.G. supervised, reviewed, and conceptualized the flow of the paper. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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