*ID: 956*

# Plant-Derived Natural Extracts and Nanoparticle Technologies for Corrosion Control in Reinforced Concrete: A Systematic Review of Mechanisms, Performance Metrics, and Emerging Hybrid Systems

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## Abstract

The corrosion of steel reinforcement remains the single most pervasive threat to the long-term durability of reinforced concrete infrastructure worldwide, with direct economic losses estimated at trillions of dollars annually. Traditional corrosion protection strategies—epoxy coatings, cathodic protection, and synthetic chemical inhibitors—are often effective but face increasing scrutiny regarding their environmental footprint, long-term reliability, and cost-effectiveness in aggressive service environments. Over the past two decades, two alternative paradigms have emerged that align with the principles of sustainable construction: plant-based "green" corrosion inhibitors and nanoparticle-modified cementitious systems. This systematic review synthesizes findings from over 150 peer-reviewed studies published between 2020 and 2026, with particular emphasis on the most recent advances in both fields. The first part of the paper examines the mechanistic basis of corrosion inhibition by botanical extracts, focusing on the adsorption behaviour of phytochemical constituents—flavonoids, tannins, alkaloids, and terpenoids—on steel surfaces under the high-pH conditions characteristic of concrete pore solutions. Electrochemical data from more than 40 plant species are compiled and critically evaluated, with inhibition efficiencies exceeding 90% reported for several species in chloride-laden simulated pore solutions at optimized concentrations. However, a recurring concern identified in the literature concerns heavy metal contamination of plant materials harvested from anthropogenically impacted environments; recent studies from Iran and elsewhere have documented measurable concentrations of lead, cadmium, and other toxic elements in medicinal plants, with significant implications for the safety of plant-derived construction additives. The second part of the review systematically evaluates the role of nanoparticles—particularly nano-silica, nano-titania, carbon nanotubes, and green-synthesised nanomaterials—in enhancing concrete durability through pore refinement, permeability reduction, and autonomous crack healing. Data from laboratory studies indicate that optimal nano-silica addition (1.5–2.5% by cement weight) can reduce water absorption by up to 41%, decrease chloride permeability by 24–40%, and improve resistance against aggressive chemical attack by 39–42%. Bacterial–nano hybrid systems for self-healing concrete have demonstrated healing efficiencies of up to 80% for cracks under 0.5 mm. The review concludes with a critical discussion of the knowledge gaps that remain, including the need for standardised testing protocols, long-term field validation, and life-cycle assessment of hybrid plant–nanoparticle systems.

***Keywords:*** *Reinforced concrete; steel corrosion; green corrosion inhibitors; plant extracts; nanoparticles; nano-silica; self-healing concrete; heavy metal contamination; sustainable construction.*

## 1. Introduction

The durability crisis in reinforced concrete infrastructure is both a technical challenge and a sustainability imperative. Concrete—the most widely consumed material on Earth after water—supports the built environment that houses, transports, and powers modern civilisation. Yet the very mechanism that gives reinforced concrete its structural capability, namely the bond between steel reinforcement and the surrounding cementitious matrix, is also its Achilles' heel. Chloride-induced corrosion of embedded steel accounts for the majority of premature deterioration of bridges, parking garages, marine structures, and other concrete elements exposed to de-icing salts or seawater. When chlorides penetrate the concrete cover and reach the steel surface, they locally disrupt the passive oxide film, initiating an electrochemical corrosion process that proceeds through a well-understood sequence of anodic dissolution of iron, cathodic reduction of oxygen, and expansive rust formation. The volumetric expansion of corrosion products—typically four to six times the volume of the original steel—generates tensile stresses that crack the concrete cover, accelerating further ingress of aggressive agents and creating a self-perpetuating cycle of deterioration [1,2].

The economic consequences are staggering. The global annual cost of corrosion is estimated at approximately 2.5 trillion US dollars, representing 3–4% of GDP in industrialised nations [3]. While not all of this is attributable to reinforced concrete, corrosion of steel reinforcement in concrete constitutes a substantial fraction. Beyond direct financial costs, corrosion-related structural failures lead to loss of service life, increased maintenance and rehabilitation expenditures, and in severe cases, risks to public safety.

Traditional strategies for corrosion protection in reinforced concrete can be broadly categorised into three approaches: (i) physical barriers that isolate the steel from the aggressive environment, such as epoxy-coated rebar, galvanised steel, and stainless steel reinforcement; (ii) electrochemical interventions, including cathodic protection systems; and (iii) chemical modifications of the concrete matrix through the addition of corrosion inhibitors or supplementary cementitious materials [4,5]. While these methods have proven effective under many service conditions, their limitations are increasingly apparent. Epoxy coatings can be damaged during handling and lose adhesion over time; cathodic protection systems require ongoing maintenance and external power sources; synthetic chemical inhibitors such as calcium nitrite and amine-based formulations are expensive, and some raise environmental and health concerns.

In response to these limitations, a growing body of research has explored two alternative pathways that align with the broader movement toward sustainable construction: (a) plant-derived natural corrosion inhibitors, and (b) nanoparticle-modified cementitious systems [6,7,8]. Each of these technologies offers distinct mechanisms of action and presents unique advantages as well as challenges.

**Plant-based inhibitors** exploit the chemical complexity of botanical extracts, which contain a diverse array of organic molecules—flavonoids, tannins, alkaloids, saponins, and terpenoids—capable of adsorbing onto steel surfaces through electron donation from polar functional groups such as hydroxyl (–OH), amino ($–NH_2$), and carboxyl (–COOH) [9,10]. Once adsorbed, these molecules form a hydrophobic barrier that impedes the transport of water, oxygen, and chloride ions to the steel surface. The adsorption process is typically well described by the Langmuir isotherm, and many plant extracts function as mixed-type inhibitors, affecting both anodic and cathodic electrochemical reactions simultaneously [11,12]. The appeal of botanical inhibitors lies in their renewable origin, low toxicity, biodegradability, and potential for extraction from agricultural waste streams—characteristics that make them attractive from both environmental and economic perspectives.

**Nanoparticle technologies**, by contrast, act primarily by modifying the concrete matrix itself rather than the steel surface [13,14]. When added to the cementitious mix at low dosages (typically 1–5% by cement weight), nanoparticles such as nano-silica (nano-$SiO_2$), nano-titania (nano-$TiO_2$), nano-iron oxide (nano-$Fe_2O_3$), nano-clay, and carbon nanotubes (CNTs) fill capillary pores, refine the pore structure, and densify the interfacial transition zone between the cement paste and aggregates [15,16]. The pozzolanic reaction of nano-silica with calcium hydroxide produces additional calcium-silicate-hydrate (C-S-H) gel, reducing permeability to chloride ions and other aggressive species. Beyond passive protection, certain nanoparticles can also enable **autonomous crack healing**: when microcracks form, nanoparticles serve as nucleation sites for the precipitation of calcium carbonate, sealing the crack and restoring impermeability [17,18]. More advanced systems incorporate bacterial spores (e.g., *Bacillus subtilis*) together with nanoparticles, achieving synergistic healing effects through microbial-induced calcite precipitation (MICP) [19,20].

The present review has three principal objectives. First, to provide a comprehensive and critical synthesis of the state-of-the-art in plant-based corrosion inhibitors for reinforced concrete, with systematic compilation of performance data and mechanistic understanding. Second, to review the application of nanoparticle technologies for corrosion control and self-healing in concrete, including recent advances in green synthesis of nanomaterials from agricultural waste and biomass. Third, to examine an often-overlooked dimension of plant-based technologies—namely, the potential for heavy metal contamination of plant materials harvested from anthropogenically impacted environments—drawing on recent studies from Iran and elsewhere that have documented elevated levels of lead, cadmium, and other toxic elements in medicinal plants [21,22]. By bringing these perspectives together, the paper aims to provide structural engineers, materials scientists, and corrosion specialists with an evidence-based framework for evaluating and implementing sustainable corrosion protection strategies for reinforced concrete infrastructure.

## 2. Corrosion of Steel in Concrete: Mechanisms and Environmental Factors

A concise understanding of the corrosion mechanism is essential before evaluating the performance of any inhibitor system. In sound concrete, the highly alkaline environment (pH 12.5–13.5) resulting from cement hydration promotes the formation of a stable passive oxide film ($\gamma$-$Fe_2O_3$ or $Fe_3O_4$) on the steel surface. The passive film is only a few nanometres thick, yet it reduces the corrosion rate of steel by several orders of magnitude relative to neutral conditions [23,24].

The passive layer can be destroyed by two principal mechanisms:

**Carbonation**: Atmospheric carbon dioxide ($CO_2$) diffuses through the concrete and reacts with calcium hydroxide ($Ca(OH)_2$) to form calcium carbonate ($CaCO_3$). This reaction progressively lowers the pore solution pH from about 13 to below 9, at which point the passive film becomes thermodynamically unstable and corrosion can initiate in the presence of oxygen and moisture.

**Chloride attack**: Chloride ions ($Cl^-$) from de-icing salts, seawater, or other sources penetrate the concrete cover and, once the concentration at the steel surface exceeds a critical threshold (the “critical chloride content”), locally disrupt the passive film, creating small anodic sites where iron dissolution occurs. The surrounding areas remain passivated, forming cathodic sites where oxygen reduction takes place. The iron ions ($Fe^{2+}$) produced at the anode react with water and oxygen to form iron hydroxides and oxides—most commonly goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), and magnetite ($Fe_3O_4$)—which occupy significantly more volume than the original steel.

The expansive rust generates hoop tensile stresses in the surrounding concrete, leading to cracking, spalling, and accelerated ingress of additional chlorides and $CO_2$ [25,26].

Chloride-induced corrosion is by far the most common and aggressive form of deterioration in reinforced concrete exposed to marine environments or de-icing salts. The critical chloride content varies with concrete composition and quality, but a commonly cited threshold is 0.4% chloride by weight of cement [27]. The time required for chlorides to reach this threshold at the steel surface depends on concrete cover depth, water-to-cement ratio, the presence of supplementary cementitious materials, and exposure conditions.

**Environmental factors** significantly influence the corrosion rate: (i) temperature accelerates electrochemical kinetics and increases diffusivity; (ii) relative humidity affects the electrical resistivity of the concrete and the availability of water for ionic transport; (iii) the presence of oxygen is necessary for the cathodic reaction; (iv) sulfate attack can exacerbate degradation by causing expansive reactions within the cement matrix [28,29].

## 3. Plant-Based Natural Corrosion Inhibitors for Reinforced Concrete

### 3.1 Mechanisms of Inhibition by Botanical Extracts

The corrosion inhibition mechanism of plant extracts involves the adsorption of organic molecules from the extract onto the steel surface, forming a protective film that impedes the transport of aggressive species to the metal surface and interferes with the electrochemical reactions of corrosion [30,31]. The adsorption process is governed by several interrelated factors: (i) the chemical structure and functional group composition of the phytochemicals; (ii) the surface charge of the steel, which depends on the pH and potential of the concrete pore solution; (iii) the concentration of the inhibitor; (iv) temperature; and (v) the nature of the corrosive environment.

The active compounds responsible for corrosion inhibition include flavonoids (quercetin, rutin, catechin), tannins (gallic acid, ellagic acid, condensed tannins), alkaloids (berberine, caffeine, vinblastine), saponins, terpenoids (thymol, carvacrol, pulegone), and steroids [32,33]. These molecules typically contain heteroatoms (O, N) and aromatic rings that facilitate electron donation to the empty d-orbitals of iron atoms on the steel surface, forming coordinate bonds. The adsorption behaviour often follows the Langmuir isotherm, indicating monolayer coverage, and the inhibition efficiency (IE%) increases with concentration up to an optimum beyond which further addition may cause desorption or precipitation [34].

The inhibition efficiency is conventionally determined by electrochemical impedance spectroscopy (EIS), potentiodynamic polarisation, and weight loss measurements. The IE% is defined as:

$$IE\% = (i_{corr,blank} - i_{corr,inhibitor}) / i_{corr,blank} \times 100$$

where $i_{corr}$ is the corrosion current density obtained from Tafel extrapolation of polarisation curves or from charge transfer resistance in EIS measurements [35,36].

Plant extracts typically behave as **mixed-type inhibitors**, affecting both anodic and cathodic reactions, although the relative strength of inhibition at each electrode may vary depending on the extract composition. The shift in corrosion potential ($\Delta E_{corr}$) provides an indication: shifts less than 85 mV generally indicate mixed-type behaviour, while larger shifts suggest predominantly anodic or cathodic activity [37].

### 3.2 Survey of Plant Species and Inhibition Performance

The literature on botanical corrosion inhibitors has expanded considerably, with studies covering more than 60 plant species in various simulated concrete pore solutions and chloride-containing environments. Table 1 presents a summary of plant species for which corrosion inhibition efficiency data are available, along with their principal phytochemical constituents and reported IE% values under optimised conditions. These species include several that have been extensively studied for their medicinal properties and heavy metal content in Iran and other regions.

From the compiled data, several observations can be made. First, the most effective plant extracts achieve inhibition efficiencies exceeding 90% under laboratory conditions, comparable to or even exceeding conventional synthetic inhibitors in some cases. Green tea (*Camellia sinensis*) and henna (*Lawsonia inermis*) are among the most widely studied, with consistently high performance across multiple independent investigations. Second, the optimal concentration typically lies between 500 and 1000 ppm; higher concentrations can lead to a decrease in IE% due to extract precipitation or competitive adsorption effects. Third, the efficiency is highly sensitive to extraction methodology: polar solvents (ethanol, water, methanol) generally yield higher IE% than non-polar solvents, as the most active polar compounds are effectively extracted by polar media [38,39].

Recent systematic reviews by Kumar et al. (2025) and El-Sherbeny et al. (2025) have reinforced these findings, emphasising that the transition from toxic synthetic inhibitors to environmentally friendly botanical extracts represents a significant paradigm shift in construction materials science [40,41]. The diversity of tested species and extraction methodologies underscores the scope for further optimisation and commercial development.

### 3.3 Influence of Exposure Parameters on Inhibition Efficiency

The performance of plant-based inhibitors is not constant but depends on the specific exposure conditions that characterise the service environment of reinforced concrete structures. Temperature plays a critical role: increased temperature accelerates electrochemical kinetics and may also affect the adsorption—desorption equilibrium of inhibitor molecules on the steel surface. Most studies report a decrease in IE% with increasing temperature, indicating that adsorption is typically exothermic and favoured at lower temperatures. However, some extracts retain moderate effectiveness even at elevated temperatures, suggesting chemisorption rather than purely physisorption [42].

Table 1. Plant species tested as corrosion inhibitors for steel in simulated concrete pore solutions or similar alkaline-chloride media

| *Plant species (common name)* | *Part used* | *Principal active compounds* | *Concentration (ppm)* | *IE% (max)* | *Test medium* | *Year* |
|---|---|---|---|---|---|---|
| *Camellia sinensis* (green tea) | Leaves | Catechins, EGCG, theaflavins | 500–1500 | 94–98 | SCPS + 3.5% NaCl | 2021–2025 |
| *Lawsonia inermis* (henna) | Leaves | Lawsone, tannins | 400–1000 | 90–95 | SCPS + 3.5% NaCl | 2022–2024 |
| *Azadirachta indica* (neem) | Leaves | Nimbolide, azadirachtin | 600–1200 | 86–92 | SCPS + 3.5% NaCl | 2020–2025 |
| *Ziziphora persica* | Leaves | Pulegone, thymol, flavonoids | 500–1000 | 90–94 | SCPS + 3.5% NaCl | 2021–2024 |
| *Cichorium intybus* (chicory) | Roots/leaves | Sesquiterpenes, tannins | 400–800 | 85–91 | SCPS + 3.5% NaCl | 2022–2025 |
| *Catharanthus roseus* (periwinkle) | Leaves | Vinblastine, vincristine | 500–1200 | 88–93 | SCPS + 3.5% NaCl | 2022–2025 |
| *Fumaria indica* (fumitory) | Whole | Fumarine, protopine, tannins | 500–900 | 83–88 | SCPS + 3.5% NaCl | 2022–2025 |
| *Psoralea corylifolia* | Seeds | Psoralen, isopsoralen | 300–600 | 85–90 | SCPS + 3.5% NaCl | 2020–2023 |
| *Glycyrrhiza glabra* (liquorice) | Roots | Glycyrrhizin, flavonoids | 400–1000 | 88–94 | SCPS + 3.5% NaCl | 2022–2025 |
| *Olea europaea* (olive) | Leaves | Oleuropein, flavonoids | 500–1500 | 82–89 | SCPS + 3.5% NaCl | 2021–2024 |
| *Mentha piperita* (peppermint) | Leaves | Menthol, menthone | 400–800 | 80–87 | SCPS + 3.5% NaCl | 2022–2025 |
| *Cornus mas* (dogwood) | Fruit | Anthocyanins, ellagic acid | 300–700 | 85–92 | SCPS + 3.5% NaCl | 2022–2025 |
| *Allium sativum* (garlic) | Bulbs | Allicin, ajoene | 500–1200 | 80–88 | SCPS + 3.5% NaCl | 2021–2025 |
| *Eucalyptus globulus* | Leaves | Eucalyptol, tannins | 400–1000 | 84–89 | SCPS + 3.5% NaCl | 2022–2025 |

*Note: SCPS = simulated concrete pore solution (pH 12.5–13.5). IE% values are approximate ranges compiled from multiple studies; actual performance varies with extraction method, concentration, and test conditions.*

**Chloride concentration** is another key parameter. In marine environments, chloride levels may reach 2–3.5% in the pore solution, while for structures exposed to de-icing salts, concentrations can be even higher locally. The competitive adsorption between chloride ions and inhibitor molecules determines the net protective effect. At high chloride concentrations, the inhibitor must exhibit a sufficiently high adsorption affinity to displace chloride ions from the steel surface. The best-performing extracts maintain IE% above 80% even at chloride concentrations up to 3.5% [43].

**Immersion time** affects inhibitor performance in two opposing ways. Initially, as the inhibitor molecules adsorb onto the steel surface, IE% increases to a maximum (typically reached within 24–72 hours). Over prolonged immersion periods (weeks to months), gradual desorption or degradation of the adsorbed film may occur, leading to a slow decline in protection. However, some extracts exhibit stable or even increasing IE% over time, suggesting the formation of a persistent, tightly bound film that continues to develop [44].

The influence of pH is particularly relevant for concrete applications, where the pore solution is highly alkaline (pH 12.5–13.5). Many organic molecules are susceptible to hydrolysis or degradation under such strongly alkaline conditions. The long-term chemical stability of plant extracts in the concrete environment remains an under-researched area; most laboratory studies are conducted over relatively short timeframes (days to weeks) and do not adequately simulate the multi-decadal service life of real infrastructure. Accelerated ageing experiments and long-term immersion studies are needed to assess the practical durability of plant-based inhibitor systems [45,46].

### 3.4 Heavy Metal Contamination: An Overlooked Concern

A substantial body of recent research has documented heavy metal contamination of medicinal plants and botanical materials collected from anthropogenically impacted environments. This literature has significant implications for the use of plant extracts as corrosion inhibitors in construction materials, because contaminated plant material could introduce toxic elements into the concrete matrix, with potential long-term environmental consequences.

A comprehensive review by Givianrad and colleagues (2025) examined the impact of heavy metals—cadmium (Cd), lead (Pb), arsenic (As), copper (Cu), chromium (Cr), zinc (Zn), and nickel (Ni)—on medicinal plants in Iran [21]. The study found that Cd and Pb contamination is particularly widespread, representing a concerning issue for consumer safety and product quality. Industrial activities, urbanisation, and the use of chemical fertilisers and pesticides were identified as major sources of heavy metal accumulation in plant tissues. Soil pollution, plant species-specific uptake characteristics, and processing methods all influence the final heavy metal concentrations in harvested plant material [47].

The quantitative analysis by Givianrad et al. revealed that Cd exceeded World Health Organization (WHO) permissible limits in 47% of the samples examined, while Pb and Zn exceeded limits in 26% and 20% of samples, respectively [21]. Cd and Pb also significantly affected plant germination rates and growth parameters. These findings are consistent with earlier studies by Alinia-Ahandani and colleagues, who documented elevated heavy metal concentrations in medicinal plant samples from northern Iran, including *Ziziphora persica*, and in soil samples from polluted regions such as Roodsar [48,49,50]. Similar contamination patterns have been reported for a broad range of plant species (more than 30) across various Iranian provinces, reflecting the widespread nature of the problem [51,52,53].

The mechanisms by which plants accumulate heavy metals include root uptake from contaminated soil and water, foliar absorption of atmospheric particulates, and the use of metal-containing fertilisers and pesticides [54]. For corrosion inhibitor applications, several specific risks arise:

1. **Direct introduction of heavy metals into concrete**: If contaminated plant material is used as the source of the corrosion inhibitor, heavy metals such as Pb, Cd, and Cr will be carried into the concrete matrix through the extract or directly as particulate contaminants.
2. **Interference with corrosion inhibition**: Some heavy metals may act as cathodic activators, accelerating rather than inhibiting corrosion, particularly if they are present as soluble ions in the concrete pore solution.
3. **Long-term environmental leaching**: Heavy metals incorporated into concrete could leach out over time, particularly if the concrete undergoes carbonation or cracking, potentially contaminating surrounding soil and groundwater.
4. **Regulatory and certification concerns**: Construction materials are increasingly subject to environmental certification requirements; the presence of heavy metals from contaminated plant additives could disqualify a material from green building certifications.

To address these risks, any practical application of plant-based inhibitors must incorporate adequate quality control measures, including (i) sourcing plant material from clean, certified agricultural sites rather than from roadsides or industrially impacted areas; (ii) pre-treatment of plant material or extracts to remove heavy metals (e.g., using chelation, ion exchange, or nanoparticle-based adsorption); and (iii) routine testing of final inhibitor products for heavy metal content prior to use in construction applications [55,56].

## 4. Nanoparticle Technologies for Corrosion Control and Self-Healing Concrete

### 4.1 Mechanisms of Nanoparticle Action in Cementitious Systems

The addition of nanoparticles to cementitious materials influences concrete performance through multiple interconnected mechanisms operating at the nanometre-to-micrometre scale. The most important pathways for corrosion protection include:

**Pore refinement and permeability reduction**: The smallest pores in cement paste are of nanometre dimensions. When nanoparticles such as nano-silica (nano-$SiO_2$) are added to the mix, they fill these pores, reducing the pore connectivity and dramatically decreasing permeability to water, chloride ions, and other aggressive species. Additionally, nano-silica acts as a highly effective pozzolan: it reacts with calcium hydroxide ($Ca(OH)_2$)—a byproduct of cement hydration—to form additional calcium-silicate-hydrate (C-S-H) gel, the primary binding phase in concrete. This secondary C-S-H gel further densifies the microstructure and refines the pore network [57,58,59]. Studies have demonstrated that chloride diffusion coefficients can be reduced by 40–60% with optimal nano-silica addition [60].

**Interfacial transition zone (ITZ) densification**: The ITZ between cement paste and aggregates is the weakest and most porous region in concrete, forming a preferential pathway for the ingress of aggressive ions. Nanoparticles concentrate in the ITZ due to their high surface area and reactivity, making this region denser and more resistant to chloride penetration [61].

**Corrosion inhibition by nanoparticles**: Some nanoparticles can directly affect the corrosion electrochemistry on the steel surface. Nano-titania (nano-$TiO_2$), for example, has been shown to form a barrier layer on steel, while nano-zinc oxide (nano-ZnO) exhibits antibacterial properties that can prevent microbially induced corrosion in certain environments [62].

**Self-healing crack repair**: Perhaps the most innovative application of nanoparticles in concrete is the development of autonomous self-healing systems. When microcracks form in concrete—as they inevitably do due to shrinkage, thermal stresses, or mechanical loading—nanoparticles can act as nucleation sites for the precipitation of calcium carbonate ($CaCO_3$) from the surrounding cement matrix or from deliberately incorporated healing agents. Crystals of $CaCO_3$ form within the crack volume, progressively filling the void and restoring impermeability and, to some extent, mechanical strength [63,64].

### 4.2 Types of Nanoparticles and Their Performance

#### 4.2.1 Nano-silica (nano-$SiO_2$)

Nano-silica is the most extensively studied and commercially advanced nanoparticle for concrete durability enhancement. The addition of nano-silica is particularly effective because it simultaneously provides filler, pozzolanic, and nucleation effects. Experimental data from multiple studies (Table 2) indicate that optimal nano-silica contents typically fall between 1.5% and 2.5% by cement weight, with higher dosages potentially causing agglomeration and loss of workability.

Table 2. Reported performance improvements for nano-silica-modified concrete

| *Property* | *Improvement relative to control* | *Nano-SiO₂ dosage (% cement)* | *Reference year* |
|---|---|---|---|
| Compressive strength (28 days) | +15 % to +30 % | 1.5–3.0% | 2023–2025 |
| Water absorption reduction | –31 % to –41 % | 1.5–2.5% | 2024–2025 |
| Chloride permeability reduction | –24 % to –40 % | 1.5–2.5% | 2023–2025 |
| Contact angle increase | +66 % | 2.0% | 2024 |
| Durability improvement (sulfate) | +39 % | 2.0% | 2024 |
| Durability improvement (chloride) | +42 % | 2.0% | 2024 |

*Note: Data compiled from [9,10,11,57,58,59].*

Recent research has extended nano-silica applications to alkali-activated concrete systems incorporating multiple solid wastes. A study by Wang et al. (2025) examined nano-silica-modified alkali-activated concrete using fly ash and steel slag as precursors [65]. The results were striking: the concrete without nano-silica experienced a 28.6% strength decrease after 90 days of immersion in high-concentration seawater, whereas the nano-silica-modified group showed only a 2.1% strength decrease, corresponding to a corrosion resistance coefficient of 97%. Furthermore, the chloride ion concentration in the surface layer (5 mm depth) of the nano-silica-modified concrete was only 10% of that in the control after 90 days of seawater exposure. The concentrations of dissolved Al and Fe in seawater were measured at 2.6 µg/L and 1.2 µg/L respectively for the nano-silica-modified material, indicating extremely low risk of metal dissolution in marine environments [65].

A study published in *Defect and Diffusion Forum* (January 2026) investigated the effect of nano-silica addition on concrete durability at dosage levels of 0, 1, 1.5, 2, and 2.5% by cement weight [9]. The experimental results demonstrated that concrete modified with 2% nano-silica exhibited water absorption decreased by 41% and contact angle increased by 66% compared to the control, while chloride permeability decreased by 24%. Moreover, the durability of the 2% nano-silica specimen increased by 39% against sulfate attack and by 42% against chloride attack. Electrochemical impedance spectroscopy confirmed significantly improved corrosion resistance of the reinforced concrete [9].

#### 4.2.2 Nano-titania (nano-$TiO_2$)

Nano-titania offers additional functionality beyond traditional corrosion protection: its photocatalytic properties can degrade organic pollutants on the concrete surface, making it attractive for urban and environmentally exposed structures. Typical dosages range from 1% to 5% by cement weight. The primary limitations of nano-titania are its relatively high cost and lower pozzolanic activity compared to nano-silica [66,67].

#### 4.2.3 Carbon nanotubes (CNTs)

Carbon nanotubes can dramatically improve the mechanical properties of concrete at extremely low dosages (0.05–0.2% by cement weight). CNTs bridge microcracks and enhance tensile strength and fracture toughness, indirectly improving corrosion resistance by reducing crack formation. However, CNT dispersion remains a significant challenge; agglomeration is common without adequate sonication or the use of surfactants. High material cost also limits widespread adoption [68,69].

#### 4.2.4 Green-synthesised nanoparticles from biomass waste

A rapidly expanding area of research concerns the production of nanoparticles from agricultural and biomass waste materials using green synthesis methods. This approach addresses two sustainability challenges simultaneously: (i) value-added utilisation of waste streams, and (ii) production of nanomaterials without the toxic precursors (e.g., tetraethyl orthosilicate, TEOS) used in conventional synthesis.

Hilal et al. (2025) compared the effect of nano date pits and nano sunflower seed shells on the properties of green cement mortar, demonstrating that agricultural waste can be effectively converted into functional nanomaterials for construction applications [70]. The study reported that nanoscale processing of these waste materials significantly enhances their performance as supplementary cementitious materials [71].

Ainomugisha Safiki (2025) systematically developed optimised protocols for engineering eco-friendly nanoparticles from sugarcane bagasse ash (SCBA) using mechanical milling and sol-gel synthesis methods [72]. The study successfully engineered small-sized SCBA nanoparticles (5–20 nm) with disfigured crystalline $SiO_2$ networks. Engineered mesoporous silica with pore diameters below 50 nm, a high surface area of approximately 700 m²/g, and silica purity up to 97% was produced. A comparison of nano-additive and clinker-replacement approaches revealed that each 1.5% nano-SCBA can effectively substitute up to 15% of cement clinker, with an 18% improvement in early cement strength. Mortars containing low-medium surface area n-$SiO_2$ (263–579 m²/g) outperformed high-SSA materials at water-to-binder ratio 0.5, with 3% n-$SiO_2$ of SSA 579 m²/g attaining compressive strength improvement of 41% [72].

### 4.3 Bacterial–Nanoparticle Hybrid Self-Healing Systems

A particularly innovative development in concrete durability is the combination of bacterial spores with nanoparticles to create autonomous self-healing systems. The microorganisms—typically spore-forming bacteria such as *Bacillus subtilis*, *Bacillus sphaericus*, and *Bacillus megaterium*—remain dormant within the concrete matrix until cracks form and water ingress activates them [73,74]. The bacteria metabolise a calcium-containing nutrient (e.g., calcium lactate or urea), converting it to calcium carbonate that precipitates within the crack, progressively sealing it.

Recent research has demonstrated that nanoparticles play a crucial facilitative role in these hybrid systems. A study published in 2025 investigated a synergistic approach combining bacterial spores of *Bacillus subtilis* with nano-silica and nano-calcium carbonate as healing agents [19]. The results showed that bacterial–nano hybrid systems achieved up to 80% healing efficiency for cracks under 0.5 mm, with significant improvements in durability indices compared to conventional self-healing approaches [19,20].

A review by the journal *Journal of Building Engineering* (Elsevier, 2025) examined the facilitative role of nanotechnology in advancing bacterial-based self-healing concrete [75]. Nanomaterials play a crucial role in protecting bacterial spores, increasing their viability and activity, promoting biomineralisation, and consequently improving the overall efficiency of microbial self-healing processes. The review also documented that bacterial self-healing has been shown to facilitate up to 22% recovery in compressive strength and 16% recovery in split tensile strength under curing conditions, with another report showing up to 74% strength recovery for concrete incorporating bacteria plus steel slag aggregates [75].

### 4.4 Long-Term Durability and Environmental Considerations

Despite the substantial laboratory evidence supporting the effectiveness of nanoparticle-modified concrete and bacterial–nano hybrid systems, several important knowledge gaps remain.

**Dispersion challenges**: The tendency of nanoparticles to agglomerate is well documented. Without adequate dispersion—typically achieved through ultrasonication, the use of superplasticisers, or surface functionalisation—the beneficial effects of nanoparticles are significantly reduced. Developing reliable, scalable dispersion methods for commercial concrete production remains an ongoing challenge [76,77].

**Long-term performance**: Most published studies report results from laboratory specimens tested over weeks or months. Few field studies have examined nano-modified concrete performance over multi-year service periods. The long-term stability of the nanoparticle–cement matrix interface and the durability of bacterial spores within the high-pH environment of concrete over decades of service are not yet fully understood [78].

**Health and safety**: The inhalation of airborne nanoparticles during concrete mixing poses potential respiratory health risks to construction workers. Adequate dust control measures and personal protective equipment are essential. Standardised occupational exposure limits for nanomaterials in construction environments are still under development [79].

**Environmental leaching**: The long-term fate of nanoparticles in aged concrete structures is uncertain. If nanoparticles are not permanently bound within the C-S-H matrix, they could leach out over time, entering soil and water systems. Preliminary studies suggest that nano-silica becomes well incorporated into the gel structure and exhibits low leachability, but more systematic environmental fate studies are needed for a broader range of nanomaterials [80].

## 5. Discussion: Synergies, Limitations, and Research Gaps

### 5.1 Comparative Assessment of Plant-Based and Nanoparticle Approaches

The two technologies examined in this review operate on fundamentally different principles and offer distinct advantages and limitations.

Plant-based inhibitors are attractive for their low cost, renewable origin, and low toxicity. They can be derived from abundant agricultural waste streams, potentially contributing to a circular economy. However, the current limitations are substantial: (i) the long-term chemical stability of organic molecules in the aggressive alkaline environment of concrete is poorly characterised; (ii) the potential for heavy metal contamination of plant materials (as documented extensively in the Iranian medicinal plant literature) must be addressed through quality control and purification; (iii) the performance of plant extracts in real concrete (as distinct from simulated pore solutions) has been minimally evaluated; (iv) the effect of plant extracts on concrete workability, setting time, and long-term mechanical properties requires systematic investigation.

Nanoparticle technologies, by contrast, offer robust, proven improvements in concrete microstructure and permeability, with a strong mechanistic understanding of their action. Nano-silica-modified concrete is already commercially available and has been used in high-performance marine structures. However, the drawbacks include higher material costs, technical challenges in nanoparticle dispersion, and potential health and environmental risks during production and construction.

### 5.2 Hybrid Strategies: Combining Plant Extracts and Nanoparticles

Emerging research suggests that combining plant extracts with nanoparticles may produce synergistic effects not achievable with either technology alone. Plant extracts can act as green dispersants for nanoparticles, preventing agglomeration through their surface-active properties. The organic molecules from the extract may additionally provide direct corrosion inhibition on the steel surface, while the nanoparticles densify the concrete matrix. A few studies have reported that such hybrid systems outperform single-component treatments [81,82], but the mechanisms remain incompletely understood, and standardised protocols for hybrid system testing are lacking.

A particularly promising direction is the green synthesis of nanoparticles using plant extracts—a method that simultaneously produces nanoparticles and coats them with organic molecules that may themselves be corrosion-inhibiting. This approach avoids the use of toxic chemical precursors and can potentially reduce the cost of nanoparticle production. The body of literature on green synthesis of nanoparticles for medical and agricultural applications (e.g., the work of Fatima et al., 2025, and Mehregan et al., 2026) [83,84] provides a foundation that could be adapted for construction material applications. However, the heavy metal contamination risk applies equally to plant extracts used for green synthesis, necessitating the same quality control measures.

**5.3 Knowledge Gaps and Future Research Priorities**

Based on this review, the following research priorities are identified:

1. **Long-term field validation**: Multi-year exposure studies of concrete specimens incorporating plant-based inhibitors and/or nanoparticles under realistic environmental conditions (marine, de-icing salt, industrial) are needed to establish practical durability.
2. **Standardised testing protocols**: The corrosion inhibition literature suffers from considerable heterogeneity in test conditions, measurement techniques, and reporting standards. The development of industry-recognised standard test methods—analogous to ASTM G109 for traditional corrosion inhibitors—would enable reliable comparison across studies and support regulatory approval.
3. **Heavy metal control and purification**: Research into cost-effective methods for removing heavy metals from plant extracts intended for construction applications is essential. Chelation, ion exchange, and nanoparticle-based adsorption (as reviewed by Hajipour et al., 2023) represent promising approaches [85,86].
4. **Alkaline stability of phytochemicals**: Systematic studies of the hydrolytic stability of flavonoids, tannins, and other active compounds under concrete-like alkaline conditions (pH 12.5–13.5, elevated temperatures) over extended timeframes (months to years) are needed.
5. **Life-cycle assessment (LCA)**: Quantitative LCA of plant-based and nanoparticle systems—including extraction, processing, transport, application, and end-of-life phases—is required to establish the net environmental benefits relative to traditional protection strategies.
6. **Scale-up and commercialisation pathways**: Research that bridges the gap between laboratory findings and industrial practice—including large-scale extraction methods, mix design optimisation, and economic analysis—is needed to support market adoption.

**6. Conclusions**

This systematic review has examined two emerging paradigms for corrosion protection in reinforced concrete: plant-based natural inhibitors and nanoparticle-modified cementitious systems. The following conclusions can be drawn from the synthesis of the available literature.

- Plant extracts from a wide range of species (more than 40) have demonstrated corrosion inhibition efficiencies exceeding 85% in simulated concrete pore solutions containing chlorides, with the best-performing extracts (green tea, henna, *Ziziphora persica*) achieving IE% above 90% under optimised conditions. The active phytochemicals—flavonoids, tannins, alkaloids—adsorb onto steel surfaces following Langmuir behaviour and function as mixed-type inhibitors.
- A substantial body of research from Iran and elsewhere has documented heavy metal contamination of medicinal plants, with Cd exceeding WHO limits in 47% of samples and Pb in 26%. These findings have direct implications for plant-based construction additives, as contaminated plant material could introduce toxic elements into concrete. Therefore, stringent quality control of raw plant material is not optional but essential for safe application.
- Nanoparticle technologies, particularly nano-silica at dosages of 1.5–2.5% by cement weight, provide robust and well-characterised improvements in concrete durability. Experimental data show water absorption reductions of up to 41%, chloride permeability decreases of 24–40%, and corrosion resistance improvements of 39–42% under aggressive chemical attack. Nano-silica-modified alkali-activated concrete has demonstrated a corrosion resistance coefficient of 97% after 90 days of seawater immersion, with chloride surface concentrations only 10% of control values.
- Bacterial–nanoparticle hybrid self-healing systems achieve up to 80% healing efficiency for cracks under 0.5 mm, with nanoparticles playing crucial roles in bacterial spore protection, nucleation site provision, and acceleration of the biomineralisation process.
- Green synthesis of nanoparticles from agricultural waste (sugarcane bagasse ash, date pits, sunflower seed shells) offers a sustainable pathway to produce nanomaterials for construction, with demonstrated compressive strength improvements of 41% at 3% n-$SiO_2$ addition. Such approaches also align with circular economy principles.
- Critical knowledge gaps remain, including the lack of long-term field validation, the absence of standardised testing protocols, and insufficient understanding of the alkaline stability of phytochemicals. Future research should prioritise these areas and integrate life-cycle assessment to guide sustainable implementation decisions.

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