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Corrosion Control in Metals: A Review on Sustainable Approach Using Nanotechnology

ABSTRACT

This study reviews previous research that employed nanotechnology to inhibit the corrosion of metals/alloys in one aspect. The other focus explored the long-term stability and durability of nanotechnology applications for corrosion control under various environmental conditions, as well as the optimization of nanoparticle dispersion and integration for maximum efficiency—two crucial but sometimes overlooked aspects of nanocoatings for corrosion prevention. While some progress had been made in preventing corrosion, achieving consistent nanoparticle dispersion and long-term efficacy remained challenging with nanocoatings. Key findings from the review of literature covering the years 2017–2023 revealed a growing body of research on various materials and techniques to enhance corrosion resistance, ranging from multilayered nanocomposites to superhydrophobic surfaces and innovative composite coatings. This research underscored the versatility and effectiveness of nanoparticle-based coatings in corrosion management, offering specialized solutions for different substrates and operating environments. Moreover, studies on the stability and durability of nanocoatings on metals demonstrated viable approaches to extending their useful lifespan, such as the use of nanolaminated coatings and the active release of corrosion inhibitors. In addition to addressing significant knowledge gaps, this review provided valuable insights for the future development of reliable and durable corrosion protection solutions.

Keywords: Corrosion prevention, Nano coatings, Corrosion resistance, Environmental conditions, Long-term stability, Nanoparticle dispersion

1. INTRODUCTION

Corrosion involves metal degradation due to chemical or electrochemical processes as it interacts with the environment [1–4]. Industrial establishments must make efforts to reduce systemic corrosion considering the fact that facilities would struggle with the effects of corrosion if corrosion control is not implemented [5]. Although it costs a fortune to prevent corrosion, doing so is less expensive than having to repair to repair or

replace damaged systems after corrosion attack. Research into effective corrosion control methods is required due to the severe economic effects of corrosion. An in-depth knowledge of the elements that actively contribute to the corrosion of metals is a necessary pre-requisite for the development of such control mechanisms. This idea has sparked research into the production of nanomaterials like nanocrystalline (NC) materials, nanogels, nanocomposites, nanoparticles, carbon dots, and nanocontainers, which have physical properties distinct from those of their commonplace microcrystalline (MC) counterparts and other corrosion inhibitors [6]. It is important to note that composites are obtained following the combination of different materials to attain improved features compared to the individual constituent materials [7–10]. On the other hand, A nanocomposite is a

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cutting edge material consisting of many nanoscale phases, each of which has dimensions between 1 and 3 nm, resulting in the creation of a distinct multi-dimensional solid material [11]. Several studies have been carried out on the use of different approaches to prevent corrosion, including the use of inhibitors [11-19], and nanotechnology [21,22]. By manipulating materials at the nanoscale, nanotechnology makes it possible to produce goods and devices with dimensions as tiny as a billionth of a metre [23,24]. While there are many advantages to using nanoparticles in corrosion prevention, there are also some drawbacks. For example, processing NC metals on a large scale can be challenging since they may have poor thermal stability and are prone to grain growth. On the other hand, the use of nanoparticles in tribo-corrosion management may cause the deposition of nanosized debris at the point of contact between two surfaces. Since they have a greater surface area and possess growth-inhibitory capabilities, synthesized nanoparticles exhibit good anticorrosion properties [25,26].

Research has been done on the enhancement of corrosion resistance utilizing nano additives [27]. To improve the corrosion resistance of the dissimilar AA5083-H111 and (AA) 6082-T6 aluminium alloys that were FSW-welded, the study investigated the use of nano additives, in particular, titanium carbide (TiC) nanoparticles, multi-walled carbon nanotubes (MWCNTS), and cerium molybdate (CeMo) containers loaded with a corrosion inhibitor (2-mercaptobenzothiazole, MBT). The findings showed that the incorporation of CeMo containers loaded with MBT during the FSW improved the corrosion resistance of the final material through the adsorption of MoO_4^{2-} ions that come from the container shell onto the surface of both dissimilar alloys, as well as the formation of stable complexes between the thiol groups of MBT and the alloying metals, preventing chloride penetration. This suggests that there is an emphasis on enhancing the robustness and lifetime of the welded joints, particularly in areas where corrosion is more pronounced [27]. Another investigation on defence against corrosion of steel in a salty environment (3.5% NaCl) reported that nanocomposite coatings based on TiO_2 provided active corrosion protection, whereas coatings based on MgO and Al_2O_3 provided barrier protection [28]. Additionally, the study on the effect of electrolyte intercalation on the corrosion of graphene-coated copper showed that the graphene coating successfully inhibited corrosion in copper single crystals [29]. On single-crystal substrates, the protective barrier created by graphene prevented the corrosion process, demonstrating its promise as a corrosion-resistant material in

particular applications. The same research, however, also showed that the protection offered by graphene covering was not as effective on polycrystalline copper substrates as it was on single copper substrates. The intercalation of electrolytes at the graphene/copper interface was found to cause corrosion in polycrystalline materials even while graphene was present. This discovery indicates a drawback in the usage of graphene covering for industrial purposes, especially when polycrystalline copper substrates are involved. The high rate of corrosion that has been observed highlights the need to develop improved graphene-coating methods for polycrystalline copper in industrial devices or to consider alternative corrosion-resistant materials.

The corrosion of three different sets of samples: stainless steel with a nickel seed layer (Ni/SS), stainless steel, a multi-layered graphene thin film stainless steel (G/Ni/SS), which are all relevant as bipolar plates for polymer electrolyte fuel cells, has been compared [30]. The graphene coating clearly outperformed steel that was only protected by nickel after three weeks of partial immersion in boiling seawater. The graphene film was found to remain intact, and the defect density was unaltered after the test. It was observed that multilayer graphene sheets, even imperfect ones, can significantly prolong the life of fuel cell bipolar plates of the next generation [30].

Although nano coatings for corrosion prevention have been developed with great success, little is known about their long-term stability and endurance in different environmental circumstances, to the best of the authors' knowledge. More research on the processes of deterioration and long-term performance is required. To maximize the efficiency of protective coatings or materials against corrosion, nanoparticles must be evenly dispersed throughout. Nevertheless, much more needs to be done on sustainable ways of integrating and dispersing nanoparticles into various matrices, while preserving their performance and stability. This study aims to investigate the long-term stability and durability of nano coatings and the necessity of optimizing nanoparticle dispersion and integration.

2. FUNDAMENTALS OF CORROSION OF METALS

Corrosion attack on metals/alloys can be through electrochemical or chemical processes. In essence, the degradation of metals can occur following cathodic and anodic half cells. The anodic corrosion region of the half-cell is where the metal

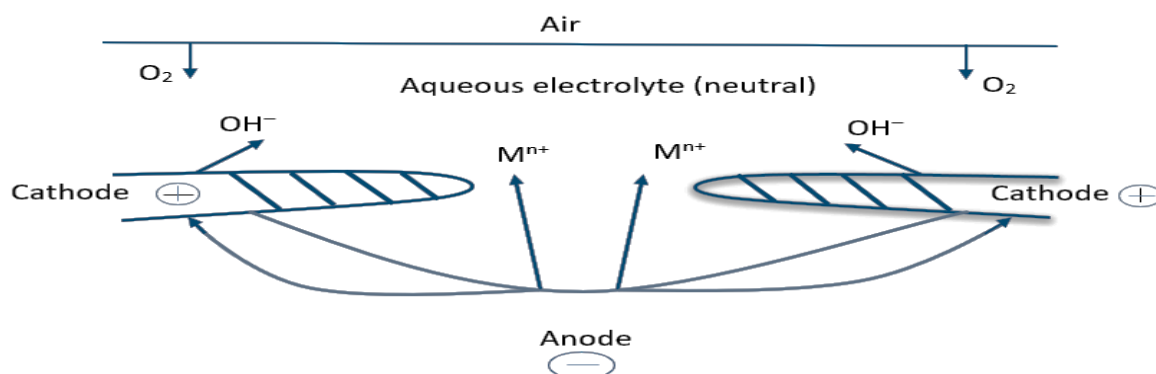
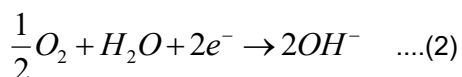


Figure 1. A cathodic surface coating rupture that results in corrosion of the metal substrate, such as nickel or millscale on steel [31] or in acidic solutions, where hydrogen is reduced as shown in Equation (3) and also in aerated acids Equation (4).

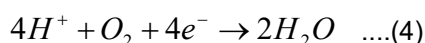
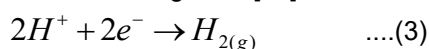
degrades, thereby going into the solution in the form of metal ions [1]. Equation (1) illustrates this phenomenon.



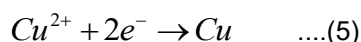
It is at the anode electrode that electrons are released. However, if there is no cathodic reaction to receive the generated electrons, they would remain on the corroding metal, forestalling further degradation [1]. For the electrochemical corrosion process, the produced electrons at the anode are subsequently received at the cathode because of the reaction at the cathodic surface. A variety of cathodic reactions are imminent, including the ones occurring in basic or neutral solutions as illustrated in Equation (2).



For instance, a rupture of the cathodic surface coating that results in corrosion of the metal substrate, such as nickel or millscale on steel as indicated in Figure 1 [31].



Furthermore, solutions that contain oxidizing agents in some chemical processes can be reduced. For instance, metallic copper can be obtained by the reduction of cupric ions as shown in Equation (5):



2.1 Gathering of information for the current study

The search for relevant information on the subject matter was conducted on Science Direct, Elsevier's database from 2017 to October 12,

2023. The initial search revealed articles that were relevant to the keywords of the current study's title. 7,664 published works were obtained, consisting of 1,968 review papers, 3,431 research papers, 168 encyclopedias and 1,710 book chapters. The search further focused on the published research papers within the range of years as earlier mentioned. The number of published papers increased as the years progressed from 9.4 % in 2017 to 19.2 % in 2022 as indicated in Figure 1. An 18.4% increase in published papers was observed after the 3rd quarter of 2023, as of October 12, 2023.

The Journal, Materials Today: Proceedings was discovered to publish the highest number of papers, relevant to the current study, followed by the *Journal of Alloys and Compounds* as shown in Figure 2. On the other hand, the indicated countries of lead authors shown in Figure 3 revealed that the lead authors from China published the highest number of research papers in Science Direct relevant to the application of nanotechnology for corrosion control.

3 OVERVIEW OF STUDIES ON THE USE OF NANOTECHNOLOGY TO PREVENT CORROSION

3.1 Corrosion control via optimization of nanoparticle dispersion and integration

Numerous studies have made substantial contributions to the field of improving nanoparticle dispersion and integration for corrosion control; each study examining distinct methods and materials to improve anticorrosive coatings. The summary of the reviewed studies in this regard is presented in Table 1. By combining mica nanosheets (MNSs) and magnetic-responsive core-shell mesoporous nanoparticles with 2-mercaptobenzothiazole ($Fe_3O_4@mSiO_2/MBT$) and

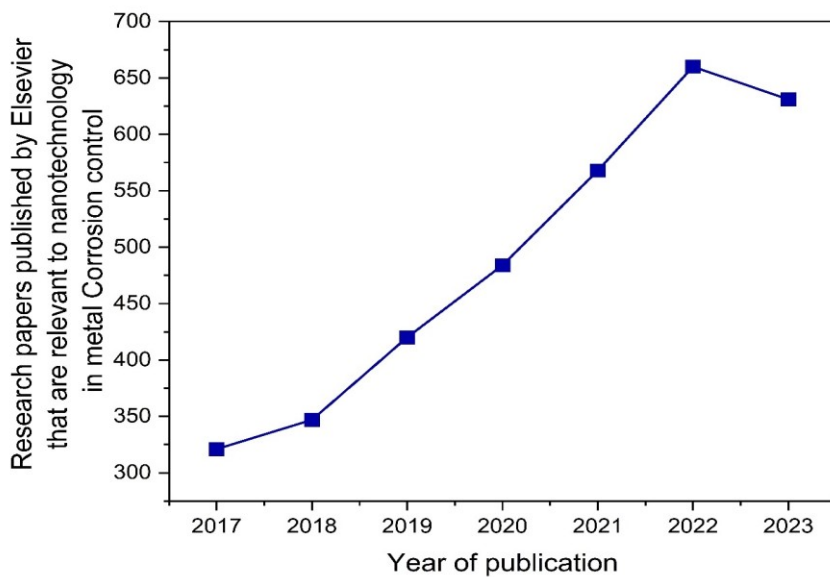


Figure 2. Total number of research papers published by Elsevier that are relevant to the keywords of the review title versus the year of publication

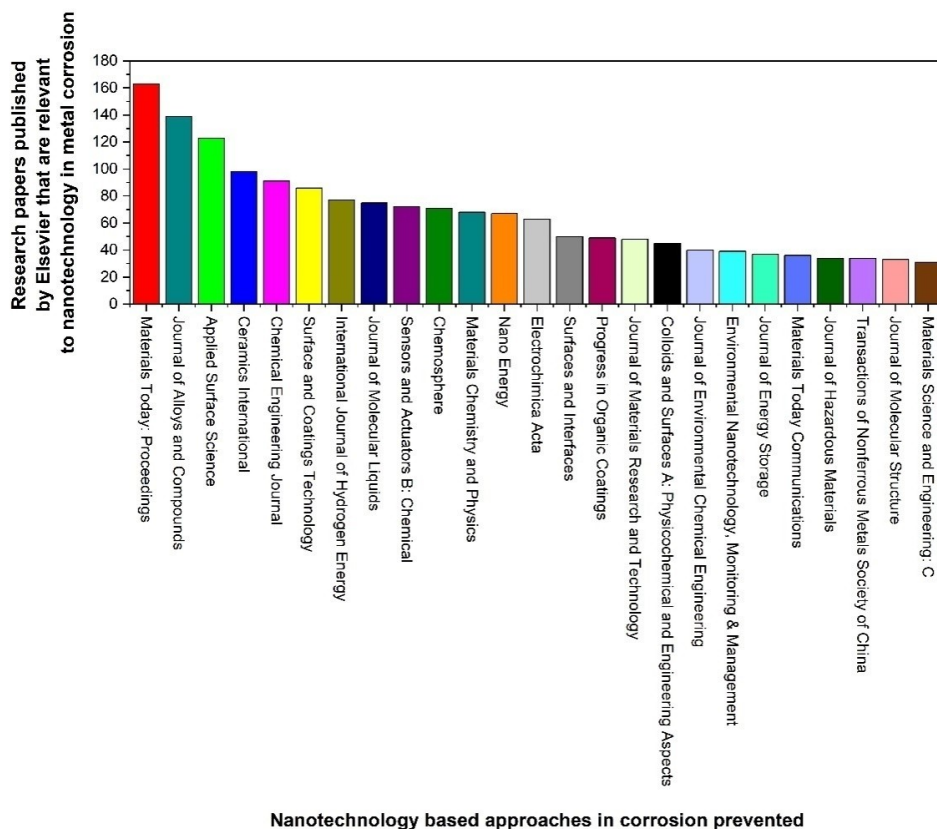


Figure 3. Elsevier journals that published research papers that are relevant to the use of nanotechnology in metal corrosion control

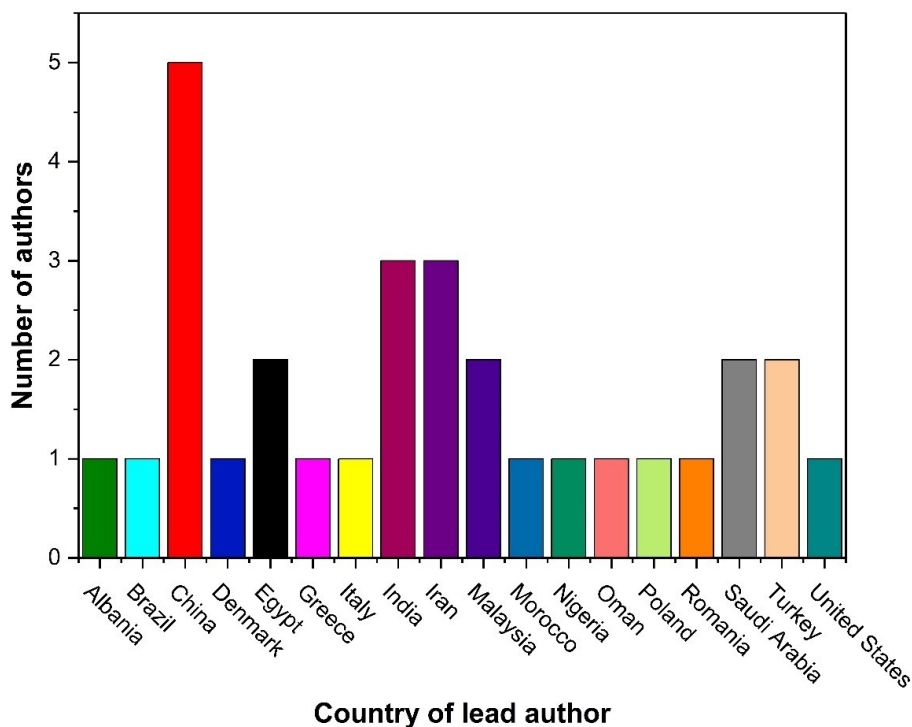


Figure 3. The countries of lead authors indicated that published papers relevant to the use of nanotechnology for corrosion control and the associated total number of authors

incubating them in a magnetic field, Pengpeng et al. [32] produced a novel anticorrosive coating. When compared to controls, this coating demonstrated a higher effectiveness of corrosion prevention and impedance modulus increased dramatically over time. The distinct dispersion of nanofillers was validated by optical microscopy and SEM-EDS, demonstrating the combined benefits of active and passive integrated anticorrosive coatings. By combining MNSs and $\text{Fe}_3\text{O}_4@m\text{SiO}_2/\text{MBT}$ nanoparticles in a magnetic field, Pengpeng et al.'s innovative anticorrosive coating increases corrosion inhibition by 30.36% when compared to controls [32]. After 30 days, there was a five-order magnitude change in the impedance modulus of this coating, which demonstrated a notable increase over time [33]. By using optical microscopy and SEM-EDS to validate the differential distribution of nanofillers, the synergistic impact of active/passive integrated anticorrosive coatings was validated [34]. Furthermore, compared to conventional coatings, nanocomposite coatings—like the one created—are renowned for their higher protective qualities, providing increased corrosion resistance through sacrificial, barrier, and active inhibitory mechanisms [35,36].

The effectiveness of a polymeric anticorrosion coating based on nanoparticles for carbon and stainless steel exposed to high-temperature molten salt conditions was studied by [37]. Their results showed reduced corrosion for both types of steel and a more uniform layer of corrosion, indicating the possibility of coatings based on nanoparticles under harsh conditions. In his investigation of ferrite nanoparticles' anticorrosion properties, Sharma [38] covered a range of forms and methods. This work provides insights into the complex processes and influencing aspects of ferrite-based nanoparticles and illuminates their potential uses in corrosion control. The examined literature emphasizes how well nanostructured coatings perform in reducing corrosion across a range of circumstances [39–43]. Surface hardness, adhesion strength, and resistance to high temperatures are three properties that nanocoatings, especially those based on nanoparticles, provide as means of improving corrosion protection [44]. Even in highly corrosive conditions like high-temperature molten salt environments, these coatings can provide a protective layer on steel surfaces, preventing corrosion and encouraging consistent corrosion patterns [45]. The research findings shed light on

Table 1. Overview of previous research that controlled corrosion by optimizing nanoparticle dispersion and integration

Metal (s) protected	Nano material used for corrosion control	Corrosion study method	Medium for corrosion study	Key findings	Ref.
Steel	Mica nanosheets, magnetic-responsive core-shell nanoparticles	EIS, PDP	NaCl (3.5 wt.%)	Enhanced corrosion inhibition efficiency, differentiated nanofiller distribution	[32]
Carbon steel and stainless steel	Polymeric materials, nanoparticles	EIS	Molten salt (40% KNO ₃ -60%NaNO ₃) @ 390-565 ^o C	Achieved homogeneous corrosion layer, reduced corrosion on carbon and stainless steel.	[37]
Carbon steel and stainless steel	Mesoporous silica nanoparticles	EIS, PDP	Na ₂ SO ₄ (2mg/ml)	The nano material demonstrated effectiveness in corrosion protection at different pH values.	[46]
Steel (X60)	Copper nanoparticles doped carbon quantum dots	EIS, PDP	Sodium lactate (0.5g/L), and sodium acetate (0.5g/L)	Significantly inhibited SRB, enhanced corrosion protection for X60 steel.	[47]
Magnesium alloy	SiO ₂ nanoparticles, polymeric materials	Hybrid film synthesis, corrosion testing.	NaCl (0.1 mol/L)	Improved corrosion resistance with nanoparticle additions.	[48]
Steel	Modified nanoparticles	Coating synthesis, characterization, corrosion testing.	NaCl (3.5 wt.%)	Enhanced corrosion resistance observed.	[49]
Carbon steel	Sn—4% Zn alloy/nanoparticle composite, nanoparticles	Synthesis, characterization, corrosion evaluation.	NaCl (3.5 wt.%)	Enhanced corrosion resistance demonstrated through measurements.	[50]
Steel	Various nanoparticles	Coating synthesis, characterization, corrosion testing.	NaCl (3.5 wt.%)	Improved corrosion resistance and mechanical properties observed.	[51]
Steel	Nanosilica	Coating synthesis, characterization, testing.	NaCl (3.5 wt.%)	Delayed coating failure observed under corrosive conditions.	[52]

the intricate mechanisms and variables that affect the anticorrosion characteristics of nanostructured coatings, such as those derived from ferrite nanoparticles, and highlight their potential for corrosion control.

Zea et al. [46] concentrated on using mesoporous silica nanoparticles packed with corrosion inhibitors to create smart anticorrosive coatings. Their work showed the efficacy of

encapsulated nanoparticles in corrosion prevention at various pH levels by using pH variations as a trigger for controlled inhibitor release. Copper nanoparticle-doped carbon quantum dots were introduced by Kalajahi et al. [47] as inhibitors against microbiologically induced corrosion (MIC). Their results demonstrated the potential of nanohybrids in the fight against MIC by showing notable suppression against sulphate-reducing bacteria (SRB) and improved corrosion protection

for X60 steel. Research conducted by Zea et al. [46] and Tian et al. [53] groups bolsters the application of nanocontainers in smart anticorrosive coatings. In their study, Zea et al. [46] examined mesoporous silica nanoparticles that were loaded with inhibitors and showed how pH variations might trigger regulated release of the inhibitors which effectively prevented corrosion [46]. Furthermore, Tian et al. [53] produced self-healing coatings using hollow mesoporous TiO_2 nanocontainers sealed with zinc oxide quantum dots [53]. These coatings demonstrated improved corrosion resistance and quick inhibitor release in response to local corrosion signals. Additionally, Lee [54] explored the application of silica nanoparticles as corrosion inhibitors for copper substrates and found that the production of surface nano-fins, which impede metal disintegration significantly reduced corrosion rates [54]. This finding suggests a different strategy for corrosion prevention. Together, this research demonstrates the variety of approaches that use nanoparticles and nanocontainers.

Using SiO_2 nanoparticles in tetraethylorthosilane (TEOS) and 3-glycidoxypropyl trimethoxysilane (GPTMS) coatings on magnesium alloy, Peres et al. [48] studied hybrid films for corrosion resistance. Their research showed that adding nanoparticles increases corrosion resistance, indicating that anticorrosion protection may be optimized by using the appropriate quantities of nanoparticles. The results of Peres et al. [48] regarding the use of nanoparticles to improve corrosion resistance in coatings are supported by studies conducted by a number of other researchers [55–59]. Ammar et al. [57] showed that SiO_2 nanoparticles enhance corrosion resistance and hydrophobicity in a polymeric matrix. Similarly, Samadianfard et al. [58] demonstrated that the corrosion resistance of sol-gel coatings was improved by adding oxidized Fullerene nanoparticles. This was confirmed by Ouyang et al. [59], who showed that SiO_2 nanoparticles greatly increased superhydrophobicity and corrosion resistance in a composite coating. Furthermore, supporting the notion that nanoparticles might improve corrosion protection is Rashid's work [55] on hybrid sol-gel coatings doped with corrosion inhibitors. Singh and colleagues [60] also discovered that TiN nanoparticles in PEO coatings on magnesium alloys enhanced the resistance to corrosion. Numerous studies have demonstrated that the corrosion protection of magnesium alloys is greatly enhanced by the incorporation of SiO_2 nanoparticles in various coating matrices, including epoxy-alkyl silane sol, superhydrophobic polysiloxane films, and slips [59,61,62]. These

nanoparticles are essential for building corrosion-resistant barriers, improving surface hydrophobicity, and closing nanopores [63]. In addition, it has been shown that the inclusion of SiO_2 nanoparticles in plasma electrolytic oxidation (PEO) coatings reduces the size and quantity of pores, improving the coatings' mechanical properties and corrosion resistance [60]. Therefore, magnesium alloys' anticorrosion characteristics may be significantly enhanced by adjusting the number and distribution of SiO_2 nanoparticles in coatings.

To ensure stability in aqueous solutions, Merino et al. [64] suggested a general approach for the growth of hybrid 3D nanoparticles with a protective shell. Their approach, which combined atomic layer deposition and vapor deposition, demonstrated the potential of functional nanoparticles in a range of conditions, including acidic liquids. Song et al. [49] examined the effects of fluoropolymer coatings with modified nanoparticles (SiO_2 , TiO_2 , and Al_2O_3) on steel substrates. They found that the coating demonstrated better dispersion and the chemical interactions with the nanoparticles improved corrosion resistance. Alshammri et al. [50] used a Sn—4% Zn alloy/nanoparticle composite on carbon steel to create a unique corrosion-resistant coating. Their work used polarization and impedance tests to demonstrate how nanoparticles (Al_2O_3 , NiO) might improve corrosion resistance. Shi et al. [51] produced homogeneous epoxy coatings with several nanoparticles (SiO_2 , Zn, Fe_2O_3 , and halloysite clay), which showed better mechanical and corrosion resistance. Their results demonstrate how nanoparticles might improve coating barrier effectiveness and anticorrosive processes. In their investigation of epoxy powder coatings using nanosilica for corrosion prevention, Fernández-Álvarez et al. [52] revealed delayed coating breakdown under corrosive circumstances. According to their research, nanoparticles may hinder the absorption of water, so postponing the onset of corrosion and enhancing the performance of coatings. The research highlighted how nanoparticles affect the performance of coatings in corrosive environments. Although Fernández-Álvarez et al. [52] proposed that nanoparticles can impede water absorption and hence improve coating performance, delaying coating breakdown [65], other studies provide different insights. The hypothesis that nanoparticles improve coating qualities is supported by Wang et al.'s [66] demonstration of enhanced corrosion resistance and durability in nano-modified composite coatings, especially those containing nano-silica and graphene nanoplatelets. On the other hand, Zaikova et al. [67] discovered that adding TiO_2

nanoparticles to floor coatings did not considerably improve their antibacterial or scratch resistance qualities, suggesting that they were ineffective in some situations. The application of nanoparticles in coatings provides important engineering and scientific insights into the prevention of corrosion. Because a protective barrier forms, which delays coating breakdown under corrosive circumstances, nanocoatings such as those containing aluminum nanoparticles display increased corrosion resistance [41,68]. Furthermore, the use of nanoparticles such as silicon dioxide and titanium dioxide in vehicle paints results in enhanced functions and self-cleaning properties, which increase surface lifetime and offer protection against environmental factors [69]. In addition, the production of metal nanoparticles for use in food packaging coatings imparts antibacterial qualities, increasing food items' shelf lives and resolving safety issues related to nanoparticle migration into food [70]. Together, these results demonstrate the wide range of use and advantages of coatings based on nanomaterials for improved performance and durability across several sectors. These investigations highlight the adaptability and efficiency of coatings based on nanoparticles in corrosion management, providing customized solutions for a range of substrates and conditions. Researchers are pushing the boundaries of the field with creative methods and material choices, opening the door for more effective and long-lasting corrosion prevention systems.

3.2 Stability and durability of nanocoatings for corrosion prevention

Several strategies are deployed to improve the stability and durability of nanocoatings for corrosion prevention. Luo et al. [71] used spray modification and femtosecond laser processing to produce micro-nanostructures on superhydrophobic surfaces to increase the corrosion resistance of aluminum alloys. With notable decreases in self-corrosion current and increases in impedance, the super-hydrophobic surfaces that were created, exhibited positive contact and slide angles as well as improved mechanical, chemical, and thermal stability, suggesting that aluminium alloys can be used sustainably. Reports showed that the stability and durability of nanocoatings for the prevention of corrosion in metals may be improved by using particular procedures. Improved corrosion resistance was achieved by using spray modification and femtosecond laser processing to form micro-nanostructures on superhydrophobic aluminum alloy surfaces [71]. Misiuk et al. [72] conducted an investigation into coating-free aluminum micro/nanopatterns that were obtained using micro-milling or laser-etching. Their findings

revealed improved wetting characteristics and super hydrophobicity [72]. Barthwal and Lim [73,74] further produced superhydrophobic coatings with superior corrosion resistance and anti-icing qualities on aluminum surfaces using chemical etching, anodization, and PDMS coating. Additionally, Tong et al. [75] demonstrated a fluorine-free technique for superhydrophobic surface preparation on aluminum alloys, focusing on increased corrosion resistance and mechanical robustness [75]. Furthermore, the application and functionality of aluminum surfaces have been further enhanced by the development of superhydrophobic coatings with anti-icing properties through affordable methods that have demonstrated promising results in delaying ice formation and encouraging self-propelled jumping behavior of water droplets [73]. The idea of using aluminum alloys sustainably through improved surface treatment is supported by all these investigations.

A summary of key findings can be found in Table 2 below. Zhang et al. [76] combined the electrochemical generation of TiO₂ nanoparticles with the modification of octadecyl trimethoxysilane (OTS) to produce long-lasting superhydrophobic coatings for aluminum alloys. Anodic oxide coating, TiO₂ nanoparticles, and the OTS network worked in harmony to provide the coating a long-lasting resistance to corrosion, potentially providing the capacity for metal corrosion protection over an extended period. This method produced the best hydrophobicity and corrosion resistance, demonstrating the cooperative effects of the TiO₂ nanoparticles, AAO layer, and OTS network [77]. The coating's outstanding corrosion resistance was made possible by its integrated components, which also made it a viable option for long-term metal corrosion protection [71]. The work fills a vital gap in the area of corrosion prevention by utilizing the distinctive qualities of each component to improve the durability and efficacy of superhydrophobic coatings for aluminum alloys [78]. Research by Zhang et al. [77] supports the development of long-lasting superhydrophobic coatings for aluminum alloys. Using HD-SiO₂ nanoparticles and PDMS binder [77] created a superhydrophobic coating that demonstrated exceptional wear resistance and 98.9% efficiency in corrosion prevention. In order to produce superhydrophobic aluminum alloy surfaces with exceptional thermal stability and corrosion protection, Zhou et al. [79] used two different techniques, resulting in water contact angles of 165° and 170°, respectively. According to Rivero et al.'s [76] concept of long-lasting corrosion resistance, these studies show how well surface microtexture and low-surface-energy materials work together to improve the toughness and

Table 2. A summary of key findings on previous studies on stability and long-term durability of nanocoatings for metal corrosion prevention

Metal/Alloy Protected	Nanomaterial Used	Corrosion Study Method	Medium for Corrosion Studies	Key Findings	Ref.
Metallic structures	Carbon nanotubes (CNT), graphene nanoplatelets (GNP), nano-silica (NS)	Electrochemical impedance spectroscopy (EIS)	-	Superior corrosion inhibition with NS and GNP-based composites	[66]
Aluminum alloy	Hydrophobic nano-silica, TiO ₂ nanoparticles	Electrochemical tests, static immersion test	NaCl solution (3.5 wt.%)	Improved corrosion resistance and durability of superhydrophobic coatings	[76]
Steel	Nanosilica, polytetrafluoroethylene (PTFE), SiO ₂ nanoparticles	TOEFL polarization, electrochemical impedance spectroscopy (EIS)	NaCl solution (3.5 wt.%)	Significant reduction in corrosion rate with PTFE coating containing SiO ₂ nanoparticles	[80]
Copper	Silica nanocapsules, corrosion inhibitors	Optical measurements, time-dependent optical extinction	Physiological environment	Prolonged anticorrosion performance with nanocapsule-loaded coatings	[81]
Copper nanodisk arrays	Al ₂ O ₃ /HfO ₂ nanolaminated coatings	Optical extinction measurements	1× phosphate-buffered saline	Extended lifetime of Cu nanodisk arrays with nanolaminated coatings	[82]
Carbon steel	Functionalized nanofluids, hierarchical surfaces	Tribo-electrochemical tests	Water flow shear	Improved lubricity and corrosion resistance with hierarchical surfaces	[83]

corrosion resistance of superhydrophobic coatings on aluminum alloys.

Haji-Savameri et al. [80] studied the use of superhydrophobic coatings — steel coated with corrosion-resistant materials — prepared by spraying polytetrafluoroethylene (PTFE) and electrodepositing a hybrid layer of nanosilica. Their research showed that the combination of low conductivity and superhydrophobic qualities greatly increased corrosion resistance, and the performance of PTFE coatings was further enhanced by the inclusion of SiO₂ nanoparticles. Regarding the application of superhydrophobic coatings for corrosion resistance, the research of Dey et al. [84] corroborates the conclusions of Haji-Savameri et al. [80]. A superhydrophobic TiO coating on steel was shown by [84] to greatly increase corrosion resistance, with a water contact angle of 160.7°

and better adhesion qualities [85]. Similarly, Xia et al. [77] improved uncoated aluminium sheets by developing a stable superhydrophobic coating with an effectiveness of 98.9%, which demonstrated outstanding corrosion prevention [84]. The two experiments demonstrate the possibility of superhydrophobic coatings to increase corrosion resistance, which is consistent with the advantages noted in the study conducted by Haji-Savameri et al. [80] about the combined benefits of low conductivity and superhydrophobic qualities for better corrosion protection.

By employing inhibitor-filled silica nanocapsules, [81] produced nanostructured multilayered coatings for copper substrates that offer corrosion mitigation and sensing capabilities. By adding these nanocapsules to the coating, this study showed promising long-term anticorrosion performance, allowing for corrosion monitoring and

inhibition [86]. By contrast, Alderete et al. [87] evaluated the application of coatings with carbon nanoparticles to safeguard copper substrates in abrasive conditions. It was discovered that the coatings made of carbon nanotubes demonstrated superhydrophobic behaviour, which qualified them as effective barriers against oxidation in coastal areas [81]. Furthermore, for longer-lasting anticorrosion effects on copper substrates, Kim et al. [88] used organosilane molecules to store organic corrosion inhibitors in mesostructured silica coatings. These studies offer different strategies for protecting copper from corrosion and enhancing its sensing abilities.

Carbon nanotubes (CNT), graphene nanoplatelets (GNP), and nano-silica (NS) were used as nanofillers to investigate the protective qualities of nano-modified composite coatings for metallic structures [83]. According to their research, composites based on NS and GNP showed better corrosion inhibition and maintained their high resistance even after extended exposure, indicating the possibility of long-term corrosion protection. The use of sub-10 nm $\text{Al}_2\text{O}_3/\text{HfO}_2$ nanolaminated coatings to prolong the lifespan of Cu nanodisk arrays in physiological conditions has been studied [82]. The results showed a linear connection between the lifespan of Cu plasmonics and the thickness of the nanolaminated coating, indicating potential for long-term anticorrosion applications. Research on the application of nanolaminated coatings for corrosion protection by Mirhashemihaghighi [89] and Farhadi [90] offers insights that are consistent with Daniel et al.'s findings [91]. With differing outcomes depending on coating thickness and substrate preparation, Mirhashemihaghighi's research on ALD Al_2O_3 coatings on Cu and Al substrates in NaCl solutions supports the usefulness of thin alumina films in corrosion protection [91]. The importance of combining decreased ice adhesion with increased corrosion resistance is emphasized by Farhadi's work on ice-releasing coatings on aluminum surfaces, highlighting the value of protective coatings for metallic substrates in harsh environments [89]. Conversely, Barulin et al. [92] discovered that aluminum structures in water experience quick photocorrosion when exposed to UV light, emphasizing the crucial constraint of aluminum instability in aqueous solutions [86]. Further investigation into the use of ALD films to mitigate copper oxidation and migration was conducted by Dogan et al. [93], who demonstrated good oxidation protection and structural changes in the passivation layers at increased temperatures [94]. The authors Wang et al. [95] introduced a novel approach to create superhydrophobic nanocomposite coatings with superior mechanical

and chemical stability: plasma-enhanced high-temperature liquid-phase-assisted oxidation and crosslinking (PHLOC). The coatings demonstrated resilience to abrasion, chemical exposure, and elevated temperatures, rendering them appropriate for extended use in challenging conditions. Wang et al. [96] improved lubricity and corrosion resistance on carbon steel substrates through the production of slippery nanofluid-injected hierarchical surfaces (SNHSs). In terms of mechanical endurance and corrosion prevention, their research showed that SNHSs reinforced with micro SiO_2 particles performed better than nanostructured surfaces [97]. Conversely, Curtis et al. [98] discovered that immersion in nanodiamond suspensions that were either positively or negatively charged had different impacts on tribological characteristics with the -ND suspensions lowering friction for surfaces made of alumina and stainless steel [99]. Schäfer et al. [99] also found that longer lubrication lives were not always the result of the structural design of surfaces coated with multi-walled carbon nanotubes, suggesting that deeper structures were not always associated with increased lubrication effectiveness [100]. These investigations provide information on various strategies and materials for improving lubricity and resistance to corrosion in a range of applications.

Zhu et al. [101] synthesized very robust superhydrophobic coatings featuring triple-scale hierarchical micro/nanostructures, exhibiting resilience against heat treatment, acid/base immersion, impact, and mechanical abrasion. The coatings showed promise for long-term useful applications due to their exceptionally high corrosion prevention effectiveness and self-cleaning qualities. Research on strong superhydrophobic coatings by Zhu et al. [101] is consistent with another study [102]. Similar to (Zhu et al. 2022)'s coatings, Huang et al. [102] produced superhydrophobic powder coatings with excellent mechanical stability, chemical resistance, and UV robustness [102]. Again, similar to Zhu et al. [101]'s coatings, Su et al. [103] suggested a dual-sized particle approach to produce superhydrophobic composites with exceptional endurance against a variety of environmental conditions. These composites demonstrated resilience to mechanical abrasion, UV radiation, and chemical exposure [86].

Li et al. (2022) investigated multilayer coatings based on carbon to improve stainless steel's resistance to tribocorrosion. According to their research, Ti—TiC_x/DLC coatings had the highest anti-tribocorrosion performance, retaining low wear and friction coefficients under prolonged testing

circumstances, which may indicate the possibility of an extended service life in tribocorrosive environments. Their results agree with those of research on carbon-based coatings for tribocorrosion improvement conducted by Zhang et al. [105], Chen et al. [106], and Uzun [107]. Ti—TiCx/DLC coatings have been shown by Li et al. [104] to have improved anti-tribocorrosion performance, retaining low wear and friction coefficients over lengthy testing, indicating a longer service life in corrosive conditions [104]. In support of this, Zhang et al. [105] demonstrated that Ti—TiCx/DLC coatings on various metal substrates had good wear resistance and low friction coefficients, particularly under high loads [105].

The significance of carbon content in augmenting coatings' resistance to tribocorrosion has been underscored [106], whereby TiAlCN/TiAlN/TiAl coatings demonstrated excellent performance. The findings were corroborated by Uzun's [107] work, which demonstrated how Ti-DLC coatings may effectively increase the tribocorrosion resistance of stainless steel [107].

In essence, Dieleman et al. [108] illustrated the advantages of constantly released corrosion inhibitors integrated in thermoset epoxy coatings by proposing inhibitory nanonetworks for active corrosion protection at damaged regions. Their research revealed the possibility of providing metallic substrates with long-term defence against damage brought on by corrosion. Interestingly, in thermoset epoxy coatings [108], added inhibitory nanonetworks to offer ongoing corrosion prevention at damaged areas [109]. On the other hand, Priyanka and Nalini [110] concentrated on improving adhesion bonds using modified graphene oxide in epoxy systems with urea-formaldehyde microcapsules to improve anti-corrosion capabilities [108]. Moreover, self-healing epoxy vitrimer/CNT nanocomposites were created by Lorwanishpaisarn et al. [111] for anti-corrosion coatings, and they showed enhanced corrosion resistance and self-healing properties [110]. While Priyanka et al. [110] concentrated on adhesion improvement, Dieleman et al. [108] emphasize continuous inhibitor release, and Lorwanishpaisarn et al. [111] highlight self-healing capabilities in anti-corrosion coatings, these research provide different strategies for battling corrosion. Together, the reviewed previous research advances our knowledge of and capacity to develop nanocoatings that protect metals from corrosion over an extended period of time. They also provide a variety of approaches to improve performance, stability, and durability under challenging conditions.

3.3 Review of nano-corrosion protection of alloys used for biomedical purposes

According to a recent work by Devadoss et al. [112], dental alloy (Ti-6Al-4V) corrosion in a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ medium may be avoided by using green production of copper oxide nanoparticles from *Murrayakoenigii*. The study showed that copper oxide nanoparticles might be used as a coating agent in dental implant alloys. When electrodeposited on Ti-6Al-4V alloy, the produced nanoparticles demonstrated clear corrosion inhibition characteristics with an inhibition efficacy of 58.15%. This discovery raises the possibility of a useful application of the nanoparticle material in dentistry, where corrosion resistance is essential to the durability and effectiveness of dental implants.

The hydrothermal approach has been successfully used to produce the nano-hydroxyapatite (nHA) matrix coatings doped with various weight percentages of graphene nanosheets (GNSs) on the Ti6Al4V alloy [113]. Due to its superior surface qualities compared to others, the nHA/5GNS coating was reported to achieve the greatest surface area and high corrosion resistance combination. The hydrothermal approach has been successfully used to produce the nano-hydroxyapatite (nHA) matrix coatings doped with various weight percentages of graphene nanosheets (GNSs) on the Ti6Al4V alloy [113]. Owing to its superior surface qualities compared to others, the nHA/5GNS coating was reported to achieve the greatest surface area and high corrosion resistance combination. The hydrothermal approach has been successfully used to produce the nano-hydroxyapatite (nHA) matrix coatings doped with various weight percentages of graphene nanosheets (GNSs) on the Ti-6Al-4V alloy [113].

In order to stop the corrosion of the alloys Ti-6Al-4V and Ti-6Al-7Nb, research has been done to produce TiO₂ nanotubes with an amorphous structure [114]. The corrosion resistance of the nanotubular oxide surfaces was examined in a chloride-containing solution (Ringer physiological solution). Results showed that the chloride-containing solution had excellent corrosion resistance since there was no transpassivation. The coating's remarkable corrosion resistance was confirmed by its low passivation current density [114].

3.4 Overview of previous work on nano-corrosion protection of steel

The summary of previous studies on the use of nanotechnology to prevent the corrosion of steel is presented in Table 3. A green corrosion prevention system for steel in 1.0 N Na_2CO_3 , and 1 N HCl)

Table 3. Summary of overview of previous studies on nano-corrosion protection of steel

Material Protected	Protective Nanomaterial	Medium	Remarks	Ref.
Steel	Silver Nanoparticles	1.0 N Na ₂ CO ₃ , 1 N HCl	Increasing nanoparticle concentrations enhance corrosion inhibition; Langmuir Isotherm-based adsorption mechanism.	[115]
Mild Steel	Titanium Nanocomposite (Ti-CO)	1.0 M HCl	Ti-CO nanocomposite inhibits corrosion; Inhibition effectiveness increases with inhibitor concentration.	[116]
Carbon Steel	Silver Nanoparticles	1.0 N HCl	Inhibitory efficiency influenced by dosage and temperature; Adhesion and adsorption via Langmuir adsorption mechanism.	[117]
Mild Steel	Polyaniline (PANI) and Titanium dioxide (TiO ₂) nanocomposites	Various Media (including 1 N NaCl, 1 N H ₂ SO ₄ , seawater)	PANI/TiO ₂ nanocomposite coatings exhibit corrosion prevention properties under different environmental conditions.	[118]
Cold-worked Tool Steel	Nanolaminate Coatings (CrN coupled with -W ₂ N or -Mo ₂ N)	-	Nanolaminate coatings (CrN/-W ₂ N and CrN/-Mo ₂ N) exhibit improved mechanical and electrochemical qualities.	[119]
Steel Pipework	Nano-scale Bio-based Nanocomposite (WHE-AgNPs)	Petroleum Wastewater	WHE-AgNPs successfully remove heavy metal ions; Acts as an anticorrosive agent for steel pipework.	[120]
Mild Steel	Multi-walled Carbon Nanotubes (MWCNTs) and Green Inhibitor/ Silver Nanoparticles (EG/AgNPs)	Saltwater	Epoxy coating with MWCNTs and EG/AgNPs provides self-healing and excellent anti-corrosion characteristics.	[121]
Iron Surface	NanoCar Inhibitors	-	NanoCar molecules form a barrier layer inhibiting corrosion by delaying the diffusion of corrosive species.	[122]
Mild Steel	Chitosan-Silver Nanocomposite (SNPs-CTNC)	Chilled Water Circuits	SNPs-CTNC inhibits corrosion effectively in chilled water circuits; Exhibits consistent inhibitory effectiveness over time.	[123]
Mild Steel	Maleic-anhydride-functionalized Graphene (MAGE) Nanofillers	3.5% NaCl, Sulphate-reducing Bacteria (SRB) Environment	MAGE coating provides improved corrosion resistance in both abiotic and aggressive microbial environments.	[124]
Stainless Steel	Copper-coated Graphene (Gr-Cu) Composite	Not specified	Gr-Cu composite exhibits dramatically improved corrosion resistance due to the presence of graphene.	[125]
Mild Steel	ZnO/NiO/CuO/PCL Nanofibre Layer	1 M HCl	Deposition of nanofibre layer results in high inhibition efficiency against corrosion.	[126]
AISI 1018 Steel	Co-doped TiO ₂ /Polypyrrole Nanocomposites	3.5% NaCl Solution	Co-doped TiO ₂ /PPy NTCs show higher corrosion resistance due to increased surface area of PPy.	[127]

acidic media has been locally developed using silver nanoparticles [115]. With increasing nanoparticle concentrations, expired drug concentrations, and reaction temperature, corrosion inhibition was seen to rise. The Langmuir Isotherm-based adsorption of nanoparticles on steel surfaces was found to be consistent with the inhibitory mechanism. For industrial cleaning and pickling processes of mild steel, a different study was done to identify effective, thermally stable, alternative, and environmentally benign anticorrosion additives [116]. The *Chromolaena odorata leaf* methanolic extract was used by the researchers to produce a titanium nanocomposite (Ti-CO). When the mild steel was exposed to 1.0 M HCl, the Ti-CO nanocomposite significantly inhibited the corrosion. At 1.0 g/L of inhibitor concentration, the inhibition effectiveness was discovered to be 92.39 %. Higher inhibitor concentrations resulted in better efficiency; however, higher temperatures resulted in lower efficiency. In accordance with the Langmuir adsorption isotherm model, it was discovered that the inhibitor molecules formed a monolayer on the metal surface, preventing corrosion.

The capacity of the produced silver nanoparticles to prevent carbon steel, a material utilized in the petroleum sector, from corroding when exposed to 1.0 N hydrochloric acid, was put to the test [117]. At various doses (from 50 to 200 ppm) and temperatures (from 303 to 333 K), the inhibitory effectiveness of the nanomaterials was investigated. The study found that higher temperatures lowered the inhibitory effectiveness while larger dosages of the nanomaterials increased it. A dose of 200 ppm of the produced nanomaterials resulted in the highest inhibitory efficiency of 98%. This inhibitory action was linked to the adhesion and adsorption of nano molecules via Langmuir adsorption on the metal surface [117]. Another investigation by Jabri et al. [118] considered the application of Polyaniline (PANI) and Titanium dioxide (TiO₂) nanocomposites to prevent mild steel from corroding in different media. These substances were used in a dip coating procedure to produce stable thin layers on mild steel specimens. The produced films were put through a variety of environmental testing, such as wet/dry tests, air tests, exposure to 1 N NaCl, 1 N H₂SO₄, and sea water. The coatings demonstrated corrosion prevention properties in these circumstances, suggesting that they may be used in real-world situations with a variety of environmental conditions.

According to Beltrami et al. [119], reactive DC reactive magnetron sputtering has been used to produce nanolaminate coatings (NLC) made up of

alternating CrN coupled with either cubic tungsten nitride (-W₂N) or molybdenum nitride (-Mo₂N) on cold-worked tool steel substrates. Coatings with higher mechanical and electrochemical qualities were produced when CrN was used in conjunction with -W₂N or -Mo₂N. The CrN/W₂N NLC combines W₂N's high hardness with CrN's low corrosion current for synergistic advantages. Similarly, the CrN/-Mo₂N NLC showed synergistic benefits over the constituent materials alone, such as increased hardness and decreased corrosion currents. This suggests that the nanolaminate structure's qualities are superior to those of its constituent layers because of the mix of several materials used to produce it. The removal of heavy metals from petroleum wastewater using a nano-scale bio-based nanocomposite (WHE-AgNPs) and its effects on piping steel corrosion have been researched [120]. At 25°C for 5 hours, the removal efficiencies for Pb were 72.6%, Cr was 81.3%, and Cd was 88.1%. Physical adsorption on WHE-AgNPs surface locations aided in the elimination process. The research showed that the newly created bio-based nanocomposite (WHE-AgNPs) was successful in treating petroleum effluent, removing heavy metal ions, and having an anticorrosive impact on steel pipework.

Ali et al. [121] used a new epoxy coating that contained multi-walled carbon nanotubes (MWCNTs) as nanocontainers filled with 5% green inhibitor (*Elaeisguineensis*)/silver nanoparticles (EG/AgNPs) to prevent mild steel from corroding in saltwater. This ground-breaking coating was developed to provide a strong corrosion inhibitor for mild steel in challenging saltwater conditions. Over the course of 42 days, the study assessed the coating's self-healing and anti-corrosion characteristics using different analyses and tests. Excellent self-healing capabilities of the coating allowed it to restore damaged coatings on the mild steel surface while the maximum inhibitory effectiveness of 97.87% was attained after 42 days of exposure to saltwater. Moreover, the corrosion rate was dramatically lowered to 0.0009 mm/year. Another study explored the relationship between NanoCar inhibitors and the iron surface to prevent corrosion using a variety of theoretical techniques, including Density Functional Theory (DFT) and Monte Carlo simulation (MC), which are based on molecular and quantum mechanics. According to the findings, NanoCar molecules formed a barrier layer by lying flat on the iron surface. Corrosion was shown to be successfully inhibited by this film's ability to delay the diffusion of corrosive species towards the metal surface [122].

An eco-friendly chitosan-silver nanocomposite has been explored by Fetouh et al. [123] as a

unique and promising corrosion inhibitor for mild steel in chilled water circuits. At a concentration of 150 ppm SNPs-CTNC, the inhibition efficiency of all produced samples was up to 97-98%. The sample that performed the best, produced for 8 hours, had an inhibitory effectiveness of more than 80% at a concentration of 100 ppm. Over the course of a year in storage, the SNPs-CTNC samples' inhibitory effectiveness and antibacterial activity were consistent. The most reliable inhibitory effectiveness was shown by the sample that had been generated for two hours; it remained over 97% even after aging. The corrosion resistance of epoxy coating on mild steel surfaces has been improved with the use of maleic-anhydride-functionalized graphene (MAGE) nanofillers in both abiotic (3.5% NaCl) and aggressive microbial (sulphate-reducing bacteria, SRB) environments. The MAGE coating provided four orders of magnitude less corrosion resistance against planktonic SRB cells, 80% less corrosion resistance against sessile SRB cells, and 19 times less corrosion resistance against 3.5% NaCl compared to unfunctionalized graphene nanoplatelets. A 99.9% maximal inhibition efficiency was achieved [124].

Copper-coated graphene (Gr-Cu) Gr/stainless steel (SS) composite material has dramatically improved corrosion resistance. A more favourable corrosion potential (-0.227 V) and a two orders of magnitude lower corrosion current density (3.8×10^6 A/cm²) were produced with the addition of 0.2wt% Gr. The low cathodic overvoltage of copper and the low ionic transfer in SS, both of which were altered by the presence of graphene, were responsible for this increase in corrosion resistance [125]. Deposition of nanofibre layer of ZnO/NiO/CuO/PCL on mild steel in HCl (1 M) has been reported to give the inhibition efficiency of 94.8 % [126]. It has been investigated how Co-doped TiO₂/polypyrrole nanocomposites in 3.5% NaCl solution may protect AISI 1018 steel against corrosion [127]. The log |Z| (impedance magnitude) of AISI 1018 coated with Co-doped TiO₂/PPy NTCs was reported to reach around 8.2, whereas for TiO₂/PPy NTCs, it was 6.0 after 30 days of exposure in the NaCl solution. In other words, Co-doped TiO₂/PPy NTCs showed higher corrosion resistance. The reason for the exceptional performance of the co-doped TiO₂/PPy NTCs was attributed to the increased surface area of the PPy obtained in the presence of co-doped TiO₂ NPs [127]. The application of nanotechnology in the form of polypyrrole, doped with montmorillonite and molybdate has been reported to prevent mild steel from corroding in NaCl (3 %) [128]. It was discovered that molybdate inhibited metal corrosion while MMT served as a barrier layer inside the nanocomposite.

3.5 Previous studies on nano-corrosion protection of metals/alloys other than steel

Researchers have investigated the use of air nanobubbles (A-NBs) to successfully prevent brass corrosion in circulating cooling water [129]. A-NBs showed strong corrosion inhibition, with a remarkable 52% inhibition efficiency found at 35 °C. According to the results, A-NBs offer a lot of promise as corrosion inhibitors. They are reported to be good candidates for industrial applications where corrosion prevention is essential, including cooling systems, because of their efficacy at resisting corrosion and impact in the underlying corrosion mechanism. Table 4 presents the summary of the overview of previous studies on the use of nanotechnology to prevent the corrosion of metals and alloys other than steel.

Copper has been shielded against corrosion via the electrophoretic deposition (EPD) of halloysite nanotubes (HNTs) [130]. The best corrosion-resistant coatings had a 50 m thickness and were produced under ideal circumstances with electrode spacing of 30 mm, voltage of 20 V, HNTs content of 4%, and deposition duration of 30 s. The coating resistance reportedly changed from 13,446 to 27,015 Ω cm² when the deposition period increased from 15 to 60 s. The coatings' versatility is demonstrated by their usefulness in several applications like thermal insulation, information concealment, and anti-corrosion measures.

A study that utilized the anodic oxidation procedure to produce nanoporous layers of aluminum oxide was carried out [131]. With the addition of 1 g/L Al₂(SO₄)₃ x 18H₂O, the procedure was carried out in a solution containing 1 M H₂SO₄. On the surface of the aluminum alloy Al1050, layers of aluminum oxide developed. In a 3.5% NaCl solution with a pH of 5.75, the nanoporous films were evaluated for their ability to prevent corrosion. When compared to the aluminum alloy (Al1050) that was not treated, all the nanoporous layers of aluminum oxide that were produced using this procedure showed better anticorrosive capabilities. This demonstrates that the anodic oxidation procedure improved the material's corrosion resistance under the designated testing condition.

Research has been conducted to improve the mechanical and biological characteristics of alumina by adding a mixture of titanium diboride micropowder and alumina nanoparticles. On a substrate made of pure titanium, this mixture was sprayed using the Atmospheric Plasma Spray (APS) method. Polarization experiments showed that the Al₂O₃-30 wt.% TiB₂ coating had the best corrosion resistance [132]. Utilizing potentiodynamic polarization (PDP) and electrochemical impedance

Table 4. Overview of previous studies on nano-corrosion protection of metals/alloys other than steel

Material Protected	Nanomaterial	Medium	Remarks	Ref.
Brass	Air Nanobubbles (A-NBs)	Circulating Cooling Water	A-NBs offer strong corrosion inhibition with 52% efficiency at 35 °C. Ideal for industrial cooling systems.	[129]
Copper	Halloysite Nanotubes (HNTs)	Electrophoretic Deposition (EPD)	HNTs coatings provide versatility in thermal insulation, information concealment, and anti-corrosion applications.	[130]
Aluminum Alloy (Al1050)	Aluminum Oxide Nanoporous Layers	3.5% NaCl Solution (pH 5.75)	Anodic oxidation produces nanoporous layers enhancing corrosion resistance under specific conditions.	[131]
Alumina	Titanium Diboride Micropowder and Alumina Nanoparticles	Atmospheric Plasma Spray (APS)	Al ₂ O ₃ -30 wt.% TiB ₂ coating exhibits superior corrosion resistance on pure titanium substrate.	[132]
Copper	Graphene Nano-sheets	Epoxy Matrix	Graphene nano-sheets enhance coating material's anti-corrosion ability in copper applications.	[133]
Aluminum Alloy	Nanoporous Alumina Coating	Palm Oil	Optimized nanoporous alumina coating provides exceptional tribo-corrosion resistance in palm oil environment.	[134]
AA2024	Colloidal ZrO ₂ Nanoparticles	Sea Water	ZrO ₂ nanoparticles block intermetallic sites, significantly reducing AA2024's corrosion rate in artificial sea water.	[135]
Aluminium Alloys	Quercetin-loaded Silica Nanocontainers	HCl Solution (pH 10)	Quercetin-loaded silica nanocontainers exhibit active anticorrosive films regulated by pH levels.	[136]
Copper	Aluminum Oxide (Al ₂ O ₃)	Defective Graphene and Boron Nitride	ALD with Al ₂ O ₃ enhances corrosion resistance on Al ₂ O ₃ /Gr/Cu and Al ₂ O ₃ /BN/Cu systems.	[137]

spectroscopy (EIS), copper corrosion and its prevention by graphene nano-sheets in the epoxy matrix have been studied. Research showed the coating material's anti-corrosion ability was noticeably enhanced [133]. Sarraf et al. [134] examined an optimized nanoporous alumina coating on an aluminum alloy with improved tribo-corrosion resistance in palm oil. When exposed to palm oil methyl ester (B100), the heat-treated specimen was found to attain exceptional corrosion resistance with a low corrosion rate of 0.079 mm(y)⁻¹ and a high corrosion protection effectiveness of 95.24% [134]. It has been investigated how stabilized colloidal ZrO₂ nanoparticles affect the corrosion resistance of AA2024 in sea water [135]. By blocking the intermetallic sites on the metal surface, ZrO₂

nanoparticles were shown to increase AA2024's corrosion resistance. Consequently, the corrosion rate of AA2024 in the artificial sea water was significantly decreased by colloidal ZrO₂ nanoparticles with a maximum inhibition efficiency of 93.6 % [135]. Quercetin (QCT) was used as a natural organic inhibitor to protect aluminium alloys in HCl solution. Active anticorrosive films were produced by loading QCT into silica nanocontainers [136]. The release and reactions of the coating's inhibitory component, especially around pH 10, were found to regulate the bio-coatings' ability to prevent corrosion. This shows that the pH levels in the area have an impact on the coating's efficacy.

For both short-term corrosion tests (10 h, 3.5 wt.% NaCl solution) and long-term exposure to

humid air (up to 18 months), the atomic layer deposition (ALD) with Al_2O_3 to passivate defective graphene and boron nitride (BN), grown on Cu, and to controllably realize superior corrosion resistance on $\text{Al}_2\text{O}_3/\text{Gr}/\text{Cu}$ and $\text{Al}_2\text{O}_3/\text{BN}/\text{Cu}$ systems has been undertaken [137]. The improved anticorrosion caused by the Al_2O_3 deposition is explained by the strong blocking impact that the Al_2O_3 —two-dimensional film/Cu contacts have on the transport of H_2O molecules [137].

3.6 Nanotechnology-Based Corrosion Prevention Method

3.6.1 Corrosion Resistance Ability Of Graphene Via CVD And LBL Techniques

In recent academic research, chemical vapor deposition (CVD) has gained substantial attention as a preferred method for forming coatings based on graphene in nanocomposite materials. CVD provided a workable way to produce dense, pure graphene coatings and enabled large-scale graphene fabrication [138]. Notably, AA2024-T3 coated with a polymer/SLGr/polymer/SLGr/polymer combination obtained a good degree of corrosion protection for up to 120 days. Samples were assessed after being soaked in a 3.5 wt.% NaCl solution for 1, 30, or 120 days. These samples included those that were bare (AA), coated with polymer alone (P-P-P), and coated with alternating polymer and SLGr layers (P-G-P-G-P).

After one day of immersion, the corrosion rate of the coated sample (20 nm/year for AA-P-P-P vs. 4 $\mu\text{m}/\text{year}$ for naked AA) was found to be two orders of magnitude lower than that of the bare AA when P-P-P coatings were applied to it. Nonetheless, as immersion time rose, the P-P-P coated sample's corrosion rate increased (to 0.3 $\mu\text{m}/\text{year}$ for AA-PP-P after 30 days compared to 20 nm/year for AA-P-P-P at one day), suggesting that the P-P-P coating was degrading. Furthermore, low current values were seen in the potentiodynamic response for AA-PG-P-G-P, and corrosion rates were less than 2 nm/year. Degradation of the coatings was also seen after the nanocomposite coatings were submerged for an additional 120 days. For these systems, it was reported that there was often good agreement between the EIS results and the polarization measurements [138].

3.7 Mechanisms of Corrosion Inhibition

3.7.1 Adsorption Isotherm Models

The inhibitor's adsorption onto the metal's surface facilitates the corrosion inhibition process [139]. The rate of adsorption is affected by a number of variables, including the temperature, the chemical makeup of the solution, the electrochemical potential at the metal-solution

interface, and the physical characteristics of the metal surface [140]. Through the use of adsorption isotherm models, the relationship between the inhibitor and the metal is clarified [139].

3.7.2 Isotherm for Langmuir Adsorption

The Langmuir adsorption isotherm model states that the inhibitor forms a monolayer on the material's surface, preventing corrosion [139]. By dividing the ions between the liquid and solid phases equally, this model guarantees homogeneous adsorption energies on the metal surface. In mathematics, the Langmuir adsorption isotherm is represented as:

$$\frac{c_r}{\theta_{Cor}} = C_c + \frac{1}{K_{ads/des}} \quad (6)$$

where, $\frac{c_r}{\theta_{Cor}}$ = the fraction of the surface coverage, C_c = the inhibitor's concentration, and $K_{ads/des}$ = the desorption/adsorption process at equilibrium.

3.7.3 Isotherm for Freundlich Adsorption

An exponential distribution of energy surrounding a heterogeneous surface is described by the Freundlich adsorption isotherm. It provides information on how the concentration of the inhibitor in the contacting liquid and on the metal surface relate to one another [139]. The Freundlich adsorption isotherm model has the following mathematical expression:

$$\theta_{Cor} = E_{df} U_{Td}^{1/r_t} \quad (7)$$

where, θ_{Cor} = the commensurate quantity of metal that was absorbed at equilibrium for each gram of the adsorbent E_{df} = the Freundlich-isotherm's constant, r_t = adsorption's intensity, and U_{Td} = concentration of adsorbate at equilibrium.

3.7.4 Isotherm of Temkin Adsorption

The decrease in adsorption heat with increasing surface coverage is linear, according to Temkin's adsorption isotherm [139]. This model, which considers the interactions between the adsorbent and adsorbate, emphasizes the uniform distribution of binding energies. The Temkin adsorption model distinguishes the interactions inside the adsorbed layer, in contrast to earlier models. In terms of math, it is stated as:

$$\theta_{OR} = P_{OP} \ln B_{QN} + P_{OP} \ln C_T \quad (8)$$

$$B_{Sorp} = \frac{RT}{b_{Tem}} \quad (9)$$

Where,

θ_{OR} = surface region that was covered.

P_{OP} = sorption's heat (constant).

B_{QN} = constant of Temkin isotherm's stability binding.

C_T = the inhibitor's concentration.

R = constant for gas (8.314J/mol/K).

T = temperature (absolute).

b_{ET} = constant for Temkin isotherm.

3.8 Recent research in the field of green synthesized nanoparticles

Natural extracts and nanotechnology were used to develop environmentally safe corrosion inhibitors for TMT rods in maritime conditions that offer long-lasting protection. The efficacy of plant extracts and biogenic silver oxide nanoparticles was demonstrated in recent research, which also showed notable corrosion resistance. Applying silver oxide nanoparticles (AgONPs) made from *Thespesia populnea* to TMT rods demonstrated a high level of corrosion resistance. A strong protective layer was demonstrated by the corrosion rate efficiencies of 97.1% for 8 mm rods and 98.7% for 16 mm rods after coating TMT rods with 10 layers of AgONPs [141]. Effective physical adsorption on the metal surface was suggested by the adsorption mechanism's adherence to the Langmuir isotherm. Similarly, at optimum doses, *Terminalia catappa* leaf extract showed an inhibitory efficacy of almost 90%, reducing the corrosion current density from 8.87 A/cm² to 5.12 μ A/cm² [142]. Because natural extracts included active ingredients with varying inhibitory efficiencies depending on concentration, their usage became more popular due to their efficacy and sustainability [143].

Leveraging their distinct characteristics and environmentally friendly production processes, biogenic iron oxide nanoparticles (FeNPs) have become successful corrosion inhibitors for TMT rods in maritime environments. FeNPs, which are made from the leaves of the *Thespesia populnea* plant, greatly increased corrosion resistance by creating protective coatings. In addition to reducing corrosion, this strategy was in line with environmentally beneficial corrosion control techniques. According to Monikandon et al. [144], adherence to the Langmuir adsorption isotherm demonstrated that physical adsorption was the main mechanism of inhibition. Maximum inhibition rates after ten FeNP coatings were 91.2% for 8 mm rods, 95.4% for 10 mm rods, and 98.7% for 16 mm rods, according to the study [144]. By using plant extracts as reducing agents, the green synthesis of FeNPs proved both economical and

environmentally safe [145]. Alternative techniques, like biogenic silver oxide nanoparticles, also showed good corrosion resistance, indicating a competitive landscape in corrosion prevention technologies, even though biogenic iron oxide nanoparticles showed encouraging findings [146].

4. FUTURE RESEARCH DIRECTIONS IN THE USE OF NANOTECHNOLOGY IN METAL CORROSION CONTROL

Future studies on the application of nanotechnology to metal corrosion control will consider the production of protective films against corrosion by using carbon allotrope-based nanocoatings, natural source-based nanocoatings, metal/metallic ion-based nanocoatings, and self-healing, environmentally sustainable corrosion inhibitors [41]. The anti-corrosive qualities of coatings are improved by nanomaterials because of their characteristics such as adhesion strength, surface hardness, and resistance to corrosion at high temperatures [53,147]. Furthermore, employing green nanoparticles as corrosion inhibitors provides an economical and sustainable approach, meeting the demand for environmentally acceptable substitutes for conventional inhibitors. The objective of these improvements is to enhance the durability of coatings against corrosive solutions and offer effective corrosion protection in a range of industrial conditions. The efficiency of nanocomposite coatings applied electrochemically, which provide superior resistance to corrosion and scratches on metal surfaces and lower maintenance costs, also needs further research [148].

To develop high-performance coatings that prevent and resist corrosion for a variety of sectors, including chemical engineering, automotive, and aerospace, researchers should concentrate on using functionalized nanomaterials [149]. Increased corrosion resistance is provided by nanocomposite coatings, which contain nanoparticles, nanotubes, and other nanomaterials [148,150]. These coatings offer long-lasting corrosion protection with characteristics including scratch resistance and self-healing capabilities [151]. Coatings may be made more resilient and long-lasting by adding nanoparticles to increase their mechanical, chemical, and optical properties [152]. Multifunctional functional coatings, such those with hydrophobicity and antifouling properties derived from nanopatterning, are essential for a number of industries, including the marine and automotive sectors [153]. Cutting-edge nano-engineered composite coatings provide protection in harsh environmental conditions by acting as shielding layers for various substrates. Therefore, for

efficient corrosion resistance in a variety of industrial applications, the strategic utilization of functionalized nanoparticles in coating development is necessary.

Future research must overcome obstacles like the large-scale manufacturing of nanocrystalline materials and possible problems with nanoparticles in tribocorrosion control in order to maximize the usage of nanomaterials for corrosion prevention [6,147]. The special qualities of nanomaterials, such as nanogels, nanoparticles, and nanocrystalline materials, can improve corrosion resistance [151,154,155]. For nanoparticles to be used as effectively as possible in corrosion prevention, challenges such as low thermal stability in large-scale manufacturing of nanocrystalline metals and the deposition of nanosized debris increase friction in tribocorrosion control must be overcome. Optimizing the efficacy of nanoparticles in preventing corrosion in a range of industrial applications will depend on overcoming these obstacles via more research and creativity.

5. CONCLUSION

After the review of the subject matter, the following conclusions can be drawn:

- i. Numerous methods for enhancing the durability and corrosion resistance of metals, especially aluminum alloys, have been made possible by research on nanocoatings. Techniques that have demonstrated significant effectiveness in improving stability and corrosion resistance include spray modification, femtosecond laser processing, micromilling, and laser etching. Furthermore, superhydrophobic coatings utilizing TiO₂ nanoparticles in combination with octadecyl trimethoxysilane, HD-SiO₂ nanoparticles, and PDMS binders have demonstrated encouraging hydrophobicity and durability. Even though these experiments show that metal lifetime can be increased, more research is required to assess the coatings' effectiveness in a range of environmental conditions and pinpoint any long-term deterioration processes.
- ii. On a variety of substrates, advanced coatings based on nanoparticles have greatly enhanced corrosion prevention. Under a magnetic field, methods that use mica nanosheets and FeO₄@mSiO₂/MBT nanoparticles have improved the impedance modulus and increased corrosion inhibition by 30.36%. However, further research is needed to determine how these coatings would behave and interact over time in practical situations.
- iii. Additionally, scaling studies for industrial applications are necessary.
- iii. An inventive method for intelligent anticorrosive systems is provided by pH-responsive nanocontainers and carbon quantum dots doped with copper nanoparticles. These coatings provide adaptive protection by releasing inhibitors in reaction to microbial activity or pH variations, which makes them perfect for manufacturing environments. But further research is needed to determine how environmental factors like humidity and temperature affect how effective these smart coatings are.
- iv. A "green" method of preventing steel corrosion in acidic environments is the use of silver nanoparticles, whose inhibition is described by Langmuir isotherm adsorption. Other coatings, such those that contain titanium dioxide (TiO₂) nanocomposites and polyaniline (PANI), work well in acidic and salty conditions. To make sure that these coatings fulfill sustainability standards without having unanticipated ecological repercussions, future study should examine their possible environmental effect and lifetime.
- v. Epoxy-based coatings have demonstrated a high (97.87%) corrosion inhibition rate in saltwater environments, especially when supplemented with multi-walled carbon nanotubes (MWCNTs) and green inhibitors. In challenging maritime conditions, its self-healing capacity holds promise for long-term protection. However, more research is required to evaluate the durability of self-healing efficacy over long periods of time and to optimize these coatings for consistent performance under a variety of environmental circumstances.

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KONTROLA KOROZIJE U METALIMA: PREGLED ODRŽIVOG PRISTUPA KORIŠĆENJEM NANOTEHNOLOGIJE

IZVOD

Ova studija se odnosi na pregled prethodnih studija koje su koristile nanotehnologiju da inhibiraju koroziju metala/legura u jednom delu. Drugo razmatranje je ispitalo dugoročnu stabilnost i izdržljivost primenjene nanotehnologije za kontrolu korozije u različitim uslovima okoline, kao i optimizaciju disperzije nanočestica i integraciju za optimalnu efikasnost – dve ključne, ali ponekad zanemarene karakteristike nano premaza za koroziju prevencija. Iako je bilo određenog napretka u sprečavanju korozije, konzistentna disperzija nanočestica i dugoročna efikasnost i dalje su bili nedostižni sa nano premazima. Ključni nalazi iz pregleda literature koja pokriva godine 2017–2023. ukazuju na sve veći broj istraživanja o različitim materijalima i tehnikama za poboljšanje otpornosti na koroziju, od višeslojnih nanokompozita do superhidrofobnih površina i inovativnih kompozitnih premaza. Svestranost i efikasnost premaza zasnovanih na nanočesticama u upravljanju korozijom je naglašena ovim istraživanjem, koje je obezbedilo specijalizovana rešenja za različite podloge i radna okruženja. Štaviše, studije o stabilnosti i izdržljivosti nanoprevlaka na metalima su pokazale da postoje održivi načini da se njihov korisni vek produži tokom vremena, kao što je upotreba premaza koji su nanolaminirani i aktivno oslobađanje inhibitora korozije. Pored zatvaranja važnih praznina u informacijama, ovaj pregled je ponudio smernice za buduću proizvodnju pouzdanih i izdržljivih uređaja za zaštitu od korozije.

Ključne reči: Prevencija korozije, Nano premazi, Otpornost na koroziju, Uslovi okoline, Dugoročna stabilnost, Disperzija nanočestica

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