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REVIEW

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Recent advances in the use of metal oxides as corrosion inhibitors: a review

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This review paper studied the potential of using metal oxides as a green corrosion inhibitor for different alloys in various aggressive corrosive environments. Metal oxides are widely used for various applications such as sensors, environmental remediation, nanoelectronics devices, solar cells, biomedical applications and clean energy production due to their unique electronic structure. Metal oxides exhibit low corrosion inhibition efficiency when used as corrosion inhibitors in bulk form but attain significantly higher inhibition efficiencies when used in nanostructured form. Increasing the concentration of the metal oxides significantly reduced the corrosion rate and enhanced the corrosion inhibition efficiency for various samples studied under different operating conditions due to the increased surface area to volume ratio as well as the enhanced adsorption of the oxides onto the surface of the substrates, thereby reducing the corrosion rate by decreasing the available sites for the dissolution reaction. However, the challenges of agglomeration and poor dispersion of nanoparticles were frequently reported at higher concentrations which contributed to observed reduced efficiencies. Barrier protection, electrochemical inhibition, synergistic interactions with other inhibitors, self-healing properties, adsorption and passivation have been widely reported as the mechanism by which metal oxides protect the various substrates studied. The chemical and thermal stability of metal oxides in aggressive salt environments is a comparative advantage over other traditional organic and green inhibitors. The various methods of synthesis and characterization of metal oxide nanoparticles as well as their cost and associated safety and environmental concerns have also been discussed.

INTRODUCTION

Corrosion is a natural phenomenon involving the degradation of metals due to chemical or electrochemical interactions with their environment, converting them into stable oxides [1]. It affects industries such as infrastructure, transportation, energy, and manufacturing, leading to substantial economic losses [2]. Different metals, including iron, steel, aluminum, and copper, undergo corrosion when exposed to moisture, oxygen, salts, or pollutants, accelerating electrochemical breakdown [3–10]. Factors like high temperatures, mechanical stress, and microbial activity further exacerbate corrosion [11–14]. The global economic impact is staggering, with annual costs estimated at $2.8–$4.7 trillion (3–5 % of global GDP), encompassing direct expenses (material replacement, maintenance) and indirect costs (downtime, environmental damage) [15–17]. Additionally, corrosion contributes to environmental harm through resource depletion, pollution, and increased energy consumption [18–20].

To mitigate these effects, strategies such as protective coatings, cathodic protection, material selection, and corrosion inhibitors are employed [21–30]. Among these, corrosion inhibitors which are chemical compounds that slow metal degradation when used in small quantities by altering the environment are vital across industries. In oil and gas, they prevent pipeline failures; in automotive and aerospace sectors, they enhance durability; and in infrastructure, they extend structural lifespans [31–44]. Their role in reducing economic losses, ensuring safety, and minimizing environmental impact underscores their importance in modern industry.

Metal oxides exhibit diverse functional properties, making them valuable in solar cells, gas sensors, optoelectronics, catalysis, and corrosion protection [45]. Their electronic structure, light absorption, and charge transport characteristics enable applications in environmental remediation and photocatalysis [46]. Notably, oxides like ZnO, NiO, and Eu_2O_3 have been explored as corrosion inhibitors due to their chemical stability and reactivity [47].

Metal oxide nanoparticles have emerged as highly effective corrosion inhibitors owing to their large surface area, chemical stability, and tunable surface chemistry [48]. Materials such as ZnO [49], TiO_2 [50], Fe_2O_3 [51], and CeO_2 [52] form protective barriers against corrosive agents while sealing microcracks in coatings [53]. Their eco-friendly nature makes them preferable over toxic alternatives, aligning with sustainability goals [54, 55]. These nanoparticles can be integrated into coatings, nanocomposites, or additives, offering versatile protection for industrial and marine applications [56–58].

For instance, ZnO nanoparticles inhibit mild steel corrosion [59–61], while CeO_2 enables self-healing coatings [62, 63]. Surface modifications further enhance their adhesion and dispersion, improving corrosion resistance [64].

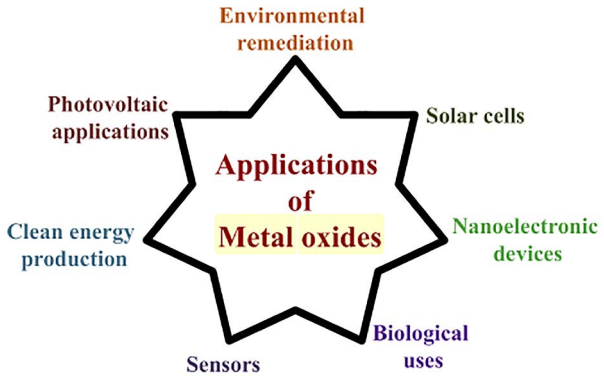


Fig. 1. Applications of metal oxides [46]

Given their superior inhibition efficiency, environmental compatibility, and adaptability, metal oxide nanoparticles represent a transformative solution for corrosion control. This review examines recent advances, mechanisms, and applications of these nanoparticles, highlighting their potential to revolutionize corrosion protection. Additionally, synthesis methods, characterization techniques, cost considerations, safety, and environmental impacts are critically discussed.

SYNTHESIS OF METAL OXIDE NANOPARTICLES

The selection of an appropriate synthesis method plays a pivotal role in determining the properties of metal oxide nanoparticles (MONPs), making it essential to choose a technique tailored to the intended application. The field of MONP synthesis is advancing rapidly, with a plethora of methods available, each offering distinct advantages and limitations. The choice of synthesis approach is largely dictated by the specific properties and applications required for the nanoparticles. MONPs can be fabricated using a diverse range of physical, chemical, and biological techniques as illustrated in Figure 2.

Physical methods

Physical synthesis methods generally employ top-down strategies, where bulk materials are broken down into nanoscale particles. Among the most common physical techniques are mechanical milling and laser ablation [66].

Mechanical milling

Mechanical milling is a simple and scalable approach for producing MONPs. This method involves grinding bulk metal oxides using high-energy ball mills, allowing for control over particle size and morphology. However, it often yields nanoparticles with broad size distributions and may introduce contamination from the milling equipment [67, 68].

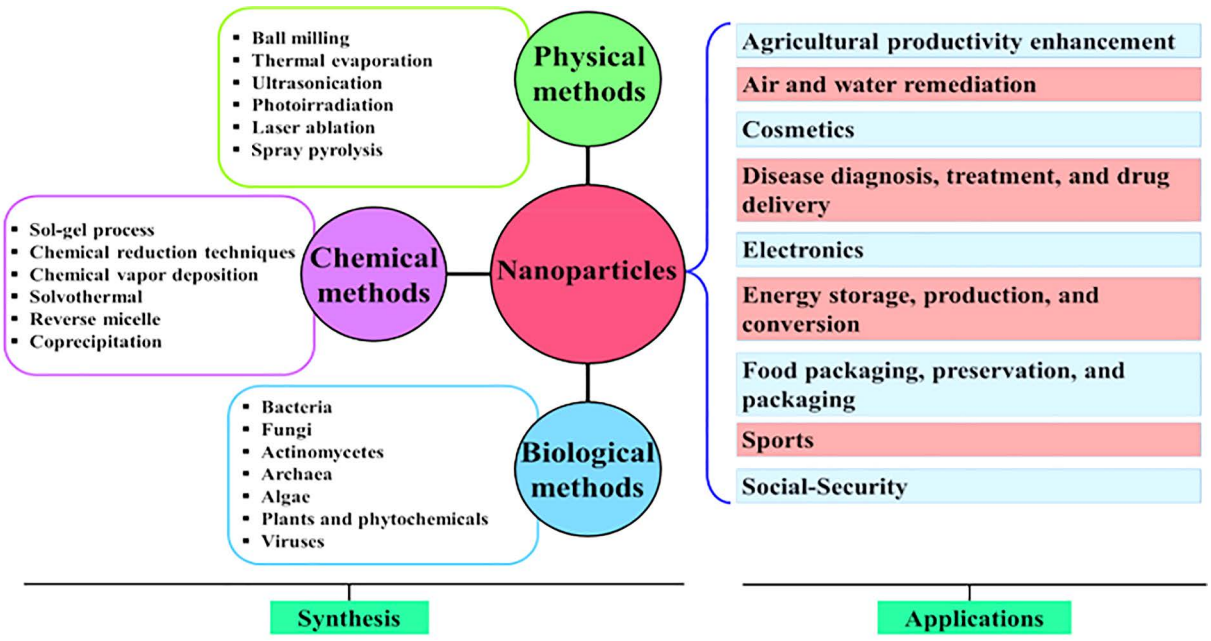


Fig. 2. Various methods for synthesis of metal oxide nanoparticles [65]

Laser ablation

Laser ablation is a highly versatile technique in which a high-power laser is used to vaporize a metal target in a liquid or gaseous medium, resulting in the formation of nanoparticles. This method is particularly effective for producing high-purity MONPs with precise control over size and shape [69, 70].

Chemical Methods

Chemical synthesis methods are the most widely utilized for MONP production due to their ability to precisely control nanoparticle size, shape, and composition. However chemical methods have several disadvantages and limitations, including environmental concerns due to use of toxic chemicals, high costs, safety risks, and challenges in scalability and reproducibility [71, 72].

Sol-gel method

The sol-gel process involves the transformation of a solution (sol) into a gel phase, followed by thermal treatment to form metal oxide nanoparticles. This technique is advantageous for producing nanoparticles with high purity, homogeneity, and controlled porosity. However, the sol-gel method often requires high-temperature calcination to convert the gel into crystalline metal oxide nanoparticles, which can be energy-intensive and costly. Furthermore, the transition from sol to gel and subsequent drying and calcination can be time-consuming, making the process less efficient for large-scale production. In addition, the use of organic solvents and precursors can lead to contamination, affecting the purity of the final product [68, 73].

Co-precipitation

Co-precipitation is a straightforward and economical method in which metal salts are precipitated in the presence of a base to form metal hydroxides. These hydroxides are then calcined to yield MONPs. This method is especially useful for synthesizing magnetic nanoparticles, such as Fe_3O_4. The limitations of this method include broad particle size distribution, agglomeration of particles which can affect their dispersibility and performance in service. Furthermore, the quality and properties of the nanoparticles are highly dependent on the purity and type of metal salts and precipitating agents used. The need for calcination or annealing to obtain crystalline nanoparticles also increases the complexity and cost of this method [74, 75].

Hydrothermal/solvothermal synthesis

Hydrothermal and solvothermal methods involve the reaction of metal precursors in aqueous or non-aqueous solvents under high temperatures and pressures. These techniques are highly effective for producing MONPs with well-defined morphologies and crystallinities [76], [77].

Microemulsion

Microemulsion synthesis is a bottom-up approach where metal precursors are reduced within nanodroplets of a microemulsion system. This method enables the production of MONPs with narrow size distributions and high surface areas [78].

Biological methods

Biological synthesis, often referred to as green synthesis, employs microorganisms, plants, or biomolecules to reduce metal ions and form MONPs. These methods are environmentally friendly and sustainable [79, 80].

Plant-mediated synthesis

Plant extracts contain various phytochemicals capable of reducing metal ions and stabilizing the resulting nanoparticles. This approach is simple, cost-effective, and yields MONPs with excellent biocompatibility [80–82].

Microbial synthesis

Microorganisms such as bacteria, fungi, and yeast can synthesize MONPs through intracellular or extracellular processes. This method is particularly advantageous for producing nanoparticles with unique shapes and sizes [65, 80].

CHARACTERIZATION METHODS FOR METAL OXIDE NANOPARTICLES

The characterization of metal oxide nanoparticles (MONPs) is an essential process for gaining insights into their physicochemical characteristics, which play a significant role in determining their effectiveness across different applications. A thorough analysis requires employing a variety of techniques to examine aspects such as size, shape, morphology, crystal structure, composition, surface properties, and other functional features of the nanoparticles. Figure 3 illustrates a summary of the most widely utilized methods for characterizing MONPs.

Structural and morphological characterization

X-ray diffraction (XRD)

XRD (X-ray diffraction) is employed to determine the crystal structure, phase composition, and crystallite size of MONPs by examining the diffraction patterns produced when X-rays interact with the atomic planes in the crystal lattice. This technique can identify crystalline phases, polymorphs, and estimate crystallite size using

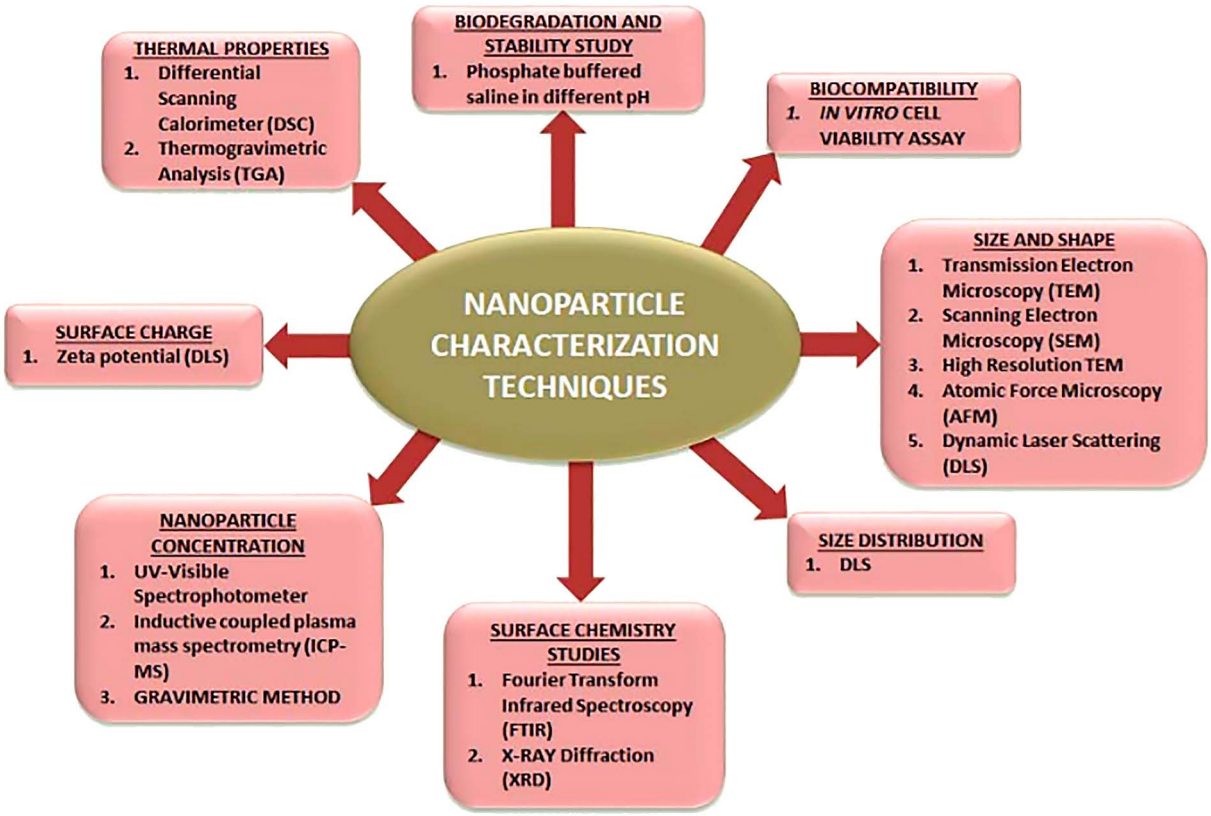


Fig. 3. Various characterization techniques for metal oxide nanoparticles [83]

the Scherrer equation, while also enabling the analysis of lattice parameters and strain. However, a limitation of XRD is its preference for crystalline materials, and it typically requires a sufficient quantity of sample to ensure accurate results [84], [85].

Scanning electron microscopy (SEM)

SEM (Scanning Electron Microscopy) produces high-resolution images by directing a focused electron beam across the sample‘s surface. It offers detailed insights into the surface morphology and topography of the sample. SEM is commonly used to visualize surface features, examine particle aggregation, and conduct cross-sectional analysis of nanocomposites. However, its limitations include the frequent need for conductive coating on non-conductive samples and its lower resolution compared to TEM (Transmission Electron Microscopy) [86, 87].

Transmission electron microscopy (TEM)

TEM (Transmission Electron Microscopy) captures high-resolution images of nanoparticles by passing an electron beam through an extremely thin sample. This technique enables the direct observation of particle size, shape, and morphology. TEM is utilized to determine nanoparticle size distribution, examine lattice fringes, and identify defects. However, its limitations include the intricate and time-consuming nature of sample preparation, as well as the need for high vacuum conditions, which can potentially alter the sample‘s properties [81, 88, 89].

Compositional and elemental analysis

Energy-dispersive X-ray spectroscopy (EDS)

EDS (Energy-Dispersive X-ray Spectroscopy) is employed alongside SEM or TEM to analyze the elemental composition of MONPs by detecting the characteristic X-rays released from the sample when exposed to an electron beam. This technique is applied for both qualitative and quantitative elemental analysis, as well as for mapping the distribution of elements. However, EDS has limitations, such as reduced sensitivity for light elements and the necessity of calibration using standards to ensure precise quantification [75, 81, 90].

X-ray photoelectron spectroscopy (XPS)

XPS (X-ray Photoelectron Spectroscopy) analyzes the kinetic energy of photoelectrons released from the sample’s surface upon exposure to X-rays, offering insights into the chemical composition and oxidation states of elements. This technique is used for surface chemical analysis, identifying oxidation states, and examining bonding environments. However, XPS is restricted to surface-level analysis, typically within a depth of a few nanometers, and necessitates ultra-high vacuum conditions for operation [91–93].

Optical and spectroscopic characterization

UV-Vis spectroscopy

UV-Vis spectroscopy analyzes the absorption of ultraviolet and visible light by nanoparticles, offering insights into their optical properties and bandgap energy. This technique is applied to determine bandgap energy and study optical absorption and scattering characteristics. However, UV-Vis is restricted to materials that are optically active and requires nanoparticles to be dispersed in an appropriate medium for accurate measurements [69, 82, 94].

Fourier-transform infrared spectroscopy (FTIR)

FTIR (Fourier Transform Infrared Spectroscopy) analyzes the absorption of infrared radiation by a sample, offering insights into molecular vibrations and chemical bonds. This technique is used to identify functional groups within the sample and study surface chemistry, as well as to examine surface modifications and coatings. However, FTIR is limited to samples that absorb infrared radiation and requires meticulous sample preparation to prevent interference from moisture [74, 95, 96].

Surface and porosity analysis

Brunauer-Emmett-Teller (BET) analysis

BET analysis determines the specific surface area and porosity of nanoparticles by adsorbing gas molecules, typically nitrogen, onto the surface and evaluating the adsorption isotherm. This method is used to calculate the specific surface area and assess pore size distribution. However, BET analysis has limitations, such as requiring a substantial amount of sample and being applicable only to materials with accessible pores [97–99].

Zeta potential measurement

Zeta potential evaluates the surface charge of nanoparticles in a colloidal suspension, offering insights into their stability and surface chemistry. This technique is used to assess colloidal stability and analyze surface charge and interactions. However, it is influenced by the pH and ionic strength of the medium and requires samples to be well-dispersed for accurate measurements [69, 92, 100].

Thermal analysis

Thermogravimetric analysis (TGA)

TGA (Thermogravimetric Analysis) monitors the mass change of a sample as it is subjected to varying temperatures, offering insights into thermal stability and composition. This technique is used to determine thermal decomposition temperatures and analyze the organic and inorganic content of a sample. However, TGA is restricted to samples that experience mass changes when heated and requires precise calibration and control of experimental conditions for accurate results [101–103].

Differential scanning calorimetry (DSC)

DSC (Differential Scanning Calorimetry) measures the heat flow related to thermal transitions in a sample, offering insights into phase changes, melting points, and crystallization behavior. This technique is used to analyze thermal transitions, stability, and determine melting and crystallization temperatures. However, DSC is limited to samples that undergo thermal transitions and requires accurate temperature control and calibration for reliable results [67, 104, 105].

SIZE, SHAPE, AND STRUCTURAL PROPERTIES OF NiO NANOPARTICLES AND THEIR IMPACT ON CORROSION INHIBITION

Smaller metal oxide nanoparticles (MONPs) exhibit a higher surface area-to-volume ratio, boosting their reactivity and interaction with metal surfaces. This greater surface area facilitates more efficient adsorption onto the metal, creating a protective barrier against corrosive agents. In contrast, larger nanoparticles, with a lower surface area-to-volume ratio, may be less effective in forming a uniform protective layer, though they can still offer substantial protection if they form a dense and stable coating. The small size of MONPs enables them to penetrate micro-cracks and defects on the metal surface, enhancing coverage and protection, particularly against localized corrosion like pitting and crevice corrosion [106]. Larger nanoparticles, however, may struggle to penetrate small defects, potentially leaving some areas exposed, though they can still contribute to corrosion inhibition by forming a physical barrier. Smaller nanoparticles are more susceptible to agglomeration due to their high surface energy, which can reduce their effective surface area and dispersion in corrosive environments, potentially lowering their corrosion inhibition efficiency. Larger nanoparticles, while less prone to agglomeration, may have limited adsorption capacity due to their lower surface area [107–109]. Spherical MONPs are often favored for their uniform size distribution and ease of synthesis, enabling the formation of dense, homogeneous coatings that provide effective corrosion protection. Rod-shaped or anisotropic nanoparticles, on the other hand, can enhance corrosion inhibition by aligning and forming interlocking structures on the metal surface, creating a more robust protective layer. Flake-shaped nanoparticles, with their high aspect ratio, offer excellent coverage and barrier properties, forming overlapping layers that block the diffusion of corrosive species. Spherical nanoparticles can produce smooth, uniform coatings, reducing surface roughness and minimizing corrosion initiation sites.

Anisotropic nanoparticles, while increasing surface roughness, can improve mechanical interlocking and adhesion of the protective layer, though excessive roughness may create sites for localized corrosion if not managed properly [56, 80, 102, 110, 111]. Crystalline MONPs, with well-defined structures, typically exhibit higher stability and better corrosion inhibition due to their predictable interactions with the metal surface. Amorphous MONPs, with their defects and unsaturated bonds, may have higher reactivity, enhancing adsorption and corrosion protection. Single-phase MONPs, such as pure TiO_2 or ZnO, often deliver consistent corrosion inhibition due to their uniform properties, while mixed-phase or composite MONPs can provide synergistic effects, combining the strengths of different phases to enhance performance. For instance, combining anatase and rutile phases in TiO_2 nanoparticles can improve both mechanical and chemical stability. Surface chemistry can be tailored through functionalization with organic or inorganic molecules, improving adhesion and the formation of a stable protective layer. The surface charge of MONPs also plays a role, influencing their dispersion and interaction with the metal surface. Positively charged nanoparticles, for example, may adsorb more effectively onto negatively charged metal surfaces, enhancing corrosion inhibition [50, 112–114].

CORROSION INHIBITION MECHANISMS OF METAL OXIDE NANOPARTICLES

The corrosion inhibition mechanisms of metal oxide nanoparticles (MONPs) are complex and involve multiple processes, including barrier protection, electrochemical inhibition, adsorption and passivation, self-healing properties, and synergistic interactions with other inhibitors. The performance of MONPs as corrosion inhibitors is influenced by factors such as size, shape, surface chemistry, and structural properties, which can be customized to enhance their effectiveness [115–117]. Barrier protection is a key mechanism through which MONPs prevent corrosion. This process involves creating a physical barrier on the metal surface that blocks the diffusion of corrosive agents like oxygen, water, and chloride ions. MONPs can form dense, uniform, and adherent coatings that isolate the metal from its corrosive surroundings. Their high surface area ensures better coverage, filling micro-cracks, pores, and defects that could otherwise initiate corrosion. Smaller nanoparticles, due to their nanoscale size, can effectively penetrate and seal micro-cracks [106]. Anisotropic nanoparticles, such as rod-shaped or platelet-shaped ones, can form interlocking structures, improving the mechanical stability and continuity of the protective layer. Functionalized MONPs, such as those enhanced with organic ligands or polymers, demonstrate improved adhesion to metal surfaces, ensuring the longevity of the protective coating. Moreover, surface hydroxyl groups on MONPs can facilitate strong interactions with the metal surface through hydrogen bonding or chemisorption, further boosting their protective performance. Metal oxide nanoparticles (MONPs) can influence electrochemical reactions at the metal-electrolyte interface, thereby reducing the corrosion rate. This is achieved by modifying both anodic and cathodic reactions [51, 118, 119]. MONPs can adsorb onto the metal surface, blocking active sites and inhibiting the dissolution of metal ions (anodic reaction). For example, TiO_2 and ZnO nanoparticles can form stable oxide layers on the metal surface, slowing down the oxidation process. Additionally, MONPs can impede the cathodic reaction (e.g., oxygen reduction or hydrogen evolution) by acting as a physical barrier or encouraging the formation of passive layers [119, 120]. For instance, Fe_2O_3 nanoparticles can reduce oxygen availability at the metal surface, thereby decreasing the rate of the cathodic reaction. Some MONPs exhibit mixed inhibition, simultaneously affecting both anodic and cathodic reactions, providing more comprehensive corrosion protection [121, 122]. Adsorption and passivation are key mechanisms by which MONPs inhibit corrosion. These processes involve the formation of a protective film on the metal surface through chemical or physical adsorption. MONPs can physically adsorb onto the metal surface via van der Waals forces or electrostatic interactions, creating a thin film that blocks corrosive agents. The surface charge of MONPs plays a significant role in physical adsorption; for example, positively charged nanoparticles can adsorb more effectively onto negatively charged metal surfaces. MONPs can form chemical bonds with metal surfaces through interactions involving surface functional groups such as –OH and –COOH. This chemisorption process creates a stable and durable protective layer. When MONPs are functionalized with compounds like silanes or phosphates, their chemisorption is further enhanced due to the formation of covalent bonds with the metal surface. Additionally, MONPs can facilitate the development of passive oxide layers on the metal surface, which are dense, stable, and capable of self-repair, offering long-term corrosion protection [118, 123, 124]. For instance, Al_2O_3 and Cr_2O_3 nanoparticles are effective in promoting passive oxide layers on aluminum and stainless steel, respectively. Some MONPs possess self-healing capabilities, allowing them to repair damage to the protective coating and sustain corrosion resistance over time. They can also be engineered to release inhibitive species, such as metal ions or organic inhibitors, in response to changes in pH or electrochemical potential at the metal surface. These species migrate to damaged areas and form new protective layers [125–127]. For example, ZnO nanoparticles release Zn^{2+} ions, which react with

hydroxyl ions to produce zinc hydroxide, sealing cracks and defects. Certain MONPs, like CeO_2 and MnO_2, exhibit redox activity, enabling them to neutralize reactive oxygen species (ROS) and reduce oxidative stress on the metal surface, thereby preventing the degradation of the protective layer. Smart MONPs can respond to environmental stimuli such as pH, temperature, or mechanical stress by releasing inhibitors or undergoing structural changes to repair the coating [56, 99, 128]. MONPs can also be combined with organic or inorganic inhibitors to achieve synergistic corrosion inhibition effects. Furthermore, MONPs can be integrated into polymer matrices or organic coatings to improve barrier properties and adhesion to the metal surface. For example, TiO_2 nanoparticles in epoxy coatings enhance mechanical strength and corrosion resistance [64, 129, 130]. MONPs can also serve as carriers for organic inhibitors, releasing them in a controlled manner to provide long-term protection. The combination of MONPs and organic inhibitors can deliver barrier protection, electrochemical inhibition, and self-healing properties simultaneously. The mechanism of corrosion inhibition of mild steel in 3.5 wt. % NaCl using epoxy-ZnO–NiO nanocomposite coating is illustrated in Figure 4.

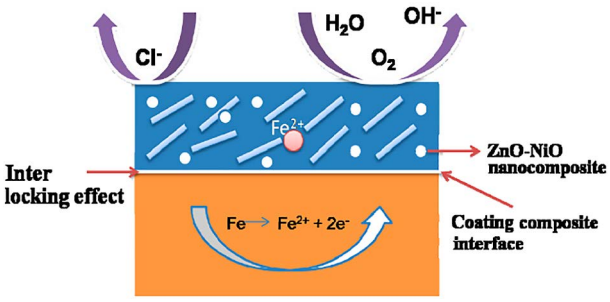
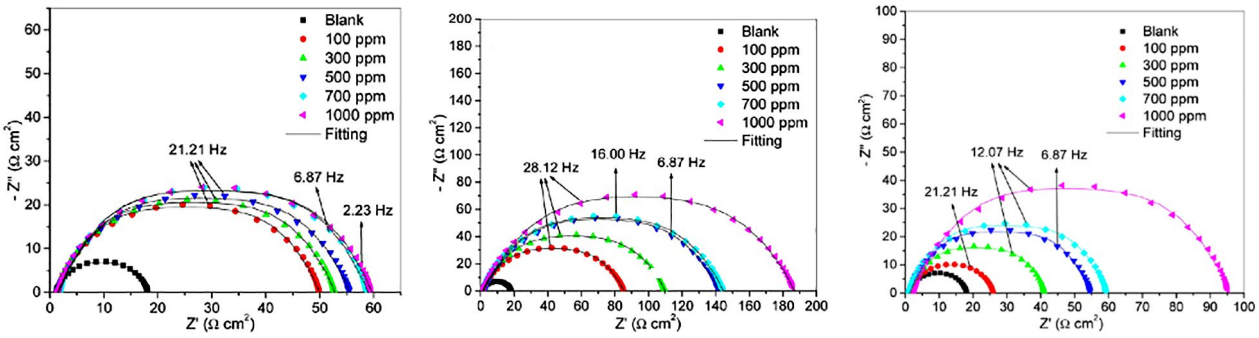


Fig. 4. Proposed mechanism of the corrosion protection by ZnO–NiO nanocomposite [131]

RECENT PROGRESS IN CORROSION INHIBITION USING METAL OXIDES

The potential of using ZnO as a corrosion inhibitor for embedded mild steel rebar in concrete in 0.2M H_2SO_4 solution was studied using gravimetric, pH and potential measurements for varying inhibitor concentrations of 25, 50, 75 and 100% prepared from 200 g of ZnO powder with distilled water. Results from the study reveal that effectiveness of ZnO as an inhibitor was limited to 25% and 50% concentrations in 0.2 M H_2SO_4 with the maximum efficiency recorded at 25%, the least concentration tested. Findings from the study showed that the immersion time had tremendous effect on both the corrosion potential of embedded steel rebar in concrete and the pH of the medium. Statistical analysis of experimental results confirmed that concentration of ZnO had greater effect on potential and pH measurements [132]. In another research work, a comparative study of the corrosion protection of mild steel in various corrosive media including fresh water, NaCl, HCl and NaOH solutions using epoxy-ZnO nanocomposite coatings was undertaken for a duration of 60 days by the gravimetric method. Results from the study showed that corrosion rate in the various media was of the order HCl > NaCl > > NaOH > fresh water. Neat epoxy samples without inhibitor showed the greatest weight loss regardless of the type of media it was immersed in compared to samples coated with epoxy resin containing 1, 2, 3, 4 and 5 wt. % ZnO Nano powder [133]. Hexagonal wurtzite nanoparticles of ZnO synthesized using natural extract of Myrrh as green capping agent were used for corrosion inhibition studies of steel in 1.0 M HCl using electrochemical techniques. Results from the electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) measurements reveal that ZnO is an effective inhibitor for steel in 1.0 M HCl. Polarization curves showed that the eco-friendly inhibitors affected anodic and cathodic reactions due to their adsorption on the steel surface, and thus, these additives functioned as cathodic mixed inhibitors [134]. The corrosion inhibition potential of synthesized nanocomposites of rod like ZnO with average particle size of 50–75 nm and three selected polymers, namely, polyethylene glycol (PEG), poly- vinylpyrrolidone (PVP), and polyacrylonitrile (PAN) were investigated for mild steel in 5% HCl solution using potentiodynamic polarization (PDP), linear polarization resistance, and electrochemical impedance spectroscopy (EIS) measurements. Findings from the study reveal that all the ZnO-polymer nanocomposites showed better corrosion protection of mild steel in 5 % HCl than the corresponding polymer alone as seen in Figure 5.Polarization studies confirmed that the inhibitors functioned primarily as mixed type while adsorption studies confirmed that the ZnO/polymer nanocomposites adsorbed onto the surface of mild steel by both physisorption and chemisorption processes, which can be explained with the Langmuir adsorption isotherm model [135]. In a bid to address clinical challenges connected to significant release of titanium (Ti) metal ions and debris due to the low corrosion resistance of orthopedics and dental implants, (ZnO) thin films were deposited onto Ti surfaces and functionalized with four different organic bifunctional molecules namely 4- aminophenylpropionic acid (APPA), 3-aminopropyltrimetoxysilane (APTMS), 3-mercaptopropionic acid (MPA), and polyethylene glycol (PEG) molecules in order to increase the corrosion resistance. Results from electrochemical testing revealed that functionalized ZnO specimens with APPA exhibited noble open circuit potentials (–0.2 V) and significant decrease in the corrosion current density (5.3×10^{-7} A/cm^2) when



a) ZnO/PEG b) ZnO/PVP c) ZnO/PAN

Fig. 5. Nyquist plots for mild steel in 5% HCl without and with different concentrations of ZnO/polymer nanocomposites [135]

compared to the values obtained for pristine Ti (–0.56 V and 2.3 × 10^{-6} A/cm^2), indicating a promising material for applications in biomedical fields [119]. ZnO–NiO nanocomposite with epoxy coating containing 1.0 and 1.8 wt. % ZnO–NiO (hexagonal and cubic) structure synthesized by the sol-gel method with an average ZnO–NiO crystallite size of 26 nm was investigated as a possible corrosion inhibitor for mild steel in 3.5 wt. % NaCl solution using electrochemical techniques.

Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization (PDP) results indicate that the corrosion resistance has improved for the nanocomposites of ZnO–NiO coated along with epoxy on steel in comparison to that of the pure epoxy-coated steel [131]. The effect of RGO–TiO_2 content in Nickel–reduced graphene oxide–titanium dioxide (Ni–RGO–TiO_2) coatings on the anti- corrosion behavior mild steel in 0.06 M citric acid and 0.1 M acetic acid was studied using electrochemical techniques. Findings from the study confirmed that a Ni/nanocomposite layer containing 20.4 wt. % RGO–TiO_2 substantially enhanced the corrosion resistance of mild steel compared to a Ni coating. Coated mild steel displayed lower corrosion rates of 0.148 and 0.189 mm/y in 0.06 M citric acid and 0.1 M acetic acid respectively compared to values of 4.252 and 1.41 mm/y, respectively recorded for bare mild steel [91]. The corrosion inhibition performance of 304L stainless steel substrates spray coated with nanoparticles of titanium dioxide (TiO_2) and nickel oxide (NiO) synthesized by chemical precipitation method in 3.5% NaCl was studied from Tafel polarization curve and electrochemical impedance spectroscopy. Results from electrochemical testing proved that there was a positive shift in the corrosion potential of the coated 304L stainless steel substrates compared to that of bare and coated samples exhibited improved corrosion resistance. NiO and TiO_2 films were also shown to be very stable in salt environment. The non-existence of rust in coated substrate exposed to salt environment (5% NaCl at 30 °C) for 390 hrs confirms that the films can act as anticorrosive coating for 304L SS substrate in adverse salt environment [129]. The influence of TiO_2 in enhancing the corrosion resistance of carbon steel coated with epoxy resin based on diglycidyl ether 4,4′-dihydroxydiphenylsulfone (DGEDDS) and 4,4′-Methylene dianiline (MDA) in 3% NaCl solution has been studied using a combination of electrochemical technique, density functional theory (DFT) studies and molecular dynamic (MD) simulations. The presence of TiO_2 in the nanocomposite coating significantly improved the corrosion inhibition performance of DGEDDS-MDA as well as stability under exposure to UV irradiation (2000 h) as illustrated in Figure 6.

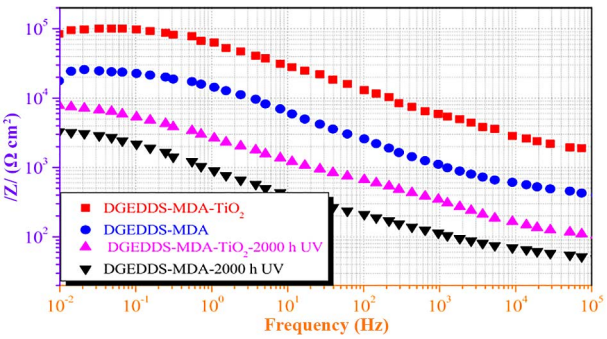
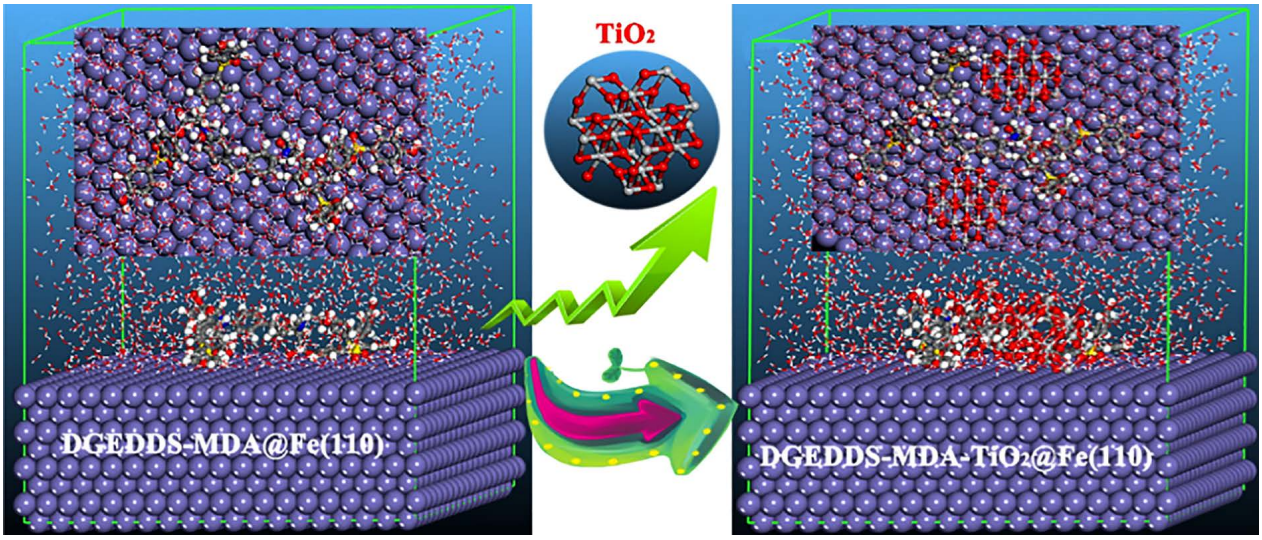


Fig. 6. Bode plot obtained for CS corrosion in 3% NaCl coated with and without DGEDDS-MDA and its TiO2 composite before and after 2000 h UV exposure [106]

Results from computational studies (Figure 7) revealed that the adsorption and orientation of the DGEDDS-MDA on the metal surface was remarkably affected by the presence of TiO_2 [106]

The electrochemical corrosion behavior of NiO NPs with average particle size of 17–18 nm synthesized using ultrasonic wave-assisted green synthesis route with Delonix elata leaf extract as a reducing and capping agent was investigated in various aqueous media including 3.5% NaCl, 6 M KOH, 1 M HCl, and 1 M H_2SO_4. Results from the study indicate that there was a drastic reduction in the corrosive nature of Zn and Mg plates that were coated with the NiO nanoparticles in all tested media as shown in Figures 8 and 9 respectively.



a) b)

Fig. 7. Side and top views of the stable adsorption configurations of: a) DGEDDS-MDA and b) DGEDDS-MDA-TiO_2 on Fe (110) surface [106]

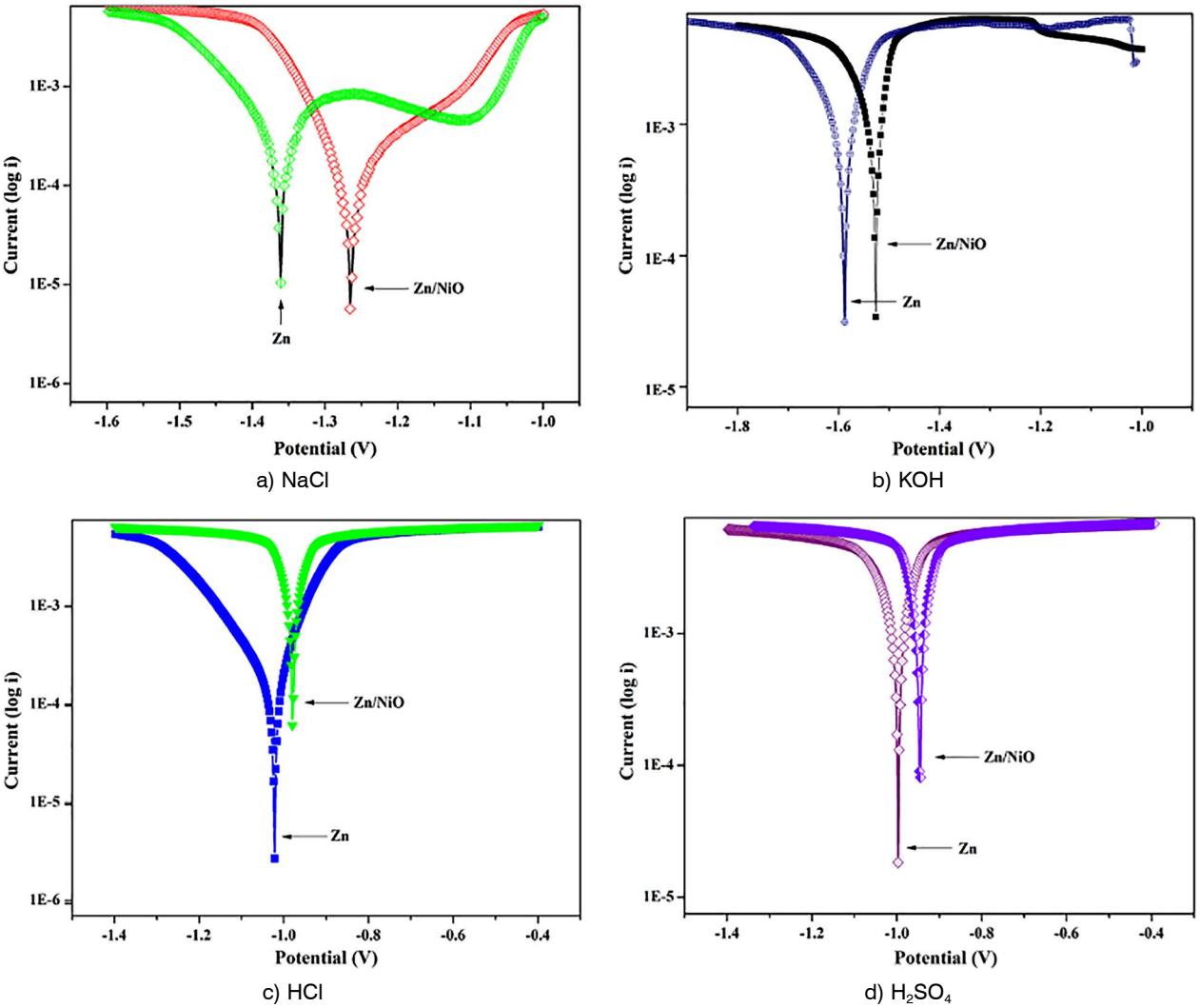


Fig. 8. Tafel plot for linear sweep voltammetry of uncoated and NiO NP-coated Zn plates in aqueous electrolytes [136]

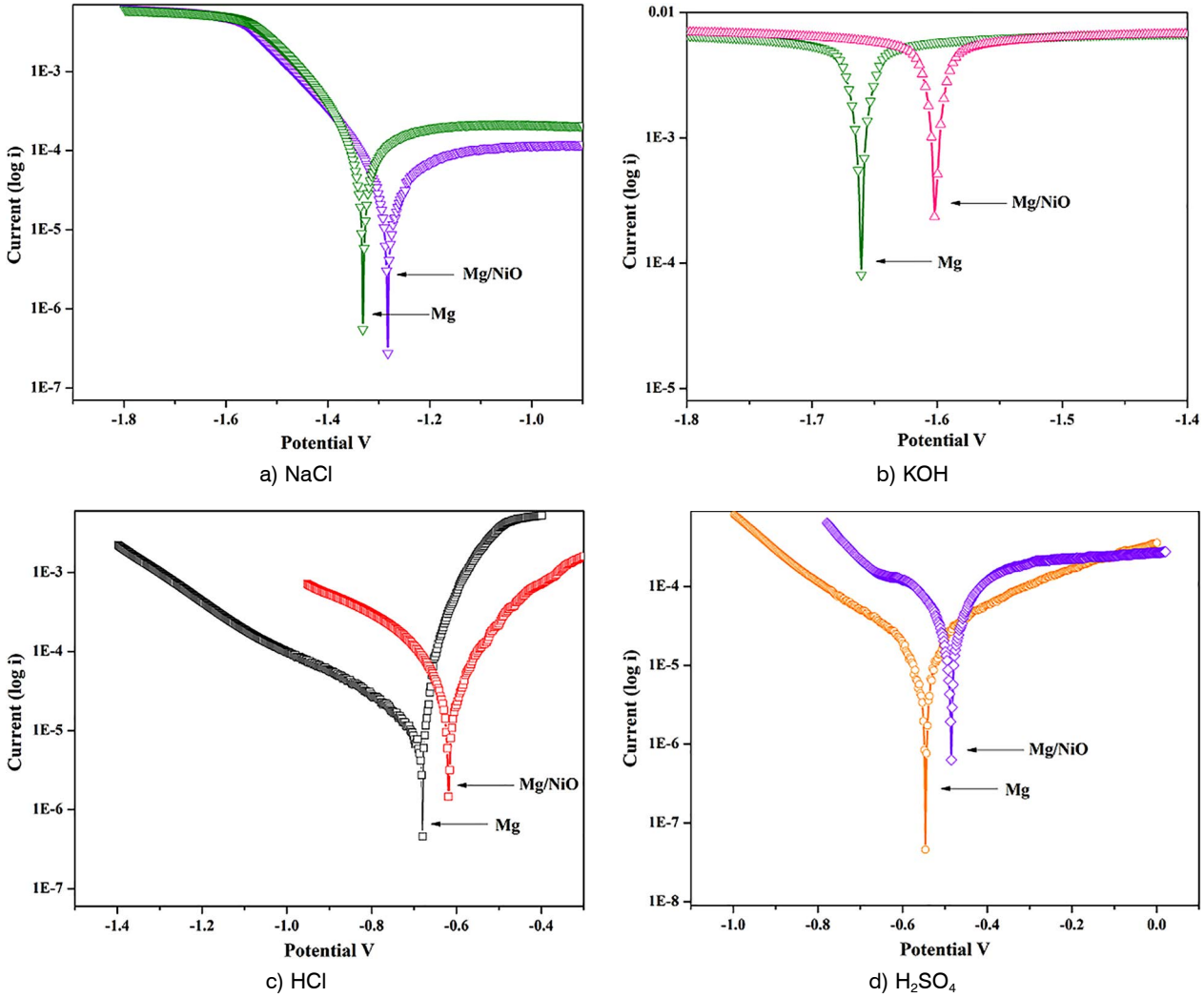


Fig. 9. Tafel plot for linear sweep voltammetry of uncoated and NiO NP-coated Mg plates in aqueous electrolytes [136]

The Zn metal plates coated with NiO nanoparticles exhibited maximum inhibition efficiency of 89% in 1 M H_2SO_4 and 68%, 76%, and 57% inhibition efficiency in 3.5% NaCl, 1 M HCl, and 6 M KOH media, respectively. In contrast, Mg metal plates coated with NiO nanoparticles displayed corrosion inhibition efficiency of 61%, 72%, 80%, and 56% in 3.5% NaCl, 1 M HCl, 1 M H_2SO_4, and 6 M KOH media respectively [136]. An ecofriendly inhibitor for corrosion protection of steel plates in marine environment has been developed and reported using approximately 30 wt. % loading of Gum Arabic (GA) into porous cerium oxide nanoparticles of average particle size below 20 nm uniformly dispersed into an epoxy formulation. Results from electrochemical impedance spectroscopy (EIS) measurements proved that the corrosion resistance of steel coated with GA loaded cerium oxide nanoparticles was significantly higher than the reference coatings. This is an indication that GA loaded CONPs act as an effective filler material for epoxy coating [99]. Environmentally benign nanoparticles of manganese oxide synthesized via ultrasonic wave assisted green synthesis using extracts of withered rose and lotus flower petals have been reported to enhance corrosion inhibition behaviour of mild steel in 1 M HCl compared to the bare mild steel sample in the test medium. Maximum corrosion inhibition efficiency of 73% and 52% were attained for mild steel samples inhibited by nanoparticles of manganese oxide prepared using lotus petal and rose petal respectively [137]. The problem of contamination of water by copper in water circulation systems whose root cause is the copper corrosion reactions in boiler feed water environment was mitigated by developing corrosion resistant Nano copper oxide coatings on copper using anodization in oxalate solution. Results from electrochemical testing of anodized and non-anodized samples conducted in two aqueous solutions containing 3.5% NaCl and 2 mg/l NH_3 respectively showed that the corrosion protection efficiencies of the anodized coating in these environments were 86 % and 75 %, respectively resulting in a seven-

fold increase in corrosion resistance of copper protected by the anodized coating in 3.5% NaCl and approximately four-fold increase in 2 mg/l NH_3 aqueous solution in comparison to the non-anodized samples in the same media. Hybrid ZrO_2/Cr_2O_3 epoxy nanocomposite coatings for corrosion protection of carbon steel have been developed by using mixed ZrO_2 and Cr_2O_3 nanoparticles synthesized using the liquid phase chemical technique with various weight ratios ranging from 0.5 to 2.5 wt. % as reinforced filler for epoxy coatings. Experimental findings from the thermogravimetric analysis and salt spray tests revealed that the addition of Cr_2O_3/ZrO_2 nanoparticles significantly enhanced the corrosion resistance and the thermal stability of epoxy coating. The nanocomposite containing 1.5 wt. % of ZrO_2/Cr_2O_3 NPs were reported to offer the optimum combination of thermal stability, corrosion resistance, adhesion, hardness, impact, and abrasion resistance due to the parallel orientation of ZrO_2/Cr_2O_3 nanoparticles to the substrate surface and barrier element to water and oxygen from the environment [125]. Green synthesized ZrO_2-Glycine nanocomposite was demonstrated as an efficient corrosion inhibitor for mild steel in 1 M HCl within the temperature range of 40–80 °C using weight loss and electrochemical methods. Results from the study show that inhibition efficiency increase with increases in both concentration and temperature up to 81% at 70 °C and then decrease slightly at 80 °C reaching up to 74% at 500 ppm. Tafel polarization curves indicated that the nanocomposite acted as a mixed type with more effect on the cathodic reaction while EIS results confirmed that the polarization resistance (R_p) increases, and double-layer capacitance (C_{dl}) decreases in the presence of the NC, which suggests its adsorption on the steel surface. Adsorption studies revealed that the adsorption was spontaneous and in accordance with the Langmuir isotherm model [57]. The corrosion resistance of mild steel in sea water has been enhanced using coatings made by embedding NiO nanoparticles modified with 3-Mercaptopropyl) triethoxysilane (MPTES) in epoxy resin. The modification which was intended to improve the dispersion of NiO nanoparticles in epoxy resin as well as enhance the interactive ability of functional groups present in MPTES on NiO nanoparticle and epoxy resin led to a significant decrease of corrosion rate of samples coated with the modified nanocomposites compared to pure epoxy coated substrate. SECM analysis revealed that lower iron dissolution in epoxy-MPTES modified NiO nanocomposite coated steel compared to pure epoxy coated sample results in decreased current of the anodic surface of steel. Enhanced resistances of film and charge transfer were obtained from the EIS studies due to the suppression of iron dissolution. The modification remarkably improved corrosion resistance by impeding the free flow of H_2O, O_2 and corrosive ions into the epoxy resin thereby lowering the chances of degradation and blistering of the coating film [118]. Environmentally benign corrosion inhibitors based on primary aminated modified cellulose (PAC) containing in-situ deposited metal oxide nanoparticles of iron, copper and nickel with particle size diameters of 10, 23 and 43 nm, respectively were synthesized and used for corrosion protection of carbon steel in HCl. Weight loss and electrochemical methods were used to assess the corrosion inhibition performance of the as-prepared PAC and PAC/MONPs nanocomposites The experimental findings proved that the protection ability increased with a rise in the inhibitor concentration with maximum corrosion inhibition efficiency of 88, 93, 96 and 99 % attained for 250 ppm of PAC/CuONP, PAC/Fe_3O_4NPs, and PAC/NiONPs, respectively. The inhibitor was shown to be mixed type with adsorption corresponding to the Langmuir adsorption isotherm [138]. The influence of varying concentrations of NiO nanoparticles on the corrosion behaviour of epoxy coatings based on diglycidyl ether of bisphenol A (DGEBA) containing 0 %, 0.25 %, 0.50 % and 1.0 % of NiO nanoparticles was investigated using the salt spray resistance technique in accordance with ASTM B-117 standard procedure. Results from salt spray testing showed that the increase in concentration of nanoparticles of NiO resulted in increase in the water barrier and anti-corrosive properties. 0.5% concentration of NiO in epoxy resin was recommended for optimum combination of corrosion resistance and abrasion resistance and was attributed to the specific morphology of the nanocomposite and interaction of the NiO nanoparticles with epoxy matrix [139]. Ecofriendly nanoparticles of NiO synthesized through the green route using *Acacia Nilotica* bark extract was demonstrated as an effective corrosion inhibitor for carbon steel in 0.5 M HCl using a combination of weight loss and electrochemical techniques. Results from weight loss measurements showed a inhibition efficiency generally increased with increase in concentration of inhibitor with a maximum inhibition efficiency of 94 % obtained at 250 ppm while the Tafel curves study reveal that the protective film is shaped on the cathodic locales of the surface of carbon steel. Electrochemical impedance spectroscopy (EIS) results confirmed that a protection layer was formed on the surface of the carbon steel to protect it from corrosion [140]. The potential of p-methoxybenzylidene-4,40-dimorpholine (p-MBDM) assembled on nickel oxide nanoparticles (NiONPs) as corrosion inhibitors for mild steel in 2 M HCl was investigated using a combination of weight loss, electrochemical impedance spectroscopy (EIS), and galvanostatic polarization techniques. Weight loss measurements revealed that the corrosion inhibition efficiency increased with increase in inhibitor concentration while polarization measurements the inhibitor acted as a mixed type inhibitor. EIS results show that the charge transfer resistance in the case of p-MBDM

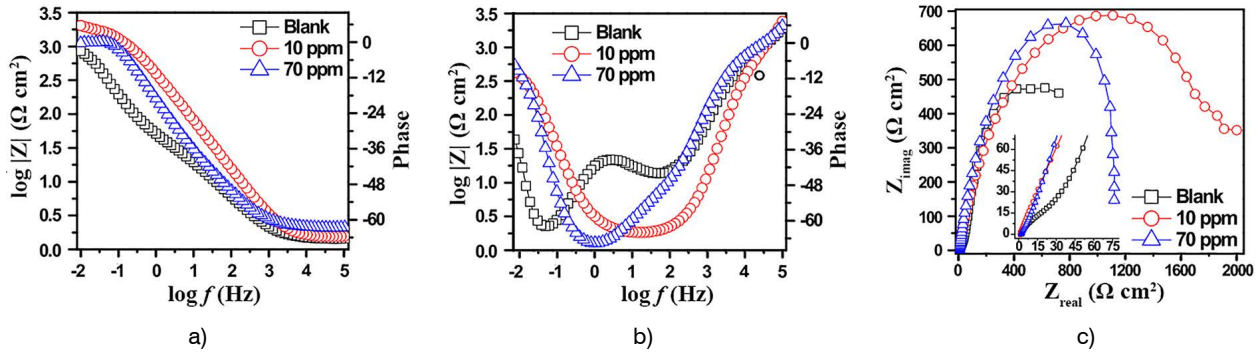


Fig. 10. Bode (a-b) and Nyquist (c) plots recorded after 5 hours immersion in 3.5 wt.% NaCl [122]

assembled on NiO NPs is significantly higher than that of p-MBDM alone [141]. It has been reported that the corrosion resistance of stainless steel 304L substrate has been enhanced by using spray coating it with thin films of nanostructured NiO. The electrochemical behaviour monitored using a combination of open circuit potential, Tafel polarization and electrochemical impedance spectroscopy revealed that the substrate had improved corrosion protection before and after salt spray test due to the presence of the thin films of nanostructured NiO. 390h exposure to salt spray test confirmed that the SS 304L substrates with NiO thin films had higher stability in salt environment and more effective corrosion protection compared to the substrate without NiO nanoparticle deposition [142]. A research conducted on corrosion protection of line pipe steel (API 5L X-80 in 3.5 wt. % NaCl medium with iron nickel oxide Nano powder using electrochemical impedance spectroscopy (EIS) revealed that corrosion inhibition occurred at low concentration, whereas higher concentration of aqueous solution produced induction behavior. The mechanism of corrosion protection was attributed to the formation of a protective film on the substrate through adsorption of metallic cations on the steel surface. the adsorption of metallic cations on the steel surface forming a protective film results from the experimental findings proved that iron nickel oxide can be effectively used as an anti-corrosion pigment in polymeric coatings as illustrated by the Bode and Nyquist plots shown in Figure 10 [122].

COST, SAFETY AND ENVIRONMENTAL CONCERNS ASSOCIATED WITH THE USE OF METAL OXIDES AS CORROSION INHIBITORS

Metal oxides are extensively utilized as corrosion inhibitors because they are both affordable and effective in preventing metal degradation. They are typically cheaper than organic inhibitors or more advanced techniques like coatings or cathodic protection. Common metal oxides such as zinc oxide (ZnO), titanium dioxide (TiO_2), and aluminum oxide (Al_2O_3) are readily available and cost-efficient to manufacture. These materials create protective barriers on metal surfaces, minimizing the need for regular upkeep or replacement of metal components, which results in significant long-term savings [49, 126, 143]. Moreover, metal oxides can be integrated into coatings or added to paints, improving their durability and cost-efficiency by prolonging the life of protective layers. However, the economic benefits of metal oxides vary depending on the application and the metal being protected. For instance, certain high-performance oxides like cerium oxide (CeO_2) may be expensive but provide exceptional corrosion resistance in extreme conditions, making their higher cost worthwhile [65, 144]. While metal oxides are generally stable and non-flammable, their safety depends on the specific compound and physical form (e.g., bulk vs. nanoparticles). Zinc Oxide (ZnO) is safe in bulk form but poses inhalation risks as nanoparticles and toxic to aquatic life at high concentrations. Nano-ZnO requires careful handling [144, 145]. Titanium Dioxide (TiO_2) is chemically inert and approved for food/cosmetics in bulk form. Nano-TiO_2 may cause oxidative stress and is classified as a possible carcinogen (IARC Group 2B) when inhaled [144, 145]. Aluminum Oxide (Al_2O_3) is non-toxic and environmentally inert, even as nanoparticles. However, it poses minimal respiratory irritation risk [146]. Bulk Cerium Oxide (CeO_2) is low in toxicity while nano-CeO_2 may induce oxidative stress but is safer than chromates [146]. Iron Oxides (Fe_2O_3, Fe_3O_4) are generally classified as non-toxic, biodegradable, and eco-friendly in all forms [146]. Chromium Oxide (Cr_2O_3) has the potential for contamination with hexavalent chromium (Cr(VI)), a carcinogen requiring strict handling protocols [147, 148]. Magnesium Oxide (MgO) is generally safe for humans and ecosystems even though it may induce mild respiratory irritation when handled in fine powdered form [149]. Copper Oxide (CuO) is often toxic in nanoparticle form, harming aquatic life and causing cellular damage [102, 138, 150]. Lead Oxides (PbO, Pb_3O_4) are highly toxic, affecting nervous systems and ecosystems; require the use of full PPE (Personal Protective Equipment) [151].

Most metal oxides are environmentally benign in bulk form, but nanoparticles raise concerns due to potential ecological accumulation and toxicity, particularly in aquatic systems [48]. Compliance with regulations like REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) in the European Union ensures responsible use [152, 153]. Safer alternatives (e.g., ZnO, Al_2O_3) are preferred over toxic options (e.g., chromates, lead oxides).

CHALLENGES AND FUTURE PERSPECTIVE

The challenges of dispersion and agglomeration are the two most significant problems limiting the applications of metal oxides as corrosion inhibitors. Other challenges encountered in the use of metal oxides as corrosion inhibitors include difficulty in application, long term stability, compatibility with substrates, dependence on environmental conditions, interference with system components and limited understanding of mechanisms. Dispersion refers to the uniform distribution of metal oxide particles within a medium (e.g., a liquid or coating) while agglomeration refers to clustering of metal oxide particles into larger aggregates, which reduces their effectiveness as corrosion inhibitors. Poor dispersion can severely limit the effectiveness of metal oxides as corrosion inhibitors. Many metal oxides, such as zinc oxide (ZnO) or titanium dioxide (TiO_2), have low solubility in water or other solvents. This makes it difficult to achieve a homogeneous dispersion in aqueous systems, which are common in corrosion inhibition applications. Poor solubility can lead to sedimentation or phase separation, reducing the availability of the inhibitor at the metal surface. The chemical nature of the dispersion medium (e.g., pH, ionic strength, or presence of surfactants) can affect the stability of metal oxide particles. For example, in highly acidic or alkaline environments, metal oxides may dissolve or react, losing their inhibitory properties. The presence of other ions or molecules in the medium can also interfere with dispersion, causing flocculation or precipitation. For optimal performance, metal oxide particles often need to be dispersed at the nanoscale to maximize surface area and reactivity. However, achieving and maintaining nanoscale dispersion is technically challenging due to the high surface energy of nanoparticles, which promotes agglomeration. Metal oxide nanoparticles have high surface energy, which drives them to agglomerate to minimize their surface area. This is particularly problematic for nanoscale inhibitors, as agglomeration reduces their surface area and reactivity [48, 53, 68, 124, 154, 155]. Agglomerated particles are less effective at forming a uniform protective layer on the metal surface, leading to uneven corrosion protection. Agglomerated particles are more likely to settle out of the dispersion medium due to their increased size and weight. This reduces the concentration of active inhibitor available in the system, compromising its protective capabilities. Sedimentation can also lead to clogging or fouling in industrial systems, causing additional operational challenges. Agglomerated particles cannot effectively cover the entire metal surface, leaving areas exposed to corrosive agents. This results in localized corrosion, which can be more damaging than uniform corrosion. Agglomerated particles are harder to apply uniformly, whether in coatings, paints, or liquid formulations. This can lead to defects in the protective layer, such as cracks or voids, which compromise its integrity [143]. To overcome the challenges of dispersion and agglomeration, certain strategies such as surface modification, use of dispersants, nanotechnology approach, sonication and mechanical mixing have been reported in previous studies. Functionalizing the surface of metal oxide particles with surfactants, polymers, or other stabilizing agents can reduce agglomeration by providing steric or electrostatic repulsion between particles. For example, coating ZnO nanoparticles with silane or organic molecules can improve their dispersion in aqueous media. Dispersants or stabilizers can be added to the medium to prevent agglomeration. These agents work by adsorbing onto the particle surface and creating repulsive forces that keep the particles apart. Common dispersants include polyelectrolytes, surfactants, and polymers [60, 119, 121, 124, 156]. Synthesizing metal oxide nanoparticles with controlled size and shape can minimize agglomeration. Techniques such as sol-gel synthesis or hydrothermal methods can produce highly dispersed nanoparticles. Encapsulation of metal oxide particles in nanocomposites or core-shell structures can also improve dispersion and stability. Ultrasonic treat-ment (sonication) or high-shear mixing can break up agglomerates and improve dispersion. However, these methods may need to be repeated periodically to maintain dispersion over time. Applying metal oxide coatings or dispersing them uniformly in a system can be technically challenging. Specialized equipment or techniques may be required, increasing the overall cost and complexity. In some cases, the application process itself may introduce defects or inconsistencies in the protective layer, reducing its effectiveness [77, 78, 116, 157–159]. Over time, metal oxide coatings or particles may degrade or be washed away, reducing their long-term effectiveness. This is particularly problematic in dynamic or harsh environments where continuous exposure to corrosive agents occurs. The formation of non-protective or porous oxide layers can also compromise the durability of the inhibition. The effectiveness of metal oxides as corrosion inhibitors depends on their ability to adhere to the metal surface. However, poor compatibility between the metal oxide and the substrate can lead to weak adhesion, reducing the protective efficacy. In some cases, metal oxides

may react with the substrate or other components in the system, leading to unintended side effects or accelerated corrosion. The performance of metal oxide inhibitors is highly dependent on environmental factors such as pH, temperature, and the presence of other ions. For example, some metal oxides may dissolve or lose their protective properties under acidic or alkaline conditions [149, 160]. In high-temperature environments, metal oxides may undergo phase changes or degradation, reducing their effectiveness as inhibitors. In industrial systems, metal oxides may interact with other components, such as polymers, lubricants, or other inhibitors, leading to reduced performance or system failure. For example, metal oxide particles can cause abrasion or wear in moving parts, negating their protective benefits. The corrosion inhibition mechanisms of some metal oxides are not fully understood, making it difficult to optimize their use or predict their performance in different environments. This lack of understanding can also hinder the development of new and improved metal oxide-based inhibitors. The corrosion inhibition mechanisms of some metal oxides are not fully understood, making it difficult to optimize their use or predict their performance in different environments. This lack of understanding can also hinder the development of new and improved metal oxide-based inhibitors. The future of using metal oxides as corrosion inhibitors looks promising, driven by advancements in nanotechnology, material science, and green chemistry [64, 115]. Development of nanoscale metal oxides with enhanced dispersion, stability, and surface reactivity for superior corrosion protection, combining metal oxides with polymers, graphene, or other nanomaterials to create synergistic effects and improve performance, focus on non-toxic, biodegradable metal oxides (e.g., cerium or zinc oxides) to meet environmental regulations, integration of metal oxides into stimuli-responsive coatings that self-heal or adapt to environmental changes, deploying Artificial Intelligence and simulations to predict and optimize metal oxide properties for specific applications as well as scaling up synthesis methods to make metal oxide inhibitors more affordable for industrial use are innovations capable of expanding the horizon of metal oxides in industries like aerospace, automotive, and marine, offering efficient and sustainable corrosion protection.

CONCLUSION

Results from many reported studies have confirmed that metal oxides especially in their nanoparticles/nanocomposite form can serve effectively as green inhibitors for mild steel, stainless steel, magnesium and zinc alloys in acidic, alkaline and saline media both at room temperature and elevated temperatures. Findings from previous studies have proved that metal oxide nanoparticles can act as mixed type inhibitors due to their effect on both the cathodic and anodic reactions. Several experimental results surveyed have established that nanocomposites of metal oxides have excellent stability under harsh operating conditions such as exposure to ultraviolet radiation, elevated temperatures, low pH and aggressive salt environment. Optimization studies and mathematical modeling of corrosion inhibition of various substrates using metal oxide nanoparticles in a variety of aggressive corrosive media is recommended for future researches. Scaling up synthesis methods especially green synthesis due to issues associated with safety, health and environment to make metal oxide inhibitors more affordable for industrial use is also highly recommended. Future work should also be focused on exploring the synergistic effect of metal oxide nanoparticles by combining them with other materials such as polymers, graphene and other nanomaterials.

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