Adsorption studies, modeling and use of green inhibitors in corrosion inhibition: An Overview of Recent Research

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Abstract

Corrosion is more than just an inevitable natural process. It is also a serious engineering problem in this modern age of technological advancement and which accounts for economic losses and irreversible structural damage. Efforts have been made to restrain the onset and thereafter destructive effects of corrosion using several preventive measures. Green Chemistry which has emerged as a new branch of environmental chemistry provides environmental friendly corrosion inhibitors specifically termed as 'green inhibitors'. Green inhibitors are non-toxic, biodegradable and eco-friendly, and have proven effective in controlling the corrosion of steel, stainless steel, mild steel, iron, aluminium, copper, 2024-T3 aluminium alloy, steel in concrete structures, carbon steel, AA5083 Al-Mg alloy, nickel and zinc. This paper reviews and discusses the use of and research on corrosion inhibitors and green inhibitors recently reported in corrosion literature.

Keywords: *corrosion, corrosion inhibitors, green inhibitors, biodegradable, steel, aluminium alloys.*

1.   Introduction

Corrosion is the damage of material resulting from exposure and interaction with the environment. It is a major problem that must be confronted for safety, environment and

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economic reasons (Thompson et al. [1]). Safety concerns are of utmost importance in every society and in all situations. Environmental concerns include corrosion caused pollution, depletion of resources such as those needed for replacement of the corroded structures and disposal of the corroded structures. To combine the technological progress with environmental safety is one of the key challenges of the millennium. Cleaner technology is new dimension that is emerging rapidly at both national and international level. Cleaner production has been identified as a key method for reconciling environment and economic development. The basic idea of cleaner production is to increase production efficiency while at the same time eliminate, or at least, minimize wastes generation and emissions at their source rather than treat them at the end of pipe only after they have been generated. The concept of cleaner production, pollution prevention or waste reduction is still relatively new, although the concepts involved are much older. Both cleaner production and sustainability came into focus with the publication of 'Our Common Future' (Brundtland [2]). This report provided a focused definition for the concept of sustainable development: "A process of change in which the exploitation of resources, the direction of investment, the orientation of the technological development and instituted change are all in harmony and enhance both current and future potential to meet human need and aspiration". According to the World Commission on Environment and Development, Brundtland Commission on Environment and Development, Brundtland Commission 1987, sustainable development is "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs." Sustainable development (Hutzinger [3], Desimone and Popoff [4]) demands change, requires doing more with lesser resource input and less waste generation. Instead of end-of-pipe technology, it requires pollution prevention philosophy, which is: "First and foremost, reduce waste at the origin-through improved housekeeping and maintenance, and modification in product design, processing and raw material selection. Finally, if there is no prevention option possible, treat and safely dispose off the waste."

In the efforts to move towards 'Sustainable Development', chemistry nowadays is at the forefront of the development of clean production processes and products. Chemistry is no doubt determining to understand and protect our environments as the world's future is strongly dependently on the chemical processes adopted. Chemistry plays an integral part of our lives and is all around us in the clothes we wear, the food, air and buildings etc. Sustainability, eco-efficiency and green chemistry are new principles that are guiding the development of next generation of products and processes (Sanghi [5]). Green Chemistry is considered an essential piece of a comprehensive program and also an alternating research

Methodology which is more eco- as well as economy friendly (Sharma et al. [6]). In its essence Green Chemistry (Anastas and Farris [7], Tundo and Selva [8], Collins [9], Wilkinson [10], Anastas [11]) is a science based, not regulatory and economically driven approach to achieving the goals of environmental protection and sustainable development.

In order to be eco-friendly, or *green*, organic synthesis (Grieco [12], Faber [13], Jessop and Leitner [14], Sanghi [15]) must meet, if not all, at least some of the following requirements: avoid waste, be atom efficient, avoid use and production of toxic and dangerous chemicals, produce compounds which perform better or equal to the existing ones and are bio-degradable, avoid auxiliary substances, reduce energy requirements, use renewable materials, use catalysts rather than stoichiometric reagents. These requirements can be easily met by the concept of green chemistry. Safety and environmental concerns tend to be very difficult to translate and quantify in terms of monetary value. However, economic concerns tend to sensibly affect the cost estimates. According to a completed study on 1998 sponsored by the Federal Highway Administration (FHWA), corrosion of metals costs the United States in excess of $276 billion per year. This loss to the economy is more than the entire gross national product of many countries around the world. This loss for 1975 was estimated at $82 billion or 4.9% of the gross National Product. However, corrosion not only affects the economy but it can also present a threat to life through the collapse of a structure or to the environment through the leakage of toxic chemicals.

Several efforts have been made using corrosion preventive practices and the use of corrosion inhibitors is one of them. *Green Chemistry* provides many environmental friendly corrosion inhibitors, called "*Green inhibitors*". The use of inhibitors for the control of corrosion of metals (Valdez et al. [16]) and alloys which are in contact with aggressive environment is an accepted practice (Taylor and Chambers [17], Khaled [18]). Large numbers of organic compounds have been studied and are being studied to investigate their corrosion inhibition potential. All these studies have revealed that organic compounds especially those with N, S and O show significant inhibition efficiency. However, most of these compounds are not only expensive but also toxic to living beings (Bothi Raja and Sethuraman [19]). It is needless to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts and organic species have therefore become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors (Rajendran et al. [20], Mathiyarasu et al. [21], Mesbah et al. [22], Okafor et al. [23], Lebrini et al. [24], Radojcic et al. [25], Refaey et al. [26], Mansour et al [27], Khamis et

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al. [28], Abdel-Gaber et al. [29]). They are the rich sources of ingredients which have very high inhibition efficiency (Little et al. [30], Bothi Raja and Sethuraman [19]) and are hence termed '*Green Inhibitors*' (Lebrini et al. [24]). These green inhibitors are non-hazardous and eco-friendly. This paper reviews and discusses the use of and research on corrosion inhibitors and green inhibitors recently reported in corrosion literature.

2.1 Observed Adsorption Mechanisms in Corrosion Inhibition

Elayyachy et al. [31] synthesized and tested two new telechelic compounds as inhibitors for the corrosion of steel in 1 M HCl solution. Weight loss measurements, potentiodynamic polarisation and impedance spectroscopy (EIS) methods were used. Elayyachy et al. [31] found that the inhibiting action increased with the concentration of methyl 4-{2-[(2-hydroxyethyl)thio]ethyl}benzoate (T2) and 11-[(2-hydroxyethyl)thio]undecan-1-ol (T3) to attain 92% at 10^{-3} M and 90% at 10^{-4} M, respectively. The investigated adsorption of T3 on the steel surface was found to obey to the Langmuir adsorption model. Elewady et al. [32] studied the role of some surfactants in the corrosion of Al in 1 M HCl using weight loss and galvanostatic polarization techniques. The results of Elewady et al. [32] showed that the inhibition occurred through adsorption of the inhibitor molecules on the metal surface. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreased with increasing temperature which is due to the fact, that the rate of corrosion of Al is higher than the rate of adsorption. The latter observation was contrary to that observed by Elayyachy et al. [31] whereby the study of the effect of temperature studied between 35 and 80⁰C showed that inhibition efficiency to have remained almost constant. Elewady et al. [32] also deduced, in contrary to many other researchers that the adsorption of these compounds on the metal surface was found to obey Freundlich adsorption isotherm. Further research by Elewady et al. [32] showed that the inhibiting action of these compounds are considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicating the joint adsorption of these compounds and iodide ions. The thermodynamic parameters for adsorption and activation processes were determined, and the subsequent galvanostatic polarization data indicated that these compounds acted as mixed-type inhibitors.

On the other hand, Fuchs-Godec [33] came to a different conclusion in the study of mixed-type inhibitors. Fuchs-Godec [33] performed electrochemical measurements to investigate the effectiveness of cationic surfactants of the *N*-alkyl quaternary ammonium salt type, i.e. myristyltrimethylammonium chloride (MTACl), cetyldimethylbenzylammonium chloride

(CDBACl), and trioctylmethylammonium chloride (TOMACl), as corrosion inhibitors for type X4Cr13 ferritic stainless steel in 2 M H_2SO_4 solution.   The potentiodynamic polarization measurements made by Fuchs–Godec [33] showed that these surfactants hindered both anodic and cathodic processes, i.e. they acted as mixed–type inhibitors. It was found that the adsorption of the N–alkyl ammonium ion in 2 M H_2SO_4 solution followed the Langmuir adsorption isotherm as observed by other researchers in their study (Quraishi and Khan [34], Yurt et al. [35], Lebrini et al [24]). The calculated values of the free energy of adsorption ΔG_{ads} by Fuchs–Godec [33] were, in cases when the charge on the metal surface was negative with respect to the point of zero charge (PZC), relatively high which is characteristic for the chemisorption. On the other hand, for positive metal surfaces Fuchs–Godec [33] assumed that SO_4^{2-} anions were adsorbed first, so the cationic species would be limited by the surface concentration of anions. Accordingly ΔG_{ads} values were lower in this case and the adsorption was attributed due to merely electrostatic attraction, which was characteristic of physisorption.

In their study, Lebrini et al. [24] studied corrosion inhibition of mild steel in perchloric acid by 3,5–bis(n–pyridyl)–4–amino–1,2,4–triazoles (n–PAT, $n = 2, 3$ and 4) at 30 °C using gravimetric and electrochemical impedance spectroscopy techniques. Protection efficiencies of 95% and 92% were obtained with 12×10^{-4} M of 3–PAT and 4–PAT, respectively; while 2–PAT reached only 65%. The inhibiting properties of n–PAT were found to depend on the concentration and the order of increasing inhibition efficiency was correlated with the modification of the position of the nitrogen atom in the pyridinium substituent. It was shown by Lebrini et al. [24] that adsorption of 4–aminotriazole derivatives on the steel surface was consistent with the Langmuir adsorption isotherm and the obtained standard free energy of adsorption values indicated that the corrosion inhibition of the mild steel in 1 M $HClO_4$ depends on both physic–and chemisorption, as opposed to the conclusions of sole physisorption from Fuchs–Godec [33]. Still with respect to research on the adsorption mechanism of corrosion inhibition, Yurt et al. [35] investigated the effect of newly synthesised three Schiff bases—2–[2–aza–2–(5–methyl(2–pyridly))vinyl]phenol, 2–[2–aza–2–(5–methyl(2–pyridly))vinyl]–4–bromophenol, 2–[2–aza–2–(5–methyl(2–pyridly))vinyl]–4–chlorophenol—on the corrosion behaviour of aluminium in 0.1 M HCl using potentiodynamic polarisation, electrochemical impedance spectroscopy and linear polarisation methods. Polarisation curves obtained by Yurt et al. [65] indicated that all studied Schiff bases were acting as mixed–type inhibitors (Fuchs–Godec [33]). All measurements made by Yurt et al. [35] showed that inhibition efficiencies increased with increase in inhibitor concentration (Quraishi and Khan [34], Amin [36], Fouda et al. [37]). This revealed that inhibitive actions of inhibitors were mainly due to adsorption on the

aluminium surface. Adsorption of these inhibitors followed the Langmuir adsorption isotherms and the thermodynamic parameters of adsorption (K_{ads}, ΔG_{ads}) of studied Schiff bases were calculated using the Langmuir adsorption isotherm. However, in the study of corrosion inhibition of copper in aerated non-stirred 3% NaCl solutions in the temperature range 15-65°C using sodium oleate as an anionic surfactant inhibitor, Amin [36] found that the sigmoidal shape of the adsorption isotherm confirmed the applicability of Frumkin's equation to describe the adsorption process rather than the much observed Langmuir isotherms.

The variation in inhibition efficiency values were found to depend on the type of functional groups substituted on benzene ring. It was also found by Yurt et al. [35] that the presence of bromine and chlorine atoms in the molecular structure of studied Schiff bases facilitate the adsorption of molecule on aluminium surface, thus partially agreeing with the observations made by Elewady et al. [32] whereby the latter showed that the inhibiting action of telechelic compounds would be considerably enhanced by the addition of KI (iodide species). Yurt et al. [35] also studied the correlation between the inhibition efficiencies of studied Schiff bases and their molecular structure using quantum chemical parameters obtained by Modified Neglect of Differential Overlap (MNDO) semi-empirical Self-Consistent Field - Molecular Orbital (SCF-MO) methods. Their results indicated that adsorption of studied Schiff bases depended on the charge density of the adsorption centres and their dipole moments. On the same line of discussion, El-Ashry et al. [38] also recently studied correlation of the quantum chemical SCF calculations of some parameters of benzimidazoles with their inhibition efficiency in case of steel in aqueous acidic medium. Geometric structures, total negative charge on the molecule (TNC), highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (E_{LUMO}), dipole moment (μ) and linear solvation energy terms, molecular volume (Vi) and dipolar-polarization (π^*) were all found to be correlated to the corrosion inhibition efficiency. The correlation between quantum parameters obtained by AM1 calculation and experimental inhibition efficiency were validated by single point calculations for the semi-empirical AM1 structure using B3LYP/6-31G* as a higher level of theory and equations (with high R^2 values) were successfully proposed using linear regression analysis to calculate corrosion inhibition efficiency. It was ultimately established by El-Ashry et al. [38] that the increase of the orbital energies E_{HOMO} favoured the inhibition efficiency toward steel corrosion.

2.2 Hybrid Coatings and Corrosion Inhibitors

Another field of extensive research on corrosion inhibition is the application of hybrid coatings preloaded with the inhibitors, and especially sol–gel derived organic–inorganic hybrid coatings (Pathak et al. [39]). Back in 2004, Pepe et al. [40] reported that chromates are among the most common substances used as corrosion inhibitors. However, these compounds are highly toxic, and an intense effort is being required (and is being undertaken) to replace them. According to Pepe et al. [40] cerium compounds seemed to fulfill the basic requirements for consideration as alternative corrosion inhibitors. The aim of the work of Pepe et al. [40] was therefore to study the effect of the incorporation of cerium ions in silica sol–gel coatings on aluminium alloys as potential replacement of chromate treatments. The main idea was to combine the 'barrier' effect of silica coatings with the 'corrosion inhibitor' effect of the cerium inside the coatings. Thin (below 1 μm for a single layer) and transparent cerium doped silica sol–gel coatings were prepared by dipping 3005 aluminium alloys in sol–gel solutions. Ultra–violet–visible spectra (UV–vis) showed that cerium ions, Ce^{3+} and Ce^{4+}, always were present in the coatings, independently of the cerium salt or firing atmosphere used. Active protection with single and two layer coatings prepared with Ce(IV) salt seemed to improve corrosion protection of the coated aluminium while coatings prepared with Ce(III) salt only entailed a protection when applied as a two layer, possibly due to sealing of pre–existent defects in the first layer. The improvement of active protection with immersion time would imply that corrosion is inhibited by cerium ions that migrate through the coating to the site of the attack (a defect in the coatings) and then react to passivate the site.

Khramov et al. [41] have developed sol–gel derived organo–silicate hybrid coatings preloaded with organic corrosion inhibitors in order to provide active corrosion protection when integrity of the coating is compromised. The incorporation of organic corrosion inhibitors into hybrid coatings has been achieved as a result of physical entrapment of the inhibitor within the coating material at the stage of film formation and cross–linking. Entrapped corrosion inhibitor become active in corrosive electrolyte and can then slowly diffuse out of the host material. To ensure continuing delivery of the inhibitor to corrosion sites and long–term corrosion protection, a sustained release of the inhibitor is achieved by a reversible chemical equilibrium of either ion–exchange of the inhibitor with the coating material or through cyclodextrin–assisted molecular encapsulation. Several organic compounds, such as mercaptobenzothiazole, mercaptobenzimidazole, mercaptobenzimidazolesulfonate, and thiosalicylic acid, have been selected and tested by Khramov et al. [41] to evaluate the effectiveness of these two approaches. Still, Lamaka et al. [42] studied the active corrosion protection of AA2024-T3 alloy provided by an environmental–friendly, well adhering pre–treatment system consisting of an inhibitor–

loaded titanium oxide porous layer and a sol-gel based thin hybrid film. As a matter of fact, Lamaka et al. [42] proposed a novel approach aimed at developing a nanoporous reservoir for storing of corrosion inhibitors on the metal/coating interface. The nanostructured porous TiO_2 interlayer was prepared on the aluminium alloy surface by controllable hydrolysis of titanium alkoxide in the presence of template agent. The morphology and the structure of the TiO_2 film were characterized with transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques. Lamaka et al. [42] found that, in contrast to direct embedding of the inhibitors into the sol-gel matrix, the use of the porous reservoir eliminated the negative effect of the inhibitor on the stability of the hybrid sol-gel matrix. Hence, TiO_2/inhibitor/sol-gel systems showed enhanced corrosion protection and self-healing ability confirmed by electrochemical impedance spectroscopy (EIS) and scanning vibrating electrode technique measurements.

Zheludkevich et al. [43] presented a new contribution to the development of a new protective system with self-healing ability composed of hybrid sol-gel films doped with nanocontainers that released entrapped corrosion inhibitor in response to pH changes caused by the corrosion process. A silica-zirconia based hybrid film was used in this work as an anticorrosion coating deposited on 2024 aluminum alloy. Silica nanoparticles covered layer-by-layer with polyelectrolyte layers and layers of inhibitor (benzotriazole) were randomly introduced into the hybrid films. The hybrid film with the nanocontainers revealed significantly enhanced long-term corrosion protection in comparison with the undoped hybrid film. The scanning vibrating electrode technique (SVET) also showed an effective self-healing ability of the defects. This effect was obtained due to regulated release of the corrosion inhibitor triggered and self-controlled by the pH feedback by the corrosion processes started in the cavities. This concept of feedback was further studied by Shchukin and Möhwald [44] wherein nanocontainers with the ability to release encapsulated active materials in a controlled way could be employed to develop a new family of self-repairing multifunctional coatings, which would possess not only passive functionality but also rapid feedback activity in response to changes in local environment. Several approaches to fabricate self-repairing coatings on plastic and metal substrates were surveyed by Shchukin and Möhwald [44]. The release of the active materials was established to occur only when triggered by specific properties of the corrosion process, which prevented leakage of the active component out of the coating and increased coating durability.

Further research was conducted by Moutarlier et al. [45] to improve the self-repair properties of sol-gel films on aluminium alloy. Moutarlier et al. [45] studied chromium(III),

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molybdate, permanganate and cerium (III) by polarisation resistance (Rp) in chloride medium and compared to the standard corrosion inhibitor, i.e. hexavalent chromium (Pepe et al. [40]). The evolution of the composition of sol-gel coatings, during the corrosion test, was examined by glow discharge optical emission spectroscopy (GDOES). Moutarlier et al. [45] have come with a fresh explanation in respect as to they showed that the morphology of sol-gel and the solubility of the additive played a determinant role in the effectiveness of corrosion protection for a long term. Additives such as molybdate and permanganate ions decreased the sol-gel network stability and were too soluble (they were rapidly lost from the sol-gel films, in an aggressive medium), decreasing the power to prevent corrosion. Incorporation of Ce(III) was not efficient for a long time, as opposed to the findings of Pepe et al. [40] due to its high solubility.

Sol-gel films containing Cr(VI) and Cr(III) seemed to provide adequate corrosion protection, due to the sol-gel stability and their low solubility. Still maintaining that the chromium (III) and (IV) species were less suited for inhibition, Poznyak et al. [46] developed Titania-containing organic-inorganic hybrid sol-gel films as an alternative to chromate-based coatings for surface pretreatment of aluminium alloys. Stable hybrid sols were prepared by hydrolysis of 3-glycidoxypropyltrimethoxysilane and different titanium organic compounds in 2-propanol solution in the presence of small amounts of acidified water. Different diketones were used as complexing agents in this synthesis for controllable hydrolysis of titanium organics. The properties of the obtained coatings were compared with those of zirconia-containing films. Electrochemical impedance spectroscopy (EIS) measurements and standard salt spray tests have been performed by Poznyak et al. [46] to investigate the corrosion protection performance of the hybrid coatings. It was revealed that their protective properties depended significantly on the nature of metalorganic precursors and complexing agents used in the process of sol preparation. The best anticorrosive protection of AA2024 in chloride solutions was provided by the titania-containing sol-gel films prepared with titanium(IV) tetrapropoxide and acetylacetone as starting materials. In the case of zirconia-containing films, better protective properties were found when applying ethylacetoacetate as a complexing agent. Equally for AA2024, Yasakau et al. [47] have worked a certain number of corrosion inhibitors for AA2024 as additives to the hybrid sol-gel formulations in order to confer active corrosion protection without damaging the coating. 8-hydroxyquinoline, benzotriazole and cerium nitrate were added at different stages of the synthesis process to understand the role of possible interaction of the inhibitor with components of the sol-gel system. SVET and EIS were employed as two main techniques to characterize the corrosion protection performance of the hybrid sol-gel films doped with inhibitors and to understand the mechanisms of corrosion protection. Yasakau

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et al. [47] have demonstrated that 8-hydroxyquinoline and cerium nitrate do not affect the stability of sol-gel films but would confer additional active corrosion protection effect. In contrast to this, benzotriazole lead to the deterioration of the corrosion protection properties of hybrid sol-gel films.

Green algae were tested as a natural additive for a paint formulation based on vinyl chloride copolymer (VYHH) to evaluate its efficiency for protection of steel against corrosion in seawater using spectrophotometry, A.C and D.C electrochemical measurements, visual inspection and surface analysis by Mansour et al. [27]. Both suspended and extracted forms of algae are utilized to achieve optimum performance of the algae-contained coatings. Poorest performance was obtained when algae added in its suspended form, whereas, the extracted form exhibited better performance based on impedance measurements. The data demonstrated that highest protection was obtained at algae threshold concentration of about 1.4 wt%. The SEM and energy dispersive X-ray (EDX) analysis together with visual inspection of coated specimens exposed to the marine environment gave very good support to the electrochemical data (Mansour et al. [27])

2.3 Modeling in Corrosion Research

The value of mathematical and computer-aided models to organize data, to consider interactions in complex systems in a rational way, to correct the conventional wisdom, and to understand essential qualitative, and at times quantitative, features of biological, electrochemical, nuclear, physical, physicochemical, mathematical and microscopic systems have been reasonably clearly documented in prior research for each of the latter field of science and engineering.

The impact of modeling research specific to corrosion inhibition (Papavinasam et al. [48], Zieliński and Sobieszczyk [49]) analysis discovery has so far been however moderate, but this will change in the future if we are adept in recognizing emerging opportunities and in integrating new concepts and tools into our research methodology. Mathematical structures and methods, allied with extraordinary contemporary computing power, are essential to the emerging field of metallurgical behaviour prediction and analysis. Important in this quest is thence a hierarchy of powerful modeling, analysis, and computational tools which can capture essential quantitative features of available experimental data and use these effectively for analysis and design of corrosion resistant structures. The few applications of computer modeling in corrosion inhibition discussed immediately below attempt at providing an overview of the level of complexity involved in the corrosion process to a point to justifiably warrant the use of powerful modeling techniques.

Isgor and Razaqpur [50] developed a robust and comprehensive finite element model for predicting the rate of steel corrosion in concrete structures. The model of Isgor and Razaqpur [50] consisted of initiation and propagation stages which were cast in the same time and space domains, that is, processes which commenced in the initiation stage, such as temperature, moisture, chloride ion, and oxygen transport within the concrete, maintained continuity into the propagation stage while active corrosion occurred contemporaneously. The model of Isgor and Razaqpur [50] was much innovative in the sense that it allowed the model to include the effects of changes in exposure conditions during the propagation stage on corrosion and the effects of the corrosion reactions on the properties of concrete. All the more, as a novel approach to corrosion inhibition analysis, Isgor and Razaqpur [50] calculated the corrosion rates on steel surface by solving the much intricate Laplace's equation for electrochemical potential with appropriate boundary conditions. These boundary conditions included the relationship between overpotential and current density for the anodic and cathodic regions. Due to the non-linear nature of these boundary conditions, a non-linear solution algorithm was used. According to Isgor and Razaqpur [50], their model being reasonably robust shall successfully enable designers to carry out comprehensive sensitivity analyses and to gauge the significance of variations in the values of certain parameters on the rate of corrosion in concrete structure, so that ultimately better corrosion resistant concrete structures be developed and cast for building and structural applications.

Kubo et al. [51] developed a mathematical model for the simulation of the changes in the pore solution phase chemistry of carbonated hardened cement paste when aqueous solutions of organic base corrosion inhibitors are applied to the surface of the material and constant current densities in the range of 1-5 A/m^2 are passed between anodes placed within the inhibitor solutions and steel mesh cathodes embedded within the paste. The model which (derived from the much used Nernst-Planck equation) was used to predict the concentration profiles of electrochemically injected inhibitors and the major ionic species present within the pore electrolyte as the corrosion reactions proceeded. For their part of scientific contribution in the mathematical modeling of corrosion inhibition, Colorado-Garrido et al. [52] presented a predictive model for corrosion polarization curves using artificial neural network (ANN). This proposed model obtained predictions of current in base of a corrosion inhibitor concentration and potential. The model of Colorado-Garrido et al. [52] was significantly different from other models developed to study corrosion inhibition in that the model took into account the variations of inhibitor concentration over steel by thermo mechanical processing to decrease corrosion rate. For the ANN, the Levenberg-Marquardt learning algorithm, the hyperbolic tangent sigmoid transfer-function

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and the linear transfer-function were dexterously used by Colorado-Garrido et al. [52]. The best fitting training data set was obtained with five neurons in the hidden layer, which made it possible to predict efficiency with accuracy at least as good as that of the theoretical error, over the whole theoretical range. On the validation data set, simulations and theoretical data test were in very good positive agreement with an R>0.985. Hence, the robustness of the model of Colorado-Garrido et al. [52] resided in its accurate predictive capacity of the current in short simulation times. On still a different scenario of corrosion inhibition, Jingjun et al. [106] recently studied the flow-induced corrosion mechanisms for carbon steel in high-velocity flowing seawater and attempted to explain the corrosive phenomena. The design methodology of Jingjun et al. [53] comprised the derivation of an overall mathematical model for flow-induced corrosion of carbon steel in high-velocity flow seawater in a rotating disk apparatus using both extensive numerical computer simulation and test methods. By studying the impact of turbulent flow using the kinetic energy of a turbulent approach and the effects of the computational near-wall hydrodynamic parameters on corrosion rates, the corrosion behaviour and mechanism were satisfactorily explored and explained by Jingjun et al. [53]. Jingjun et al. [53] held that their overall modeling and simulation approach could enable to understand afresh and in depth the synergistic effect mechanism of flow-induced corrosion. Jingjun et al. [53] also maintained for a first time that it was indeed scientific and reasonable to investigate carbon steel corrosion through correlation of the near-wall hydrodynamic parameters, which could accurately describe the influence of fluid flow on corrosion. The subsequent computational corrosion rates obtained by the model of Jingjun et al. [53] were in good agreement with actual measured corrosion data. Jingjun et al. [53] also succeeded in showing that serious flow-induced corrosion is caused by the synergistic effect between the corrosion electrochemical factor and the hydrodynamic factor, while the corrosion electrochemical factor plays a dominant role in flow-induced corrosion.

3.   Green Inhibitors

All synthetic processes or engineering methods involve the use of different chemicals and materials which may cause corrosion to metals during the specific process. Some of them are very hazardous and environmentally problematic in nature. To control corrosion with conventional 'toxic' corrosion inhibitors, they pose significant adverse effects on the environment and at the end of the chain, to mankind. Such corrosion inhibitors are called "Grey inhibitors" as have been discussed in the earlier sections. However, Green Chemistry provides many environmental friendly corrosion inhibitors, called "*Green Inhibitors*" which are non-hazardous and eco-friendly (Little et al. [30], Bothi Raja and Sethuraman [19], Davó

et al. [54], Bendahou et al. [55], Craddock et al. [56], Deacon et al. [57], Taha [58], Scendo [59]).

3.1 Natural Derivatives for Green Corrosion Inhibitors

The safety and environmental issues of corrosion inhibitors arisen in industries have always been a global challenge. Chromates for example are used in the pretreatment of aluminium alloys (Hinton et al. [60]). Since chromates are suspected to be toxic as well as carcinogenic (Costa and Klein [61]), many alternative corrosion inhibitors are being developed to reduce the jeopardizing effects on humans, animals and environment. *Green Inhibitors* are environment friendly corrosion inhibitors and range from rare earth elements (Kilbourn [62], Bethencourt et al. [63], Virtanen et al. [64], Bethencourt et al. [65], Powell et al. [66], Arenas et al. [67], Hughes et al. [68]) to organic compounds (Choi et al. [69], Davis et al. [70], Cano et al. [71], Aballe et al. [72], El-Maksoud [73], Solmaz [74], Moretti et al. [75], El-Sawy et al. [76], Khamis and Al-Andis [77]).

3.2 Research on Green Corrosion Inhibitors

The following digest of only some of the umpteen researches being carried out on the development and testing of green corrosion inhibitors exemplify potential for the very wide array of green derivatives that can be synthesized and extracted for the said purpose. Many of the reported researches (over 3000) in literature may be broadly classified in the following categories of green derivatives for corrosion inhibitors: organic, amino acids, plant extracts and rare earth elements based.

3.2.1 Organic-Based Green Inhibitors

Khaled [18] synthesized a new safe corrosion inhibitor namely N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-yl)-guanidine (NTG) and its inhibitive performance towards the corrosion of mild steel in 1M hydrochloric acid and 0.5 M sulphuric acid has been investigated. Corrosion inhibition was studied by weight loss, the Tafel extrapolation method and electrochemical impedance spectroscopy. These studies of Khaled [18] have shown that NTG was a very good inhibitor in acid media and the inhibition efficiency could be reached as high as up to 99% and 96% in 1M HCl and 0.5M H_2SO_4, respectively. Khaled [18] intensified the research and made polarization measurements reveal that the investigated inhibitor is cathodic in 1M HCl and mixed-type in 0.5M H_2SO_4. The activation energies of the corrosion process in the absence and presence of NTG were obtained by

measuring the temperature dependence of the corrosion current density. Khaled [18] successfully demonstrated that the adsorption of the NTG inhibitor on the metal surface in the acid solution was found to obey the Langmuir's adsorption isotherm as has been observed with many of the conventional, but toxic, corrosion inhibitors (Elayyachy et al. [31], Quraishi and Khan [34], Yurt et al. [35], Lebrini et al [24]). Gao and Liang [78] tested β–amino alcohols compounds in the series of 1,3–bis–dialkyl (C_nH_{2n+1}) aminopropan–2–ols as volatile corrosion inhibitors for brass in simulated atmospheric water using potentiodynamic, potentiostatic current transient, electrochemical impedance spectroscopy, gravimetric, and volatile inhibition ability measurements. The evolution of the inhibition effect of the investigated compounds has been monitored by Gao and Liang [78] according to the length of alkyl chain. The results obtained by Gao and Liang [78] indicated that the inhibition efficiency increased with increasing the alkyl chain length and also inhibitor concentration. Polarization curves deduced by Gao and Liang [78] clearly supported that these compounds acted as good anodic inhibitors in water. Gao and Liang [78] discussed the inhibition mechanism in light of the chemical structure of undertaken inhibitors and came to the same, but widely validated, conclusion that the adsorption of the alcohol–based inhibitors on the brass surface followed the Langmuir adsorption isotherm model.

3.2.2 Amino Acids–Based Green Inhibitors

Barouni et al. [79] studied the inhibition effect of five amino acids on the corrosion of copper in molar nitric solution by using weight loss and electrochemical polarization measurements. Valine (Val) and Glycine (Gly) were found to accelerate the corrosion process; but Arginine (Arg), Lysine (Lys) and Cysteine (Cys) inhibited the corrosion phenomenon, with cysteine being the best among the three inhibitors. Its efficiency increased with the concentration to attain 61% at 10^{-3} M. Ismail [80] further investigated the efficiency of cysteine as a non-toxic corrosion inhibitor for copper metal in 0.6 M NaCl and 1.0 M HCl by electrochemical studies. Potentiodynamic polarization measurements and electrochemical impedance spectroscopy were equally employed by Ismail [80] to study the effect of cysteine on the corrosion inhibition of copper. Ismail [80] observed that a higher inhibition efficiency of about 84% could be achieved in the chloride solutions. The potentiodynamic polarization measurements made by Ismail [80] showed that the presence of cysteine in acidic and neutral chloride solutions affected mainly the cathodic process and decreased the corrosion current to a great extent and then shifted the corrosion potential towards more negative values. The experimental impedance data obtained by Ismail [80] were analyzed according to a proposed equivalent circuit model for the electrode/electrolyte interface. The results obtained from potentiodynamic polarization and

impedance measurements by Ismail [80] were in good agreement, and the adsorption of cysteine on the surface of Cu, in neutral and acidic chloride solutions, followed the Langmuir adsorption isotherm very well with an adsorption free energy of cysteine on Cu of 25kJ/mol revealing a strong physical adsorption of the organic-based inhibitor on the metal surface.

3.2.3 Plant Extracts-Based Green Inhibitors

Bendahou et al. [55] evaluated the effect of natural rosemary oil as non toxic inhibitor on the corrosion of steel in H_3PO_4 media at various temperatures. The oil was initially hydro-distilled and used as inhibitor in various corrosion tests with gravimetric and electrochemical techniques being used to characterise the corrosion mechanisms. Chromatographic analysis by Gas Chromatography showed that the oil was rich in 1,8-cineole. Bendahou et al. [55] demonstrated good agreement between the various methods explored for corrosion inhibition analysis. The polarisation measurements showed that rosemary oil acted essentially as a cathodic inhibitor. The efficiency of the oil increased with the concentration (to attain 73% at 10g/L) but decreased with the rise of temperature in the 25-75^{0}C range. According to novel results of Bendahou et al. [55], the natural oil could thus be used in chemical cleaning and pickling processes, thereby validating the originality of their work in finding of a safe and cheap inhibitor from natural plants. In Bothi Raja and Sethuraman [19], the corrosion inhibitive effect of the extract of black pepper on mild steel (MS) in 1 M H_2SO_4 media was evaluated by conventional weight loss studies (33-50^{0}C), electrochemical studies namely Tafel polarization, A.C impedance and SEM. Results of weight loss study reveal that black pepper extract acts as a good inhibitor even at high temperatures. The inhibition is through adsorption which is found to follow Temkin adsorption isotherm. Polarization curves revealed the mixed mode inhibition of black pepper extract. Analysis of impedance data has been made with equivalent circuit with constant phase angle element for calculation of double layer capacitance value. SEM studies provide the confirmatory evidence for the protection of MS by the green inhibitor.

El-Etre et al. [81] tested the aqueous extract of the leaves of henna (lawsonia) as a corrosion inhibitor of steel, nickel and zinc in acidic, neutral and alkaline solutions, using the polarization technique. El-Etre et al. [81] found that the extract acted as a very good corrosion inhibitor for the three tested electrodes in all tested media. The inhibition efficiency increased as expected with the concentration of extract when increased. El-Etre et al. [81] postulated that the degree of inhibition depended on the nature of the metal and the type of the medium. For C-steel and nickel, the inhibition efficiency increased in the

order: alkaline < neutral < acid, while in the case of zinc it increased in the order: acid < alkaline < neutral, thereby reconciling with the much observed concept of the lawsonia extract being a mixed inhibitor as has been the case with umpteen grey inhibitors. The inhibitive action of the extract was discussed in view of adsorption of the complex lawsonia molecules onto the metal surface. El-Etre et al. [81] found that this adsorption followed Langmuir adsorption isotherm in all tested systems. El-Etre et al. [81] proposed, as a fresh explanation, that the formation of a complex between the metal cations and lawsone was an additional inhibition mechanism of steel and nickel corrosion. In their research with plant extracts for corrosion inhibition, Oguzie et al. [82] appraised the inhibiting effect of Ocimum basilicum extract on aluminium corrosion in 2M HCl and 2M KOH solutions, respectively, at 30 and 60°C. The corrosion rates were determined using the gas-volumetric technique and the values obtained in absence and presence of the extract was used in the calculation of the inhibition efficiency by Oguzie et al. [82]. Oguzie et al. [82] estimated the mechanism of inhibition from the trend of inhibition efficiency with temperature. According to Oguzie et al. [82] the Ocimum basilicum extract was believed to inhibit aluminium corrosion in both the acidic and alkaline environments. Inhibition efficiency increased with extract concentration but decreased with rise in temperature, again suggesting physical adsorption of the organic matter on the metal surface. These results were corroborated by kinetic and activation parameters for corrosion and adsorption processes evaluated from the experimental data at the temperatures studied by Oguzie et al. [82]. On further testing, Oguzie et al. [82] found that halide additives synergistically improved the inhibition efficiency of the extract. Hence, the research of Oguzie et al. [82] provided new information on the possible application of Ocimum basilicum extract as an environmentally friendly corrosion inhibitor. Oguzie et al. [82] maintained that the mixed extract – iodide formulation provided an effective means for retarding aluminium corrosion even in highly aggressive alkaline environments. Yet a 'sweeter' research was undertaken by Radojčić et al. [25] in their study of the influence of natural honey (chestnut and acacia) and natural honey with black radish juice, on the corrosion of tin in aqueous and sodium chloride solutions using weight loss and polarization techniques. Radojčić et al. [25] observed that the inhibition efficiency of acacia honey was lower than that of chestnut honey, while the addition of black radish juice increased the inhibition efficiency of both honey varieties. The mechanism of corrosion inhibition was explained from a new perspective by Radojčić et al. [25] in that the process of inhibition was attributed to the formation of a multilayer adsorbed film on the tin surface, still following the established Langmuir adsorption isotherm.

Sethuraman and Bothi Raja [83] on their side have evaluated the corrosion inhibition potential of Datura metel in acid medium on mild steel (MS) with a view to develop new green corrosion inhibitors. The methodology of Sethuraman and Bothi Raja [83] consisted in studying an acid extract of the D. metel for its corrosion inhibitive effect by electrochemical and weight loss methods. Using weight loss measurement data, an attempt was made by Sethuraman and Bothi Raja [83] to probe the mechanism of inhibitive action by fitting the different established adsorption isotherms. Sethuraman and Bothi Raja [83] were much convincing in showing significant corrosion inhibitive effect in acid medium on MS. Sethuraman and Bothi Raja [83] explained based on their findings that inhibition was through adsorption of the phytoconstituents on MS following both the Temkin and Langmuir adsorption isotherms. According to Sethuraman and Bothi Raja [83], the Datura metal plant was being investigated for the first time by them for its corrosion inhibitive and their developed green inhibitor could possibly find use in the inhibition of corrosion in industries where MS is used as a material of choice for the fabrication of machinery.

Acid cleaning of mild steel dissolution by 1M sulphuric acid/10% methanol (test solution) in presence of Arghel herb extract as green inhibitor were monitored by potentiodynamic and electrochemical impedance techniques in the temperature range 30–60ºC by Khamis et al. [28]. At all temperature, the corrosion rate decreased with increasing inhibitor concentration. Potentiodynamic polarization measurements indicated that the inhibitor has strong effect on the corrosion behavior of the steel and behave as mixed type inhibitor (Khamis et al. [28]). Impedance results indicate that the charge transfer controls the dissolution mechanism of steel across the phase boundary in the absence and the presence of the inhibitor. The inhibition efficiency obtained from various employed methods was in good agreement. Thermodynamic and activation parameters obtained from this study indicated that the presence of the Arghel increases the activation energy, and the adsorption process of the inhibitor on the metal surface is spontaneous (Khamis et al. [28]).

Inhibition of aluminium corrosion in 2M sodium hydroxide solution in the presence and absence of 0.5M NaCl using damsissa (*Ambrosia maritime*, L.) extract has been studied employing different chemical and electrochemical techniques by Abdel–Gaber et al. [29]. Chemical gasometry technique showed that addition of chloride ions or damsissa extract to sodium hydroxide solution decreases the volume of the hydrogen gas evolved. Potentiodynamic results manifested that chloride ion retard the anodic dissolution of aluminium, below the pitting potential, in sodium hydroxide solution. Damsissa extract, in presence or absence of chloride ion, influenced both the anodic dissolution of aluminium and the generated hydrogen gas at the cathode indicating that the extract behaved as

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mixed-type inhibitor. The decrease in the observed limiting current with increasing damsissa extract concentration indicated that the anodic process is controlled by diffusion. Nyquist plots present two capacitive semicircles at higher and lower frequencies separated by an inductive loop at intermediate frequencies (Abdel-Gaber et al. [29]). The inductive loops were clarified by the occurrence of adsorbed intermediates on the surface. A proposed equivalent circuit was used to analyze the impedance spectra for aluminium in alkaline solutions. The results showed that the damsissa extract could serve as an effective inhibitor for the corrosion of aluminium in alkaline solutions. The impedance measurements verified the remarkable stability of the extracts during storage up to 35 days. Damsissa extract was found more effective in presence of chloride ions than in its absence. Inhibition was found to increase with increasing concentration of the extract but decreases with increasing temperature. The associated activation parameters were determined and discussed (Abdel-Gaber et al. [29]).

The inhibition of corrosion of aluminium using a package composed mainly of the extract of *Lupine* and *Damsissa* plants in addition to surfactant has been studied using potentiodynamic and impedance techniques. Inhibition effect of surfactant in the inhibitor package is shown to increase at composition around its critical micelle concentration. The extract of *Arghel* that introduced into concrete during its mixing has a pronounced effect on reducing the attack of chloride ions to the steel reinforcement. Polarization measurements illustrated that *Arghel* behaved as anodic type inhibitor in simulated seawater solutions. EIS data revealed that *Arghel* has a pronounced effect on the diffusion process (Khamis et al. [84]).

Khamis et al. [85] investigated the dual function of *olive* (Olea europaea L) extract as antiscalent for $CaCO_3$ deposit and corrosion inhibitor for steel in alkaline $CaCl_2$ brine solution. The antiscalent properties of this extract were studied using conductivity measurements, EIS, and chronoamperometry techniques in conjunction with microscopic examination. The inhibitive characteristics were investigated using EIS and potentiodynamic polarization curves measurements. Mineral scales were deposited from the brine solution by cathodic polarization of the steel surface at -0.9V. The extract was found to impede $CaCO_3$ supersaturation and decreases the time of nucleation (Khamis et al. [85]). The scaling steps of nucleation, crystal growth and total coverage of the surface regions were characterized by chronoamperometry technique and different impedance spectra. The surface area occupied by the scale deposits decreased with increasing extract concentrations. Potentiodynamic polarization curves indicated that plant leaves extract inhibits the corrosion of steel by controlling the cathodic oxygen reduction process. The

data were compared with that previously obtained using *fig* leaves (Ficus carica L.) extract. The results showed that *olive* and *fig* leaves extract can decrease corrosion and scale build-up under the conditions tested (Khamis et al. [85])

3.2.4 Rare Earth Elements-Based Green Inhibitors

Considerable research efforts have been made to develop non-toxic and equally performing green corrosion inhibitors from rare earth elements. In principle, the rare earth element is selected from cerium, terbium, praseodymium, or a combination thereof, and at least one rare earth element should be in the tetravalent oxidation state. An inorganic or organic material is then used to stabilize the tetravalent rare earth ion to form a compound that is sparingly soluble in water. Specific stabilizers are chosen to control the release rate of tetravalent cerium, terbium, or praseodymium during exposure to water and to tailor the compatibility of the powder when used as a pigment in a chosen binder system. Stabilizers may also modify the processing and handling characteristics of the formed powders. Many rare earth-valence stabilizer combinations have been shown to equal the performance of conventional hexavalent chromium systems.

Blin et al. [86] investigated the corrosion inhibition mechanisms of new cerium and lanthanum cinnamate based compounds through the surface characterisation of the steel exposed to NaCl solution of neutral pH. Blin et al. [86] used Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy to identify the nature of the deposits on the metal surface and confidently demonstrated that after accelerated tests the corrosion product commonly observed on steel (which is lepidocrocite, γ-FeOOH) is absent. The cinnamate species were clearly present on the steel surface upon exposure to NaCl solution for short periods and appeared to coordinate through the iron. At longer times the rare earth metal oxyhydroxide species were proposed by Blin et al. [86] to have formed as identified through the bands in the 1400-1500 cm^{-1} regions. According to Blin et al. [86], the protection mechanism appeared to involve the adsorption of the REM-cinnamate complex followed by the hydrolysis of the REM to form a barrier oxide on the steel surface, this being a novel mechanism involved and observed in corrosion inhibition. Blin et al. [87] further intensified their research on rare earth elements by demonstrating through a combination of linear polarisation resistance (LPR) and cyclic potentiodynamic polarisation (CPP) measurements that the lanthanum-4 hydroxy cinnamate compound could inhibit both the cathodic and anodic corrosion reactions on mild steel surfaces exposed to 0.01 M NaCl solutions. However, the dominating response was shown to vary with inhibitor concentration. At the concentrations for which the highest level of protection was achieved,

both REM-4 hydroxy cinnamate (REM being lanthanum and mischmetal) displayed a strong anodic behaviour for mild steel and their inhibition performance, including their resistance against localised attack, improved with time.

4.   Concluding Remarks

The diverse set of research summarized and discussed advocate that intense research efforts are being deployed to tackle the much problematic phenomenon of corrosion. Although it is realized that the preceding discussions are modest, the essence remains that a wide variety of chemical, biological, physical, mechanical, electrical, metallurgical, nuclear, electrochemical and computational techniques are being employed to make progress the current research to shift from grey corrosion inhibitors to green corrosion inhibitors. Green corrosion inhibitors are being more and more synthesized from organic, amino acids and plant extracts and tested in their inhibition efficiencies, while modeling research is attempting to address and elucidate the mechanism of the chemical reactions involved in the corrosion process and in corrosion inhibition with the use of modeling techniques like finite element modeling and artificial neural network. Grey corrosion inhibitions unanimously adhere to the Langmuir adsorption model while several findings of research on equally performing and inhibitive green inhibitors have supported additional adsorption mechanisms captured rightly by the Frumkin's equation, Freundlich and Temkin adsorption isotherms. Latest corrosion protection techniques involve the use of nanomaterials but the use of green inhibitors remains a much safer and environmentally secure way of protection against corrosion. It is not only environment friendly but also a cost effective method with the added advantage of waste minimization. Therefore, it may inferred that the applications of green inhibitors have a wide scope of research and development yet to be fully explored.

Acknowledgements

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