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The Impact of Green Corrosion Inhibitors on the Protection Performance of Hybrid Silane Sol-Gel Coatings: A Review

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ABSTRACT

In man-made structures, corrosion is one of the most important problems and environmentally friendly protective coatings are one of the vital requests in different industries. In this article, silane-based sol-gel coatings, as a substitution to toxic coatings based on chromates, have been evaluated. The role of using different green additives, extracted from plants, to deal with corrosion in different corrosive media has been investigated. However, different parameters can affect the efficiency of these materials such as pH, temperature, concentration, substrate type, media, compatibility, etc. The comparison of the anti-corrosion performance of silane sol gel coatings containing these green inhibitors showed that there is much potential for the broader application of these safe materials for maintenance of structures.

1.Introduction

Steels are highly vulnerable in corrosive environments and, therefore, require protection against corrosion [1]. One of the primary techniques for defending metals against corrosive environments is to apply coatings [2-4]. One type of coating is conversion coatings, such as chromate and phosphate, which establish strong bonds with the substrate and inhibit the degradation of coatings. Additionally, they increase adhesion to the subsequent layer. Among coatings, chromate-based ones provide excellent protection against corrosion, but they are unfortunately harmful to human health [5, 6].

Owing to environmental concerns caused by chromate conversion coatings, one alternative to chromate conversion coatings is silane-based hybrid coatings [7].

Hybrid organic-inorganic materials synthesized by the sol-gel method have been attended in the last decade [8]. Neat silane-based hybrid coatings can act as protective obstacles versus corrosive agents [9]. Although, over time, these corrosive agents penetrate the matrix through cavities and reach to the surface of the metal, causing electrochemical reactions, followed by the formation of corrosion products underneath the coating and finally causing the coating delamination from the substrate [9]. To enhance the performance of the metals, various strategies have been used. Still, generally, the use of corrosion inhibitors is the most practical and affordable method provided that they are encapsulated for controlled release [10]. The use of organic compounds containing electron-rich atoms such as oxygen, phosphorous, and sulfur, along with aromatic rings, is effective in boosting the corrosion resistance of metals [11].

These groups are absorbed on the metal surface through their active centers [11].

Unfortunately, the method of synthesis of organic compounds is complex and expensive. Several researches have been done to replace organic inhibitors, in which much attention has been paid to environmentally friendly plant-based materials [12]. Plant-based corrosion inhibitors form complexes with metal ions through their functional groups, and these complexes cover a large area by blocking the metal surface and protecting the metal from destructive factors in the solution [12].

The sol-gel process enables the formation of an inorganic network through hydrolysis and condensation reactions [13]. An organic network can

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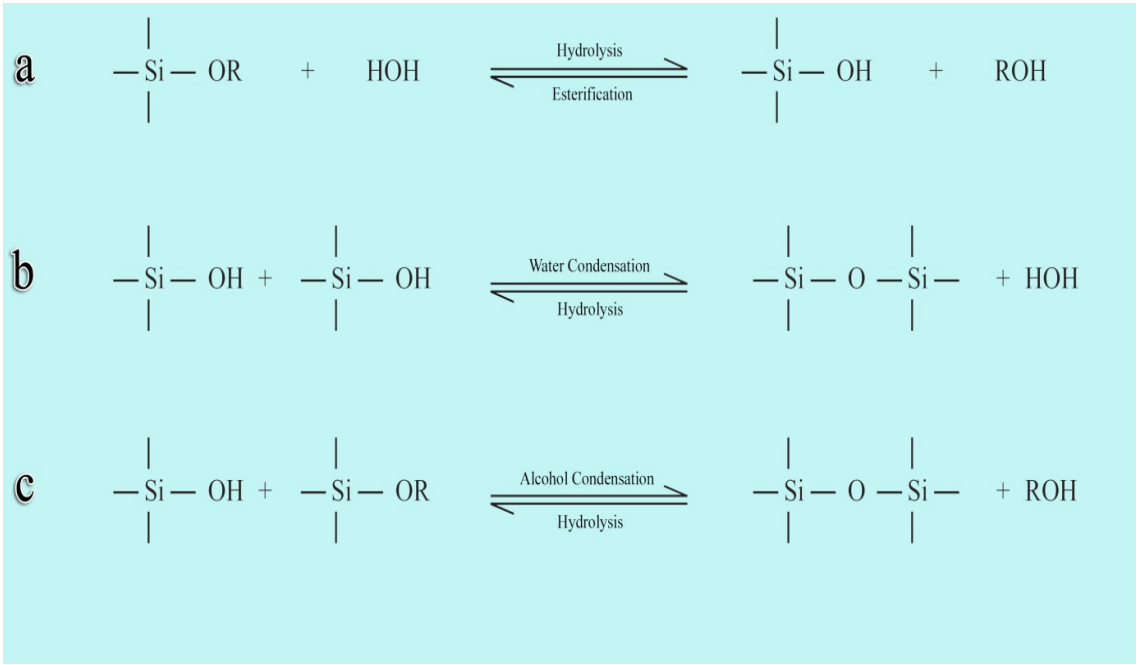
be created alongside or in conjunction with the inorganic one [14]. In addition to modifying the properties of the final network, secondary networks can be created within the inorganic network to keep and enhance the properties of organic and inorganic networks together [15]. The presence of organic compounds in the hybrid network causes a decrease in the stress relaxation temperature and densification of these materials at much lower temperatures compared with inorganic materials. Therefore, it will be possible to prepare multicomponent materials and organic materials with polymerizable groups, control the dimensions of phases in the network, and apply coatings on various types of surfaces [16]. To synthesize hybrid organic-inorganic coatings, the sol-gel method is frequently employed due to its relatively easy preparation conditions, the cost-effectiveness of the equipment, and its compatibility with other processes [17]. Generally, in the sol-gel process, the hydrolysis reaction occurs with an increase in the water content as well as the replacement of alkoxy groups (OR) with OH groups (Schematic 1(a,b)) [18]. Then, successive condensation reactions occur between the Si-OH and Si-OR groups, and Si-O-Si is produced along with alcohol and water as by-products (Schematic 1c) [18]. Under these conditions, condensation begins before the hydrolysis reaction is completed [18]. However, factors such as pH, H_2O/Si molar ratio, and catalyst can be the terminating force of hydrolysis before the condensation starts [18]. In addition, since water and alkoxide are immiscible, hydrolysis becomes easier in the vicinity of a homogenizing agent such as alcohol because of the miscibility of alkoxide and water [19]. Gradually, the number of silicon bonds increases, and separate molecules come together as a bridge, and in the sol state, they bond together. When the coalescence of sol particles occurs, the gel is obtained by closing from the inside and wrinkling the network [13,17]. During drying, volatile materials, water, and alcohol exit the system, and the network shrinks, which is accompanied by condensation [20]. It should be emphasized that increasing the solution content may cause increased esterification and polymerization in the opposite direction of these reactions [13]. Using this process, an organic network can be bonded to an inorganic one, and hybrid organic-inorganic coatings with very interesting properties can be prepared [17]. These coatings can be applied to various surfaces by dipping, spraying, and spin coating methods with thicknesses in the range of 4-20 μm [21]. Organic-inorganic coatings have special mechanical properties such as abrasion resistance, corrosion resistance, and wear resistance [22,23]. In this paper, the effect of green inhibitors in silane coatings to reduce the corrosion of metallic substrates has been reviewed. Different factors affecting the efficiency of silane coatings, such as curing conditions, pH, porosity, and type of inhibitor, have been mentioned.

The reason that distinguished this review paper from the published review ones is that in other papers, the effect of organic and inorganic chemical inhibitors was investigated, whereas in this work, the emphasis is only on green inhibitors.



Schematic 1. Hydrolysis and condensation reaction in sol-gel processes [18].

2.Parameters affecting the anti-corrosion properties of silane-based hybrid sol-gel coatings:

2.1.Effect of curing conditions, pH, particle size, surface preparation, thickness, and method of application

Silane coatings can act as primers by creating a physical barrier to limit access of corrosive species to the metal surface and provide protection against corrosion. The performance of silane coatings depends on the formation of a no defect layer with appropriate adhesion [24]. The formation of a silane coating is influenced by factors such as curing conditions, pH of the solution, surface preparation, thickness, method of application, and particle size in the matrix [24].

The curing condition of a coating is a determining factor for final coating properties, such as thickness and barrier quality. The crosslinking of the coating during the curing process, through Si-O-Si bonds, delays the diffusion of aggressive agents to the metal surface [25]. Therefore, the crosslinking density is crucial, and the presence of areas with low crosslinking densities, as well as defects such as cracks, facilitates the formation of electrolyte penetration and aggressive agents [26]. Curing conditions of coatings such as temperature and time can directly affect the level of defects in the coating, such as cracks, as well as the level of crosslinking. Many endeavors have been made to ameliorate the barrier properties of silane coatings [27,28]. For this purpose, the curing conditions have been studied by various researchers as a significant factor affecting the barrier properties [29].

Phanasgaonkar *et al.* [30] used thermogravimetric analysis (TGA) and demonstrated that the variation of mass loss is almost constant in the temperature range about 150 to 400 °C, but there is a remarkable mass loss at 400 °C, indicating the presence of cracks in the coating. Therefore, they suggested that the suitable temperature range to cure the coating is 150 to 350 °C.

Rafiaei *et al.* [31] evaluated the effect of curing temperature and time on the corrosion properties of a silane coating applied on 304L stainless steel. They showed that as the curing time and temperature increase, the crosslinking of the coating increases. Another report suggests that a temperature of 150 °C and a curing time of 45 minutes are the optimal conditions for curing [32].

Another influential factor is the pH of the silanol solution. Figure 1 shows the dependency of hydrolysis and condensation reactions on pH. It can be observed that in acidic conditions, the rates of both reactions are high, whereas, in neutral pH, they are slow. When OH^- is the reaction catalyst, the rates of condensation and gelation reactions are high. However, when H^+ is the reaction catalyst, the rate of hydrolysis reaction is high, but that of the gelation reaction is slow. Hydrolysis and condensation occur concurrently unless one of them is restricted due to special conditions [33].

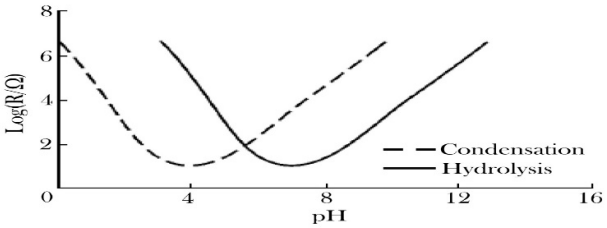


Figure 1. Rate of hydrolysis and condensation reactions for a silane sample [33].

Asadi *et al.* [34], investigated the impact of sol pH (2.8 and 4) on the hydrophobicity and hydrophilicity behavior of silane coatings applied on steel. The measured contact angle results showed that at pH=2.8, the contact angle was higher, indicating the creation of a more hydrophobic film. The reason for the hydrophilicity of the silane coating at pH=4 is due to the presence of more unreacted silanol groups (SiOH) due to the low crosslinking density caused by a low degree of hydrolysis. Surface preparation is considered an essential parameter in the formation of metalosiloxane (Me-O-Si) bonds. In fact, the presence of OH groups on the metal surface is necessary to establish crosslinking with SiOH groups [24].

Franquet *et al.* [35] assessed the influence of various surface preparation conditions of an Al alloy with a silane coating in an alkaline environment and concluded that the adsorption rate of silane molecules on the surface of the prepared samples increased with increasing the number of hydroxyl (OH^-) groups.

Rouzmeh *et al.* [36] studied the impact of acidic preparation using H_2SO_4 at different pH values on the protective performance of the silane coating on mild steel samples. They reported that the corrosion protection performance of silane coatings is about 4 times higher than alkaline cleaning, and therefore, acid pickling is much more effective. They also found that the optimal conditions for acidic surface preparation

of the mild steel were at pH=3. The thickness of the silane coating can restrict the penetration of water, oxygen, and chloride ions to the coating/metal interface. Increasing the amount of polymer or organic compounds leads to the formation of thicker coatings [17]. The coating method can also affect the coating thickness [37]. For instance, electrodeposition can result in the formation of thick and crack-free coatings compared with dipping or spin coating processes [37]. In addition, by electrodeposition, it is possible to synthesize thick coatings using dilute sols, which causes an increase in the stability of the sol as well as the ease of the process [37]. Finally, by decreasing the particle size to the nanoscale, fewer cracks can be seen in the silane coating [38]. Thus, the decrease in the particle size improves the morphology of the film formed [39].

2.2.Effect of adding eco-friendly inhibitors

The presence of fine porosities in hybrid sol-gel coatings can cause the occurrence of corrosion in the substrate. Therefore, in addition to organic compounds, other additives like inhibitors can be added to the sol-gel system to improve the corrosion resistance of the substrate. Green corrosion inhibitors extracted from various parts of plants have absorbed much attention owing to their low price, accessibility, and non-toxicity compared with organic and inorganic inhibitors [40-45].Ghuzali *et al.* [46] dispersed ethanolic and aqueous extracts of Clitoria Ternatea flower (CT) with concentrations of 25-100 ppm in a silanol matrix [tetraethyl orthosilicate (TEOS) and 3-Glycidyloxypropyl) trimethoxysilane (GPTMS)] and applied it on mild steel. They assessed the anti-corrosion performance of the coatings in a 0.5 M HCI environment using electrochemical impedance spectroscopy (EIS) and molecular simulation studies. The EIS results showed that the sol-gel coating containing 75 ppm of the ethanolic extract of CT exhibited the highest corrosion inhibition efficiency (83.78%). In molecular simulation studies, by using the energy parameter of the highest filled molecular orbitals (E_{HOMO}), it is possible to understand the electron donating ability of the inhibitor molecules as a main factor of inhibition efficiency. Therefore, the inhibition efficiency can be enhanced by rising E_{HOMO}. The results of molecular simulation indicated that the bioactive ingredient quercetin in CT has higher (less negative) E_{HOMO} values of -8.755 eV than other compounds, as a result it provides electrons more easily to the d orbital of iron metal and formed stronger absorption. Hamidon *et al.* [47] applied caffeine extracted from tea leaves with concentrations of 25-100 ppm in a sol-gel matrix [tetraethyl orthosilicate (TEOS) and 3-aminopropyl triethoxysilane (APTES)] on a mild steel grade and investigated the corrosion resistance behavior of the coatings in a 3.5% NaCl solution using EIS. The EIS results (Table 1) showed that the sol-gel coating containing 100 ppm of the caffeine extract exhibited a corrosion inhibition efficiency of about 84.22% and ranked first among the coatings tested in this research. The electron exchange between the molecules of caffeine and unoccupied electrons of the iron atom leads to the surface absorption of this inhibitor on the metal surface. In addition, the presence of caffeine not only causes reduced dissolution in anodic regions but also inhibits the hydrogen evolution reaction in cathodic regions. Since caffeine shifts the potential toward negative values, it is classified as a cathodic inhibitor.

Table 1. Electrochemical impedance parameters for steel samples with and without sol-gel coatings [47].

Sample	Coating resistance $\Omega.cm^2$	Charge transfer resistance $\Omega.cm^2$	Inhibitiona Efficiency (%)
Mild steel	-	981.25	-
Neat Sol-gel Coating	178.25	1954.95	49.81
Sol-gel Coating containing 25 ppm Caffeine	287.87	2441.65	59.80
Sol-gel Coating containing 50 ppm Caffeine	329.91	2934.94	66.57
Sol-gel Coating containing 75 ppm Caffeine	341.54	3726.41	73.67
Sol-gel Coating containing 100 ppm Caffeine	576.24	6218.02	84.22

Norizan *et al.* [48] dispersed the ethanolic extract of Beta vulgaris in a silanol matrix (TEOS+APTES) with different concentrations and applied it on a mild steel grade. They evaluated the corrosion resistance behavior of the coating in a 3.5% NaCl solution using EIS and polarization. The EIS results showed that the sol-gel coating containing 400 ppm of the ethanolic extract of Beta vulgaris exhibited an inhibition efficiency of about 83.03% and increased corrosion resistance. The polarization results (Figure 2) revealed that the presence of the Beta Vulgaris inhibitor in the matrix led to the shift of potential toward negative values and acts as a mixed inhibitor.

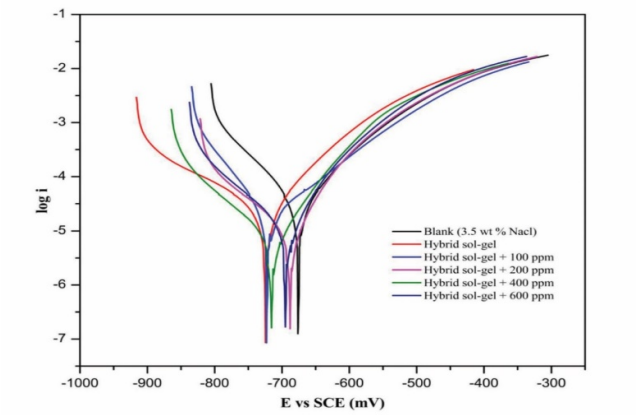


Figure 2. Polarization diagrams of mild steel coated with sol-gel coatings in presence and absence of Beta Vulgaris green inhibitor [48].

Zakaria *et al.* [49] incorporated winged bean extract into a silanol matrix [polydimethylsiloxane (PDMS) + tetraethyl orthosilicate (TEOS)] and evaluated the corrosion resistance behavior of the silane coating in a 0.5 M HCl solution using the electrochemical techniques. The results of the electrochemical test showed the presence of flavonoid and phenolic bioactive materials, such as myricetin, catechin, galic acid, Ferulic acid and quercetin in the silane matrix, induced active protection of the resultant coating.

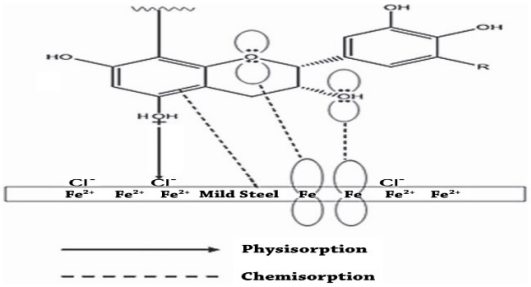
Hamidon *et al.* [50] studied the corrosion behavior of mild steel coated with silane films containing 25-100 ppm of tea leaf aqueous extract in a 3.5% NaCl solution at 303 K using polarization tests. The polarization results (Table 2) showed that the presence of 75 ppm of tea leaf extract in the silane coating decreased the corrosion rate significantly and increased the inhibition efficiency to 0.41 CR/mpy and 85.66%, respectively.

Table 2. potentiodynamic polarization parameters for steel samples with and without sol-gel coatings [50].

Sample	Corrosion Rate (mpy)	Inhibition Efficiency (%)
Mild steel	2.85	-
Pure Sol-gel Coating	1.43	49.43
Sol-gel Coating containing 25 ppm Tea leaves extract	1.29	54.67
Sol-gel Coating containing 50 ppm Tea leaves extract	1.02	66.99
Sol-gel Coating containing 75 ppm Tea leaves extract	0.41	85.66
Sol-gel Coating containing 100 ppm Tea leaves extract	0.57	79.75

In another research work, Hamidon *et al.* [51] evaluated the corrosion behavior of AA6061 alloy coated with silane films containing methanolic and acetonic extracts of mangrove bark tannins in a 3.5 wt.% NaCl solution using polarization tests. The polarization results showed that the sol-gel coating containing 100 ppm of the above-mentioned acetonic extract could decrease the corrosion current density and corrosion rate and enhance the inhibition efficiency. In addition, the mangrove bark acetonic extract led to the simultaneous blocking of both anodic and cathodic sites.

Abdulmajid *et al.* [52] assessed the corrosion behavior of a mild steel substrate coated with sol-gel films containing methanolic and acetonic extracts of tamarind shell in a 0.5 M HCl solution using EIS and contact angle measurements. The EIS results showed that the sol-gel coating containing methanolic extract of tamarind shell exhibited better anti-corrosion performance compared to the sol-gel coating containing acetonic extract of tamarind shell. In addition, the contact angle measurement results showed that the sol-gel coating became more hydrophobic in the presence of methanolic extract, and the contact angle of the water droplet reached θ=107.64°. The performance mechanism of this inhibitor can be described as follows (Schematic 2): At first, adsorption occurred through electrostatic interaction between inhibitor cations and Cl^- ion adsorbed on the metal surface. Therefore, the metal complex was formed from Fe^{2+} and the inhibitor. Then, these complexes could connect to the mild steel surface through Van der Waals forces, create a physical barrier between the corrosive environment and the substrate, and inhibit corrosion [53].



Schematic 2. Inhibition mechanism of tamarind shell extract in 0.5 M HCl on mild steel [53].

Sheydaei *et al.* [54] synthesized anti-corrosion hybrid nano-pigments based on CT and sodium montmorillonite nanoclay (Na^+-MMT), followed by dispersing them (1.5 and 3 wt.%) in a silanol matrix. They studied the anti-corrosion performance of the coatings in a 3.5% NaCl solution after immersing them for 72 hours by the EIS test. The results showed that the presence of sol-gel coatings containing 3 wt.% CT-MMT nano-pigment, charge transfer resistance, coating resistance, and inhibition efficiency were increased to 5106 $\Omega.cm^2$, 687 $\Omega.cm^2$, and 86%, respectively. Compared with pure samples and containing 1.5 wt.% CT-MMT, the resistance was better. The high anti-corrosion performance of CT-MMT nano-pigment was because of the flake-like structure of MMT and hydrophobic bioactive materials present in CT (Figure 3).

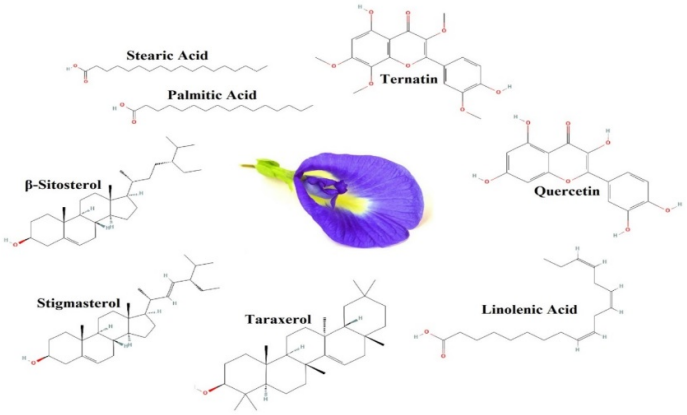
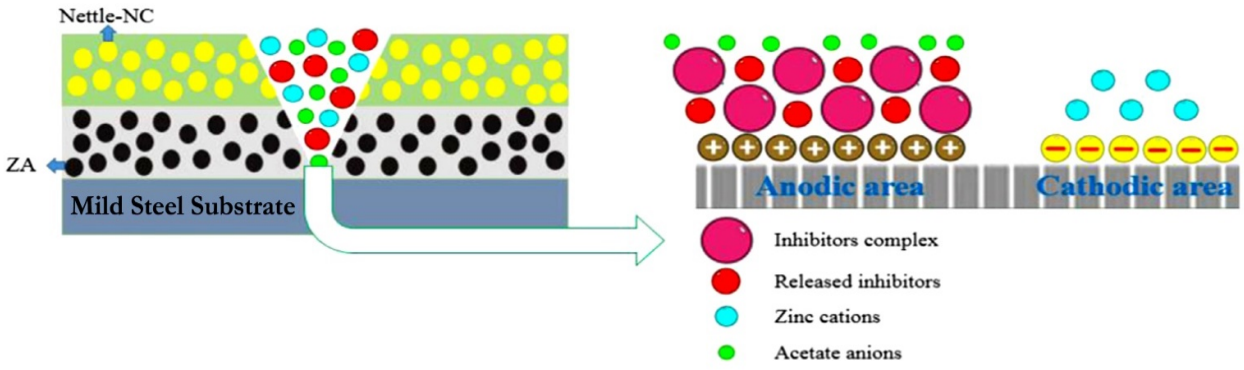


Figure 3. Molecular structure of the anti-corrosion important active ingredient of Clitoria Ternatea [54].

Ishak *et al.* [55] dispersed ethanolic and aqueous extracts of Curcumin in a silanol matrix and applied it on a steel coupons to evaluate the anti-corrosion behavior of coatings in 0.5M HCl using the EIS method. The capacitive loops in the Nyquist plots, which represents charge transfer resistance, was bigger for the sol-gel coating containing 100 ppm of ethanolic extract of Curcumin compared with that of other samples, which indicated the better durability of this coating. However, the active ingredients present in Curcumin contain benzene rings and oxygen atoms, through which they could exchange electrons with the steel surface and were surface chemisorbed and blocked anodic and cathodic active sites. On the other hand, the sol-gel coating containing 100 ppm of the ethanolic extract of Curcumin could increase the hydrophobicity of the surface to θ=100.2°.Izadi *et al.* [56] encapsulated the Nettle extract eco-friendly inhibitor during a layer-by-layer process. Fe_3O_4 nanoparticles were first considered the core, followed by the deposition of a layer of polyaniline on the surface of Fe_3O_4. Then, the Nettle inhibitor was loaded on the surface of polyaniline, followed by coating the Nettle surface with a layer of polyacrylic acid. They also applied two layers of silane coating on the surface of the mild steel substrate. The first and the second layers contained zinc acetate and nano reservoirs containing the Nettle inhibitor. The corrosion protection performance of the scratched coating was evaluated in a 3.5% NaCl environment. As shown in Schematic 3, by scratching the coating, the Nettle extract was released from the reservoir and, along with the anion acetate, interacted with the products achieved from the dissolution of anodic regions (Fe^{2+}). On the other hand, zinc cation reacted with hydroxyl ions present in cathodic regions and blocked it, and induced active protection.

Izadi *et al.* [57] employed two layers of sol-gel conversion coatings to increase the adhesion of an organic epoxy coating to its substrate. This protection system consisted of three layers. At first, a sol-gel coating containing the zinc acetate inhibitor was applied as a primer by the immersion method on a mild steel substrate. Then, the sol-gel coating containing anti-corrosion nanocapsules loaded with the nettle inhibitor was applied on the primer as an intermediate layer by the same immersion method. Finally, after curing this bi-layer, the epoxy resin mixed with the polyamide hardener was used as the top coat (with a thickness of 100 μm) that was applied on this bi-layer using a film applicator. The salt spray test was used to compare the corrosion resistance of the coatings and the results showed that the epoxy coating applied alone and as a single layer on the mild steel was severely degraded after 90 days. Moreover, blisters and corrosion products surrounded the scratch and covered the whole coating surface while in the three-layer system, as soon as a scratch was created in the coating, the acetate blocked the cathodic regions in the first layer of the inhibitor, the nettle was released from the nanocapsule in the second layer and blocked the anodic regions. The last layer, as a physical barrier, slowed down the diffusion of corrosive agents, and as a result, blisters and corrosion products were much less in this sample compared with those in the control sample.



Schematic 3. Anti-corrosion performance mechanism of Nettle extract released from nanoreservoirs in the scratched bilayer silanol coatings [56].

Izadi *et al.* [58] modified the surface of Na^+-MMT using an aqueous extract of Nette and used it as anti-corrosion nano-pigments in a silanol matrix to mitigate the corrosion of a mild steel grade in saline

environments. According to Bode plots and the absolute value of impedance at both low and high frequencies, it could be deduced that the sol-gel coating containing the above-mentioned nano-pigments exhibited a higher resistance than the pure sol-gel coating at all immersion times.

Mohamad Azran *et al.* [59] used silanol coatings containing 750 ppm of aqueous and ethanolic extracts of Mulberry to inhibit the corrosion of a low-carbon steel grade in a saline medium. The results of polarization and contact angle measurements showed that the sol-gel coating containing 750 ppm of the ethanolic extract of Mulberry exhibited inhibition efficiency about 85.57%. This indicated a mixed-type (anodic-cathodic) inhibition for this inhibitor and led to the higher hydrophobicity of the surface.

Santos *et al.* [60] dispersed garlic peel and cocoa shell powders with a mixture ratio of 2:1 in a silanol matrix and applied the dispersed mixture on carbon steel surfaces to evaluate the anti-corrosion performance of the coatings in a saline environment. The EIS results confirmed that the used green inhibitors led to the increased resistance of final silane coatings. In addition, the Tafel curve showed that the silane coating containing the inhibitor had a higher anti-corrosion potential compared with the pure silane coating.

Nikpour *et al.* [61] assessed the corrosion behavior of a grade of mild steel coated with silane films containing 100-400 ppm of Mentha longifolia extract in a 0.1 M NaCl solution. The electrochemical results showed that the sol-gel coating containing 200 ppm of the extract could play an effective role in the active protection of the coating and led to improved corrosion properties owing to containing important active ingredients such as Pulegone, Carvone, Cineole, and Menthol.

Nasr-Esfahani *et al.* [62] employed silanol coating containing rosemary extract to inhibit the corrosion of 304L stainless steel in a saline medium. Since Rosemarinic acid and tannic acid are the active ingredient of rosemary extract containing phenolic compounds, and these compounds can easily form complexes with bivalent and trivalent ions to create layers, which are adsorbed on the surface and act as a barrier between the metal surface and the corrosive solution to decrease the corrosion rate.

Ashassi-Sorkhabi *et al.* [63] investigated the surface preparation of Mg AZ91 alloy using a modified silane solution containing various wt.% (0.1, 0.5, 1, and 5) of Aspartic acid as a green inhibitor. They stated that adding 1 wt.% Aspartic acid to the silane solution led to an enhancement in the inhibition properties of the silane film along with a decreased corrosion rate of the metal surface compared with the absence of the modified silane solution. The reason was that the presence of three active sites in the Aaspartic acid structure allows the inhibitor to be adsorbed on the metal surface and protect the Mg surface against the corrosive medium.

In another study, Ashassi-Sorkhabi *et al.* [64] modified the surface of Na^+-MMT nanoparticles with an amino acid of the L-methionine type. They dispersed it as an anti-corrosion nanopigment within a silanol matrix and then applied it on Mg AZ91 alloy. Ultimately, the corrosion resistance of the coatings was evaluated in a 3.5% NaCl environment. The results showed that due to a synergistic effect, the sol-gel coating containing MMT-methionine anti-corrosion nanopigment exhibited better corrosion protection performance compared with the sol-gel coating without the aforementioned nanopigment.

Ashraf *et al.* [65] incorporated TiO_2 nanoparticles and Cystine green inhibitor in a silanol matrix and applied the product on the surface of Mg AZ91 alloy to evaluate the corrosion behavior of the coatings in a saline medium. The results showed that the sol-gel coating containing 0.5 wt.% Cysteine along with 1 wt.% TiO_2 could act as an effective protective system to be exposed to a saline aggressive medium for a long time.

Sfameni *et al.* [66] modified the surface of graphene oxide (GO) nanoparticles with Phytic Acid (PA) green inhibitor and used it as ananti-corrosion nanofiller in a silanol matrix to protect the surface of AQ-36 Al. The results of the salt spray test showed that the sol-gel coating PA-GO nanofiller could protect the surface of the Al substrate after 1300 hours presence in the salt fog cabin, so that no blistering and rusting or corrosion products were seen on the surface and in the scratch zone.

Gobara *et al.* [67] dispersed the extract of the powder of fish-scale collagen as a green inhibitor in a silanol matrix, applied it on AA2024 alloy, and investigated the corrosion behavior of the coatings in a 3.5% NaCl medium. The EIS results showed that the sol-gel coating, which did not contain the green inhibitor, could not exhibit long-term resistance, whereas the presence of the green inhibitor improved the anti-corrosion performance of the coating. Collagen has amide functional groups in its molecular structure. The nitrogen in the amide formed an insoluble complex (N-Al) with the aluminum surface through coordinative bonding, which caused the greatest possible inhibition properties. This complex, in turn, prevented the dissolution of the aluminum substrate by creating an insulating film, thus reducing the corrosion rate.

Balaji *et al.* [68] modified the surface of TiO_2 nanoparticles with Chitosan and incorporated it as an anti-corrosion compound in a silanol matrix to apply it on Al. They evaluated the anti-corrosion performance of the coatings in a 3.5% NaCl medium. The atomic force microscopy (AFM) images (Figure 4) of the coated samples after immersing in the electrolyte showed that the average surface roughness of the sol-gel coating with TiO_2 was about 9.41 nm, while that of the sample containing Chitosan-modified TiO_2 nanoparticles decreased to 5.37 nm. This confirmed an increase in the smoothness (uniformity) of the anti-corrosion film.

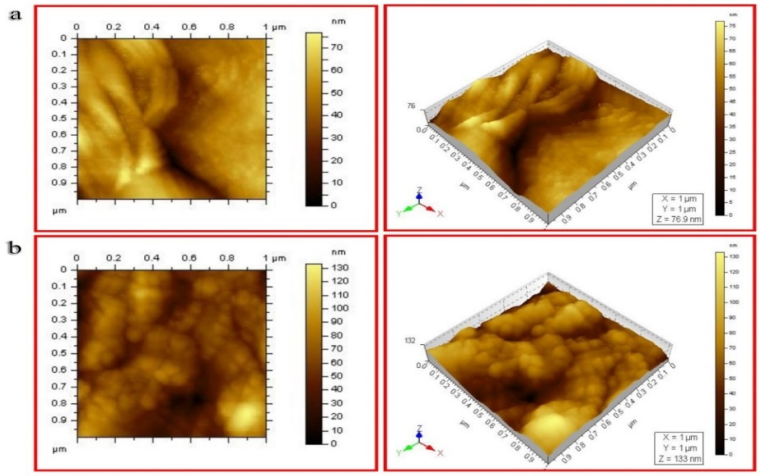


Figure 4. AFM images of the surface of Al samples coated with a) sol-gel coating containing TiO_2, b) sol-gel coating containing Chitosan-surface modified TiO_2 [68].

Khoshkou *et al.* [69] studied the corrosion behavior of a carbon steel grade coated with silane films containing various contents of Henna extract (1, 3, 6, and 9 wt.%) in a 0.1 M HCl medium. The results indicated that with the presence of the sol-gel coating containing 3 wt.% Henna extract, compared with other samples, both the corrosion current density and corrosion rate decreased significantly and reached to 0.048 $\mu A/cm^2$ and 0.02 MPY, respectively. Also, the corrosion potential shifted toward positive values, where the potential difference was < +85 mV. This indicated the ruling of the mixed inhibition (anodic-cathodic) mechanism of the Henna extract. On the other hand, the inhibition efficiency increased to 95.6%. One of the important active ingredients of Henna is lawsone, which plays a crucial role in the inhibition process, i.e., lawsone molecules reacted with the cations of the metal surface and formed Chelate and prevented the surface adsorption of Cl anion on the metal surface.

Motalebi *et al*. [70] investigated the anti-corrosion performance of 316L stainless steel by applying silane coatings containing different contents of Henna extract (0.012, 0.25, 0.05, 0.1 wt.%) in a simulated body fluid solution for biomedical applications using polarization tests. The results showed that the sol-gel coatings contained 0.1 wt.% Henna extract, with a polarization resistance of 500 $k\Omega.cm^2$ and an inhibition efficiency of 92.53%, exhibited the best anti-corrosion performance among all the samples. Also, the presence of 0.1 wt.% Henna extract could significantly reduce the porosity percentage of the coating surface to about 0.04%.

Hosseini *et al*. [71] incorporated the Nigella Sative extract along with zinc nitrate in a metal-organic framework (MOF), and used it as an anti-corrosion pigment in a silanol matrix. The anti-corrosion performance of the synthesized scratched coatings in a saline environment was evaluated. They found that ,as soon as the coating was scratched, the inhibitor species were released from the MOF and adsorbed on the surface of the scratched region to form the protective film. In addition, the corrosion protection performance of the steel surface coated with the silane coatings was improved significantly with the presence of the above-mentioned pigment.

Li *et al.* [72] employed sol-gel coatings containing Levodopa green inhibitor to protect Mg AZ31 alloy in a 0.1 M NaCl solution. The results showed that as soon as the silane coating containing the inhibitor was scratched, Levodopa, with the self-polymerization capability, filled the scratched regions and exhibited an excellent stability after 14 days of immersion in the saline environment. However, the silane coating that did not contain Levodopa lost its performance after three days of immersion.

Li *et al.* [73] used a sol-gel conversion coating containing the Catecholamine green inhibitor to

enhance the adhesion and protection performance of a Water-Based Polyurethane (WBPU) coating applied to an Mg AZ31 substrate because the WBPU coating could not be applied solely on the mentioned substrate due to the hydrogen evolution reaction and the occurrence of coating delamination. The results revealed a significant increase in the adhesion and interlayer cohesion, and the bilayer adhesion to the substrate from 1.49 MPa to 2.75 MPa. On the other hand, the EIS results showed that the WBPU coating applied on the sol-gel coating containing the inhibitor exhibited a resistance of about $1.7x10^7$ $\Omega.cm^2$ after immersing for 120 days in a 3.5% NaCl solution. Nonetheless, the WBPU coating that was applied on the sol-gel coating without the inhibitor after the same immersion time exhibited a much lower resistance of about $4.9x10^4$ $\Omega.cm^2$, which indicates the active protection of the Catecholamine inhibitor.

In another investigation, Li *et al.* [74] used a sol-gel coating containing Cathechol (CA) and Lysine (Lys) green inhibitors with a thickness of about 9 μm to protect Mg AZ31 alloy in a 0.1 M NaCl environment. The EIS results showed that the presence of 4 mg/ml of CA/Lys inhibitors in the silanol matrix led to an increase in the corrosion resistance of the coating after 18 hours of immersion in the saline solution. However, the corrosion resistance of the sol-gel coating without the above-mentioned inhibitors decreased significantly after immersion for 3 days and lost its performance.

Rodriquez-Alonso *et al*. [75] used L-Cysteine amino acid as the corrosion inhibitor in a silanol matrix to protect Mg AZ61 alloy in a saline environment. The results indicated that the presence of L-Cysteine in the silanol matrix led to excellent inhibition performance in the coating. The performance mechanism of L-Cysteine can be described as follows: This inhibitor contains functional groups such as carboxyl, amine, and thiol in its molecular structure. Due to having a pair of non-bonding electrons, the oxygen atom in carboxyl, nitrogen atom in amine, and sulfur atom in thiol exchanged electrons with the MgAZ61 surface and were absorbed on its surface physically, forming a protective film and prevented the corrosive agents from reaching the substrate.

Tang *et al.* [76] loaded the Phytic Acid (PA) green inhibitor and the azole benzotriazole inhibitor (BTA) on SiO_2 nanoparticles using polyallylamine hydrochloride through the layer-by-layer technique. They utilized this as an anti-corrosion nanocapsule in a silanol matrix to protect mild steel in a 3.5% NaCl solution and evaluated its performance using EIS. The Nyquist and Bode plots clearly indicated (Figure 5a and 5b) that the silane coating containing the PA +SiO_2 nanocapsule, compared with the silane coating containing the BTA + SiO_2 nanocapsule and the silane coating without the nanocapsules, exhibited greater charge transfer resistance and higher absolute impedance values (at lower frequencies) after immersing for 5 hours in the saline solution, indicating favorable corrosion inhibition performance of this coating.

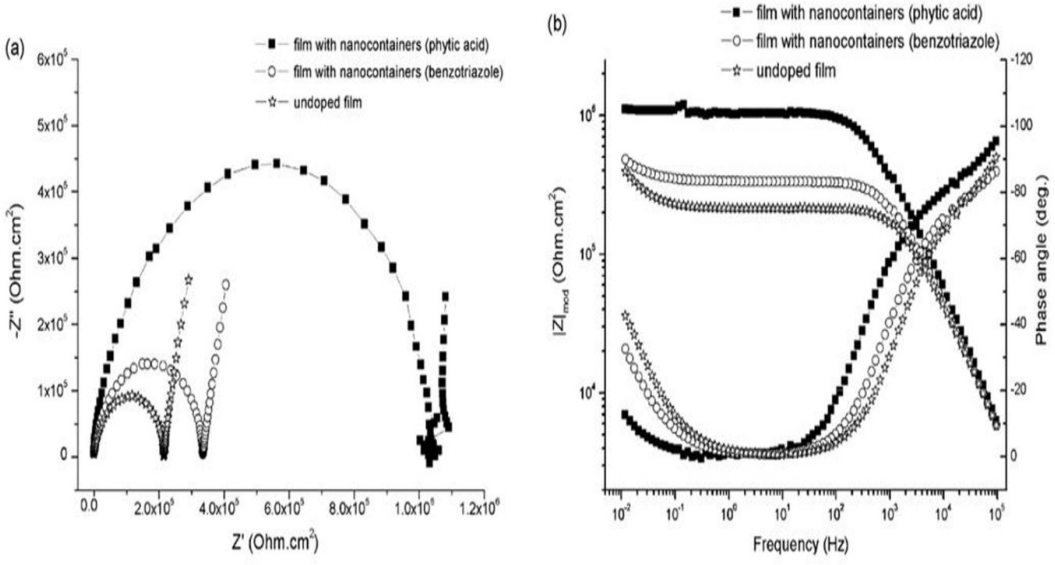


Figure 5. a) Nyquist and b) Bode plots of the sol-gel coatings with and without the anti-corrosion nanocapsules [76].

Upadhyay *et al.* [77] employed sol-gel coatings containing green inhibitors such as diazolidinyl urea (DZU), Betaine (BET), quinaldic acid (QDA), and Dopamine hydrochloride (DOP) to protect Mg AZ31 alloys in a 3.5% NaCl environment, The results demonstrated that among the aforementioned inhibitors, QDA could cover the surface micro- and nano-porosities of the silanol matrix, preventing the penetration of corrosive agents (chloride anions) to the metal surface. This led to an enhancement in inhibition efficiency as well as a reduction in the corrosion rate

3. Conclusion

Silane based sol-gel coatings can be used for protection of metals and alloys ,as replacement of toxic Chromate conversion coatings. However, uaing of green extracts of plants can be increasd the efficiency of these coatings. Several mechanisms have been mentioned regarding the causes of the increase in anti-corrosion performance due to the presence of these plant inhibitors, among which the surface adsorption ,the occupation of corrosion sites by plant agents and the prevention of the passage of corrosive agents due to the filling of micropores are important.With attention to the efficiency and acceptable performance of these materials in various corrosive conditions and also their compatibility with the environment, it is expected that, in the future, a wider application will be found for these materials in the structure of sol gel coatings.

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