

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Green Methods for Corrosion Control

---

Khadija M. Emran, Shimaa M. Ali and  
Hamedh A. Al Lehaibi

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.72762>

---

## Abstract

Corrosion of metals is a serious environmental problem. Most of the corrosion inhibitors are synthetic chemicals that are hazardous to environments and expensive. Today, there has been an increasing search for green corrosion inhibitors, due to the toxicity of some inhibitors. Green corrosion inhibitors are biodegradable and free of heavy metals or other toxic compounds. There is an intensive effort underway to develop new plant origin corrosion inhibitors for metal subjected to various environmental conditions. Salts of rare earth elements can be also used as inorganic alternative nontoxic corrosion inhibitors. Sol-gel coatings can be recommended as green protective films for metal corrosion. The origin of sol-gel process, its advantages and limitations, and the type of coating method are presented in this chapter, as well as a brief summary of recent literature concerning the use of hybrid inorganic-organic sol-gel and nanostructured sol-gel protective coatings for metal corrosion in different media.

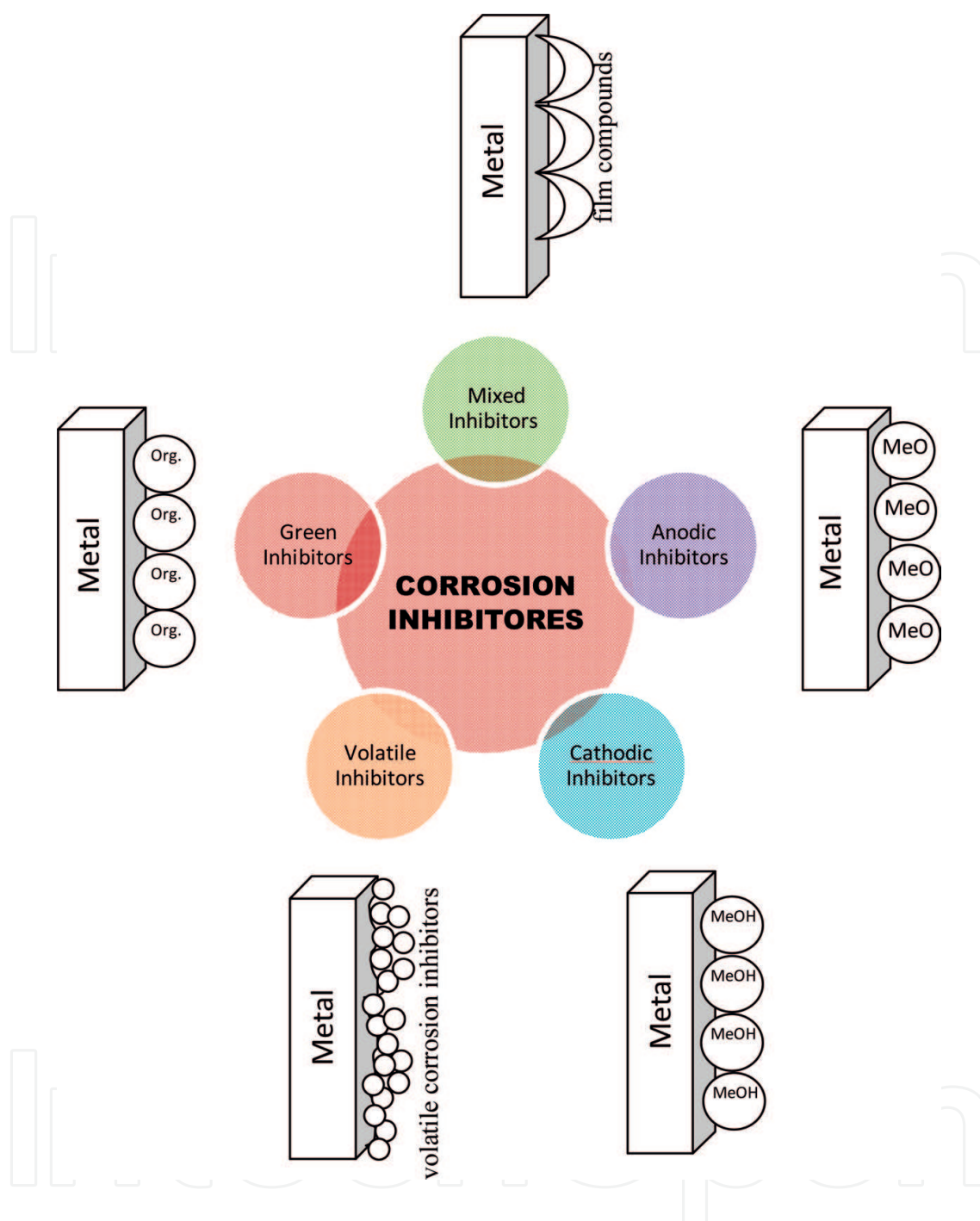
**Keywords:** corrosion, green inhibitors, plant extracts, protective films, sol-gel process

---

## 1. Introduction

Metallic materials are the pre-eminent important materials used in structural and decorative applications and are still the most widely used group of materials particularly in both mechanical engineering and transportation industry [1]. The usefulness of these metals is constrained by one common problem known as corrosion. The corrosion, deterioration or destruction of metals is an unavoidable but controllable process by means of optimum corrosion management practices.

One of the established methods of protection against corrosion damage is the use of corrosion inhibitors. A corrosion inhibitor is a solid or liquid substance when added in a suitable



**Figure 1.** Types of corrosion inhibitors and their possible mechanisms.

concentration to an environment reduces the corrosion rate by reducing the corrosivity of the environment [2]. Corrosion inhibitors can be divided into two broad categories: passive film formation and adsorbing on the metal surface. In both cases, a barrier was created on the surface that prevents access of corrosive agents to the metal surface [3]. Corrosion inhibitors have always been considered to be the first line of defiance against corrosion. According to their action, there are four types of corrosion inhibitors: anodic inhibitors, cathodic inhibitors, mixed inhibitors and volatile corrosion inhibitors (VCI). Anodic inhibitors usually cause a

large anodic shift of the corrosion potential to reach passivation region by forming a protective oxide film on the metal surface. Cathodic inhibitors act by selectively precipitating on cathodic areas. This blocking of cathodic areas limits the diffusion of reducing species to the surface. Also, they can slow the cathodic reaction itself. Mixed inhibitors work by reducing both the cathodic and anodic reactions by forming film compounds that block both anodic and cathodic sites. Volatile corrosion inhibitors (VCI) compounds have sufficient vapor pressures to allow vaporization and subsequent condensation and adsorption on metal surfaces as a monomolecular passivating layer and control the corrosion attack. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine, and hexamethylenamine are used [4–6]. When choosing an inhibitor, there are several factors including cost and amount, easy availability and, most importantly, safety to environment need to be considered.

Another newly established method for corrosion control, covered in this chapter, is employing green sol-gel coatings. Sol-gel science, early discovered in the 1800s and studied in detail since the 1930s, has attracted researchers' interest to a great extent. As inorganic gels can be formed at low temperatures and converted to glasses without the need of melting process.

Sol-gel materials encompass a wide range of inorganic and organic-inorganic hybrid materials which share a common preparation strategy: the sol-gel process. It involves the generation of colloidal suspensions, "sols" [7]. During the process, inorganic networks grow by sol (colloidal suspension) formation then the sol undergoes gelation (gel). Metal alkoxides, mainly alkoxysilane, are most commonly used precursors for the sol synthesis as they react easily with water. Deposition of a protective layer can be a proper way to enhance the corrosion resistance of a substrate. This can be done by a variety of ways such as chemical [8] or physical [9] vapor deposition, laser cladding [10], thermal spraying [11] and sol-gel [12]. Upon comparison, the sol-gel method has advantages of being simple, deposition can be achieved at low temperatures. The low-temperature reaction makes it possible to incorporate organic modifiers into the inorganic network, thus providing new materials which have combined reactants' properties [13–15]. In conclusion, types of corrosion inhibitors with their possible mechanisms are summarized in **Figure 1**.

## 2. Green inhibitors

Green corrosion inhibitors or "eco-friendly inhibitors" are biodegradable compounds and do not contain heavy metals or other toxic compounds. They are biocompatible with nature. Similar to the general classification of "inhibitors," "green inhibitors" can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

### 2.1. Organic green inhibitors

The organic green inhibitors are the quinine, alkaloids, phenol, phenylpropanoid flavonoids, organic acid and other natural products obtained from natural sources like plants. It also includes synthetic compounds with negligible toxicity. Herein, plant extracts, gums, drugs

and oils have been considered as green corrosion inhibitors. The use of wastes from plants as corrosion inhibitors can be another way of extending the beneficial use of these plants and so enhance municipal waste management. Some of the notable developments on organic green inhibitors, especially plant extracts, are discussed here.

Aquatic plants contain some organic compounds that provide definite physiological actions on the human body and these bioactive substances include alkaloids, terpenoids, steroids, phenolic compounds, tannins and flavonoids and most of them are known to have corrosion inhibition efficiency.

Plant material extracts contain many active principles. They contain polar or hetero atoms such as S, N, O, P and aromatic rings, favoring the adsorption by donor-acceptor interaction between  $\pi$  electrons of donor atoms S, N, O, P and aromatic rings of inhibitors, and the vacant d-orbitals of metal surface atoms [16]. Because of adsorption of inhibitor molecules on the metal surface, protective film is formed that isolates the metal from the aggressive environment. Thus, corrosion is controlled.

Large numbers of organic extracts of plant materials have been used to prevent a variety of metals such as mild steel [17–28], various types of steel [29, 30], cast iron [31] aluminum and its alloys [32–34], zinc and its alloys [35–38], copper [39–41], nickel [42, 43] and tin [44, 45].

According to corrosive medium, extracts of plant materials have been used to prevent corrosion of metals in various medium. Most studies were conducted in acidic medium [31] than in basic [34] and neutral medium [35]. Different parts of plants that include roots, leaves, bark, flowers and fruits (shell, juice and seed) were used to reduce the corrosion. Many methods have been employed such as hydrogen evolution, weight loss method, thermometric methods, electrochemical studies and so on to evaluate corrosion inhibition efficiencies of inhibitors extracted from plants. The protective film has been analyzed by various surface analyses techniques such as fourier-transform infrared spectroscopy (FTIR) spectroscopy, UV-visible spectroscopy, scanning electron microscope (SEM), energy dispersive X-rays analysis (EDXA) and atomic force microscope (AFM).

Overtime, plants extracts have been used as corrosion inhibitors, alone or in combination with other inhibitors. The mixture of plants extracts shows better inhibition efficiency than individual members, which is called synergistic effect. Many additives have been used to improve the inhibition efficiency of plant extracts. For example  $Zn^{2+}$ , methylene dichloride, n-butanolic extract [46–51], KI [22, 52, 53], KCl, KBr [54–58], formaldehyde, diethylamine [59], ethyl acetate [60], and dimethyl sulfoxide [61].

### *2.1.1. Advantages and limitations of plant extract use*

Plant extracts are environmental friendly, nontoxic, low cost and easily biodegradable. Despite these features as environmentally acceptable, readily available and renewable source for a wide range of green inhibitors, they have some main drawbacks. The drawback of most reports on plant extracts as corrosion inhibitors is that the active ingredient has not been identified. Also, they are easily biodegradable and contaminated by microorganisms which limit the storage of liquid extract or even the solid extract for a long

term. According to a number of research works published in the last two decades on these groups of products, plant extracts occupy the first place by 68% for aluminum and its alloys corrosion inhibition (**Figure 1**) [16].

It is important to consider the type of plant extract (water, alcohol, acid). The quality of the ingredients present in plant extracts consequently affects the effectiveness of the extracts in inhibiting corrosion.

### 2.1.2. Mechanism of action of green inhibitors

Many theory mechanisms have been put by several workers. These mechanisms are being summarized in the following points:

- Organic substances may form onium ions in acidic solutions and are adsorbed on the cathodic sites of the metal surface.
- Organic substances in some plant extracts contain an alkaloid berberine which has a long chain of aromatic rings, an N-atom in the ring, and O atoms as H atoms substitution. The free electrons on the O and N atoms form bonds with the electrons on the metal surface.
- Allyl propyl disulfide, which is an S-containing unsaturated compound, exists in many plant extracts and affects the potential cathodic process of metals such as steel.
- Pyrrolidine in neutral and alkaline aqueous media ionizes, and the N-atom acquires a negative charge, and the higher charge on free electrons on N results in stronger bond between the pyrrolidine and metals.
- The N-atom in alkaloid ricinine is in the ring attachment of the  $-OCH_3$  favoring the interaction with the metal surface.

## 2.2. Inorganic green inhibitors

Green inhibitors display substantially improved environmental properties as compared to the existing inhibitors whose toxic level is above 50%. The action of inorganic green inhibitors is to improve the passivity of a metal and alloys. According to that, most inorganic green inhibitors are compounds or metal ions that have more positive redox potential than the metal surface and also improve the passivity of a metal by favoring the electropositive metal to be reduced and deposited on the surface. There are several inorganic salts that are less toxic than chromate inhibitors. Among the metals used for corrosion inhibitor are: mercury (Hg) [62], lanthanide salts (La) [63, 64], samarium (Sm) [63], cerium salts [64–68] and platinum (Pt) [69] (**Table 1**).

Moreover, there are inorganic anions providing passivation protection to metal surfaces through their incorporation into the oxide layer; the most widely used of these are: chromate ( $CrO_4^{2-}$ ), nitrate ( $NO_2^-$ ), molybdate ( $MoO_3^-$ ), phosphate ( $H_2PO_3^-$ ) and silicates [70].

Inhibitor medium	Metal and medium	Reference
La(NO <sub>3</sub> ) <sub>3</sub> , Sm(NO <sub>3</sub> ) <sub>3</sub> , LaCl <sub>3</sub> , SmCl <sub>3</sub>	AISI 434 SS in NaCl	[65]
CeCl <sub>3</sub>	Aluminum alloy in NaCl	[66]
CeCl <sub>3</sub>	AA5083 alloy and galvanized steel in NaCl	[67]
CeCl <sub>3</sub>	Sn-Fe alloy in NaCl	[68]
CeCl <sub>3</sub>	AA6964 Al-Zn alloy in NaCl	[69]
(Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O)	Tinplate in citric-citrate	[70]
Tryptamine (TA)	ARMCO iron in 0.5 M deaerated H <sub>2</sub> SO <sub>4</sub>	[71]

**Table 1.** Model inorganic green inhibitors.

### 2.2.1. Mechanism of inhibitors

In neutral and alkaline media, the oxygen reduction reaction is more favored as cathodic reaction Eq. (1).



The cathodic reaction in Eq. (1) of oxygen reduction increases local pH by generating a high concentration of OH<sup>-</sup> ions. These OH<sup>-</sup> ions formed over the cathodic sites react with metal ions present in the solution according to Eqs. (2) and (3).



These reactions give rise to the precipitation of lanthanide oxides or hydroxides over cathodic sites and block them. Blocking the cathodic active sites by these compounds decreases the available cathodic current and therefore reduces the corrosion process.

### 2.3. Sol-gel protective coatings

The sol-gel process involves several stages as shown in **Figure 2** [71]:

- Hydrolysis of the precursors with the formation of hydroxide species;
- Condensation with the formation of oxide species;
- Gelation with the formation of a “spanning cluster” yielding a network which entraps the remaining solution;
- Ageing with the formation of further crosslinks which change the structure in pore sizes and pore wall strengths;

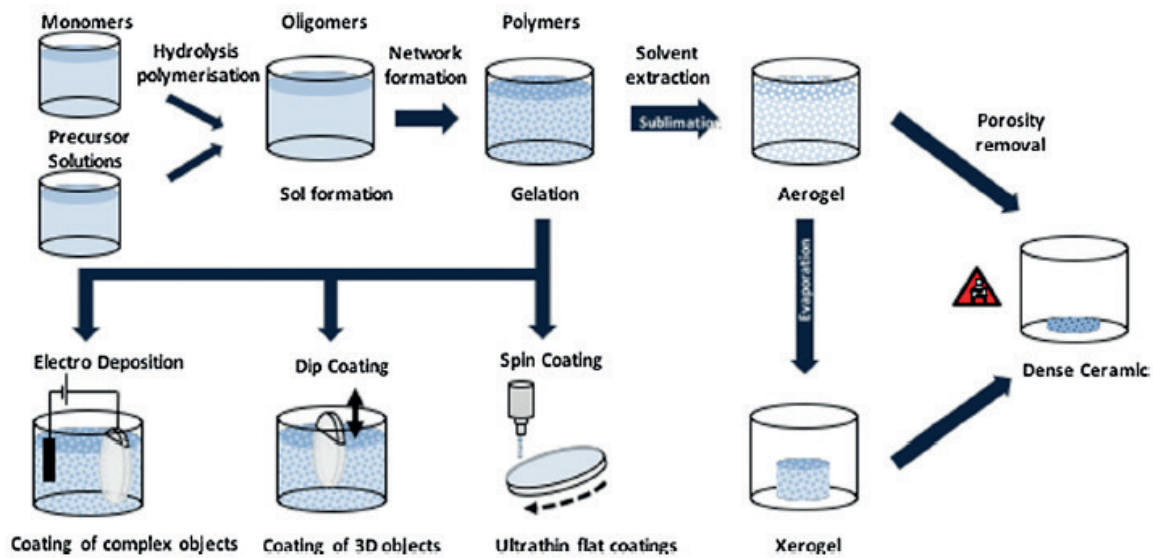


Figure 2. Sol-gel process and possible coatings routes [71].

- Drying with the loss of solvent and the associated development of capillary stress; and
- Densification with the collapse of the open structure and formation of a dense material.

### 2.3.1. Advantages of sol-gel coatings

There are many advantages using sol-gel coatings, and some of the most important features are listed as follows [72]:

1. Excellent chemical stability.
2. Enhanced corrosion resistance for metal substrates.
3. An environmentally friendly technique of surface protection “green coating” (Replacement of toxic pretreatments and coatings which have traditionally been used for increasing corrosion resistance of metals).
4. Sol-gel process can be achieved at room temperature, thus degradation or thermal volatilization of incorporated organic species can be avoided.
5. Cast coating is possible without the need for complicated processes. Since used precursors are in the liquid form.
6. These are economical and fast and can be used for all types of surfaces to control the size and porosity of the resultant thin film.
7. Precursor such as metal alkoxides and mixed alkyl/alkoxides are frequently volatile and easily purified to very high levels using techniques developed for the microelectronics industry.



8. Highly porous materials and nanocrystalline materials may be prepared in this way.
9. Since liquid precursors are used, it is possible to cast ceramic materials in a range of complex shapes and to produce thin films or fibers as well as monoliths, without the need for machining or melting.
10. Hybrid silica sol-gel coatings are of growing interest as corrosion protection materials for metals as these coatings have good adhesion to metallic substrates and offer good corrosion resistance by combining properties of organic polymers and properties of ceramics [73, 74].

### 2.3.2. Limitations of sol-gel coatings

Common sol-gel limitations can be summarized in the following points [7]:

- Precursors are sensitive to moisture;
- Precursors are expensive, limiting large-scale manufacture;
- The process is time-consuming; and
- The dimensional change can occur on densification, shrinkage, cracking on drying, require attention.

### 2.3.3. Applications of sol-gel coatings

#### 2.3.3.1. Spin-coating

Spin coating has been used for several decades for the application of thin films. In this process, a small drop of the coating material is loaded onto the center of a substrate, which is then spun at a controlled high speed. In the spin-coating process, the substrates spin around an axis which should be perpendicular to the coating area. As a result, the coating material spreads forming a thin film on the surface. Film properties, such as thickness, will be affected by several factors such as: viscosity, surface tension, drying ease and the rotation speed [75].

#### 2.3.3.2. Dip coating

This method can be achieved by immersing a metal into a tank containing the coating material then withdrawing it to obtain a homogeneous film. Compared to the spin coating, the film obtained by dip coating is thicker [76].

#### 2.3.3.3. Spray coating technique

Spray coating technique is a process in which molten or softened particles are applied by impact onto a substrate to produce a coating. This is done by using a vessel under pressure that pumps loading through a spray gun. The operation occurs in a totally enclosed system to minimize radiation of coating and product wastes [75].

#### 2.3.3.4. Flow-coating process

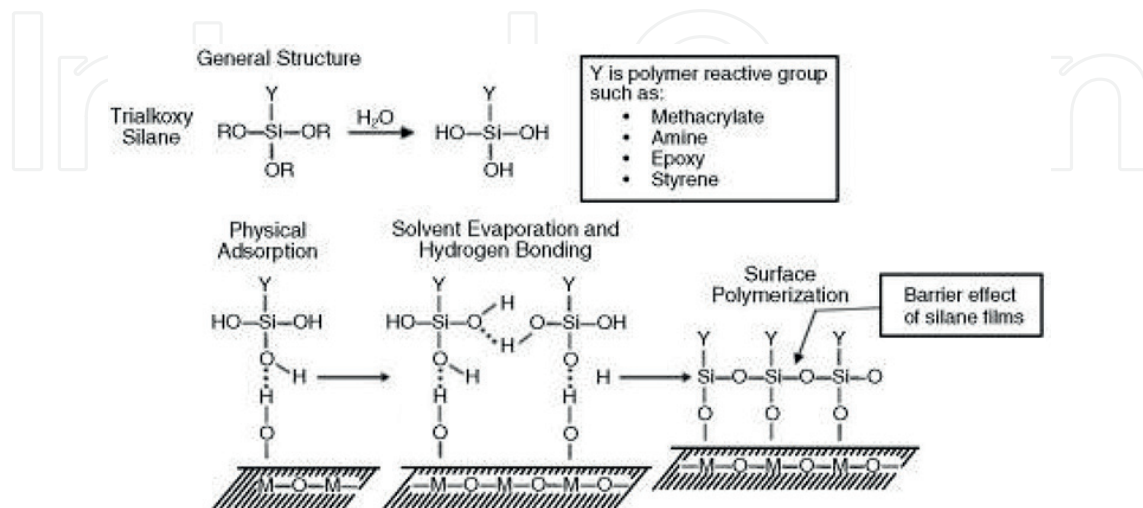
In flow-coating process, the liquid-coating system is more or less poured over the substrate to be coated. The coating thickness depends on the angle of inclination of the substrate, the coating-liquid viscosity and the solvent evaporation rate. Thus, nonplanar large substrates can be readily coated [76].

There are many studies, investigate the ability of the sol-gel method to protect metals from corrosion, will be discussed in the following section.

#### 2.3.4. Corrosion control by using sol-gel coatings

Sol-gel-coated layers can exhibit good adhesion to the metal substrate due to the formation of chemically adsorbed M—O—Si bonds, as shown in **Figure 3**, resulting in a good anticorrosion performance. The following section summarizes a brief collection of recent and novel studies concerning the use of sol-gel coatings for corrosion control in metals and metal alloys.

Al-Cu-Fe alloy powder, a highly effective lubrication-oil additive, was coated by conventional sol-gel method employing tetraethyloxysilane (TEOS) as the precursor for purpose of improving its corrosion resistance [78]. The sol-gel method was modified by employing ultrasound to study the effects of both ultrasonic power and irradiation time on the coating process. The coated powder had a high corrosion resistance in the acid media of pH 1. Vignesh et al. used 3-mercaptopropyltrimethoxysilane (MPTMS) as the precursor for sol-gel coating on aluminum metal [79]. The results brought to light the potential of MPTMS as a precursor in the development of sol-gel coating over Al metal. The FTIR studies revealed the mechanism of the gelation of MPTMS and the formation of Si—O—Al linkage on the metallic substrate. The formed film was found to be stable up to 350°C as evident from thermogravimetric analysis. The X-rays diffraction (XRD) data also confirmed the formation of sol-gel coating on the metal surface. The electrochemical impedance spectroscopy (EIS) analysis of MPTMS coating on aluminum showed the inhibition of the corrosion by acting as a barrier to the electrolyte by impeding its contact with the metal



**Figure 3.** Bonding of silane precursors to the metallic surface [77].

surface. The polarization studies revealed that MPTMS sol-gel coating on aluminum blocked the anodic sites of the metal and thereby reduced the metal dissolution into the electrolyte solution, while SEM confirmed the protective nature of the MPTMS coating over aluminum substrate.

Seifzadeh et al. have studied the novel and crack-free nanocomposites based on sol-gel process for corrosion protection of copper [80]. The best results have been obtained after addition of sodium montmorillonite nanoclay at 0.01% concentration. Also, the phenyltrimethoxysilane sol-gel coating becomes more hydrophobic after addition of nanoclay at low concentrations (0.01 and 0.1%). Results indicated that phenyltrimethoxysilane coating provided a high protection from corrosion when compared with copper substrate. The addition of nanoclays resulted in a crack-free sol-gel coating and enhanced protective properties of the coating. A conversion coating was formulated and applied on mild steel prior to sol-gel  $\text{Al}_2\text{O}_3$  coating to improve the corrosion resistance of mild steel reported by Tiwari et al. [81]. The comparison was made between conversion coated and conversion followed by sol-gel  $\text{Al}_2\text{O}_3$ -coated mild steel. The modified surfaces, produced by conversion coating and conversion followed by sol-gel  $\text{Al}_2\text{O}_3$  coating, were characterized by XRD and X-ray photoelectron spectroscopy (XPS) and SEM. The corrosion resistance of the sol-gel coating was evaluated in 3.5 wt.% NaCl solution by one-component plasma (OCP), polarization and EIS measurement. By examining the surface morphology of solgel after  $\text{Al}_2\text{O}_3$  coating ( $0.36 \pm 0.03 \mu\text{m}$  thickness), the surface seems smooth with featureless topography. The sol-gel  $\text{Al}_2\text{O}_3$  coating is free from any defect and is homogeneous. No change in the coating morphology is seen after long immersion (240 h) in 3.5 wt.% NaCl solution and repeated anodic polarization. The conversion coating by using silica sol and aluminum oxyhydroxide followed by heat treatment at  $500^\circ\text{C}$  produced mild steel surface suitable for sol-gel  $\text{Al}_2\text{O}_3$  coating. The conversion coating formed a composite oxide containing  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  on the surface. The  $\text{Al}_2\text{O}_3$  coating is amorphous and stable for 240 h in 3.5 wt.% NaCl solution. The protective nature of a coating composed of a hybrid sol-gel and a phosphate-based conversion layer for magnesium-alloy corrosion was investigated by Li et al. [82]. The sol-gel coating itself has a good anticorrosion performance; however, the presence of an additional conversion layer highly enhanced the protection ability. The corrosion process was examined by EIS which showed that the presence of the conversion layer increases the system resistance upon immersion in a 0.05 M NaCl solution, as compared to the single sol-gel coating. Hassannejad et al. studied the effects of cerium doping on corrosion resistance of amorphous silica-titania coating [83]. Potentiodynamic polarization and EIS spectroscopy have been used to study the corrosion behavior of composite coating in 3.5% NaCl solution. Results showed that ceria doping presented higher corrosion resistance than undoped silica-titanium composite layer and also the passive region of the doped films in potentiodynamic tests expanded with respect to undoped silica-titanium composite layer. The film corrosion resistance is noticed due to the inhibition action of cerium. There is a critical cerium concentration, above it cracking occurs, this can be related to the high expansion coefficient of cerium oxide. Mei et al. examined the effects of cerium salts on corrosion behaviors of Si-Zr hybrid sol-gel coatings [84]. The Si-Zr hybrid sol-gel coatings on aluminum substrate were prepared through hydrolysis and condensation of GPTMS and zirconium(IV) n-propoxide, used as inhibitors for corrosion, three types of cerium salts ( $\text{Ce}(\text{NO}_3)_3$ ,  $\text{CeCl}_3$  and  $\text{Ce}(\text{CH}_3\text{COO})_3$ ) were doped into the sol-gel coatings. The corrosion process is retarded

by the addition of cerium salts due to its self-healing abilities. The sol-gel coating doped with  $\text{Ce}(\text{CH}_3\text{COO})_3$  has the highest corrosion resistance due to the utilized hydrolysis and condensation provided by  $\text{CH}_3\text{COO}^-$ . Ali et al. investigated the corrosion behavior of zinc substrates in 0.5 M HCl solution pretreated with various mono- and bilayered sol-gel films [85]. It was found that the bilayer morphology is similar to that of the outer layer. The protection abilities of mono- and bi-films are discussed in terms of film structure and functionality. The hybrid bifunctional organic coating (i.e. contains two different organic functional groups) is more efficient than monofunctional one. Hybrid monolayer has higher protection ability than its corresponding bilayers. Rahimi et al. reported the corrosion- and wear-resistance characterization of environmentally friendly sol-gel hybrid nanocomposite coating on aluminum. The hybrid nanocomposite coatings have been synthesized from TEOS and GPTMS precursors. The multilayer coatings were prepared by dip-coating technique. Effects of different layers on corrosion and wear resistance were studied. The coatings were found to increase the electrochemical corrosion resistance of aluminum. The maximum corrosion resistance properties, as determined by using electrochemical cyclic polarization testing, were observed for triple sol-gel-coated layer. The results suggested that crack-free plain organic-inorganic hybrid nanocomposite coatings with Si-O-Si structure backbone and  $\text{CH}_2$  group incorporated into a silica network could be obtained on aluminum substrate by sol-gel synthesis. Atomic-force microscopy height images showed smooth nanostructural surface with root mean square less than 4 nm and the existence of organic and inorganic components in coatings could be a result of excellent wear and mechanical properties. Shi et al. studied that the sol-gel coatings were prepared using GPTMS and TEOS as precursors, diethylenetriamine as curing agent. Inhibition effect of 2-methyl piperidine on magnesium alloy in 0.005, 0.05 and 0.5 wt.% NaCl solution is investigated.

The protection abilities of unmodified and modified GPTMS-VTMS sol-gel films with different Ti- and Al-alkoxides concentrations against zinc corrosion in 0.5 M HCl solution are reported by Ali et al. [85]. It was shown that the presence of the modifiers, either Ti or Al, facilitates the formation of the network structure and increases slightly the thermal stability of sol-gel materials. Weight-loss and electrochemical measurements proved that the highest protection ability of sol-gel coatings is assigned with low modifiers concentrations. The protection efficiency is increased from 69.2 to 96.2% and 95.8% upon modification with 0.005 M of Ti and Al modifiers, respectively. On the other hand, higher modifier concentrations may cause a galvanic corrosion which results in lower protection efficiency values. Corrosion inhibitors and nanoparticles can be added in the silane sol-gel network to improve corrosion resistance [86]. Balan et al. examined the effect of adding activated cerium nitrate nanoparticles into a coated sol-gel matrix on low-carbon steel substrates. Hybrid sol-gel films have been prepared from mixture of TEOS and GPTMS. Silica, alumina and their equimolar mixtures are used as nanoparticles with a concentration of 250 ppm. The SEM confirmed crack-free surface for prepared substrates with different pretreatments. Inorganic corrosion inhibitor was introduced into the coating via encapsulation in the nanoparticles reported by Tavandashti et al. [87]. Organosiloxane sol was prepared by mixing GPTMS, TEOS and isopropanol to obtain a sol with 75 mol.% organic content. The high corrosion-resistance performance of such coatings is due to the presence of encapsulated cerium nitrate corrosion inhibitor that can be released at

the defects within the coating, hindering the corrosion reactions at defective sites. Asadi et al. investigated the cloisite concentration effect on the protective performance of sol-gel coating, prepared from GPTMS, TEOS and methyltriethoxysilane on mild steel substrate [88]. The optimum concentration of nanoparticles was determined. The data indicated superiority of the hybrid film embedded with 1000 ppm of cloisite nanoparticles. Confirming the electrochemical data, FTIR spectra and water contact angles showed that the nanoparticles well dispersed in the silane film might improve barrier properties moreover, a good trend correlation was observed between the noise resistance and low-frequency *IZI* data. Naderi et al. studied the synergistic effect of incorporation of nanoclay along with cerium nitrate as a corrosion inhibitor into an eco-friendly silane layer consisting of GPTMS, TEOS and methyltriethoxysilane applied on pure Al [89]. EIS and polarization results showed that the high protective nature of film containing cerium is due to film deposition on cathodic regions, thus preventing entrance of aggressive species to the surface. FTIR spectra proved the presence of the inhibitor in the film structure. N-nanoparticles silane coating in the presence of cerium salt provided higher corrosion protection compared to the film with only incorporated nanoclay.

## Author details

Khadija M. Emran<sup>1\*</sup>, Shimaa M. Ali<sup>1,2</sup> and Hamedh A. Al Lehaibi<sup>1</sup>

\*Address all correspondence to: kabdalsamad@taibahu.edu.sa

1 Department of Chemistry, Collage of Science, Taibah University, Madinah, Kingdom of Saudi Arabia

2 Department of Chemistry, Collage of Science, Cairo University, Giza, Egypt

## References

- [1] Roberge PR. Handbook of Corrosion Engineering. Columbus, OH: McGraw-Hill Companies; 2000
- [2] Malik MA, Hashim MA, Nabi F, Al-Thabaiti SA, Khan Z. Anti-corrosion ability of surfactants: A review. International Journal of Electrochemical Science. 2011;6:1927-1948
- [3] Abd El-Lateef HM, Abbasov VM, Aliyeva LI, Ismayilov TA. Corrosion protection of steel pipelines against CO<sub>2</sub> corrosion—A review. Chemical Journal. 2012;2(2):52-63
- [4] Zhang D, An Z, Pan Q, Gao L, Zhou G. Comparative study of bis-piperidiniummethyl-urea and mono-piperidiniummethyl-urea as volatile corrosion inhibitors for mild steel. Corrosion Science. 2006;48(6):1437-1448. DOI: 10.1016/j.corsci.2005.06.007
- [5] Chen Z, Huang L, Zhang G, Qiu Y, Guo X. Benzotriazole as a volatile corrosion inhibitor during the early stage of copper corrosion under adsorbed thin electrolyte layers. Corrosion Science. 2012;65:214-222. DOI: 10.1016/j.corsci.2012.08.019

- [6] Belarbi Z, Farelas F, Singer M, Nešić S. Role of amines in the mitigation of CO<sub>2</sub> top of the line corrosion. *Corrosion*. 2016;**72**(10):1300-1310
- [7] Brinker CJ, Hurd AJ, Schunk PR, Frye GC, Ashley CS. Review of sol-gel thin film formation. *Journal of Non-Crystalline Solids*. 1992;**147-148**:424-436. DOI: 10.1016/S0022-3093(05)80653-2
- [8] Zheludkevich ML, Salvado IM, Ferreira MGS. Sol-gel coatings for corrosion protection of metals. *Journal of Materials Chemistry*. 2005;**15**(48):5099-5111
- [9] Wang H, Akid R, Gobara M. Scratch-resistant anticorrosion sol-gel coating for the protection of AZ31 magnesium alloy via a low temperature sol-gel route. *Corrosion Science*. 2010;**52**(8):2565-2570. DOI: 10.1016/j.corsci.2010.04.002
- [10] Makhlof AH, Tiginyanu I. *Nanocoatings and Ultra-Thin Films: Technologies and Applications*. New Delhi: Woodhead Publishing Limited; 2011
- [11] Attia SM, Wang J, Wu G, Shen J, Ma J. Review on sol-gel derived coatings: Process, techniques and optical applications. *Journal of Materials Science and Technology*. 2002;**18**(3):211-218
- [12] Brinker CJ, Clark DE. *Better Ceramics through Chemistry*. 3rd ed. Philadelphia, PA: Materials Research Society; 1988
- [13] Liang B, Wang G, Zhang B, Zhang X. Corrosion resistance of Al-Cu-Fe alloy powder coated with silica using an ultrasound-assisted sol-gel method. *Corrosion Science*. 2013;**73**:292-299. DOI: 10.1016/j.corsci.2013.04.018
- [14] Alvarez D, Collazo A, Perez C. The use of sol-gel film as pre-treatment for tinplate used in the canning industry. *Progress in Organic Coatings*. 2013;**76**(12):1819-1826. DOI: 10.1016/j.porgcoat.2013.05.023
- [15] Li YS, Ba A, Mahmood MS. An environmentally friendly coating for corrosion protection of aluminum and copper in sodium chloride solutions. *Electrochimica Acta*. 2008;**53**(27):7859-7862. DOI: 10.1016/j.electacta.2008.05.062
- [16] Xhanari K, Finšgarv M, Hrnčič MK, Maver U, Knez Ž, Seiti B. Green corrosion inhibitors for aluminium and its alloys: A review. *RSC Advances*. 2017;**7**(44):27299-27330
- [17] Chauhan LR, Gunasekaran G. Corrosion inhibition of mild steel by plant extract in dilute HCl medium. 2007;**49**(3):1143-1161
- [18] Okafor PC, Ikpi ME, Uwah IE, Ebenso EE, Ekpe UJ, Umoren SA. Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. *Corrosion Science*. 2008;**50**(8):2310-2317
- [19] Okafor PC, Ebenso EE, Ekpe UJ. *Azadirachta indica* extracts as corrosion inhibitor for mild steel in acid medium. *International Journal of Electrochemical Science*. 2010;**5**(7):978-993
- [20] Singh MR. A green approach: A corrosion inhibition of mild steel by *Adhatoda vasica* plant extract in 0.5 M H<sub>2</sub>SO<sub>4</sub>. *Journal of Materials and Environmental Science*. 2013;**4**(1): 119-126

- [21] Ji G, Shukla SK, Dwivedi P, Sundaram S, Prakash R. Inhibitive effect of *Argemone mexicana* plant extract on acid corrosion of mild steel. *Industrial and Engineering Chemistry Research*. 2011;**50**:11954-11959. DOI: 10.1021/ie201450d
- [22] Eduok UM, Umoren SA, Udoh AP. Synergistic inhibition effects between leaves and stem extracts of *Sidaacuta* and iodide ion for mild steel corrosion in 1M H<sub>2</sub>SO<sub>4</sub> solutions. *Arabian Journal of Chemistry*. 2012;**5**:325-337
- [23] Benali O, Benmehdi H, Hasnaoui O, Selles C, Salghi R. Green corrosion inhibitor: Inhibitive action of tannin extract of *Chamaerops humilis* plant for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. *Journal of Material and Environmental Science*. 2013;**4**:127-138
- [24] Mourya P, Sitashree B, Singh MM. Corrosion inhibition of mild steel in acidic solution by *Tagetes erecta* (Marigold flower) extract as a green inhibitor. *Corrosion Science*. 2014;**85**:352-363
- [25] Ji G, Anjum S, Sundaram S, Prakash R. *Musa paradisiaca* peel extract as green corrosion inhibitor for mild steel in HCl solution. *Corrosion Science*. 2015;**90**:107-117
- [26] Mathina A, Rajalakshmi R. Corrosion inhibition of mild steel in acid medium using *canna Indica* as green corrosion inhibitor. *Rasayan Journal of Chemistry*. 2016;**9**:56-66
- [27] Ibisi NE, Ihejirika AV. Inhibitory potentials of *Bamboosa vulgaris* leaves extract on corrosion inhibition of mild steel in 1M HCl solution. *Saudi Journal of Engineering and Technology*. 2017;**2**:211-218
- [28] Ogwo KD, Osuwa JC, Udoinyang IE, Nnanna LA. Corrosion inhibition of mild steel and aluminium in 1 M hydrochloric acid by leaves extracts of *Ficus sycomorus*. *Physical Science International Journal*. 2017;**14**:1-10
- [29] Faustin M, Lebrini M, Robert F, Roos C. Corrosion studies of C38 steel by alkaloids extract of a tropical plant type. *International Journal of Electrochemical Science*. 2011;**6**:4095-4113
- [30] Faustin M, Maciuk A, Salvin P, Roos C, Lebrini M. Corrosion inhibition of C38 steel by alkaloids extract of *Geissospermum laeve* in 1M hydrochloric acid: Electrochemical and phytochemical studies. *Corrosion Science*. 2015;**92**:287-300
- [31] Emran KM, Al-Ahmadi AO, Ahmed NM, Torjoman BA, Sheekh SN. Corrosion and corrosion inhibition of cast iron in hydrochloric acid (HCl) solution by cantaloupe (*Cucumis melo*) as green inhibitor. *African Journal of Pure and Applied Chemistry*. 2015;**9**,3:39-49
- [32] Ating EI, Umoren SA, Udousoro II, Ebenso EE, Udoh AP. Leaves extract of *Ananas sativum* as green corrosion inhibitor for aluminium in hydrochloric acid solutions, green. *Chemical Letters Review*. 2010;**3**:61-68
- [33] Fetouh HA, Abdel-Fattah TM, El-Tantawy MS. Novel plant extracts as green corrosion inhibitors for 7075-T6 aluminium alloy in an aqueous medium. *International Journal of Electrochemical Science*. 2014;**9**:1565-1582
- [34] Singh A, Ahamad I, Quraishi MA. *Piper longum* extract as green corrosion inhibitor for aluminium in NaOH solution. *Arabian Journal of Chemistry*. 2016;**9**:S1584-S1589

- [35] Abd-El-Naby BA, Abdullatef OA, Abd-El-Gabr AM, Shaker MA, Esmail G. Effect of some natural extracts on the corrosion of zinc in 0.5 M NaCl. *International Journal of Electrochemical Science*. 2012;7:5864-5879
- [36] Bright A, Michlin Ruphina Maragatham S, Malar vizhi I, Selvaraj S. Corrosion behavior of zinc in 1.0 n hydrochloric acid with *Cnidioscolus chayamansa*: A green approach. *International Journal of Recent Scientific Research*. 2015;6:3594-3601
- [37] El-Housseiny S. Inhibition of the acid corrosion of zinc by cannabis plant extract. *American Journal of Chemistry*. 2017;7:6-15
- [38] Patel BB, Vashi RT. *Azadirachta indica* (neem) extract as green inhibitor for corrosion of brass in nitric acid media. *Journal of Applied Chemistry*. 2017;6:340-349
- [39] Sangeetha TV, Fredimoses M. Inhibition of mild copper metal corrosion in HNO<sub>3</sub> medium by acid extract of *Azadirachta indica* seed. *Journal of Chemistry*. 2011;8(S1):S1-S6
- [40] Deyab MA. Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution. *Journal of Industrial and Engineering Chemistry*. 2015;22:384-389
- [41] Fouda AS, Elmorsi MA, Abou-Elmagd BS. Adsorption and inhibitive properties of methanol extract of *Euphorbia heterophylla* for the corrosion of copper in 0.5 M nitric acid solutions. *Polish Journal of Chemical Technology*. 2017;19:95-103. DOI: 10.1515/pjct-2017-0014
- [42] El-Etre AY, Abdallah M, El-Tantawy ZE. Corrosion inhibition of some metals using Lawsonia extract. *Corrosion Science*. 2005;47(2):385-395
- [43] El-Etre AY, El-Tantawy Z. Inhibition of metallic corrosion using Ficus extract, Portugaliae. *Electrochimica Acta*. 2006;24:347-356
- [44] Ibrahim ME, El-Khrisy AM, Al-Abdal-lah EM, Baraka A. Evaluation of the inhibitor action of certain natural substances used as corrosion inhibitors. 1. In the dissolution of tin in nitric acid. *Mo Metalloberflanche Beschichten won Metall und Kunststoff*. 1981;35(4):134-136
- [45] Sharma SK, Peter A, Obot IB. Potential of *Azadirachta indica* as a green corrosion inhibitor against mild steel, aluminum, and tin: A review. *Journal of Analytical Science and Technology*. 2015;6:26-1-16
- [46] Djeddi N, Benahmed M, Akkal S, Laouer H, Makhloufi E, Gherraf N. Study on methylene dichloride and butanolic extracts of *Reutera lutea* (Desf.) Maire (Apiaceae) as effective corrosion inhibitions for carbon steel in HCl solution. *Research on Chemical Intermediates*. 2015;41:4595-4616
- [47] Rajenderan S, Shanmugapriya S, Rajalakshmi T, Amal Raj AJ. Corrosion inhibition by an aqueous extract of rhizome powder. *Corrosion*. 2005;61:685-692
- [48] Priya SL, Chitra A, Rajenderan S, Anuradha K. Corrosion behaviour of aluminium in rain water containing garlic extract. *Surface Engineering*. 2005;21(3):229-231
- [49] Njoku VO, Oguzie EE. Inhibitory properties of *Baphia nitida* extract in acid mild steel corrosion. *EUROCORR*. 2009. pp. 849-870



- [50] John Amalraj A, Wilson Sahayaraj J, Peter Pascal Regis A, Sahayaraj A, Pandian P, Johnraj P, Kasthuri A, Kumar C. Synergistic effect of *Allium cepa*-Zn<sup>2+</sup> system on the corrosion of carbon steel in ground water. *Engineering*. 2013;**5**:178-183
- [51] Kavitha N, Manjula P, Anandhakumar N. Synergistic effect of *C. papaya* leaves extract-Zn<sup>2+</sup> in corrosion inhibition of mild steel in aqueous medium. *Research Journal of Chemical Science*. 2014;**4**:88-93
- [52] Arab ST, Al-Turkustani AM, Al-Dhahiri RH. Synergistic effect of *Azadirachta indica* extract and iodide ions on the corrosion inhibition of aluminium in acid media. *Journal of the Korean Chemical Society*. 2008;**52**:281-294
- [53] Obot IB, Obi-Egbedi NO, Umoren SA, Ebenso EE. Synergistic and antagonistic effects of anions and *Ipomoea involucrata* as green corrosion inhibitor for aluminium dissolution in acidic medium. *International Journal of Electrochemical Science*. 2010;**5**:994-1007
- [54] Sharma S, Parihar PS, Nair RN, Verma PS, Sharma A. Influence of ion-additives on inhibitory action of extract of *Trigonella foenum graecum* seeds for AA6063 in acid medium. *Rasayan Journal of Chemistry*. 2012;**5**:16-23
- [55] Ridhwan AM, Rahim AA, Shah AM. Synergistic effect of halide ions on the corrosion inhibition of mild steel in hydrochloric acid using mangrove tannin. *International Journal of Electrochemical Science*. 2012;**7**:8091-8104
- [56] Krishnaveni K, Ravichandran J. Effect of aqueous extract of leaves of *Morinda tinctoria* on corrosion inhibition of aluminium surface in HCl medium. *Transactions of Nonferrous Metals Society of China*. 2014;**24**(8):2704-2712
- [57] Chidi OBI, Stella Wegwu N. Corrosion inhibitive dynamics of *Pennisetum purpureum* (elephant grass) on aluminum metal in acidic media. *International Journal of Innovation Science and Engineering*. 2016;**4**(3):1-15
- [58] Njoku VO, Oguzie EE, Obi C, Ayuk AA. *Baphia nitida* leaves extract as a green corrosion inhibitor for the corrosion of mild steel in acidic media. *Advanced Chemistry*. 2014; **2014**: Article ID 808456, 10 pages
- [59] Zhang J, Zhang Q, Chen G, Zhao JR, Tang DY. Modification of *Punica granatum* Linne husk extract as eco-friendly corrosion inhibitors in oil fields. *Applied Mechanics and Materials*. 2014;**488**:273-276
- [60] Dekmouche M, Saidi M, Hadjadj M, Ghiaba Z, Yousfi M. Green approach to corrosion inhibition by ethyl acetate extract from *Pistacia atlantica* galls in hydrochloric acid solution. *International Journal of Electrical Science*. 2014;**9**(7):3969-3978
- [61] FelipeM BMC, Silva DR, Martinez-Huitle CA, Medeiros SRB, Maciel MAM. Effectiveness of *Croton cajucara* Benth on corrosion inhibition of carbon steel in saline medium. *Material Corrosion*. 2013;**64**(6):530-534
- [62] Cui Y, Zhao D, Qu H, Qu G, Liu J, Ren P. The study of composite substituting mercury corrosion inhibitors for zinc in zinc-manganese battery. *Advanced Material Research*. 2014;**881-883**:102-107

- [63] Bernal S, Botana FJ, Calvino JJ, Marcos M, Perez-Omil JA, Vidal H. Lanthanide salts as alternative corrosion inhibitors. *Journal of Alloys and Compounds*. 1995;**255**:638-641
- [64] Hinton BRW, Arnott DR, Ryan NE. The inhibition of aluminum alloy corrosion by cerous cations. *Metals Forum*. 1984;**7**:211-217
- [65] Arenas A, Bethencourt M, Botana FJ, de Damborenea J, Marcos M. Inhibition of 5083 aluminium alloy and galvanized steel by lanthanide salts. *Corrosion Science*. 2001;**43**:157-170
- [66] Arenas MA, Conde A, de Damborenea JJ. Cerium: A suitable green corrosion inhibitor for tinplate. *Corrosion Science*. 2002;**44**:511-520
- [67] Shi H, Han E, Liu F. Corrosion protection of aluminium alloy 2024-T3 in 0.05 M NaCl by cerium cinnamate. *Corrosion Science*. 2011;**53**:2374-2384
- [68] Mora N, Cano E, Polo JL, Puente JM, Bastidas JM. Corrosion protection properties of cerium layers formed on tinplate. *Corrosion Science*. 2004;**46**(3):563-578
- [69] Moretti G, Guidi F, Grion G. Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid. *Corrosion Science*; **46**(2):387-403
- [70] Bethencourt M. Lanthanide compounds as environmental friendly corrosion inhibitors of aluminium alloys: A review. *Corrosion Science*. 1998;**40**(11):1803-1819
- [71] Owens GJ, Singh RK, Foroutan F, Alqaysi M, Han C, Mahapatra C, Kim H, Knowles JC. Sol-gel based materials for biomedical applications. *Progress in Materials Science*. 2016;**77**:1-79
- [72] Seifzadeh D, Golmoghani-Ebrahimi E. Formation of novel and crack free nanocomposites based on sol gel process for corrosion protection of copper. *Surface and Coatings Technology*. 2012;**210**:103-112. DOI: 10.1016/j.surfcoat.2012.08.073
- [73] Lakshmi RV, Bharathidasan T, Basu BJ. Superhydrophobic sol-gel nanocomposite coatings with enhanced hardness. *Applied Surface Science*. 2011;**257**(24):10421-10426. DOI: 10.1016/j.apsusc.2011.06.122
- [74] Lakshmi RV, Yoganandan G, Mohan AVN, Basu BJ. Effect of surface pre-treatment by silanization on corrosion protection of AA2024-T3 alloy by sol-gel nanocomposite coatings. *Surface and Coatings Technology*. 2014;**240**:353-360. DOI: 10.1016/j.surfcoat.2013.12.051
- [75] Tiwari SK, Sahu RK, Pramanick AK, Singh R. Development of conversion coating on mild steel prior to sol gel nanostructured Al<sub>2</sub>O<sub>3</sub> coating for enhancement of corrosion resistance. *Surface and Coatings Technology*. 2011;**205**(21-22):4960-4967. DOI: 10.1016/j.surfcoat.2011.04.087
- [76] Murillo-Gutierrez NV, Ansart F, Bonino JP, Menu MJ, Gressier M. Protection against corrosion of magnesium alloys with both conversion layer and sol-gel coating. *Surface and Coatings Technology*. 2013;**232**:606-615. DOI: 10.1016/j.surfcoat.2013.06.036
- [77] Zaferani SH. The science of anti-corrosion thin films. *Corrosionpedia*. 2016

- [78] Poznyak SK, Zheludkevich ML, Raps D, Gammel F, Yasakau KA, Ferreira MGS. Preparation and corrosion protective properties of nanostructured titania-containing hybrid sol-gel coatings on AA2024. *Progress in Organic Coatings*. 2008;**62**(2):226-235. DOI: 10.1016/j.porgcoat.2007.12.004
- [79] Ali SM, Allehaibi H. Protective sol-gel coatings for zinc corrosion: Precursor type effect. *Surface and Coatings Technology*. 2017;**311**:172-181. DOI: 10.1016/j.surfcoat.2017.01.010
- [80] Li YS, Tran T, Xu Y, Vecchio NE. Spectroscopic studies of trimethoxypropylsilane and bis(trimethoxysilyl)ethane sol-gel coatings on aluminum and copper. *Spectrochimica Acta: Part A Molecular and Biomolecular Spectroscopy*. 2006;**65**(3-4):779-786. DOI: 10.1016/j.saa.2005.12.040
- [81] Nemeth S, Liu YC. Mechanical properties of hybrid sol-gel derived films as a function of composition and thermal treatment. *Thin Solid Films*. 2009;**517**(17):4888-4891. DOI: 10.1016/j.tsf.2009.03.099
- [82] Li Y, Lu W, Wang Y, Tran T. Studies of (3-mercaptopropyl)trimethoxysilane and bis(trimethoxysilyl)ethane sol-gel coating on copper and aluminum. *Spectrochimica Acta Part A*. 2009;**73**(5):922-928. DOI: 10.1016/j.saa.2009.04.016
- [83] Shi H, Liu F, Han E. Corrosion protection of AZ91D magnesium alloy with sol-gel coating containing 2-methyl piperidine. *Progress in Organic Coatings*. 2009;**66**(3):183-191. DOI: 10.1016/j.porgcoat.2009.07.004
- [84] Shi H, Liu F, Han E. Corrosion behaviour of sol-gel coatings doped with cerium salts on 2024-T3 aluminum alloy. *Materials Chemistry and Physics*. 2010;**124**(1):291-297. DOI: 10.1016/j.matchemphys.2010.06.035
- [85] Ali SM, Allehaibi H. Nano-structured sol-gel coatings as protective films against zinc corrosion in 0.5 M HCl solution. *Journal of Saudi Chemical Society*. 2017;**21**(4):473-480. DOI: 10.1016/j.jscs.2016.12.001
- [86] Balan P, Shelton MJ, Ching DOL, Han GC, Palaniandy LK. Modified silane films for corrosion protection of mild steel. *Procedia Materials Science*. 2014;**6**:244-248. DOI: 10.1016/j.mspro.2014.07.030
- [87] Tavandashti NP, Sanjabi S. Corrosion study of hybrid sol-gel coatings containing boehmite nanoparticles loaded with cerium nitrate corrosion inhibitor. *Progress in Organic Coatings*. 2010;**69**(4):384-391. DOI: 10.1016/j.porgcoat.2010.07.012
- [88] Asadi N, Naderi R, Saremi M. Determination of optimum concentration of cloisite in an eco-friendly silane sol-gel film to improve corrosion resistance of mild steel. *Applied Clay Science*. 2014;**95**:243-251. DOI: 10.1016/j.clay.2014.04.018
- [89] Naderi R, Fedel M, Deflorian F, Poelman M, Olivier M. Synergistic effect of clay nanoparticles and cerium component on the corrosion behavior of eco-friendly silane sol-gel layer applied on pure aluminum. *Surface and Coatings Technology*. 2013;**224**:93-100. DOI: 10.1016/j.surfcoat.2013.03.005