Eco-friendly green corrosion inhibitors in overview

Waled Abdo Ahmed[1], Mohammed H. Al-Mashhadani[2*], Mustafa Abdallh[2], Zainab Hussain[3], Emad Yousif[2*]

[1] Department of chemistry, Faculty of Education, Thamar University, Thamar, Yemen

[2] Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

[3] Department of Chemistry, College of Science, Misan University, Misan-Iraq

Correspondence: mo_chemical@yahoo.com; emad_yousif@hotmail.com

https://orcid.org/0000-0001-8185-833X

Article History:
Received: 2020-05-13
Revised: 2020-06-24
Accepted: 2020-06-28
Published: 2020-07-01

Keywords:
corrosion
corrosion Inhibitors
green inhibitors

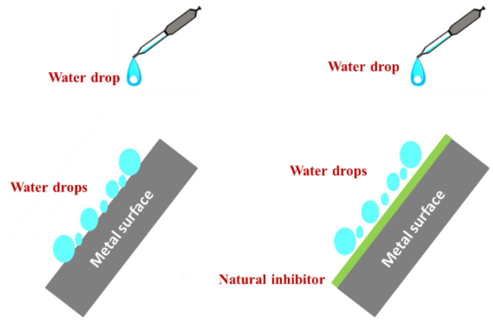
How to cite?

Abstract

Green inhibitors are substances obtained from natural sources and used to stop aggressive dangerous of the metallic corrosion without damaging the eco-system of the environment. Nowadays corrosion causes problems in a wide range of industries such as oil and chemical productions. This paper includes a literature review of the most important corrosion green inhibitors which are used in industry. It is also presenting the categories of green inhibitors such as organic green inhibitors, inorganic green inhibitors, and natural polymers. The synthetic materials without any hazards also considers as a green inhibitors. The mechanism of inhibitive process between the eco-friendly inhibitor and the metallic surface was also described in this work.

Public Interest Statement

This short review focuses on utilizing environment friendly green corrosion inhibitors as the eco-system on the planet is in a real danger due to the development of industry and consuming too much of energy. Therefor this abstract includes highlighting the importance of using green materials which do not badly influence the environment. Metallic corrosion causes word wide economic problems and using synthesized inhibitors cost a lot of money and in the same time could negatively affect the environment. Hence natural inhibitors are cheaper and consider eco-friendly materials.



Green corrosion inhibitors

The biologically acceptable inhibitors in nature are called either eco-friendly or green corrosion inhibitors. These inhibitors can response in a proper way to prevent the corrosion without damaging the eco-system of the environment. Generally, this kind of inhibitors obtains from plant by using extraction process due to the biological nature of the plant. The synthetic inhibitors without any toxicity are also considers as green inhibitors. Eco-friendly or green inhibitors can be classified into two main categories which are organic green inhibitors and inorganic green inhibitors.[1,2]

Organic green corrosion inhibitors

This kind of eco-friendly inhibitors could be obtained from natural resources such as plants. Figure 1 shows the most common organic green inhibitors which are used to stop the metallic corrosion.[3]

Figure 1: Examples of the most common organic green inhibitors.[3]

Inorganic green corrosion inhibitors

Inorganic elements or metals have a crucial role in living organisms, when they are at trace amounts.[4] The higher concentrations of many metals cause toxicity to all forms of lives. It is also applicable for the derivatives of metals. For example, chromium compounds, mainly chromates have been broadly utilized as potential inhibitors in aqu systems due to their high efficiency.[5] Besides the high inhibition efficiency, chromates show extraordinary toxicity thus they have been banned to utilize in industrial applications.[6] In search of alternatives for chromate inhibitors, lanthanide salts are found to show excellent inhibition properties.[7,8] In the same time they have showed very low toxicity such as lanthanide chloride toxicity was stated similar to the sodium chloride toxicity.[9] Hence lathanide salts can also be considered as green inhibitor or eco-friendly inhibitor (Table 1). A few research studies were reported on the corrosion inhibition properties of lathanides during the last decade. For example, Arenas et al reported the application of $CeCl_3$ as an inhibitor for an aluminium alloy (AA5083) and galvanized steel in aerated NaCl solutions.[10] The study has provided evidence for the formation of an inhibitor layer on the surface of alloy as well on galvanized steel. The presence of Ce^{4+} was observed which was due to the oxidation of Ce^{3+}. The phenomenon of "over precipitation" of cerium particles was observed on some areas of galvanized steel surface.[11] This was attributed to the loss in the film coherence that occurs when it reaches critical thickness. The yellow coloration of the layer formed on the galvanized steel was not observed for the aluminium alloy, which may be due to the microscopic sizes of the precipitates. In another attempt by Arenas et al, $CeCl_3.7H_2O$ was employed as corrosion inhibitor for tinned iron or tin plate in NaCl solutions.[12] The coulometric studies revealed the cathodic nature of the inhibitor, which was similar to their previous report. Similarly, Bernal et al reported the inhibitive effects of lanthanum nitrate, samarium nitrate ($Sm(NO_3)_3$), lanthanum chloride ($LaCl_3$), and samarium chloride ($SmCl_3$) for corrosion.[13] Even though the nitrate ion is considered as an anodic inhibitor, the studied rare earth nitrates $Sm(NO_3)_3$) , and $La(NO_3)_3$, were demonstrated as mixed inhibitors, which attributed to presence of lanthanide ions in the solutions. Interestingly, for rare earth chlorides decrease in inhibition efficiency was observed on increasing the inhibitor concentration. This undesirable influence was understood because of the increasing in the concentration of the chloride ions.

Table 1: Inorganic-green inhibitors.

Inhibitor	Metal	Medium
$CeCl_3$	AA5083 galvanized steel	NaCl
$CeCl_3.7H_2O$	Tinned iron	NaCl
$Sm(NO_3)_3$, $La(NO_3)_3$, $LaCl_3$ and $SmCl_3$	AISI 434 SS	NaCl

Natural Polymers

Polymers are the materials that have excellent adhesive properties on metal surfaces. A wide range of polymers has been studied for their anti-corrosive properties in the form of both pre-coating[14] on the metal as well as inhibitor in a variety of corrosive fluids[15] (Table 2). Guar gum, (Figure 2) a naturally-occurring polysaccharide was examined as inhibitor for carbon steel inside sulfuric acid solutions.[16] It was suggested an adsorption mechanism for the inhibitive nature of the Guar gum. Increasing in the ratio of the inhibitor had improved the efficiency to pitting corrosion, which was supported by the shifts in the pitting potentials. The interaction between the oxygen atoms present on the side chains, and ferrous ions were probably impossible. Therefore, the possible mode of coordination type bonding was assumed to occur between the ferrous ions and the oxygen atoms present in the backbone of the polymer. In an attempt to compare the inhibition efficiencies of a natural polymers and synthetic polymers, Umoren et al[17] studied gum Arabic and polyethylene glycol for inhibitions of mild steel mixed with H_2SO_4. The synergistic effects of halide derivatives were also studied. The authors have also reported inhibitors (Exudate gum) using to reduce the aluminum corrosion in acidic solutions.[18] Though the time dependence of the inhibition efficiencies of exudates gum followed almost similar trend to gum Arabic, the effect of temperature was different. The inhibition efficiency was increasing on temperature scale for the former, where as it was decreasing for the later. Therefore, the exudate gums was proposed to have physically adsorbed on the surface of aluminum in various acidic medium.[19]

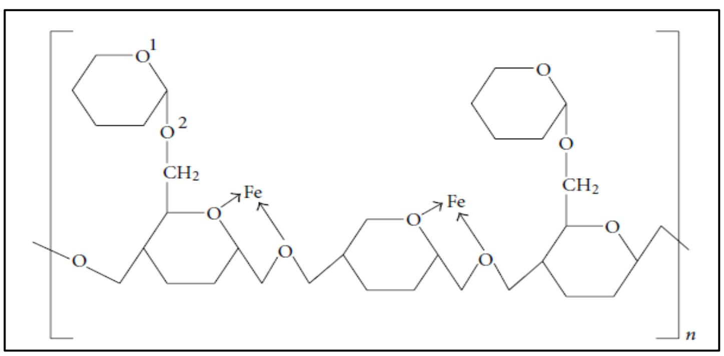


Figure 2: Chemical structure of Guar gum.

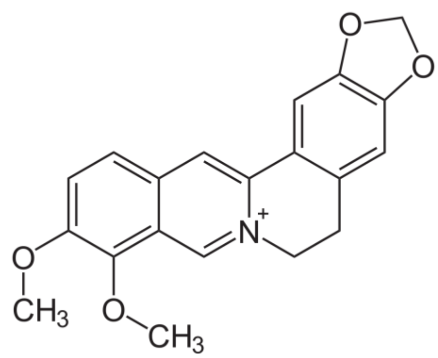
Table 2: List of natural polymers and derivatives studies as corrosion inhibitors

Inhibitor	Metal	Medium
Guar Gum	Carbon steel	H_2SO_4
Gum Arabic	Mild steel	H_2SO_4
Exudate Gums	Alumminium	HCl
Carboxymethyl cellulose	Mild steel	HCl

Inhibition Mechanism of Some Green Inhibitors

Several theories were developed that demonstrate the behavior of green inhibitors. Where the proposal was made by the world mann organic matter. The theory considers that the anions in acidic medium could be absorbed by the metallic surface to compete the cathodic process which leads to reduce the corrosion process. Thus, there are many mechanisms of action that explain the process of inhibiting corrosion of metallic materials by using eco-friendly products. Below is going to describe some of natural inhibitors.[20]

1- **Argemone Mexicana** is a bright yellow flower found in Mexico and it is toxins for grazing animals see Figure 3a. This plant contains an alkaloid berberine molecules see Figure 3b. Berberine is an aromatic compound contains quaternary ammonium salts, two methoxy groups and hetero cyclic ring. This compound works as inhibitor *via* making a bond between the metallic surface and the free unpaired electrons of the oxygen and nitrogen atoms.



a) **b)**

Figure 3: a) Argemone Mexicana plant. b) Berberine chemical structure.

2- **Garlic** contains allyl propyl disulfide. Perhaps, these S-containing unsaturated molecules affect probably the cathodic reaction on the metallic surface.

3- **Carrot** has pyrrolidine molecules (see Figure 4) which are easily loss a proton then the nitrogen atom gains a negative charge which leads to make a strong bond with the metallic surface. Thus carrots are not protected in acids because they are not ionized in acidic media.

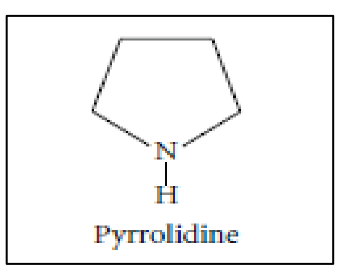


Figure 4: Pyrrolidine chemical structure.

4- Castor Seed contains methoxy group and nitrogen atom which is part of the ring. The ricinine is attached to the nitrogen atom as shown in Figure 5.

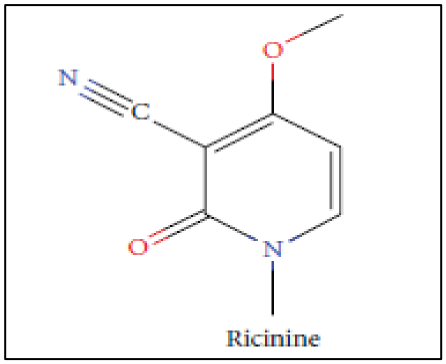


Figure 5: Ricinine.

The researchers have been used so many other natural products as a corrosion inhibitors such as black pepper,[21] mangosteen fruit,[22] pericarp of G. mangostana (see Figure 6).[23] soya bean, and caffeic acid.[24]

Figure 6: a) Mangostana fruit.[22] b) Pericarp.[23]

Conclusion

As general, corrosion inhibitors demonstrated excellent results to reduce the influence of metallic corrosion in a wide range of industrial application. However, many inhibitors show side effects on the environment through damaging the eco-system of it. Green inhibitors or eco-friendly inhibitors revealed outstanding outcomes by stopping the metallic corrosion in the same time do not damage the environment. The most common green inhibitors were reviewed in this paper and the mechanism of inhibition was also described.

Biographies

Waled Abdo Ahmed lives in Yemen, Taiz city, Bachelor of Science (Chemistry-physics) - Taiz University, Taiz, Yemen, with excellence (90.8%). MSC and PhD degree from a world-ranked leading Malaysian University, Universiti Kebangsaan Malaysia; abbreviated UKM, in chemistry science, specialized in Organic Chemistry (industrial chemistry). Currently he is working at Thamar University, faculty of education as assistant professor in organic chemistry and head of chemistry department. He got his Possessing excellent administrative, verbal and written communication skills along with effective teaching methods for inspired learning environments. Having the ability to conduct independent research, leading research projects team, and supervising undergraduate/ postgraduate students in the areas related to Organic Chemistry. His interested researches are Synthesis and production of renewable bio-based/oleochemical lubricant, Bio-modification of fats and oils, Synthesis of oleochemical compounds from biodegradable sources and Analytical method development.

Mohammed H. Al-Mashhadani is a member staff in Chemistry Department / College of Science / Al-Nahrain University, Baghdad, Iraq. BSc. In chemistry, Chemistry Department, Collage of Science, Al-nahrain University, with score 81.2%. Rank: 1st out of 23 students. MSc. In chemistry, Chemistry Department, Collage of Science, Al-Nahrain University, (Removable study of some phenols and acids compound from aqueous solutions by (Triethanolamine-glycerylmaleate) polymer surface), with score 84.42%. Ph.D In organic chemistry, School of Natural Science, Bangor University, UK (Dibenzothiophene-S,S-dioxide Based Conjugated Molecular and Polymeric Materials for Organic Electronics), with very minor corrections. His position is a lecturer and he is teaching organic chemistry for undergraduate students. He is also supervising them when they are doing their experiments in the laboratory. He is helping with the supervising postgraduate students. His research interesting is synthesizing new semiconductor organic materials which are suitable to for organic electronics applications such as solar cells, OLEDs, transistors..etc.

Mustafa Abdallh received his BSc and Master degrees in chemistry in 2004 and 2007, from Al-Nahrain University in Iraq, respectively. In 2013, He went to Australia and studied at Monash University under supervision of Associated Professor Kei Saito. After obtaining his PhD degree in 2018, he is appointed as a lecturer at Al-Nahrain University, Iraq. His current research focuses on the design and synthesis of sustainable, stimuli responsive and self-healing materials.

Zainab Hussein, Master of Science in Chemistry, University of Baghdad, Zainab currently works at the Department of Chemistry, University of Misan, Zainab does research in physical chemistry, Photochemistry, Adsorption and Nanochemistry.

Emad Yousif graduated from Al-Nahrain University (Ph. D), in 2004, with a focus on inorganic chemistry. In 2004, Yousif took up a post as lecturer at Al-Nahrain University, and was promoted to professor in 2015. Yousif's research covers the inorganic, photochemistry, synthesis structure, processing and properties of polymers, and oleo-chemistry. In particular, he is interested in the antibacterial, optical and lubricant properties of such polymers. Yousif has published many scientific articles in national and international journals, and has also published many books, which reflect his interest in public engagement in science. In addition, based on his international publications, he has recently been honored as TWAS fellow.

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