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NATURAL SCIENCES

SOURCES OF GREEN CORROSION INHIBITORS AND THEIR APPLICATION.

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Abstract. Green inhibitors are important today because they are mainly obtained from natural sources and are less toxic than chemically synthesized corrosion inhibitors. Today, the importance of corrosion inhibitors in the protection of metal-based structures in industry from external aggressive environments is enormous. This review article provides information on the sources and types of green corrosion inhibitors and their applications. The mechanism of inhibitive process between the eco-friendly inhibitor and the metallic surface was also described in this work.

Keywords: eco-friendly inhibitor, green inhibitors, corrosion inhibitors.

Importance of corrosion inhibitors and their application

Protection of metals against corrosion in different corrosive environments can be achieved using corrosion inhibitors, which are compounds added in small quantities to a corrosive solution to reduce or minimize the corrosion rate[1]. *The economic impact of corrosion is substantial; for instance, according to international research by NACE (IMPACT 2016), the annual global economic damage due to corrosion amounts to approximately 2.5 trillion US dollars*[2]. *This represents about 3.4% of the average gross domestic product (GDP) of each country* [3].

In recent years, there has been growing interest in environmentally friendly corrosion protection methods to reduce pollution from waste and toxins. Green inhibitors, such as plant extracts, are not only environmentally friendly but also more cost-effective than chemically synthesized inhibitors [4]. *Various plant parts, including leaves, stems, fruits, roots, and seeds, have been used as green inhibitors.*

Corrosion is the destruction of materials, especially metal and metal-based structures, as a result of chemical reactions or electrochemical processes. Corrosion mainly occurs as a result of exposure of metal (iron) to oxygen and water. In general, this process is sometimes called reverse metallurgy, because corrosion can be included in the type of spontaneous processes due to the reduction of the thermodynamic free energy of metals. In general, corrosion reduces metals to oxides or sulfides, which are thermodynamically stable in their natural state [5].

At the same time, corrosion is causing great damage not only to industrial infrastructures, but also to cultural heritage. We can say that there is no sector that does not suffer from the corrosion process, for example: energy, transport, chemical and chemical technology, food and drinking water system, oil and gas production industry, pharmaceutical, engineering, construction. did not Corrosion of metal and reinforced concrete structures, pipelines carrying hydrocarbons and water, air, land and sea transport infrastructure, bridges, piers, marine structures, chemical plants and nuclear reactors, power plants, electronic devices, body implants, cultural heritage sites, causing unprecedented damage to artifacts and many other structures.

One of the truths that we have to recognize is that the corrosion process is always one of the processes that prevent us from maintaining metal and metal-based devices in a stable condition. As a result, humanity is not only suffering cultural damage, but also witnessing huge economic losses[6].

Green corrosion inhibitors based on plant extracts

Although the inhibitors synthesized by chemical methods have high efficiency, they cause great damage to the environment, are not environmentally safe, and are associated with the wide use of different types of corrosion inhibitors in various processes. -environmental problems appeared. Corrosion inhibitors currently in use can significantly slow down the rate of corrosion, but their only drawback is that they are environmentally hazardous. For example, Cr^{+6}-based inhibitors have proven to be highly effective for copper and its alloys, but such cationic corrosion inhibitors are toxic [7,8]. In order to eliminate the above-mentioned problems, the issues of development of environmentally harmless, non-toxic corrosion inhibitors and their implementation are being promoted. Taking into account these requirements, a number of scientific researches on the use of natural resources and compounds have been conducted in recent years. As a result of scientific research, the term "Green inhibitor" appeared in the world "corrosion inhibitors" community.

In general, as the main source of green inhibitors of this type, we can cite compounds obtained by extraction from plants and their various parts (leaf, fruit, stem, seed, flower) [9,10].

The use of "green" corrosion inhibitors is not only economically beneficial, but also ecologically important in ensuring the stability of metal-based devices in water treatment, industrial cooling systems, and water transmission systems. For this purpose, until now, researches on obtaining green inhibitors from various plants and using them in practice have been conducted around the world.

In the literature, green inhibitors have been obtained from plants growing in the desert regions of Baja California, Mexico, by ethanol and water extraction, and they have been widely used on an industrial scale [11,12].

A number of studies are being carried out to replace toxic and chemical inhibitors with ecologically safe and non-toxic green inhibitors by extracting green inhibitors from plants, which are natural sources in nature. Extracts from several plants have been suggested as green inhibitors by a number of research scientists. Most of them have been found to have inhibitory properties with high efficiency (90%)[13,14].

In this regard, many scientists of the world have conducted scientific research on the methods of obtaining green inhibitors from various types of plants and their practical application in various aggressive environments.

Singh P and his co-authors used naphthyridine-based derivatives as green corrosion inhibitors to protect mild steel from corrosion in hydrochloric acid environments. Its inhibition efficiency was studied by means of metal surface morphology and electrochemical studies [15].

When studies were conducted on the use of the extract obtained from *Catharanthus roseus* (*Vince rosea*) and *Turmeric (Curcuma longa)* plants as a green inhibitor in 1 M HCl solution medium, it was found that its inhibition efficiency was not inferior to that of chemically synthesized corrosion inhibitor [16].

Using a heterocyclic compound based on glucosamine and pyrimidine as a corrosion inhibitor, its inhibition efficiency was studied in 1 M hydrochloric acid medium. Inhibition efficiency was analyzed using gravimetric, electrochemical, surface morphology (SEM, AFM and EDX) and computational methods. The obtained heterocyclic corrosion inhibitor has a high inhibition efficiency due to the presence of electron acceptor ($-NO_2$) and electrodonor ($-CH_3$ and $-OH$) functional groups. According to the analysis of potentiodynamic analysis, it was determined that this inhibitor belongs to the class of cathode-type inhibitors [17].

According to the research carried out in [18], the effectiveness of indole alkaloids extracted from the leaves of *Alstonia angustifolia* (*A. latifolia*) in the medium of 1 M HCl solution for steel structures was determined. Acacia fruit extract was used to prevent corrosion of bronze (Cu-10Sn) alloy in 0.5 M sodium chloride solution. In this case, the concentration of the inhibitor was taken from 200 mg/l to 1800 mg/l. According to the results of the study, the inhibition efficiency increased with the increase of the inhibitor concentration and reached 93.5% at a concentration of 1800 mg/l. The experiment was carried out for 4 weeks, and the analysis of the sample taken in the second week using SEM-EDX showed that the amount of chlorine decreased from the initial weight (8.47%) to 3.20%.

The effectiveness of indole alkaloids extracted from the leaves of *Alstonia angustifolia (A. latifolia)* in 1 M HCl solution for steel constructions was studied. In this experiment, the temperature was 303 K and the concentration was 3 to 5 mg/l. As a result of practical experiments, it was determined that the inhibition efficiency is higher than 80%. It is important that this extract, according to the results of the polarization value, the inhibitor does not change the mechanism of anodic or cathodic reactions, and it can be added to the group of mixed type inhibitors [19].

Abdel-Gaber A. and other researchers studied the mechanisms of adsorption, potentiodynamic polarization and electrochemical impedance spectroscopy of the extract of *Eucalyptus (Eu)* plant leaves in 0.5 M H_2SO_4 and 0.5 M H_3PO_4 solutions. It has been found in practice that eucalyptus leaf extract works as a mixed inhibitor and that eucalyptus leaf extract has a higher inhibition efficiency in medium with 0.5 M H_2SO_4 than in 0.5 M H_3PO_4 [20].

The inhibitory properties of tryptamine (TA) for a 0.5 M H_2SO_4 solution were studied in the temperature range of 25°C to 55°C and time durations of 1, 24 and 72 hours, resulting in potentiodynamic curves of the engorgement process (PCM) and electrochemical impedance spectroscopy (EIS) was obtained. According to the obtained results, the corrosion efficiency was from 90% to 99% even at 55°C and 72 hours, but the corrosion rate increased at higher temperatures and times[21].

Authors such as Khaled K.F and Monte Carlo studied the inhibitory property of the extract of the leaves of *Emilia sonchifolia* (ES) to prevent copper corrosion in 2 M hydrochloric acid solution. The electrochemical potential of the inhibition process and the surface of the sample taken for the experiment were also studied by methods of analysis [22]..

Asadi N and other authors studied the mechanism of inhibition of light steel constructions using green inhibitor obtained from *Lemon Balm* extract in 1 M HCl solution using electrochemical and theoretical methods. The inhibitory active components of *Lemon balm extract* (LB. E) and their functional groups were studied by UV spectroscopy, Fourier Transmission infrared (spectroscopy) (FT-IR) and Raman spectroscopy methods. It was found that the inhibition efficiency of this green inhibitor is 95% at a concentration of 800 mg/l. The results of potentiodynamic polarization analysis showed that the rate of cathodic corrosion was significantly reduced when using LB extract and was classified as a mixed type inhibitor [23].

Tridax procumbens and *Chromolaena odorata* extracts were taken and the corrosion resistance of stainless steel (UNS S31254) used in the extraction of oil from acidic oil fields saturated with carbonic anhydride was determined based on the Tafel method. In addition, these green inhibitors have been shown to have high inhibitory efficiency in protecting other alloys around us from corrosion. Both of the above inhibitors were found to be 90% effective at a concentration of 100 mg/l for acidic media [24].

Two types of industrial substances such as *Rolliniastatin-1* and *Motrilin* were isolated from the extract of *Rollinia occidentalis* and tested in acidic solutions for carbon steel constructions. A 1 M solution of hydrochloric acid was mainly used as an acidic medium, and the temperature ranged from 25 to 55 0C, and the concentration showed the maximum inhibition efficiency at 0.4 mg/l. The authors classified green inhibitors of this type as mixed-type inhibitors. Using the Langmuir adsorption isotherm, the adsorption mechanism of the inhibitor and the dependence of inhibition on temperature and concentration were studied [25].

In this study, *Hibiscus sabdariffa* plant extract was used as a green corrosion inhibitor to protect aluminum from corrosion in 5 M sulfuric acid environment [26].

According to the purpose of the research carried out by Alibakhshi E and his co-authors, extracting from the *Glycyrrhiza glabra* plant and using the obtained extract as a green inhibitor in 1 M solution of hydrochloric acid to prevent corrosion of light steel constructions was studied. Also, the inhibition mechanism and effectiveness of this type of green inhibitor were studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. Based on the results of the polarization analysis, the authors showed that this green inhibitor can be included among the mixed type inhibitors, that is, *Glycyrrhiza glabra* extract significantly slows down the rate of anodic and cathodic reactions. From the obtained results, it can be seen that the corrosion current density for the steel sample without the inhibitor was 260 $\mu A/cm^2$, while with the inhibitor at the concentration of 800 mg/l it was 40.2 mA/cm2. In comparison, it was found that the corrosion rate slowed down by 6.5 times. The maximum inhibitory efficiency of *Glycyrrhiza glabra* extract was 88% at a concentration of 800 mg/l for 24 hours. Due to this, a number of organic substances such as glycyrrhiza, 18b-glycyrrhetinic acid, licuritigenin, licochalcone contained in *Glycyrrhiza glabra* extract have been shown to adsorb molecules due to the reduction of hydrophilicity of the steel surface[27].

By Abdel-Gaber A and other authors, several green inhibitors obtained from plants such as *Chamomile* (*Chamaemelum mixtum*), *Halfabar* (*Cymbopogon proximus*), *Black cumin* (*Nigella sativa L.*), *Kidney bean* (*Phaseolus vulgaris L.*) in a solution of 1 M H_2SO_4 its effect on steel corrosion was studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. According to the researchers, the extracts of such plants can be classified as a mixed type of inhibitor. It has been shown in practice that it has the highest efficiency when the inhibition mechanisms and efficiency are studied in relation to 1 M H_2SO_4 solution [28].

Authors such as Vijayalakshmi P.R and Subhashini S conducted their study to determine the mechanism of absorption of *Palmyra* extract(*Borassus flabellifer Linn*) plant extract in 0.5 M H_2SO_4 and 1 M HCl acid environments to prevent corrosion of steel by electrochemical and gravimetric methods. those who did. These two co-authors stated that when the obtained extract was used as a green inhibitor, the inhibition efficiency increased as the concentration of the green inhibitor increased, and the efficiency results were 97.65% and 98% when tested in the aforementioned acidic solutions for 24 hours. reached 11%. Adsorption isotherms and electrochemical parameters of this inhibitor were studied, and it was noted that it is a mixed type inhibitor [29].

An extract from the leaves of *Emblica officinalis* was obtained by Saratha R and co-authors and used as a green inhibitor to prevent the corrosion of mild steel in 1 N HCl environment. In this case, when the concentration of green inhibitor was 2%, the inhibition efficiency was 87.9% [30].

Two co-authors, Ameh P.O and Eddy N.O, used *Commiphora pedunculata* (CP) extract for corrosion protection of AA3001 aluminum alloy in hydrochloric acid environment and investigated the inhibition efficiency using gravimetric and thermodynamic methods [31].

In the literature, the extraction process using *Argan hulls* plant bark extract as a corrosion inhibitor for steel in 1 M hydrochloric acid environment was studied and the best efficiency was found to be 97.3% at a concentration of 5 g/l [32].

Kamal C and a number of other researchers conducted the anti-corrosion inhibition process of *Hydroclathrus clathratus* extract in two types of 1 M hydrochloric acid and 1 M sulfuric acid medium at temperatures of 25, 35 and 550C. It was studied by electrochemical and scanning electron microscope (SEM) analysis [33].

Also, *Diospyros Kaki* leaf extract, 97.3% inhibitory efficiency in 1 M hydrochloric acid medium [34], *Croton persimilis* leaf extract is a very good inhibitor for 1 M hydrochloric acid and 0.5 M sulfuric acid medium [35], *Matricaria C hamomilla* inhibition efficiency of 4.5 g/l hydrogen sulphide oil in hydrogen sulfide medium was up to 96% [36], *Morinda citrifolia* extract is an effective inhibitor for salt water [37].

R. S. Al-Moghrabi and H. T. Rahal, co-authors, found that the extract obtained from the leaves of *Crataegus oxyacantha* and *Prunus Avium* plants in a 0.5 M solution of hydrochloric acid has a high inhibitory efficiency [38].

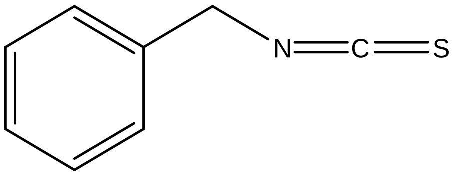
Authors such as Sneha Kagatikar stated that research was conducted using glycogen as a biopolymer green corrosion inhibitor in 3.5% NaCl medium to prevent corrosion of 6061Al-15 %(V)SiC(P) composite[39].

Ashassi-Sorkhabi H in order to prevent corrosion of Al7075 aluminum alloy, 3.5% sodium chloride solution was used and its electrochemical corrosion under these conditions was also analyzed [40,41].

The extract obtained from the leaves of plants such as *Polycarpaea corymbosa*(PC) and *Desmodium triflorum*(DT) in 1.0 M hydrochloric acid solution was also studied by gravimetric method and electrochemical measurements of steel corrosion resistance. According to the results of the experiment conducted in the temperature range of 27 and 47±1 0C, the inhibition efficiency is from 91.78% to 92.99%. They also pointed out that this type of inhibitor can be used as a mixed type of inhibitor, and thermodynamic parameters such as free energy of adsorption (ΔG ads) and enthalpy of adsorption (ΔH ads) were determined [42].

Protection of metal structures from corrosion in industry has become one of the urgent problems not only in acidic or sodium chloride environments, but also in the environment of calcium carbonate solution. It is important to prevent the corrosion of metals used in places where the content of salts is several times higher than the norm. For this reason, the inhibition mechanism of *Lycium Essential Oils* (LEO) as green inhibitor in $CaCO_3$ medium was studied using methods such as membrane technology with nanoparticles, electrochemical impedance spectroscopy (EIS) and chronoamperometry. This green inhibitor contains antioxidants, which prolong the settling time of $CaCO_3$ by forming complexes with calcium cations [43,44].

Chemicals currently used in industry for corrosion inhibitors are highly toxic to humans and the environment. These inhibitors can disrupt the biochemical process of any enzyme system in the body. Therefore, it is possible to use green inhibitors and protect the health of the process controller. For this purpose, in this study, using the extract of *Papaya seeds* for low-carbon steel in 0.5 to 3 N sulfuric acid environment, its annealing efficiency was studied. Increasing the concentration slowed down the corrosion rate. This green inhibitor contains Benzylisothiocyanate.



Benzylisothiocyanate.

This organic substance adsorbs very well on the steel surface and increases the level of corrosion protection[45].

The absorption of *Valoniopsis pachynema* plant extract for H3PO4 medium was studied by mass loss, potentiodynamic and electrochemical impedance spectroscopy methods. Activation energy of inhibition process, free energy, enthalpy and entropy change from thermodynamic parameters and rate constant and half-life from kinetic parameters were calculated [46].

The effectiveness of the extract obtained from the seeds of the *Elaeocarpus plant* in 3 M hydrochloric acid environment of mild steel constructions was determined. Inhibition efficiency was analyzed by gravimetric method, and corrosion protection mechanism was analyzed by Tafel diagram, electrochemical and scanning electron microscope methods. The obtained analysis results showed that the inhibition efficiency of *Elaeocarpus extract* was 93.370, 97.111, 89.015 and 90.528%. In addition, when mathematical and quantum chemical studies were carried out, the same analysis as the above analysis was reported[47].

Environmentally friendly corrosion inhibitors are not only plant extracts, but also organic inhibitors.

The following green corrosion inhibitor was synthesized as a result of the reaction of fatty acids obtained by hydrolysis of *Castor oil* with vanillin. Vanillin esters (VE15, VE20, VE40 and VE60) obtained as a result of the reaction of the obtained compounds with monoethanolamine were synthesized. The chemical structure of the obtained compounds was determined by FT-IR spectroscopy and 1HNMR spectroscopy. The mechanism of corrosion inhibitors in the medium of 0.5 M HCl was studied by potentiodynamic polarization curves and Langmuir adsorption isotherm and it was noted that it is a mixed type corrosion inhibitor [47].

In this work [48], the adsorption of *Matricaria Chamomilla* oil on the surface of carbon steel and the inhibition mechanisms and inhibition efficiency were investigated in hydrogen sulfide medium at room temperature. In this case, the results obtained at the inhibitor concentration of 4.5 g/l proved that the inhibition efficiency is up to 96%.

Together with Zakir Hossain SM and other co-authors, the inhibition efficiency of *Cyanamide aldehyde* was tested in a 3% aqueous solution of sodium chloride. According to the test results, the inhibition efficiency of the corrosion inhibitor was 70% at a concentration of 50 mg/l. According to the mechanism of inhibition, it was studied by the method of polarization curves that it is a mixed type of inhibitor. Accordingly, *Elaeocarpus extract* simultaneously reduced the density of cathodic and anodic currents[49-54].

Conclusion

This analytical article provides information on the use of green corrosion inhibitors in various aggressive environments based on extracts from various parts of several plants. This article is important to get general information about green corrosion inhibitors.

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