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PLANT EXTRACTS AS GREEN INHIBITORS OF CORROSION OF METALLIC MATERIALS - A REVIEW

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Abstract: *The paper reviews corrosion protection by inhibitors, and more specifically – by green corrosion inhibitors. The conventional corrosion inhibitors are usually toxic to the living organisms, and their use leads to environmental pollution, killing different biological species. Thus, a need for environmentally friendly inhibitors had appeared in recent years. Nowadays, there are numerous reports on the possibility of using plant extract as corrosion inhibitors. When used as corrosion inhibitors, plant extracts give the advantage of environmental safety. These corrosion inhibitors are called green, as they do not pose environmental risks. However, as plants chemical composition is dependent on different non-controllable factors, the chemical composition of plants extracts is also non-controllable, and this requires careful testing of plants extracts for their inhibitory properties.*

Keywords: *Corrosion, Inhibitors, Protection, Green, Toxicity, Metals.*

INTRODUCTION

Corrosion of metallic materials is a spontaneous and irreversible process of destruction during the interaction of metals with the environment. In essence, corrosion is a phenomenon that counteracts human activities to obtain metallic materials from natural resources. This counteraction has thermodynamic foundations, so to prevent or slow down corrosion processes, targeted efforts are needed.

Due to the conditions on our planet, corrosion processes are more often associated with the flow of electric current, i.e. the more common type of corrosion is electrochemical corrosion. It usually develops slowly over time until catastrophic destruction occurs. The result has: 1) an adverse economic effect; 2) an adverse effect on the environment; 3) tragic consequences for safety. An example of the latter is the incident in the Echemishka tunnel, where a person died in 2017 due to corrosion of a metallic structure. Thus, even if we ignore the other two adverse effects of corrosion processes, we should not let these processes develop uncontrollably, but we should slow them down and monitor them, and when possible - prevent them completely.

Nowadays, various methods are used to prevent and slow down corrosion. These include the correct choice of material for the specific corrosion environment, design that is tailored to the operation of the structure and the environment, alloying to impart or increase corrosion resistance, heat treatment to obtain a more resistant microstructure, the application of protective coatings, environmental control, electrochemical protection.

One of the ways used in practice to prevent corrosion processes or reduce their speed is environmental control. It has several varieties (Bardal, 2004), (Roberge, 2008), (Popov, 2025), (Mattsson, 2001), (Pedeferri, 2018): 1) controlling the temperature of the medium; 2) controlling the speed of movement of the medium; 3) controlling the composition (content of aggressive ions, oxygen and protons) in the medium; 4) adding corrosion inhibitors.

Due to their effectiveness, combined with accessibility and ease of use, corrosion inhibitors are the most widely used. Historically, the first substances purposefully developed and used as corrosion inhibitors were usually toxic to living organisms. This has necessitated the search and development of environmentally safe inhibitors, known as green ones, in recent decades.

EXPOSITION

Corrosion inhibitors (CI)

According to the ISO 8044 standard, a corrosion inhibitor is "a chemical substance which, when present in a corrosion system in an appropriate concentration, reduces the rate of corrosion without significantly changing the concentration of any corrosive agent".

Corrosion inhibitors (CIs) interact with the metal surface in such a way as to imitate the processes of in situ coating deposition (Jones, 1996). CIs are substances which, when added in small but sufficient quantities to the aggressive environment, reduce the rate of electrochemical corrosion to a predetermined value, or reduce it to zero (Dariva & Galio, 2014), (Bardal, 2004), (Jones, 1996), (Mattsson, 2001), (Pedeferri, 2018), (Popov, 2025), (Roberge, 2008).

The classification of CIs is made according to various characteristics. For example, relatively early in (Putilova, Balezin, & Barannik, 1958), a division of CIs according to several characteristics was described. One is the nature of the inhibitor's action – if it creates a protective layer on the metal surface, it is type A, and if it only reduces the aggressiveness of the environment – type B, and it is possible to have inhibitors of mixed type AB. The same authors [9] distinguish between safe and dangerous CIs, and by dangerous CIs they mean those that, under certain conditions, do not form a dense protective layer on the metal surface.

In modern scientific literature, CIs are classified according to one of the following features (Dariva & Galio, 2014), (Pedeferri, 2018), (Landolt, 2007), (Sastri, 2011), (Mattsson, 2001), (Popov, 2025), (Roberge, 2008), (Bardal, 2004):

1) chemical nature – organic and inorganic CIs;

2) effect on electrochemical half-reactions – anodic, cathodic, mixed CIs;

3) area of application – for industrial cooling waters, for natural waters, for drinking water; for protection during chemical cleaning of metallic parts; in the oil industry; for packaging; for protection of reinforced concrete, etc.; for basic environments; for acidic environments; for neutral environments; for coatings; for atmosphere – volatile CIs;

4) efficiency – dangerous and safe CIs; this classification is essentially the same as that presented in (Putilova, Balezin, & Barannik, 1958);

5) mechanism of inhibitor reaction – adsorption; passivation; formation of a protective layer by deposition of mineral salts or poorly soluble organic compounds; removal of the oxidant.

The inhibitory effect of CIs is manifested in one of the following two ways (Sastri, 2011): 1) interaction of the inhibitor with aggressive particles from the environment and their neutralization; 2) interaction of the inhibitor with the metal surface (adsorption) and isolation of this surface. Thus, (Sastri, 2011) divides CIs into two large groups (included in the fifth classification above): I) modificators of the environment and II) inhibitors, that interact with the metallic surface. This division repeats what was previously done by (Putilova, Balezin, & Barannik, 1958) of CIs of group A and group B.

Today, the most used classification of CIs is the one that considers the effect of the inhibitor on the reaction that determines the corrosion rate, i.e. the second classification listed above.

Traditionally, chromates, benzimidazole derivatives, phosphates, silicates, borates, molybdates are used as CIs, and in some cases CIs also contain arsenic (Mattsson, 2001), (Jones, 1996), (Dariva & Galio, 2014), (Pedeferri, 2018), (Roberge, 2008), (Bardal, 2004), (Nnanna, Uchendu, Ikwuagwu, John, & Ihekoronye, 2016), (Sheydaei, 2024). Some of them are toxic substances. This fact has imposed the need to develop and use CIs that are safe for living organisms and the environment.

Green corrosion inhibitors (GCIs) obtained from plants

Environmentally safe and non-toxic CIs are known as green. The idea behind the concept of GCIs is the principle of "green chemistry", which includes efforts to manage the risk of using various chemically active substances (Zakeri, Bahmani, & Aghdam, 2022). According to the same authors, to be classified as a "green" corrosion inhibitor, a substance must be non-bioaccumulative (not accumulate in living organisms), biodegradable, and have zero or minimal toxicity to the marine environment – these are criteria adopted by the Paris Commission PARCOM, currently the OSPAR Convention (Zakeri, Bahmani, & Aghdam, 2022).

Extracts from various plants, herbal extracts, and plant essential oils meet these requirements, and the specialized literature presents the results of numerous experiments with them, proving their suitability to perform the role of GCI.

For the first time, plant extracts – dried stems and leaves of celandine (Chelidonium majus) – were used as CIs in 1930 to protect steels in sulfuric acid pickling baths (Sanyal, 1981), and natural CIs were used as early as the Middle Ages – for example, gunsmiths added flour, yeast, bran to acidic solutions to remove scale (Putilova, Balezin, & Barannik, 1958).

GCIs obtained from plants belong to organic ICs. Their effectiveness depends on the following factors (Sanyal, 1981):

1) size of the molecule;
2) aromaticity (aromatic nature of the molecule) and/or conjugated bonds;
3) length of the carbon chain;
4) bond energy with the metal surface;
5) type, number and manner of bonding of atoms or molecules (π or σ bonds);
6) the ability of the layer formed by the inhibitor to remain compact or to crosslink;
7) the ability to form a complex with the atoms of the metal lattice in the form of a solid;
8) appropriate solubility in the aggressive medium.

The electrolyte required for electrochemical corrosion is generally water or an aqueous solution. Its properties affect both the corrosion processes and the ability of the inhibitor to protect the metal surface (Sanyal, 1981). For example, increased electrolyte temperature increases the corrosion rate, while at the same time reduces the effectiveness of the inhibitor. The latter is due to the desorption of previously absorbed CI, as well as the reduced amount of oxygen required for the beneficial effect of some non-oxidative inhibitors. The increased speed of movement of an electrolyte with added CI also negatively affects the protective properties of the inhibitor, and the presence of chlorides leads to the need for higher CI concentrations. There is no universal CI – usually substances show inhibitory action only in acidic solutions, others – only in basic ones, and still others – only in neutral ones. Similarly, the corrosion rate of different metals is affected by different substances, so that if a given CI reduces the corrosion rate of iron, it does not affect the corrosion of aluminium (Sanyal, 1981).

It becomes clear that all these facts must be considered when developing and selecting CIs. When substances derived from plants are used as CIs, the problem is further aggravated by the characteristic features of plants.

Green corrosion inhibitors derived from plants are "molecules extracted from plants" (Abbout, 2020). The chemical composition of plants is studied by phytochemistry. It deals with plants as a source of physiologically or biologically active substances. These substances include secondary metabolites of plants (Petkov, 1982), which metabolites are widely tested for green corrosion inhibitors. Some of them have strong physiological activity, and are toxic in larger doses – they are obtained from plants containing alkaloids with strong action, toxic peptides, etc. Widely distributed plants produce secondary metabolites with weak physiological activity and are rarely toxic (Petkov, 1982).

The chemical composition of a plant, respectively the extracted secondary metabolites, varies within "very wide limits" (Petkov, 1982). This may be caused by the vegetative phase of the plant – a well-known factor that also determines the period of collection of the plants. For some plants there are also chemical forms (races) – this is the case of two plants that are botanically indistinguishable but have quantitative or qualitative differences in chemical composition. This is due to inherited differences in the enzyme systems involved in plant metabolism, and these differences are preserved in generations, regardless of the proximity of the two races (Petkov, 1982). In (Petkov, 1982), chamomile growing in Northern Bulgaria and chamomile found in Southern Bulgaria are given as examples of chemical races. In addition to these two influences, the chemical composition of plants also depends on random factors. They are due to changes in the environment - atypical temperatures, precipitation, lighting, hail and mechanical damage, parasites and diseases, changes in the chemical composition of the soil. These are factors that affect plant metabolism, and from there - on the quantity and quality of secondary metabolites (Petkov, 1982). All this shows that obtaining a quality extract with a repeatable chemical composition from plants is difficult.

In addition, modern scientific publications do not always report which substances extracted from plants act as GCIs - these substances are still not fully known.

In modern scientific literature, results of numerous experiments with plant extracts have been reported, studying the ability of extracts to act as GCIs. Below are several examples from recent years that demonstrate the relevance of the topic considered here.

In work (Vimala, Vimala, Nivetha, Amala, & Agila, 2025), it was found that Malabar nut extract acts as a GCI for the protection of carbon steel in an acidic environment. The protective effect of Malabar nut extract reaches 79.72% at a concentration of 95 ppm and is manifested by adsorption and cathodic control in HCl solution. The authors found that the protective effect of the extract is due to the alkaloids and flavonoids contained in it.

Nepalese watercress extract also exhibits inhibitory properties towards carbon steels, with the degree of protection reaching 98.35% at low concentrations in sulfuric acid solution by forming a barrier layer (Kumari, et al., 2025), with the protective components of the extract not being specified.

The extract of the leaves of creeping thistle also acts as a mixed CI on carbon steels in acidic media, as reported in (Ellaite, Forsal, & Lahmady, 2024), with the inhibitory efficiency being 94% at an extract content of 600 ppm. The authors of (Ellaite, Forsal, & Lahmady, 2024) also do not report the active components, but they demonstrate that they adsorb onto the steel surface and thus block the access of the corrosive components of the electrolyte.

Peppermint extract (peppermint oil), obtained by Soxhlet extraction, has been successfully tested as a CI for the protection of structural steels in reinforced concrete in acidic environments (Iglesias, et al., 2024), where it is known that the passive layer on iron and its alloys, formed in the presence of concrete hydration products, is degraded. The extract was applied as a coating on the protected surface.

The aqueous extract of sandwort leaves (beach grass) has shown an efficiency of protecting carbon steel, reaching 84% at a concentration of 700 ppm in acidic environments (Jebali, et al., 2024). The authors of (Jebali, et al., 2024) found that the protective effect is manifested by adsorption, and the extract acts as a mixed CI, but did not indicate its active components.

The leaves of the white star apple have also been used to obtain an extract that has shown inhibitory efficiency of over 94% at contents of 400 to 1600 mg/l in aqueous solutions of HCl and H_2SO_4 (Okeke Pamela, et al., 2025), and the authors have identified the active phytocomponents.

What is common for extracts from different plants is the presence of bioactive phytochemicals, such as flavonoids, alkaloids and polyphenols - their presence ensures effective adsorption of the extract molecules and formation of a protective layer. The results published in scientific literature are from studies conducted in laboratory conditions, which do not fully reproduce the conditions in which metallic products and structures operate.

CONCLUSION

The examples given here are only a small part of the numerous studies on the possibility of using plant extracts as green inhibitors of corrosion of metal materials. From them follows the conclusion that plant extracts successfully perform the action of corrosion inhibitors, while not leading to toxicity. The main problems with plant extracts acting as corrosion inhibitors are their inconsistent chemical composition and incompletely defined active ingredients. This may require that, when using a particular plant extract, it be pre-tested for optimal protective concentration.

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