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Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.5937/zasmat2202183E

Zastita Materijala 63 (2)
183 - 202 (2022)

Plant materials as green corrosion inhibitors for select iron alloys: a review

ABSTRACT

The importance of corrosion studies brings to the forefront economic losses, damage, and safety issues of metals deterioration in the construction industry. Although the choice of a material and use of inhibitors can contribute to its resistance to environmental corrosion behavior, the structural deterioration of metals can be exacerbated under operation conditions. In this review, highlights of research findings published in the past five years on the use of plant materials as corrosion inhibitors for variants of steel: carbon steel, mild steel, stainless steel are provided. It elucidates the meaning of green inhibitors and their types. It also presents the methods employed to ascertain the inhibition efficiencies of the plants/plant parts listed and the parameters considered in the corrosion inhibition analyses. The major gaps or limitations identified in the reported research findings include experimentation at constant temperatures and short immersion periods for the alloys. Due to the fact that, if these extracts were to be deployed for industrial use, they'd be subjected to more hazardous conditions, such as higher temperatures, pressures, etc., this paper proposes that their investigations as potential inhibitors on the laboratory/pilot scale be performed at higher temperatures and longer immersion times which may as such provide more comprehensive knowledge on the environmental/climatic requirements for their application. Additional improvement strategies are also suggested. The list of extracts, however, is not exhaustive.

Keywords: *mild steel, carbon steel, corrosion, plant extracts, green corrosion inhibitors,*

1. INTRODUCTION

Corrosion is an issue of global concern as it is responsible for the deterioration of materials, especially metals and alloys used in almost every industry. This is because they are usually exposed to acids in industrial processes for purposes such as oil well acidizing, acid pickling and acid descaling [1]. Some other major corrodents (sources of corrosion) in industries are hydrogen sulfide, caustic alkalis as well as ammonium hydroxides, corrosion of steel at hydrocarbon–electrolyte interfaces and in emulsified two-phase environments, oxygen, naphthenic acids, carbon dioxide, as well as water cut [2].

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Paper received: 19. 01. 2022.
Paper accepted: 10. 02. 2022.
Paper is available on the website: www.idk.org.rs/journal

Corrosion inhibitors are usually added to the acid solutions to prevent or slow down the metal loss and acid consumption rate [3–5]. However, some of these corrosion inhibitors are toxic to the environment and this has prompted the search for eco-friendly (bio-sourced) corrosion inhibitors for metals in acid solutions and other corrosive environments [6,7]. This is due to their abundance, cheapness and low toxicity [8]. They are mainly extracted from plants [9–21] and seaweed biomass [22–24] and classified as green inhibitors.

1.1. Corrosion in Steel

Steel is a widely used iron-carbon alloy for construction of articles, structures, and vessels of everyday use. The preference for the use of steel is due to its excellent mechanical properties (high tensile strength, durability, toughness, etc.) and economy [25,26]. Steels tend to deteriorate in acid medium due to corrosion. It was reported that the loss due to metallic corrosion is greater than the loss due to any natural disasters [27]. Hence, the corrosion inhibition of steels in acid medium became an intensive field of research [28].

Figure 1: Pitting corrosion on a stainless-steel stator housing operating in seawater [29]

Slika 1. Piting korozija na kućištu statora od nerđajućeg čelika koje radi u morskoj vodi [29]

1.2. Corrosion in Steel Rebars

Deicing salts and salt-water spray can lead to serious corrosion problems for reinforced concrete bridge structures. These problems can cause costly and labor-intensive repair and even replacement of the structure. Surface applied corrosion inhibitors are potentially a useful and cost-effective way to prolong the life of existing structures. Mild steel, also known as plain-carbon steel, is widely used as it provides material properties that are acceptable for many applications [25,26]. However, the challenge is that it has low corrosion resistance especially in acidic or corrosive environments. Substances such as chloride, carbon dioxide, oxygen, and moisture can penetrate through weak pores in concrete, triggering the corrosion of reinforcing steel bars in concrete and finally inducing cracks in the concrete. This inadvertently affects the load-carrying capacity of the reinforcing steel bar and impairs its ductility, which presents a serious problem for the safety of structures in seismically active areas. The use of many inorganic and synthetic inhibitors on RC structures in coastal environment can result in serious threat to aquatic life in addition to its high cost of production [6]. Natural products such as plant extract, amino acids, proteins, and biopolymers have been reported to be eco-friendly, cheap, and biodegradable and efficient in corrosion mitigation [1,7]. Plant extracts are a rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [1,7]. This review gives an overview of recent work on the inhibitive effect of various plant extracts particularly for mild steel in acidic medium to provide the engineering community with vital comparative literature for possible large-scale use of these natural inhibitors. This will contribute to sustainable and green manufacturing. The effects of temperature, concentration, and reaction medium on the inhibition efficiency were discussed.

2. GREEN CORROSION INHIBITORS

Green corrosion inhibitors can be classified into two groups, namely, organic green corrosion inhibitors and inorganic green corrosion inhibitors [29]. The organic green inhibitors consist of synthetic substances that are nontoxic to the environment [30], while the inorganic group consists of inhibitors that are vastly utilised in aqueous systems due to their high productivity [31]. As reported in [30], Wei et al. [32] stated the advantage of organic green inhibitors over the inorganic inhibitors. Fig.2 gives a diagram of groups of green corrosion inhibitors.

2.1. Plant-Based Corrosion Inhibitors

2.1.1. Plant extract preparation

An extract can be defined as a substance consisting of the active agents (phytochemicals) of a plant or its parts and obtained using a solvent [33]. They are commonly obtained from the whole plant or the parts containing higher concentrations of the phytochemicals [34,35]. Examples of these phytochemicals include, those found in the stems and roots including flavonoids, saponins, alkaloids and steroids; those found in the leaves which include anthocyanins, flavones, sinapyl esters, isoflavonoids and psoralens; coumarin found in the flowers, and those found in fruits including tricarboxylic acid, terpenoids, tannins, flavonols and aromatic acids [33]. A summary of the extracts of some plants examined as corrosion inhibitors and the gaps established is presented in Table 1.

2.1.2. Methods used in the preparation of plant extracts

There are many methods employed for extracting active agents or phytochemicals from plants/plant parts. These can be classified as traditional and non-traditional methods. Traditional extraction methods include maceration, infusion, decoction, digestion, and percolation [33,36]. The method applied depends on what is desired as product. In maceration, dried or undried materials are crushed, smashed, or cut into bits. They are then immersed in the extraction solvent for periods of at least 3 days in continuous mixing. The diffusion of the solvent in the material of interest solubilizes the active compounds which leads to their possible extraction. The suspended particles (solids) in the resulting mixture can then be separated by filtering. The advantage of this technique is that the entire substance is extracted unchanged in composition with the phytochemicals being soluble). In the infusion method, the extract is produced by maceration in boiling water for a short period of time. This enables a very efficient extraction of the most soluble constituents. The decoction process consists of the crude substance being boiled in a definite volume of water for a specified period. A disadvantage of this method is the fact that the extract obtained will contains a large quantity of water-soluble impurities [37]. The digestion method requires that the raw materials are macerated in slightly warm solvent. This improves the solubility of the solvent for extraction thus preventing the decomposition of the phytochemicals. The percolation method is essentially a filtration process performed at room temperature. The raw material is dampened and placed inside a conical container (the percolator) with an adjustable closure. The percolator is then filled with a solvent and covered up. The extract then drops from the filter into a receiving container. One advantage of this method is that it gives a high yield of the extract within a short period of time. A second advantage is that the needed raw materials are inexpensive [38].

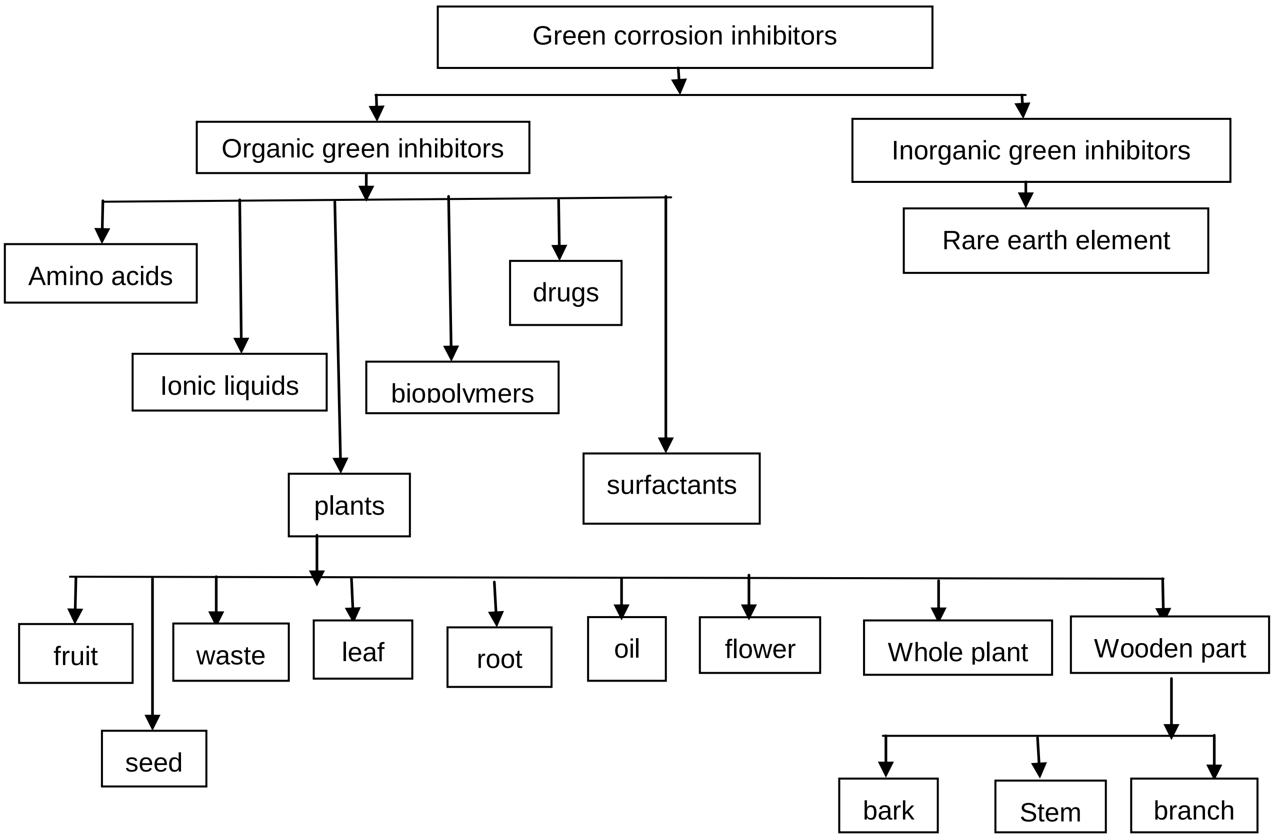

Figure 2. Groups of green corrosion inhibitors

Slika 2. Grupe zelenih inhibitora korozije

The non-traditional methods are more sophisticated. They include the hot continuous extraction method and the ultrasound extraction or sonication [38]. The first one uses the Soxhlet apparatus consisting of a glass body with boiling flask, a siphon arm, thimble, extraction chamber, and condenser. The boiling flask containing the solvent is heated and the vapors produced are condensed. The resultant liquid falls into the thimble containing the raw material. The extract then fills the extraction chamber. This causes the siphon arm to return the liquid into the boiling flask. The reflux process must be stopped up to obtain the degree of the extraction desired. Sonication is a process that uses high energy ultrasounds to improve permeability of cell walls, producing cavitation to disrupt cellular membranes [39,40]. Consequently, sonication breaks the cells, releasing their content for further extraction.

Liquids obtained by the methods introduced above are then refined by filtration or decantation.

Zhang et al [37] have, however, included the following extraction methods as modern or greener extraction methods, that have also been applied in natural products extraction: super critical fluid extraction (SFC), pressurized liquid extraction (PLE) and microwave assisted extraction (MAE), They asserted that these methods have added advantages such as lower organic solvent consumption, shorter extraction time and higher selectivity. Others listed are, pulsed electric field extraction, enzyme assisted extraction, reflux extraction, hydro distillation and steam distillation.

2.1.3. Factors affecting the yield and quality of plant extracts during preparation

Type of solvent: Solvents used for extraction of phytochemicals affect their physical, chemical and antioxidant properties and even the yield, [41-44] hence the right choice of solvent for a given extraction is very vital [33]. Regularly used solvents include, water, ethanol, methanol, acetone, ethyl acetate…etc. [45-48]. Temperature has a significant effect on extract preparation. At low temperatures, the solubility of the phytochemicals may be reduced while at high temperatures, decomposition of these substances/compounds may occur[40]. According to [49,50], the recommended temperature for an ideal extraction falls between the range of 60–80^{0}C. However, when drying of the material is to be considered, oven drying is advisable, because drying at room temperature can take a long time to accomplish. [34]. Other factors include extraction time, solvent–to-feed ratio, number of repeated extractions of the sample and material pretreatment [51].

3. CHARACTERIZATION TECHNIQUES

Potentiodynamic polarization (PDP) measurement: Polarization tests, such as PDP, are based on the evaluation and analysis of the current produced by a variable potential in a working electrode. This method is one of the most used DC electrochemical methods in corrosion measurements. Here, the potential in a wide range is applied on the test electrode, and as a result, an adequate current is generated. The presentation of the potential in the function of current density (I) (or log I) for each measured point results in the polarization curve. The polarization curve can be used to determine the corrosion potential and the corrosion rate of the metal in the given condition (Tafel slope). The advantage of this method is the likelihood of a localized corrosion detection, easy and quick determination of the corrosion rate, efficiency of the corrosion protection, etc. [52].

Cyclic Potentiodynamic Polarization (PDP). This is also widely used to determine resistance to localized corrosion or degradation rate in a short time [53]. It is performed like a potentiodynamic scan, but with an addition: the voltage is swept across a range but reversed back to the starting potential. This allows a return to the original potential. The surface is likely to be changed by the reactions during the scan, so often the data from the return voltage sweep do not superimpose upon the data from the forward sweep.

Electrochemical Impedance Spectroscopy (EIS) [54]. This technique is used to determine the impedance of a system in terms of the frequency of a variable potential. The analysis of EIS results relies on models with equivalent electrical circuits, with the most recurrent graphical representations of its results being Nyquist plots [55]. EIS shows more information, for example, mechanism and different resistance of the system.

Linear polarization resistance (LPR) is a technique used to obtain the corrosion rate by determining the relationship between electrochemical potential and generated currents on charged electrodes [56].

Weight Loss Method (WL): This technique is based on the mass lost by the metal, which is directly monitored to get the corrosion rate. The loss of metal due to corrosion is measured by exposing the metal specimen of known area to the environment for a period of time and the difference in weight before and after exposure is calculated [57].

Surface characterization is usually studied by means of spectroscopy and microscopy techniques. Some of these are:

Scanning Electron Microscope (SEM) provides a clear comparison between the metal surface with and without a corrosion inhibitor, as well as other morphological information [58,59].

Atomic Force Microscope (AFM) obtains information regarding the shape of the metal surface for comparison purposes and topography imaging [60–63].

X-Ray Photoelectron Spectroscopy (XPS) is recurrently used for oxidation states, stoichiometry, and electronic state determination [64–67].

Fourier transform infrared (FTIR) spectroscopy is used to obtain information on the functional groups and vibrational modes on the corrosion inhibitors [33].

Ultraviolet–Visible (UV–VIS) spectroscopy helps to explain functional groups, electronic transitions, and optical band gaps.

Table 1. Summary of research gaps for plant-based green corrosion inhibitors from 2016 to 2021 for steel. -Note: DEIS – Dynamic EIS; HPLC - high-performance liquid chromatography; IE- Inhibition efficiency;; ATR-FTIR – Attenuated total refraction FTIR;;; EDX – Energy Dispersive X-ray spectroscopy; SVET - Scanning vibrating electrode technique; WAXD - wide-angle X-ray diffraction; VPSEM – Variable pressure SEM; GC – Gas Chromatography; MC – Mass spectroscopy; DFT – Density functional theory; temp. – temperature; inh. – inhibitor; conc. – concentration; MD - molecular dynamics; MC - Monte Carlo; QM - quantum mechanics.

Tabela 1. Rezime istraživačkih nedostataka za inhibitore zelene korozije na bazi biljaka od 2016. do 2021. za čelik. -Napomena: DEIS – Dinamički EIS; HPLC - tečna hromatografija visokih performansi; IE-Efikasnost inhibicije; ATR-FTIR – FTIR prigušene ukupne refrakcije; EDX – Energetska disperzivna X-ray spektroskopija; SVET - Tehnika skenirajuće vibracione elektrode; WAXD - širokougaona difrakcija rendgenskih zraka; VPSEM – SEM promenljivog pritiska; GC – gasna hromatografija; MC – Masena spektroskopija; DFT – Teorija funkcionalne gustine; temp. – temperatura; inh.. – inhibitor; conc. – koncentracija; MD - molekularna dinamika; MC - Monte Karlo; QM - kvantna mehanika.

Inhibitor	**Alloy**	**parameters**	**analysis**	**Gap**	**Ref.**
Gentiana olivieri extracts	mild steel	inh. conc; 200 400, 600, 800mg/L temp.; 20, 30, 40, 50^{o}C.	FTIR, UV-VIS, EDX, SEM, HPLC, PDP, EIS,	Constant immersion time. Suggestion: Vary immersion time from 3 -30 days	[68]
Highest IE obtained was 93.7% with the highest inhibitor concentration					
Black tea leaves extract	mild steel	inh. conc.; 2, 4 6, 8, 10 and 12 drops immersion time; 1, 2, 3hrs for the WL method	FTIR, EDX, SEM WL	constant temp. Suggestion: Vary temp. from 30^{o}C to 80^{o}C	[69]
Note: I drop equals 0.005ml Highest IE obtained was 97% with the highest inhibitor concentration					
Coffee husk extract	carbon steel	inh. conc.; 10% 20%, 30% (v/v)	SEM, PDP, LPR EIS, WL	constant temp. (25^{o}C) and immersion time (4hr) for the WL method. Suggestion: Vary immersion time from 3 to 30 days and temp. from 25 to 90^{o}C	[70]
Highest IE obtained was 97% with the highest inhibitor concentration					
Castor bark powder extract	carbon steel	inh. conc. (0.44, 0.77, 1.11, 1.44, 1.77 g/L) immersion time (2, 6, 12, 24hrs)	FTIR, SEM, PDP, EIS, SVET, WL	constant temp. Remark: Vary temp from 25^{o}C to 90^{o}C	[71]

The highest IE attained was 83% at the highest inhibitor concentration					
Juniperus procera leaves extract	carbon steel	Inh. Conc.; 0.5, 1.0 1.5, 2.0, 2.5g/L Immersion time (6hrs) . temp.: 25, 35, 45, 55^{o}C	WL, EIS, PDP	Constant immersion time Remark: Vary the immersion time from 3 – 30 days.	[72]
The highest IE attained was 87.2% at the highest inhibitor concentration					
Ligularia fischeri green extract	mild steel	inh. conc.; 100 200, 300, 400, 500ppm, temp.; 30, 40, 50, 60 ◦C	FTIR, UV–visiblle Raman, SEM, EDX AFM, WAXD, PDP EIS, AAS, WL	Constant immersion time (3hr) Remark: Vary immersion time from 3 to 30 days	[73]
Results: 500 ppm gave the highest IE of 92%; IE decreased with temperature					
Tragia plukenetii extract	mild steel	inh. conc.; 100 200, 300, 400, 500ppm; temp. (30, 40, 50, 60◦C)	FTIR, UV–visible Raman, SEM, EDX AFM, WAXD, PDP EIS, AAS, WL	Constant immersion time (3hr) Remark: Vary immersion time from 3 to 30 days	[74]
Results: 500 ppm gave the highest IE of 88%; IE decreased with temperature					
Magnolia Kobus extract	mild steel	inh. conc.; 100 200, 300, 400, 500ppm, temp. (30, 40, 50, 60◦C)	FTIR, UV–visible AFM, AAS, SEM, PDP, EIS, WL EDX	Constant immersion time (3hr) Remark: Vary immersion time from 3 to 30 days	[75]
Results: 500 ppm gave the highest IE of 95.01 %; IE decreased with temperature					
Saccocalyx satureioides extract	carbon steel	Inh. Conc.; 200, 400, 600, 800, 900mg/L. temp.: 20, 30, 40, 50^{o}C	SEM, EIS, PDP, WL	Constant immersion time Remark: Vary the immersion time from 3 – 30 days.	[76]
Results: 900 ppm gave the highest IE of 87%; IE decreased with temperature					
Borage flower	mild steel	Inh. Conc. (200, 400, 600, 800 ppm) Maximum Immersion time of 5hrs	WL, EIS, PDP FTIR, UV-VIS, SEM, AFM	Constant temperature (25 ◦C) Remark: Vary the temp. from 25 up to 90^{o}C	[77]

Results: Highest IE of 93% obtained with 800 ppm conc. for the WL method; and 91% IE With 800ppm at 5hrs for the EIS method.					
Rice straw extract	steel	Immersion time (7, 14, 21, 28, 35, 42 days)	FTIR, VPSEM, EDX, cyclic polarization, WL	Constant temp. (25°C) Remark: Vary temp. from 25 up to 90°C	[78]
Results: Immersion time of 7 to 14 days and 85% IE					
Glycyrrhiza glabra (Pea and bean)	mild steel	Inh. Conc. (200, 400, 600, 800 ppm)	EIS, PDP, AFM, contact angle, MD, MC, QM	Constant immersion time (24h) Remark: Vary the immersion time from 3 up to 30 days	[79]
Results: 800 ppm gave 88% maximum IE					
Lemon Balm extracts	mild steel	inh. conc.; 200 (400, 600, 800ppm immersion time (0.5, 2, 4, 6, 12, 24hrs)	EIS, PDP, contact angle, SEM, AFM Raman spectroscopy FTIR, MC, MD, QM, UV – VIS.	Constant temp, Remark: Vary temp from 25 °C up to 90°C.	[80]
Result: 800 ppm with immersion time of 24 h and 94.6% IE					
Ptero-carpus Santali-noides leaves extract	low carbon steel	Inh. conc. (0.1–0.7 g/L) temp. (25°C and 60°C)	EIS, LPR, PDP, SEM, EDAX, AFM FTIR, UV – VIS	Limited temp. (25°C and 60°C). Remark: Extend temp to 90°C and vary immersion time up to 30 days.	[81]
Result: Highest IE (95.64%) obtained at 0.7 g/L PSLE extract at 60°C from PDP experiment					
Ficus *religiosa* leaf, bodhi tree	mild steel	conc (100–500 ppm) temp. (25, 35, 45 ◦C)	EIS, WL, SEM quantum chemical study	Constant immersion time (24 h). Remark: Vary immersion time from 3 30 days	[82]
Results: 50 ppm gave 88.29% IE					
Myristica Fragrans (nutmeg fruit)	mild steel	conc. (100, 200, 300, 400, 500 ppm)	WL, UV – VIS FT-IR spectroscopy, NMR analysis, quantum chemical	Constant temp. 25°C and immersion time (24hr) Remark: Vary temp.	[83]

			studies, SEM	from 25 up to 90°C and extend immersion time from 3 to 30 days	
Results: 500 ppm gave 87.81% IE					
Sunflower seed hull (flower)	mild steel	Inhibitor conc. (50, 100, 200, 300, 400ppm), Temp; 25, 40, 50, 60°C	FT-IR, UV-VIS, Gas chromatography, PDP and EIS	Constant immersion time (24hr) Remark: Vary the Immersion time from 3 up to 30 days	[84]
Result: 400 ppm gave 98.46% IE at 60 ◦C					
Gongronema latifolium (utazi herb)	mild steel	Inhibitor conc. (0.5, 1.0, 2.5, 5.0 and 10.0 g/L), temp. (30, 40, 50, 60°C)	Gasometric	Immersion ime not stated and only one major experiment carried out. Remark: Vary immersion time from 3 to 30 days	[85]
Results: i. Maximum IE of 95.4% obtained with the 10g/L conc. at 30°C for EEGL ii. Maximum IE of 96.5% obtained with the 10g/L conc. at 50 ◦C for SEGL					
Ficus leaves extract	Carbon steel	Inh. Conc. (25 to 200 mg/L.) and temp. (25, 35, 45°C)	PDP, EIS, FTIR, SEM and quantum chemical studies	constant immersion time (24 h) Remark: Vary the immersion time from 3 to 30 days	[86]
Results: Maximum IE was 95.8% at 25°C and conc. of 200mg/L. Obtained high efficiencies at higher temps.					
Xanthium Struma- rium	low carbon steel	Inh. conc. (2, 4, 6, 8, 10mL/L) temp. (30, 40, 50, 60°C)	WL, FTIR, SEM, mathematical and statistical modelling	constant immersion time, Remark: Vary immersion time from 3 – 30 days.	[87]
Result: Maximum IE was 94.82% at the optimum concentration of 10 mL/L.					
Cuscuta reflexa (Morning, glory family) fruit extract)	mild steel	Inh. Conc. (100, 200, 300, 400, 500 ppm)	WL, electrochml UV – VIS spectroscopy, surface analysis, quantum chemical studies, FTIR spectroscopy	Constant immersion time (24h) used. Remark: Vary the immersion time from 3 to 30 days	[88]

Results: 500 ppm gave 95.47% maximum IE					
Tunbergia fragrans extract	mild steel	Inh. Conc. (100, 200, 300, 400, 500 ppm)	WL, PDP, EIS, SEM, EDS	Constant immersion time (2 h) and constant temp Remark: Extend immersion time up to 30 days and immersion temp. up to 90^{o}C	[89]
Results: 500 ppm gave 81.1% maximum IE					
Euphorbia Heterophylla L. extract	mild steel	Inh. Conc. (1g/L, 1.5g/L, 2g/L) immersion time (3hr, 5hr, 7hr) Immersion temp. (40, 50, 60, 70^{o}C)	WL, Thermodynamic and adsorption studies	Short immersion time Remark: Extend immersion time to 30 days.	[90]
Result: Highest IE obtained with Ig/L 7hr immersion time.					
Diospyros Kaki leaves extract	St37 steel	inh. conc. (90, 135 180, and 225 ppm) immersion time; 6hr	PDP, EIS, DEIS, SEM, EDAX, FTIR	constant immersion time and temp. Remark: Vary immersion time up till 30 days and immersion temp. up to 90^{o}C	[91]
Result: Maximum IE of 91% was obtained at 225ppm from PDP measurements					
Sida Acuta leaves and stem	mild steel	inh. conc.; 0.1, 0.2, 0,3, 0.4, 0.5g/L. temp.; 30, 40, 50, 60^{0}C)	WL, hydrogen evolution measurement AAS, FTIR, UV-VIS	Constant immersion time. Remark: Vary the immersion time from 3 to 30 days.	[92]
Results: 0.5g/L gave 85% (leaves) and 52% (stem) IE at 30 ◦C. IE decreased with temperature.					
Aloysia Citrodora Leaves Extract	mild steel	inh. conc. (200, 400, 600, 800ppm), immersion time, 0.5, 2,5, 5 hrs)	PDP, EIS, AFM, FTIR, UV-VIS, SEM,	Constant temp. (room temp.) Remark: Extend temp. to 80^{o}C.	[93]
Result: Highest IE (94%) obtained with the 800ppm conc. at 2.5hrs (EIS)					

Ammi visnaga umbels extract	mild steel	Inh. conc.; 150 ,250 450, 700ppm. temp.; 30, 40, 50, 60^oC	GC, MS WL, EIS PDP, SEM, DFT, MD.	Short immersion time range. Remark: Vary immersion time from 3 – 30 days.	[94]
Result: Maximum IE of 84% obtained at the highest inh. conc. (700ppm) and the lowest temp. of 30^oC, though IE remained relatively high at other temperatures.					
Rosa canina fruit	mild steel	inh. Conc. (200, 400, 600, 800 ppm) immersion time (2, 4, 6, 24, 48 h)	FTIR, UV-VIS FE-SEM, EDS, PDP EIS. MD, QM simulations	Constant temperature (25^oC) Remark: Vary temp. from 25 to 90^oC	[95]
Result: 800 ppm gave 85.35% IE at immersion time of 24 hrs					
Lychee waste	mild steel	inh. Conc. (300, 400, 500, 600, 700ppm immersion time Extraction process (blank Etoh-U, Etoh-R, H_2O-U)	WL, EIS, SEM FTIR spectroscopy, and computational studies	Constant temperature (25oC) Remark: Vary temp. from 25 to 90^oC	[96]
Results Etoh-U: 97.95% IE 1.5 h: 97.95% IE 600 ppm: 97.95% IE					
Musa paradisica peels (banana)	mild steel	Acid solution (1M HCl and 0.5M H_2SO_4 and inh. conc. (200, 300, 400ppm)	EIS, LPR, Tafel polarization, FTIR, SEM, AFM analysis	Constant temp. temp. (25^oC and immersion time (24hr). Remark: Vary temp. from 25 to 90^oC and extend immersion time from 3 up to 30 days.	[97]
Results: 1 M HCl, 400 ppm gave 90% maximum IE					
Longan seed and peel	mild steel	Inh. conc. (300 400, 500, 600ppm) and temp. (25, 35, 45, 55^oC)	EIS, Weight loss FTIR, SEM, computational studies	Constant immersion time (24hr) Remark: Vary the immersion time from 3 to 30 days	[98]
Results: 600ppm: 92.93% IE 55 ◦C: 89.29% IE					

Peganum harmala seed extract	mild steel	inh. conc. (200, 400, 600 and 800 ppm) immersion time (0.5hr, 2.5hr, 5hr)	PDP, EIS, FTIR, UV-VIS, SEM, AFM contact angle, MD DFT and MC	Constant temp. and short time of exposure, Remark: Extend temp. to 90°C and immersion time.	[99]
Result: Maximum IE was 95% at 2.5hrs and 800ppm extract					
Capsicum Annuum fruit paste	mild steel	Immersion time (24, 96, 168 h)	WL, contact angle measurements, FTIR, SEM,	Constant temperature (25°C) and conc. Remark: Vary the temperature from 25 up to 90°C	[100]
Results: Maximum IE of 96.48% at immersion time of 24hrs					
Taraxa-cum officinale	stainless steel	inh. conc. (0.1, 0.3, 0.7, 1.5, 3.0g/L)	WL, EIS, PDP SEM, UV - VIS and FTIR Thermometric measurement	Constant time temp. for the WL method Remark: Vary temp. from 25°C up to 90°C and immersion time from 3 – 30 days	[101]
Result: Maximum IE was 99.3% at the maximum inhibitor conc. of 3.0g/L					
Litchi peels	mild steel	inh. conc. (25, 75, 100, 150, 200, 300ppm)	Weight loss, EIS, PDP, surface analysis	Constant temperature (25°C) and immersion time (24 h). Remark: Vary the temperature from 25 up to 90 ◦C and then immersion time from 3 to 30 days.	[102]
Results: 300 ppm gave a maximum IE of 97.8%.					
Water-rmelon Waste (rind, seed and peels	mild steel	Inh. conc. (10, 50, 100, 200ppm)	EIS, SEM, UV-vis and FTIR spectroscopy	Constant temp. (25°C) and immersion time (24h) Remark: Vary temp. from 25 to 90°C and immersion time from 3 to 30 days	[103]
Results: Rind: 200 ppm, 79.86% IE Seed: 200 ppm, 83.67% IE Peel: 200 ppm, 72.42% IE					

Apricot Juice extract	mild steel	Inh. conc. (100 200, 300) 400pp and temp.: 30, 40, 50, 60 °C)	Weight loss	Constant immersion time (24 h) Remark: Vary the immersion time from 3 to 30 days	[104]
Results: 400 ppm gave the maximum IE of 75% IE at 30 ◦C					
Ginkgo Leaf Extract	X70 Steel	inh. conc. (25, 50, 100 and 200 mg/L) temp. (25, 35, 45° C)	PDP, EIS, FTIR, SEM	Limited temp. range. Remark: Extend temp. to 90°C.	[105]
Result: Approximately 90% maximum IE in the presence of 200 mg/L GLE at all tested temp.					
Carrot (*Daucus Carota L.*) Peels	mild steel	inh. conc. (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5% v/v)	Weight loss, PDP, optical microscopy	Constant time of 6hrs. Remark: Extend immersion time from 3 days to 30 days	[106]
Result: The maximum IE 88.08% obtained 0.5v/v conc. at 25°C from PDP experiment, IE reduced with temp.					
Tabernae-montana Divaricate extract	steel	inh. conc. (100, 200, 300, 400, 500ppm)	Weight loss, EIS, PDP, SEM-EDS, Analysis	Constant time and temp. Remark: Increase time of Immersion from 3 – 30 days and temp. up to 90°C	[107]
Result: A maximum of 95% IE was achieved by using 500ppm of inhibitor.					
Myrobalan extract	mild steel	inh. conc. (200, 400, 600 and 800 ppm) immersion time (0.5hr, 2.5hr, 5hr)	PDP, EIS, AFM, UV-VIS, SEM, MC, MD, DFT simulations	Constant temp. Remark: Vary temp. from 25°C to 90°C	[108]
Results: Maximum IE of 91% by 800 ppm extract from EIS analysis at 2.5hrs.					
Chinese goose-berry fruit extract	mild steel	inh. conc. (400, 600, 800 and 1000 ppm) immersion time (0.5hr, 2.5hr, 5hr)	PDP, EIS, FTIR, SEM, AFM, MC,	Constant temp. Short time of of exposure, Remark: Extend temp. to 90°C and immersion time to 30 days.	[109]

Result: Maximum IE of 94% obtained during 5hrs immersion at 25 °C and 1000 ppm of extract for WL experiment.					
Garcinia indica (Binda) Fruit rind extract	mild steel	inh. conc. (1%, 2%, 3% and 4% v/v extract in acid solution) immersion time (24, 48, 72, 96hr)	PDP, EIS, FTIR, WL SEM, AFM, UV-VIS	small conc. values increased Suggestion: Increase conc.	[110]
Result: Maximum IE was obtained at 97.28%, (4%v/v and 24hrs for WL method). For the rest of immersion time, IE remained in the range 93.14% - 96.46%.					
Gloriosa superba seeds extract	low carbon steel	inh. conc. (100, 200, 300, 400, 500, 600, 700mg/L)	PDP, EIS, FTIR, UV-VIS, SEM, AFM WL, MD, DFT.	constant temp. and time Remark: Vary temp. up to 90°C and time up to 30 days.	[111]
Result: Maximum IE of 93.84% obtained at 700 mg/L from the EIS experiments.					
Paprika Extract	carbon steel	inh. conc. (50, 100, 150, 200 250, 300ppm) Temp.: 25, 30, 35, 40°C	ATR-FTIR, SEM, EDX PDP, EIS, WL	short immersion time Remark: Vary immersion time from 3 to 30 days and temperature up till 90°C	[112]
Result: Maximum IE was about 95% observed at 40°C.					
Avocado Seed powder (Persea Americana) extract	SAE 1008 carbon steel	inh. conc. (0.44, 0.77, 1.11, 1.44, 1.77 g/L) immersion time (2hrs for WL method)	FTIR, PDP, EIS, WL, optical microscopy	short immersion and constant temp. Remark: Vary time from 3 to 30 days. and temp. from 30 to 90°C.	[113]
Maximum IE was 92% for the WL method and 98% for the EIS analysis at the highest inhibitor concentration					
Coreopsis tinctoria extract	mild steel	inh. conc.; 100 200, 300, 400, 500ppm temp.; 30, 40, 50, 60°C	Raman, SEM, EDX EIS, AAS, WL	Constant immersion time (3hr) Remark: Vary immersion time from 3 to 30 days	[114]

Results: 500 ppm gave the highest IE of 80.62 %; IE decreased with temperature					
Ficus carica extract	carbon steel	Inh. conc.; 50, 100 150, 200, 250 300ppm, temp.: 25, 35, 45, 55^{o}C for the WL method	PDP, EIS, EFM WL, AFM FTIR	Too short a period of immersion, Suggestion: Increase immersion time from 3 to 30 days and temp. to 90^{o}C	[115]
Results: Maximum IE of about 95.7% with the highest concentration and the highest temperature using the WL method.					
Ecballium Elaterium extract	carbon steel	Inh. conc.; 50, 100 150, 200, 250 300mg/L, temp.: 25, 30, 35, 40 45^{c}C for the WL method	PDP, EIS, EFM WL, AFM, FTIR DFT	Too short a period of immersion (3hrs), Suggestion: Increase immersion time from 3 to 30 days and temp. to 90^{o}C	[116]
Results: Maximum IE of about 97.5% with the highest concentration, highest immersion time, and the highest temperature using the WL method.					
Conyza bonariensis extract	carbon steel	Inh. conc.; 10, 20, 40, 60, 80, 100ppm, temp.: 30, 35, 40, 45^{o}C for the WL method	PDP, EIS, EFM WL, AFM, SEM EDX,	Too short a period of immersion (3hrs), Suggestion: Increase immersion time from 3 to 30 days	[117]
Results: Maximum IE of about 93.3% with the highest concentration using the WL method. IE reduced with temperature increase.					
Ambrosia maritima	Carbon steel	Inh. conc.; 100, 150, 200, 250, 300ppm. Temp.; 25, 30, 35, 40, 45^{o}C for the WL	PDP, EIS, EFM, SEM, FTIR, AFM	Too short an immersion time used Suggestion: increase immersion time from 3 to 30 days	[118]
Results: Maximum IE of about 92.7% with the highest concentration for the WL.					
Wihania somnifera	Carbon steel	Inh. conc.; 100, 200, 300, 400. 500, 600ppm. temp.; 25, 30, 40, 45^{o}C	PDP, EIS, EFM, FTIR, AFM, WL	Too short an immersion time Suggestion: increase immersion time from 3 to 30 days.	[119]
Results: Maximum IE of about 90.4% with the highest concentration for the EIS method. IE decreased with increase in temperature.					

Pulicaria undulate	carbon steel	Inh. conc.; 50 100, 150, 200, 250ppm. Temp. 25, 30, 35, 40, 45°C.	EIS, PDP, EFM AFM, WL, ATR-IR	Too short an immersion time Suggestion: Increase immersion time to 30 days and temp. to 90°C	[120]
Result: Maximum IE obtained as 92.34% with the highest concentration and highest temperature for the (WL method). IE increased with increase in temperature.					

4. CONCLUSION

The work presented a review of the literature on various corrosion inhibitors in mitigating the corrosion process of iron alloys. It is obvious that natural plant extracts are effective green corrosion inhibitors against these alloys. Findings indicate that some of these plant-based inhibitors exhibited high efficiencies at low temperatures and short immersion times. In addition, studies on the real-world application are limited. Due to the limitations of the test media and environmental variables in these literatures, it is recommended that more studies at elevated temperatures be conducted to determine the optimum temperature for the inhibitors' application in corrosive media such as seawater environment. The immersion time should be extended to determine the optimum time for the inhibition efficiencies of the plant-based substances. It was observed that some inhibitors' efficiencies decreased as temperature increased as a result of their thermal instability. While experimental approaches such as electrochemical impedance spectroscopy, weight loss, and potentiodynamic polarization techniques were utilized in these literature, further research should analyze the structure of the extracts to understand the process of inhibition and any possibility of toxic properties to the deployed environment.

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IZVOD

BILJNI MATERIJALI KAO INHIBITOR ZELENE KOROZIJE ZA ODABRANE LEGURE GVOŽĐA: PREGLED

Značaj studija korozije stavlja u prvi plan ekonomske gubitke, štete i bezbednosna pitanja propadanja metala u građevinskoj industriji i privredi. Iako izbor materijala i upotreba inhibitora mogu doprineti njegovoj otpornosti na ponašanje korozije u okolini, strukturno propadanje metala može biti pogoršano u uslovima rada. U ovom pregledu daju se istaknuti nalazi istraživanja objavljenih u poslednjih pet godina o upotrebi biljnih materijala kao inhibitora korozije za varijante čelika: ugljenični čelik, meki čelik, nerđajući čelik. Razjašnjava značenje zelenih inhibitora i njihove vrste. Takođe, predstavlja metode koje se koriste da bi se utvrdila efikasnost inhibicije navedenih biljaka/delova biljke i parametri koji se razmatraju u analizama inhibicije korozije. Glavne praznine ili ograničenja identifikovana u prijavljenim nalazima istraživanja uključuju eksperimentisanje na konstantnim temperaturama i kratkim periodima potapanja za legure. Zbog činjenice da bi, ako bi se ovi ekstrakti koristili za industrijsku upotrebu, bili izloženi opasnijim uslovima, kao što su više temperature, pritisci, itd., ovaj rad predlaže da se njihova istraživanja kao potencijalni inhibitori u laboratoriji/pilot skala se izvodi na višim temperaturama i dužim vremenima potapanja što kao takvo može pružiti sveobuhvatnije znanje o ekološkim/klimatskim zahtevima za njihovu primenu. Takođe, predlažu se dodatne strategije poboljšanja. Spisak izvoda, međutim, nije konačan.

Ključne reči: *meki čelik, ugljenični čelik, korozija, biljni ekstrakti, zeleni inhibitori korozije,*

Naučni rad

Rad primljen: 19. 01. 2022.

Rad prihvaćen: 10. 02. 2022.

Rad je dostupan na sajtu: www.idk.org.rs/casopis