Chapter 3

Green Corrosion Inhibitors from Biomass and Natural Sources

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Abstract

Considering the fact that corrosion of metals and alloys presents a significant problem all over the world, the one of most recently utilized approaches to combat this problem necessitates the researches for employment of new materials, which satisfied the green chemistry idea. In this connection, the development of sustainable corrosion inhibitors is highly demanded due to the increasing of awareness of green chemistry principles not only in corrosion discipline, but also in all branches of science and technology. Due to natural and biological origin as well as their eco-friendly extraction, the plant materials and biomass derived from various waste sources could be applied as beneficial substances for metals and alloys protection in different corrosion environment. Therefore, this work reports the main findings regarding their employments as green anticorrosion substances.

Keywords

Natural Sources, Biomass Waste, Green Corrosion Inhibitors, Metal Surface, Corrosion Media

Contents

Green Corrosion Inhibitors from Biomass and Natural Sources	46
1. Introduction.....	47
2. Corrosion	49
2.1 Corrosion Inhibitors.....	50

2.2	Corrosion inhibitors from plant sources	51
2.3	Corrosion inhibitors from biomass waste	58
References		62

1. Introduction

The corrosion of metals and alloys is a serious industrial issue all over the world, which could be minimized or stopped by suitable approaches. One of them involves the application of corrosion inhibitors [1], i.e. the substances which are able to slow down the corrosion reactions when added in low concentration. Due to the fact that corrosion involves the movement of the metal ions into the aggressive solution from the more (anode) to less (cathode) active areas, with an ionic current in the solution, and an electronic current in the metal, the addition of inhibitors reduced the corrosion rate by increasing or decreasing the anodic and/or cathodic reactions [2]. These molecules generally contained heteroatoms, such as oxygen, nitrogen and sulfur, through are adhered onto the metal, forming a barrier for further corrosion attack. Although, the literature reports [1,3] showed that various organic compounds are successful anticorrosion substances for metals and alloys in different environments, unfortunately their use is limited due to their toxic nature and expensive synthesis.

Nowadays, with increasing of “green chemistry” concept in all branches of science, technology and engineering, a set of principles that causes reduction of environmental pollution, and increase of eco-friendly chemicals are influenced also in the corrosion science, regarding the employment of inhibitors derived from natural resources and biomasses [4]. In that connection, the plants as natural products have been recently proposed [5,6] as a green corrosion inhibitor due to its cheap, environmentally acceptable, abundant, readily available, and effective anticorrosion properties. There is a rich source of bioactive compounds such as tannins, phenols, flavonoids, acids, alkaloids, catechins, terpenoids, amino acid and proteins, polysaccharides and vitamins [4,5].

The numerous plant extracts have been prepared from various parts of plants, including leaf, root, stem, bark, pulp, fruit, etc., and investigated as green corrosion inhibitors for many metallic surface [7,8]. Among various phytochemicals in plant extracts seem that polyphenols classes satisfy the most of the demands of anticorrosion inhibitors [9], including that they are less toxic than other natural compounds, for instance alkaloids. Due to the fact that phytochemicals are extracted from various parts of plants, the proportion of constituents responsible for anticorrosion performance differ among them, and consequently attribute to different inhibition efficiency. It is certain that plant extracts and

oils gained from leaf emerge to be an effective type of inhibitors to corrosion and could be successfully used on an industrial level, due to the high inhibition efficiency, up to 88 % [10]. However, the plant extracts could not resist high temperatures, and are not efficient in extremely aggressive environments [7].

Although efficient in anticorrosion activity, their exact mechanism is difficult to explain, due to its complex chemical structure. It could be anodic, cathodic or mixed. Usually, the anodic acted by creating a defensive oxide layer on the superficial of the metal, while cathodic ones are capable to reduce the cathodic reaction due to its selective precipitation on the cathodic areas of metal. When the inhibitors are able to provide both, cathodic and anodic actions, which is the one of usual characteristic of the numerous of green corrosion inhibitor then they could be classified as mixed types. Their adsorption on metallic surface is frequently associated by the presence of the double or triple bonds or V and VI groups of elements with free electron couples, i.e. N, P, S and O. It is also important to mention that certain types of inhibitors are strongly specific for one type of metal or alloy, and are not able to provide efficient inhibition of others.

Due to the fact that phytochemicals in plant extracts are the mixture of various constituents, it is necessary to provide the efficient qualitative or quantitative examination of plant extracts, in order to gain the idea which of the compound(s) is responsible for anticorrosion activity on metals or its alloys. Although, some attempts of corrosion scientists [10-14] have been made to connect the anticorrosion activity with certain chemical characterization of plant extracts, further investigations should be done. For instance, did the individual components act synergistically or antagonistically? In addition, if the active component showed by itself a very high degree of inhibition, particularly in aggressive medium, should it be isolated from the mixture? If the plant extracts could not withstand very high temperature (decomposition of some components), do scientists need to find and isolate a component that will show a high degree of inhibition even at higher applied temperatures? Thus, the future studies on application of plant extracts as corrosion inhibitors should be directed on isolation of the targeted, active molecule, which is responsible for the anticorrosive action.

Besides application of plant extracts as corrosion inhibitors, the employment of value-added compounds originated from un-utilized biomasses [15-32] as anticorrosion substances extended the investigations to another promising and superior candidates. Their chemical structures, similar to those of traditional inhibitors, and the fact that they are generated from low-cost and abundant waste biomasses opened new strategies towards to circular economy happen. Thus, in that connection the present paper summarized some of the natural resources and waste biomasses, which extracts are employed as green corrosion inhibitor.

2. Corrosion

The corrosion process [33] which could be chemical or electrochemical in nature requires at least two reactions that could occur in a corrosive environment. These reactions are classified as anodic and cathodic, and are defined by follow example, i.e. for metal M immersed in sulfuric acid solution the metal oxidation occurs through an anodic (1) and reduction through cathodic (2) reactions:

Although, there are no unique classifications of the types of corrosion, the two common categories are established [34]: *i*) general (atmospheric, galvanic, high-temperature, liquid-metal, molten-salt, biological and stray-current, and *ii*) localized (crevice, filiform, pitting, oral, biological and selective leaching).

The tendency of a metal to corrode depends of various factors, which are mostly connected to metal itself, i.e. its composition and structure, degree of damage (macro or micro defects), and environmental conditions, i.e. type of corrosion medium, pH and acid content, the quantity of corrosion accelerators (oxygen, nitrate, sulfur, chloride and phosphate compounds in corrosion medium), as well as temperature and time of metal/metal alloys exposure to the corrosive medium, which significantly influenced on kinetics of metal oxidation and reduction of species in solution.

In order to avoid the corrosion damages, it is necessary to predict all possible failure, starting from metallic substrate to its final, desirable application, making technical, economic and environmental benefits. In that connection, the selection of appropriate metal or alloy, its testing, before and after interaction with environment, as well as analyses of environmental parameters involved in corrosion phenomena are important facts and must be considered.

Although, the different metallic materials needed to be protected from corrosion, the steel, aluminum, tin, zinc, copper and its alloy are frequently evaluated, due to their broad range of applications. For instance, the steels (carbon steel, alloy steel stainless steel and tool steel) have a wide range of applications (construction, manufacturing, transport, shipbuilding, energy and packaging) due to its highly durable, corrosion resistant, tensile and affordable properties. Tin as soft, silvery - white metal also possesses numerous properties, among which a un-toxicity and excellent resistance to aggressive attacks are

more pronounce. Tin is usually integrated with other metals in order to make the alloys, which are possessed beneficial characteristic of tin. For instance, the tinplate (steel sheet coated with a layer of tin), efficiently expressed the corrosion resistance and low toxicity of tin with strength of steel. Although, the tin makes a minor proportion of tinplate, its addition to steel sheet made tinplate one of the frequently used materials for cans manufacture. Besides tinplate utilization in food and drinks industry (90 %), other applications involved cosmetics, fuel, oil, paints and other industry. Aluminium is used in the enormous number of products, such as cans, foils, kitchen utensils, window frames, beer kegs and airplane parts. It has a low density, great thermal conductivity and good corrosion resistance. It could be easy cast, manufactured and modeled. Aluminium is un-toxic and does not release any odors or taint products with which it is in contact, and thus in forms of aluminum foils and sheets is suitable in food packaging and pharmacy. The good corrosion resistance, excellent mechanical properties and capability to galvanize other metals made zinc currently one of the frequently utilized metals in various industrial branches. The copper as one of non-ferrous materials also possesses excellent properties, i.e. good electric conductivity, strength, ductility and corrosion resistance, which provided its broad application in electronics, energy, petrochemical, transportation, machinery, metallurgy and other industries.

2.1 Corrosion Inhibitors

Corrosion inhibitors are the substance that effectively reduces or prevents the corrosion of exposed metal in a corrosive environment [35]. Added in a small quantity, they are able to diminish the progression of corrosion, maintaining a protective, inhibitive film on metal superficial.

Corrosion inhibitors are classified as organic or inorganic compounds and over the last century, inorganic inhibitors such as chromates, vanadates, various nitrates etc. have been systematically used in various corrosive media [36] due to its remarkable inhibitory properties on different metals and alloys. However, their use is prohibited due to high toxicity, and thus the researches have been carried out on utilization of different organic compounds, especially newly synthesized heterocyclic molecules [3]. At the moment when it is understood that their preparation is extremely expensive, and when a large amount of hazardous organic solvents is used for their synthesis, the application of such compounds is avoided. Although, it has been proven that the vast majority of organic inhibitors protect the metal from the aggressive medium, mostly by adsorption, through atoms that possesses free electron pairs (N, S, O and P) or through double and triple bonds in the molecule, their utilization is also avoided due to the risks to human life and its environment [3].

The increasing of awareness of “green principles”, i.e. ecological, economic and environmentally-friendly (e^3 concept) [37] in all fields of science and technology have been influenced also in the corrosion discipline. In that connection the use of traditional, synthetic organic compounds has been limited, and replaced by green organic compounds, usually extracted by conventional or innovative processing technology, such as pulsed electric fields, ultrasound, microwave, supercritical fluid and high hydrostatic pressure [38]. The green corrosion inhibitors are renewable, bio-degradable and non-toxic, which made them a superior anticorrosion candidate than their synthetic counterparts. They are employed as inhibitors for various metallic materials in different media, such as HCl, H₂SO₄, H₃PO₄ and HNO₃. Nowadays, the plant extracts have acquired a numerous examination and application as green corrosion inhibitor, due to its natural origin. Additionally, the new compounds isolated from the under-utilized waste biomass as corrosion inhibitors have also gained the high attention due to transformation of waste into value-added product with anticorrosive activity, providing beneficial to the producer and environment.

In order to evaluate the inhibition activity of green corrosion inhibitors in various corrosive medium, the several standard analyses, including gravimetric test (weight loss), and potentiodynamic polarization and impedance spectroscopy analyses are employed [4,5]. The weight loss test is the simplest technique used to calculate the corrosion rate, and it is based on metal weight measurements before and after immersion in corrosive medium for a certain period. In comparison with weight loss analysis, the potentiodynamic polarization technique is able to provide a number of useful information regarding the rate of metal dissolution and its protection. For instance, current density, (i_{corr}), potential (E_{corr}) and Tafel slopes (β_a and/or β_c) are some of the polarization parameters frequently reported. Electrochemical impedance spectroscopy requires alternating current, and the output is Nyquist plot for charge transfer or diffusion control process. It could be used to determine polarization resistance R_p , which in turn is inversely proportional to the i_{corr} value. Besides these methods, the atomic force microscope (AFM) and scanning electron microscopy (SEM) are also two of powerful techniques applied to investigate the surface morphology, at nano to microscale. Both of them are capable to provide valuable information regarding the generation and progression of corrosion at the metal-solution interface. Nowadays, the computational studies and quantum chemical calculation are also in the progress, and they are so important for prediction of anticorrosion mechanism.

2.2 Corrosion inhibitors from plant sources

Plant extracts are extensively investigated since their main components have no notable side effect on human population and its surrounding, and since they are cheap, renewable

and easy applicable. Besides these properties the extracts derived from plant sources contained the phytochemicals with similar characteristic and structure to organic corrosion inhibitors, i.e. they possess the heteroatom(s) and/or free electrons in the last orbital, making them as good candidates for inhibiting of metal corrosion in different media.

In order to employ plant extracts as anticorrosion substances for metals and alloys protection, the various methods and parameters for their preparation are available. For instance, the selection of the appropriate solvents is very important for efficient extraction of targeted compound(s). Although, water possesses the excellent properties (inexpensive, readily available, non-toxic, non-flammable and non-hazardous) in comparison with other solvents, the preparation of plant extracts requires mostly aqueous solution of organic solvents (ethanol and methanol), due to its better diffusion into plant cells. The second parameters, which must be considered is extraction temperature, and usually range from 60 to 80 °C. The extraction carried out from these optimal ranges could limit the solubility of targeted compounds or could cause its decomposition.

Nowadays, the uses of plant extracts in corrosion control are considered as green and environmental-friendly approach due to excellent solubility of plant phytochemicals in water. Organic acids, phenols and flavonoids, alkaloids, terpenoids amino acids and proteins, polysaccharides and vitamins are the usual constituents of a numerous of plant extracts [39]. Each of them could interact with a metal surface and retard the corrosion reactions due to the presents of polar functional groups such as -OH, -COOH, -COOC₂H₅, -OCH₃ etc. These groups are capable to increase the solubility of the compounds in a common corrosion media, such as water solution of inorganic acids, salts and alkali. The anticorrosion efficiency of mentioned constituents depends on the adsorption layers formed under particular conditions, and it is usually related with the origin and charge of the metal surface, the chemical composition of the inhibitor (functional groups, aromaticity, possible steric effects, etc.) and at least but not negligible the type of aggressive electrolyte [1]. As it is pointed above, the main mechanism of metals protection in aqueous media is the adsorption of inhibitor on metal surface. If the molecules of inhibitor existed in the system as protonated species (very acidic solutions), the inhibitor is capable to adsorbed on the metal surface by electrostatic feature, and the inhibitor act through so-called physisorption mechanism. [40]. If the inhibitor molecules existed in a solution as neutral molecules, they could donate their electron pairs to vacant orbital of a metal to make a covalent or coordinate types of bond, and in that case the chemisorption mechanism is achieved. Increase of system temperatures is favorable to this type of adsorption, i.e. the rises of temperature lead to increase of inhibitor activity. Although, the chemisorption mechanism of plant extracts has been observed on metal surface, it is the most likely that physisorption and chemisorption occurred on the same metal surface [41].

When the plant materials are considered as potential corrosion inhibitors, they are mostly evaluated on the basis of their bioactive constituents. They contain the particular functional groups, responsible for anticorrosion activity. For instance, the essential oil as concentrated hydrophobic liquids with pleasant odor and essence, usually extracted by steam distillation due to high volatility from various plant parts (flowers, stems, leaves, fruits, seeds and roots etc.) presented the complex mixture of constituents, at a quite different concentration. Their complex chemical compositions, among which aromatic and aliphatic compounds, and hydrocarbon terpenes (isoprenes) and terpenoids (isoprenoids) played a vital role in green anticorrosion performance. The essential oils also contained aldehydes (geranial, citronellal, etc.), ketone (pulegone, carvone, pinocarvone, etc.), alcohols (geraniol, citronellol, nerol, menthol, carveol, etc.), esters (linalyl acetate, isobornyl acetate, etc.) and ethers (1,8-cineole, menthofurane, etc.) [42], and as revealed Table 1 made them as suitable corrosion inhibitors for various metals and alloys, in different environments [43-59].

For instance, the corrosion inhibition efficiency of argan oil on corrosion of C38 steel in 1 M HCl solution obtained by potentiodynamic polarization analysis is 81 % with inhibitor concentration of 3 g/L [43]. Although the authors did not specify which of the components is responsible for the anticorrosion activity of oil, on the basis of calculated thermodynamic parameters they reported that the molecules from oil are physically adsorbed on the steel surface. The same technique is used for determination of inhibition activity of carob oil on steel (type C38) in 1 M hydrochloric acid [45]. Its inhibition action is conditioned by employed concentration, and with 0.5 g/L reached the 86.7 % efficiency. In spite of the fact that the chemical composition of carob oil is quite similar to argan oil (Table 1), the authors claim that molecules of inhibitors are adsorbed chemically on the steel surface. The fatty acids are also the main constituents of chamomile oil, which effectively blocked the steel corrosion in acidic medium depending on applied temperatures, i.e. 90 % at 298 K and 86 % at 328 K [47]. Limonene is the one of the components of several essential oils including verbena [44], fennel [48] and dill [54]. Although these investigations are performed in high acidic solutions, this cyclic monoterpene could not be protonated, and thus according to authors the molecules in the extracts are adsorbed by chemisorption on C38 steel, carbon steel and aluminum surfaces, respectively.

Table 1 Natural oils from plants as green corrosion inhibitors.

Natural oil	Main components	Material	Medium	Inhibitor concentration	Highest inhibition efficiency (%)	Refs.
Argan	Oleic acid, linoleic acid, spinasterol, γ -Tocopherol	C38 steel	1 M HCl	3 g/L	81.0	[43]
Verbena	Geranial, neral, limonene			5.0 g/L	85.5	[44]
Carob seed	Linoleic acid, palmitic acid, oleic acid			0.5 g/L	86.7	[45]
Rosemary	1,8-cineole	Steel	2 M H_3PO_4	10 g/L	73.0	[46]
Chamomile	Linoleic acid, oleic acid, palmitic acid		1 M HCl	2 g/L	90.0	[47]
Fennel	Limonene, β -pinene	Carbon steel	1 M HCl	3 mL/L	76.0	[48]
Garlic	Monoterpens			2.5 g/L	95.8	[49]
Menta	Menthol	Mild steel	1 M HCl	1 g/L	86.0	[50]
Pelargonium	Citronellol, geraniol, izometanon			4 ml/L	90.6	[51]
Laurel	1,8-cineole, methyl eugenol, linalool	Aluminium	1% CH_3COOH	45 mg/L	76.8	[52]
Basil	Linalool, eugenol, 1,8-cineol		0.5 M HCl	5.7 g/L	78.4	[53]
Dill	Carvone, limonene		1 M HCl	300 ppm	98.0	[54]
Cinnamon	Cinnamaldehyde, δ -cadinene	Copper	0.5 M H_2SO_4	150 ppm	89.6	[55]
Artemisia	Camphor, β -thujone	Tinplate	0.5 M HCl	5 g/L	81.0	[56]
Thymus	Borneol, α -terpineol			6 g/L	87.0	[57]
Lavander	Linalool, linalyl acetate	AA5754 alloy	3% NaCl	20 ppm	99.0	[58]
Laurel	1,8-cineol, methyl eugenol, linalool			50 ppm	82.4	[59]

Essential oils of different plants, especially those of the Mediterranean climate, such as laurel, lavender and basil, show very high protection of aluminium in acetic [52] and hydrochloric [53,54] acids, and neutral 3 % NaCl solution [58,59]. For instance, the degree of inhibition of essential oil extracted from basil oil [53] on aluminium in 0.5 M HCl solution gained by potentiodynamic polarization analysis is 90.1 % with oil concentration of 5.7 g/L. The authors revealed that linalool (2,6-dimethyl-2,7-octadien-6-ol) as major component of oil, and lower of eugenol and 1,8-cineole could be easily protonated, forming protective layer on aluminum by physisorption. Additionally, the lavender and laurel essential oils provided the excellent inhibition of aluminium alloy in 3 % NaCl against pitting corrosion due to presence of linalool [58,59]. The authors also assumed that besides physical adsorption on metal surface, the high inhibition efficiency (99.0% for lavender and 82.4% for laurel oils) is connected with the appearance of different adsorption centers, which are able to act synergistically to form a polymeric and coherent film on aluminium alloy. The study of rosemary oil on the corrosion of steel in 2 M H₃PO₄ solution [46] confirmed that its inhibition efficiency increases with increases of oil concentration, and the maximum value of 73 % is obtained with 10 g/L. Although 1,8-cineole as the major component of rosemary oil is responsible for anticorrosion activity, the authors suggested that intermolecular synergistic effect in which are participate all other active molecules in oil are also meritorious for excellent inhibition.

Besides essential oil, some of corrosion inhibitors derived from plant extracts [12,13,60-75] with the major components worthy for inhibition are shown in Table 2. For instance, the investigation of mild steel protection in 0.5 M sulphuric acid indicates that phytochemicals (methoxypyrazine, wine lactone and bisphenol A) found in the extracts of *Armoracia rusticana* [60] are responsible for its inhibition performance. The electrochemical measurements showed that this extract protected the mild steel with inhibition efficiency of 95.74 %, at concentration of 100 mg/L. The authors revealed that numbers of heteroatoms (N and O) in the molecules of methoxypyrazine, wine lactone and bisphenol A are able to create coordinate bonds, and thus through them are easily adsorbed on the surface of mild steel. Similarly, the *Azadirachta indica* extract contain a significant number of oxygen, sulfur and nitrogen atoms accountable for its inhibition activity [61]. Although, the authors revealed that it is difficult to assign which of the 300 compounds in *Azadirachta indica* extract is liable for the anticorrosion effect, and protection of mild steel. In the work of Chevalier et al. [12] is showed that anibine as major alkaloid (95.4 %) of *Aniba rosaeodora* extract is responsible for mild steel protection in high acidic solution by chemisorption. Although, the bamboo leaf extract contains flavonoids, amino acids and amylose, with O and N atoms in their functional groups (-OH, C-O, N-H and O-heterocyclic rings), the authors did not indicate which of the compounds is responsible for

remarkable protection of steel in 1 M HCl (90.3 %) and 0.5 M H₂SO₄ (79.2 %) solutions after addition of 200 mg/L of extracts [62]. These authors [63] also studied the inhibition performance of *Ginkgo* leaves extract, rich of flavonoids, ginkgolides and amino acids, on steel surface in contact with HCl and H₂SO₄ solutions. They pointed out that the molecules from *Ginkgo* leaves extract as protonated in acid media formed the coordinate bond by partial transference of electrons from O and N atoms to vacant d orbits of Fe, providing excellent adsorption and protection of the steel surface. Similarly, the ginseng root extract as a mixture of glycoside, saponin, phenolic acids, alkaloids and lignin also acted as a good corrosion inhibitor of aluminium in HCl solution due to presence of heteroatoms in their structure [64]. According to the authors it is difficult to assign, which of the constituents is responsible for the inhibitive effect.

The black pepper extract also acted as excellent corrosion inhibitor of C38 steel in HCl medium, where the highest protection of 95.8 % are gained by 2 g/L [65]. At the same time, the authors have done the comparative study using piperine, which is isolated from black pepper powder. Its inhibition attains 99 % at 0.001 M concentration.

The influence of *Borage* flower extract on mild steel corrosion in 1 M HCl solution is studied by EIS and potentiodynamic polarization methods [66]. EIS results showed that maximum inhibition performance of 91 % is obtained at 800 ppm. In order to get the additional information regarding the anticorrosion mechanism of substances found in extracts, i.e. lactic acid, nicotinic acid and carotene, the authors are used the theoretical methods based on molecular simulations and quantum chemical calculations. They observed that all of three anticorrosion components, in neutral and protonated forms protected the steel surface with a flat molecular orientation. The other extract, such as that obtained from *Geissospermum* leave also showed a good protection of C38 steel in 1 M HCl, due to presence of alkaloid geissospermine. Its molecules are adsorbed onto the steel surface by physisorption of protonated species and chemisorptions of aromatic ring [67]. The authors also indicated that the high inhibition performance (over 90%) is gained by large size of geissospermine molecules, which covered the wide areas of steel surface and thus retarding the corrosion.

The adsorption and inhibitive efficiency of ethanolic extract of the leaves of *Chlomolaena odorata* L. on mild steel corrosion in acidic solution is probably attributed to the presence of different flavones [68]. However, the mutual effects of phytochemicals in the extract also may contribute to its high inhibition efficiency.

Aluminium corrosion in NaOH solution is studied after addition of aqueous extract of *Hibiscus sabdariffa* leaves [69]. The author revealed that the protection of aluminium surface is based on two phenomena, i.e. the first is the development of potentials at the

metal-solution interface, and the second one is the presence of an oxide film. Considering the fact that the pH values of zero charge for aluminum oxide is 9.0-9.1, it is more likely that positively charged species in *Hibiscus* extract (thiamine and anthocyanins) tend to adsorb under the electrostatic attractions (physical adsorption mechanism). However, its constituents may also act synergistically to inhibit Al corrosion in the tested solutions. The *Saraca ashoka* extract [70], although contains the tannins, saponins and flavonoids, only epicatechin as flavonoids has ability to inhibit the corrosion of mild steel. As results showed the inhibition efficiency of 95.48 % is gained with 100 mg/L of inhibitor.

Overall, it is evident that most of the extracts contained the mixture of phytochemicals, and according to the authors it is difficult to interpret which of the substances possessed the anticorrosion activity. In this context, the future application of extracts derived from various plant materials as corrosion inhibitor must be focused on isolation of the specific active molecule, which is responsible for the anticorrosive properties.

Table 2. Plant extracts as green corrosion inhibitors

Plant extract	Main component	Material	Medium	Inhibitor concentration	Highest inhibition efficiency (%)	Type of adsorption	Refs.
Bamboo leaves	Flavonoids, amino acids	Steel	1 M HCl	200 mg/L	87.4	Mixed	[62]
			0.5 M H ₂ SO ₄		78.8		
Ginko leaves	Flavonoids, ginkgolides, amino acids		1 M HCl	100 mg/L	91.4		[63]
			0.5 M H ₂ SO ₄		81.6		
Geissospermum leaves	Geissospermine	C38 steel	1 M HCl	100 mg/L	90.0	Physisorption	[67]
Black peper	Piperine		1 M HCl	2 g/L	95.0	Chemisorption	[65]
<i>Jasminum nudiflorum</i>	Favonoids, phillyrin, verbascoside	Cold roled steel	1 M HCl	50 mg/L	93.0	Mixed	[71]
<i>Ficus tikoua</i>	Allantoin, 5 methoxypsoralen, methyl caffeate	Carbon steel	1 M HCl	200 mg/L	95.8	Chemisorption	[72]
<i>Saraca ashoka</i>	Epicatechin	Mild steel	0.5 M H ₂ SO ₄	100 mg/L	95.5	Mixed	[70]

<i>Armoracia rusticana</i>	Methoxypyrazine, wine lactone, bisphenol A		0.5 M H ₂ SO ₄	100 mg/L	95.4	Mixed	[60]
<i>Chlomolaena odorata</i>	Mixture of flavones		0.5 M H ₂ SO ₄	5 % v/v	95.0 89.0	Physisorption	[68]
<i>Artemisia annua</i>	Artemisinin		2 M H ₂ SO ₄	4 g/L	95.5	Physisorption	[13]
<i>Azadirachta indica</i>	Terpenoids-azadirachtin		2 M H ₂ SO ₄	4 g/L	60.4	Physisorption	[61]
					66.8		
					81.8		
<i>Aniba rosaeodora</i>	Anibine		1 M HCl	200 mg/L	91.0	Chemisorption	[12]
<i>Cuminum cyminum</i>	Cuminaldehyde		1 M HCl	300 ppm	93.0	Physisorption	[73]
Borage flower	Lactic acid, nicotinic acid, carotene		1 M HCl	800 ppm	91.0	Mixed	[66]
<i>Rosa canina</i>	Marein, ascorbic acid, pectin, tannin		1 M HCl	800 ppm	86.0	Mixed	[74]
Fig leaves	Psoralene, vanillin, β -sitosterol	2 M HCl	200 ppm	87.0	Physisorption	[75]	
Ginseng	Unknown complex mixture	Aluminium	1 M HCl	50 % v/v	93.1 63.1	Physisorption	[64]
<i>Hibiscus sabdariffa</i>	Thiamine, niacine, ascorbic acid, anthocyanins		0.5 M NaOH	1.5 g/L	85.0	Physisorption	[69]

2.3 Corrosion inhibitors from biomass waste

Nowadays, the cost effective prevention of metals and its alloys utilizing natural compounds is of a great priority for industries. Several authors have employed various valuable components derived from un-utilized biomasses to yield efficient protection of metallic surfaces. For instance, Gapsari et al. [15] applied the extracts derived from the honeycomb waste as the inhibitor of stainless steel, type 304, in 0.5 to 2.0 M H₂SO₄ solution. They found that corrosion rate of stainless steel increases up to 2000 mg/L of inhibitor, and decreases with a concentration of 3000 to 4000 mg/L. The highest inhibition efficiency of 97.29 % is reached by inhibitor concentration of 2000 mg/L in 0.5 M H₂SO₄. According to the authors, its inhibition performances is associated to the adsorption

behavior of honeycomb extracts due to presence of quercetin, luteolin, vitexin, fisetin, isohamnetin, isoferulic, apigenin and pinobanksin.

The extracts from other waste materials, such as eggshell is found to significantly alter the corrosion resistance of austenitic stainless steel, type 316 [16]. The authors showed that the increase of inhibitor concentration hinders the formation of a passive film, and the highest protection of 94.74% is gained by weight loss analysis.

In the work of Montoya et al. [17] it is found that the two primers with organic corrosion inhibitors extracted from *Pinus radiata* bark, from the waste generated by the timber and paper industries could be used as inhibition of 1020 steel due to formation of tannin-Fe protecting coatings.

Cruz-Zabalegui et al. [18] have used a non-ionic gemini surfactant (N,N-diethylaminedialkyldiamide) synthesized from the fatty acids derived from avocado oil as CO₂ inhibitor of API X-52 steel. By the test performed at 50 °C, during 24 h with inhibitor concentration of 10 to 50 ppm, the authors pointed out that this compound assured good protection due to physical adsorption onto the steel. In the work of Liao et al. [19] is showed that the waste of lychee (peel and seed) is possible to recycle and used as environmentally friendly inhibitor of mild steel in 0.5 M HCl solution up to concentration of 600 mg/L to achieves the maximum protection.

Although, the *Prunus dulcis* (almond) is one of the frequently used fruits in human diet, its peels are thrown out as a waste material. However, the idea of utilizing this waste material for protection of mild steel in 0.1 M HCl solution is gained by Pal et al. [20]. They showed that methanolic and aqueous extracts of almond protected the mild steel with efficiency of 93 and 85 %. The more pronounced inhibition performance of methanolic than aqueous extract, the authors supported this by SEM and AFM analyses. By UV/Vis and FTIR spectroscopy analyses, the authors showed that methanol contain more phytochemicals than water, among which the isorhamnetin-3-O-rutinoside, chlorogenic acid and catechin are those responsible for mild steel inhibition. The authors also revealed that extracts are classified as mixed type, where the adsorption is neither pure physical nor pure chemical.

Tiwari et al. [21] used the ethyl acetate extract of *Musa Paradisica* peels for mild steel protection in hydrochloric and sulphuric acids. The results of electrochemical study strongly validate that extract of *Musa Paradisica* peels retards mild steel corrosion in both acidic medias, due to abundancy of heteroatoms (oxygen and nitrogen) and aromatic rings, which are adhered on the surface via chemical or electrostatic interaction with iron atoms. Although banana peel extract contains several bio-active compounds, each of them could contribute to some extent in the total inhibition performance of the extract. According to the authors the inhibition activity is primarily controlled by the gallocatechin molecule.

In the work of Soares Rodrigues [22], the biomass of the microalgae *Spirulina maxima*, a cyanobacterium that synthesizes high levels of protein is studied as a natural inhibitor of carbon steel in 1 M HCl. This biomass acted as a good corrosion inhibitor reaching an efficiency of 96.4 %, after 72 h of immersion with 100 mg/L of inhibitor. Furthermore, the chitosan extracted from exoskeletons of crustaceans in the sea food waste led to about 88 % of corrosion inhibition through chemical and physical types of adsorption onto carbon steel. The corrosion inhibition efficiency of extracellular polymeric substances (EPS) extracted from waste activated sludge on carbon steel in 3.64 % NaCl solution saturated with CO₂ at 25 °C is examined by Go et al. [24]. In comparison with waste activated sludge alone with EPS extracted from the waste showed that the better inhibition performance of around 80 % is gained by extracellular polymeric substances with its concentration of 1.000 mg/L. This compound acted as a mixed-type of inhibitor with O-H, N-H, C-N, C=O and C-H groups, which contributed to adsorption on steel.

In the work of Dehghani et al. [25], the Chinese gooseberry fruit shell is used as green corrosion inhibitors of carbon steel, in HCl solution. Its aqueous extract composed of sucrose, maltose and folate, with concentration of 1000 ppm assured 92 % of inhibition, after 2.5 h of steel immersion. The results obtained by EIS are also supported by molecular simulation findings, which point out that among three major organic constituents the folate possessed the higher inhibition activity than sucrose and maltose. As authors declared the hydroxyl and carbonyl, and imine and amine groups with oxygen and nitrogen centers are responsible for a stronger inhibition activity of folate in comparison with two others.

Adewuyi et al. [26] are used *Khaya senegalensis* fatty hydroxylamide (KSFA) for inhibition of aluminium in 0.5 M HCl. The authors started from un-utilized seed oil, and in more steps, including esterification, transesterification, hydroxylation and amidation they synthesized KSFA. This compound with concentration of 0.001 mg/L exhibited 90.43 % of efficiency with concentration of 0.001mg/L, which is also related with the presence of heteroatoms in the KSFA.

Besides them, the agro-industrial waste based on rice bran oil is used to prepare a green corrosion inhibitor for the 1018 steel surface [27]. The authors showed that the addition of 10 and 25 ppm of inhibitor improves the inhibition of steel above 99 %. Fiori-Bimbi et al. [28] are used pectin from citrus peel as corrosion inhibitor of mild steel in HCl solutions. They have shown that pectin with concentration of 2.0 g/L assured efficient inhibition (94.2 %) of steel, at 45 °C by cathodic and anodic protection of metallic surface. Furthermore, the works of Ninčević Grassino et al. [29,30] showed that pectin isolated from tomato peel waste generated by canning industry act as eco-friendly corrosion inhibitor of tin. Corrosion tests performed in a NaCl/acetic acid/citric acid, at 25 °C pointed out that pectin

is an efficient inhibitor (73 and 65.8 % for potentiodynamic polarization and electrochemical impedance spectroscopy), even at very low concentrations of 4 g/L.

Overall, the isolation of valuable-added compounds from abundant and under-utilized resources opens opportunity for production of new classes of inhibitors, which could be utilized as anticorrosion substances after their complete qualitative and quantitative analyses.

Table 3. Green corrosion inhibitors from biomass waste.

Waste source	Main components	Material	Medium	Inhibitor concentration	Highest inhibition efficiency (%)	Refs.
Honeycomb	Quercetin	Stainless steel 304	0.5 M H2SO4	2000 mg/L	97.29	[15]
Egg shell	n.d.	Stainless steel 316	0.5 M H2SO4	2 - 10 g	94.74	[16]
Avocado oil	N, N-Diethylaminodialkyl diamide	API X-52 pipeline steel	3.5 % NaCl	10 ppm	94	[18]
<i>Pinus radiata</i> bark	Catechin, taxifolin	Steel	3.5 % NaCl (w/v)	n.r.	n.r.	[17]
Rice brain oil	Imidazoline		3.5 % NaCl	10 ppm	99.69	[27]
				25 ppm	99.65	
Lychee`s peel and seed	Epicatechin, epigallocatechin, cyanidin-3-glucoside	Mild steel	0.5 M HCl	600 mg/L	97.95	[19]
<i>Prunus dulcis</i>	Isorhamnetin-3-O-rutinoside, catechin, chlorogenic acid		0.1 M HCl	11.80 mg/L	93	[20]
<i>Musa paradisa</i> peel	Gallocatechin		1 M HCl	400 mg/L	91	[21]
			0.5 M H2SO4		85	
Citrus peel	Pectin			1 M HCl	2 g/L	94.2
<i>Spirulina maxima</i>	n.d.	Carbon steel	1 M HCl	100 m/L	96.40	[22]
Shrimp shell	Chitosan		1 M HCl	10 ⁻⁵ M	88.50	[23]
Sludge	n.d.		3.64 % NaCl	1000 mg/L	78.89	[24]

Gooseberry fruit shell	Sucrose, maltose, folate		1 M HCl	1000 ppm	91.9	[25]
Khaya senegalensis seed	Fatty acids (C18:1)	Aluminium	0.5 M HCl	0.001 mg/L	90.43	[26]
Tomato peel	Pectin	Tin	2 % NaCl%, 1 % acetic acid and 0.5 % citric acid	4 g/L	72.98	[29]
Tomato peel	Pectin		2 % NaCl%, 1 % acetic acid and 0.5 % citric acid	4 g/L	65.8	[30]

n.d. = not detected; n.r. = not reported

References

- [1] G. TrabANELLI, V. Carassiti, Mechanism and phenomenology of organic inhibitors, in: M.G. Fontaine, R.W. Stachle (Eds.), *Advances in Corrosion Science and Technology*, Plenum Press, New York, 1970, pp. 147-20. https://doi.org/10.1007/978-1-4615-8252-6_3
- [2] P.B. Raja, M.S. Sethuraman, Natural products as corrosion inhibitor for metals in corrosive media - A review, *Mater. Lett.* 62 (2008) 113-116. <https://doi.org/10.1016/j.matlet.2007.04.079>
- [3] J. Aljourani, K. Raeissi, M.A. Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1 M HCl solution, *Corros. Sci.* 51 (2009) 1836-1843. <https://doi.org/10.1016/j.corsci.2009.05.011>
- [4] S. Marzorati, L. Verotta, S.P. Trasatti, Green corrosion inhibitors from natural sources and biomass wastes, *Molecules*. 48 (2019) 1-24. <https://doi.org/10.3390/molecules24010048>
- [5] A. Ninčević Grassino, Plant extracts as a natural corrosion inhibitors of metals and its alloys used in food preserving industry, in A. Méndez-Vilas (Ed.), *Science within Food: Up to date Advances on Research and Education Ideas*, Food Science Book Series 1, Formatex Research Center, Badajoz, 2017, pp. 185-193.

- [6] L.T. Popoola, Organic green corrosion inhibitors (OGCIs): a critical review, *Corros. Rev.* 37 (2019) 71-102. <https://doi.org/10.1515/corrrev-2018-0058>
- [7] S.A. Umoren, M.M. Solomon, I.B. Obot, R.K. Suleiman, A critical review on the recent studies on plant biomaterials as corrosion inhibitors for industrial metals, *J. Ind. Eng. Chem.* 76 (2019) 91-115. <https://doi.org/10.1016/j.jiec.2019.03.057>
- [8] C. Verma, E.E. Ebenso, I. Bahadur, M.A. Quraishi, An overview on plant extracts as environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media, *J. Mol. Liq.* 266 (2018) 577-590. <https://doi.org/10.1016/j.molliq.2018.06.110>
- [9] L.C. Pirvu, Polyphenols and herbal-based extracts at the basis of new antioxidant, Material Protecting Products, in: M. Aliofkhazraei (Ed.), *Developments in Corrosion Protection*, Intech Open, London, 2014, pp. 181-198.
- [10] A. Dehghani, G. Bahlakeha, B. Ramezanzadeh, Green Eucalyptus leaf extract: A potent source of bio-active corrosion inhibitors for mild steel, *Bioelectrochemistry*. 130 (2019) 107339. <https://doi.org/10.1016/j.bioelechem.2019.107339>
- [11] A. Ostovari, S.M. Hoseinie, M. Peikari, S.R. Shadizadeh, S.J. Hashemi, Corrosion inhibition of mild steel in 1M HCl solution by henna extract: a comparative study of the inhibition by henna and its constituents (Lawson, Gallic acid, α -d-Glucose and Tannic acid), *Corros. Sci.* 51 (2009) 1935-1949. <https://doi.org/10.1016/j.corsci.2009.05.024>
- [12] M. Chevalier, F. Robert, N. Amusant, M. Traisnel, C. Roos, M. Lebrini, Enhanced corrosion resistance of mild steel in 1 M hydrochloric acid solution by alkaloids extract from *Aniba rosaeodora* plant: Electrochemical, phytochemical and XPS studies, *Electrochim. acta* 131 (2014) 96-105. <https://doi.org/10.1016/j.electacta.2013.12.023>
- [13] P.C. Okafor, V.E. Ebiekpe, C.F. Azike, G.E. Egbung, E.A. Brisibe, E.E. Ebenso, Inhibitory action of *Artemisia annua* extracts and Artemisinin on the corrosion of mild steel in H₂SO₄ Solution, *Int. J. Corros.* 2012 (2011) 1-8. <https://doi.org/10.1155/2012/768729>
- [14] A. Saxena, D. Prasad, R. Haldhar, G. Singh, A. Kumar, Use of *Saraca ashoka* extract as green corrosion inhibitor for mild steel in 0.5 M H₂SO₄, *J. Mol. Liq.* 258 (2018) 89-97. <https://doi.org/10.1016/j.molliq.2018.02.104>
- [15] F. Gapsari, K.A. Madurani, F.M. Simanjuntak, A. Andoko, H. Wijaya, F. Kurniawan, Corrosion inhibition of honeycomb waste extracts for 304 stainless steel in sulfuric acid solution, *Materials*. 12 (2019) 1-15. <https://doi.org/10.3390/ma12132120>

- [16] O. Sanni, A.P.I. Popoola, O.S.I. Fayomi, Enhanced corrosion resistance of stainless steel type 316 in sulphuric acid solution using eco-friendly waste product, *Results Phys.* 9 (2018) 225-230. <https://doi.org/10.1016/j.rinp.2018.02.001>
- [17] L.F. Montoyaa, D. Contreras, A.F. Jaramillo, C. Carrascoc, K. Fernándezd, B. Schwederski, D. Rojas, M.F. Melendrez, Study of anticorrosive coatings based on high and low molecular weight polyphenols extracted from the Pine radiata bark, *Prog. Org Coat.* 127 (2019) 100-109. <https://doi.org/10.1016/j.porgcoat.2018.11.010>
- [18] A. Cruz-Zabaleguia, E. Vazquez-Velezb, G. Galicia-Aguilara, M. Casales-Diazb, R. Lopez-Sesenesc, J.G. Gonzalez-Rodriguezd, L. Martinez-Gomez, Use of a non-ionic gemini-surfactant synthesized from the wasted avocado oil as a CO₂- corrosion inhibitor for X-52 steel, *Ind. Crops Prod.* 133 (2019) 203-211. <https://doi.org/10.1016/j.indcrop.2019.03.011>
- [19] L.L Liao, S. Mo, H.Q. Luo, N.B. Li, Corrosion protection for mild steel by extract from the waste of lychee fruit in HCl solution: experimental and theoretical studies, *J. Colloid. Interf. Sci.* 520 (2018) 41-49. <https://doi.org/10.1016/j.jcis.2018.02.071>
- [20] S. Pal, H. Lgaz, P. Tiwari, I.M. Chung, G. Ji, R. Prakash, Experimental and theoretical investigation of aqueous and methanolic extracts of *Prunus dulcis* peels as green corrosion inhibitors of mild steel in aggressive chloride media, *J. Mol. Liq.* 276 (2019) 347-361. <https://doi.org/10.1016/j.molliq.2018.11.099>
- [21] P. Tiwari, M. Srivastava, R. Mishra, G. Ji, R. Prakash, Economic use of Waste *Musa Paradisica* peels for effective control of mild steel loss in aggressive acid solutions, 6 (2018) 4773-4783. <https://doi.org/10.1016/j.jece.2018.07.016>
- [22] L. Soares Rodrigues, A. Ferreira do Valle, E. D'Elia, Biomass of microalgae *spirulina maxima* as a corrosion inhibitor for 1020 carbon steel in acidic solution, *Int. J. Electrochem. Sci.* 13 (2018) 6169-6189. <https://doi.org/10.20964/2018.07.11>
- [23] M.H.M. Hussein, M.F.El-Hady, H.A.H. Shehata, M.A. Hegazy, H.H.H. Hefni, Preparation of some eco-friendly corrosion inhibitors having antibacterial activity from sea food waste, *J. Surfact. Deterg.* 16 (2013) 233-242. <https://doi.org/10.1007/s11743-012-1395-3>
- [24] L.C. Go, W. Holmes, D. Depan, R. Hernandez, Evaluation of extracellular polymeric substances extracted from waste activated sludge as a renewable corrosion inhibitor, *Peer. J.* (2019) e7193. <https://doi.org/10.7717/peerj.7193>.
- [25] A. Dehghani, G. Bahlakeha, B. Ramezanzadeh, A detailed electrochemical/theoretical exploration of the aqueous Chinese gooseberry fruit shell extract as a green and cheap corrosion inhibitor for mild steel in acidic solution, *J. Mol. Liq.* 282 (2019) 366-384. <https://doi.org/10.1016/j.molliq.2019.03.011>

- [26] A. Adewuyi, R.A. Oderinde, Synthesis of hydroxylated fatty amide from underutilized seed oil of *Khaya senegalensis*: a potential green inhibitor of corrosion in aluminium, *J. Anal. Sci. Technol.* 9 (2018) 1-26. <https://doi.org/10.1186/s40543-018-0158-9>
- [27] G. Salinas-Solano, J. Porcayo-Calderon, L.M. Martinez de la Escalera, J. Canto, M. Casales-Diaz, O. Sotelo-Mazon, John Henao, L. Martinez-Gomez, Development and evaluation of a green corrosion inhibitor based on rice bran oil obtained from agro-industrial waste, *Ind. Crops Prod.* 119 (2018) 111-124. <https://doi.org/10.1016/j.indcrop.2018.04.009>
- [28] M. Fiore-Bimbi, P.E. Alvarez, H. Vaca, C.A. Gervasi, Corrosion inhibition of mild steel in HCl solution by pectin, *Corros. Sci.* 92 (2015) 192-199. <https://doi.org/10.1016/j.corsci.2014.12.002>
- [29] A. Ninčević Grassino, J. Halambek, S. Djaković, S. Rimac Brnčić, M. Dent, Z. Grabarić, Utilization of tomato peel waste from canning factory as a potential source for pectin production and application as tin corrosion inhibitor, *Food Hydrocoll.* 52 (2016) 265-274. <https://doi.org/10.1016/j.foodhyd.2015.06.020>
- [30] A. Ninčević Grassino, S. Djaković, T. Bosiljkov, J. Halambek, Z. Zorić, V. Dragović-Uzelac, M. Petrović, S. Rimac Brnčić, Valorisation of tomato peel waste as a sustainable source for pectin, polyphenols and fatty acids recovery using sequential extraction, *Waste and Biomass Valorization*, 4 (2019). <https://doi.org/10.1007/s12649-019-00814-7>
- [31] A.S. Abbas, É. Fazakas and T.I. Török, Corrosion studies of steel rebar samples in neutral sodium chloride solution also in the presence of a bio-based (green) inhibitor, *Int. J. Corros. Scale Inhib.* 7 (2018) 38-47.
- [32] A. Marciales, T. Haile, B. Ahvazi, T.D. Ngo, J. Wolodko, Performance of green corrosion inhibitors from biomass in acidic media, *Corros. Rev.* 36 (2018) 239-266. <https://doi.org/10.1515/corrrev-2017-0094>
- [33] K.E. Heusler, D. Landolt, S. Trasatti, Electrochemical corrosion nomenclature, *Pure Appl. Chem.* 61 (1989) 19-22. <https://doi.org/10.1351/pac198961010019>
- [34] N. Perez, *Electrochemistry and Corrosion Science*, Kluwer Academic Publisher, Boston, 2004. <https://doi.org/10.1007/b118420>
- [35] B.N. Popov, Corrosion inhibitors, in: B.N. Popov (Ed.), *Corrosion Engineering, Principles and Solved Problems*, Elsevier, Amsterdam, 2015, pp. 581-597. <https://doi.org/10.1016/B978-0-444-62722-3.00014-8>

- [36] O. Gharbi, S. Thomas, C. Smith, N. Birbilis, Chromate replacement: what does the future hold?, *Mater. Degrad.* 12 (2018). <https://doi.org/10.1038/s41529-018-0034-5>
- [37] A. Režek Jambrak, Non-thermal and innovative processing technologies, in: P. Ferranti, E.M. Berry, J.R. Anderson (Eds.), *Encyclopedia of Food Security and Sustainability*, Elsevier, 2019, pp. 477-483. <https://doi.org/10.1016/B978-0-08-100596-5.22285-3>
- [38] J. Azmir, I.S.M. Zaidul, M.M. Rahman, K.M. Sharif, A. Mohamed, F. Sahena, M.H.A. Jahurul, K. Ghafoor, N.A.N. Norulaini, A.K.M. Omar, Techniques for extraction of bioactive compounds from plant materials: A review, *J. Food Eng.* 117 (2013) 426-436. <https://doi.org/10.1016/j.jfoodeng.2013.01.014>
- [39] D.C. Costa, H. Costa, T.G. Albuquerque, F. Ramos, M.C. Castilho, A. Sanches-Silva, Advances in phenolic compounds analysis of aromatic plants and their potential applications, *Trends Food Sci. Tech.* 45 (2015) 336-354. <https://doi.org/10.1016/j.tifs.2015.06.009>
- [40] K. Xhanari, M. Fingšar, M. Knez-Hrnčić, U. Maver, Ž. Knez, B. Seiti, Green corrosion inhibitors for aluminium and its alloys: a review, *RSC Adv.* 7 (2017) 27299-27330. <https://doi.org/10.1039/C7RA03944A>
- [41] M. Srivastava, P. Tiwari, S.K. Srivastava, A. Kumar, G. Ji, R. Prakash, Low cost aqueous extract of *Pisum sativum* peels for inhibition of mild steel corrosion, *J. Mol. Liq.* 254 (2018) 357-368. <https://doi.org/10.1016/j.molliq.2018.01.137>
- [42] S. Burt, Essential oils: their antimicrobial properties and potential application in foods-A review, *Inter. J. Food Microb.* 94 (2004) 223-253. <https://doi.org/10.1016/j.ijfoodmicro.2004.03.022>
- [43] L. Afia, R. Salghi, L. Bammou, El. Bazzi, B. Hammouti, L. Bazzi, A. Bouyanzer, Anti-corrosive properties of Argan oil on C38 steel in molar HCl solution, *J. Saudi Chem. Soc.* 18 (2014) 19-25. <https://doi.org/10.1016/j.jscs.2011.05.008>
- [44] D.B. Hmamou, R. Salghi, A. Zarrouk, H. Zarrouk, M. Errami, B. Hammouti, L. Afia, L. Bazzi, L. Bazzi, Adsorption and corrosion inhibition of mild steel in hydrochloric acid solution by verbena essential oil, *Res. Chem. Intermed.* 39 (2013) 973-989. <https://doi.org/10.1007/s11164-012-0609-7>
- [45] D.B. Hmamou, R. Salghi, A. Zarrouk, O. Benali, F. Fade, H. Zarrok, B. Hammouti, Carob seed oil: an efficient inhibitor of C38 steel corrosion in hydrochloric acid, *Int. J. Ind. Chem.* 3 (2012) 1-9. <https://doi.org/10.1186/2228-5547-3-25>

- [46] M. Bendahou, M. Benabdellah, B. Hammouti, A study of rosemary oil as a green corrosion inhibitor for steel in 2 M H_3PO_4 , *Pigm. Resin Technol.* 35 (2006) 95-100. <https://doi.org/10.1108/03699420610652386>
- [47] D. Ben Hmamou, R. Salghi, A. Zarrouk, B. Hammouti, S.S. Al-Deyab, L. Bazzi, H. Zarrok, A. Chakir, L. Bammou, Corrosion inhibition of steel in 1 m hydrochloric acid medium by chamomile essential oils, *Int. J. Electrochem. Sci.* 7 (2012) 2361-2373.
- [48] N. Lahhit, A. Bouyanzer, J.M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss, L. Majidi, Fennel (*Foeniculum Vulgare*) Essential oil as green corrosion inhibitor of carbon steel in hydrochloric acid solution, *Port. Electrochim. Acta.* 29 (2011) 127-138. <https://doi.org/10.4152/pea.201102127>
- [49] L. Afia, O. Benali, R. Salghi, E.E. Ebenso, S. Jodeh, M. Zougagh, B. Hammouti, Steel Corrosion inhibition by acid garlic essential oil as a green corrosion inhibitor and sorption behavior, *Int. J. Electrochem. Sci.* 9 (2014) 8392-8406.
- [50] M. Chraibi, K. Fikri Benbrahim, H. Elmsellem, A. Farah, I. Abdel-Rahman, B. El Mahi, Y. Filali Baba, Y. Kandri Rodi, F. Hlimi, Antibacterial activity and corrosion inhibition of mild steel in 1.0 M hydrochloric acid solution by *M. piperita* and *M. pulegium* essential oils, *J. Mater. Environ. Sci.* 8 (2017) 972-981.
- [51] Y. El Ouadi, A. Bouyanzer, L. Majidi, J. Paolini, J.M. Desjobert, J. Costa, A. Chetouani, B. Hammouti, S. Jodeh, I. Warad, Y. Mabkhot, T. Ben Hadda, Evaluation of Pelargonium extract and oil as eco-friendly corrosion inhibitor for steel in acidic chloride solutions and pharmacological properties, *Res. Chem. Intermed.* 41 (2015) 7125-7149. <https://doi.org/10.1007/s11164-014-1802-7>
- [52] J. Halambek, M. Cvjetko Bubalo, I. Radojčić Redovniković, K. Berković, Corrosion behaviour of aluminium and AA5754 alloy in 1% acetic acid solution in presence of laurel oil, *Int. J. Electrochem. Sci.* 9 (2014) 5496-5506. <https://doi.org/10.1016/j.eoenv.2013.10.019>
- [53] J. Halambek, A. Žutinić, K. Berković, *Ocimum basilicum* L. oil as corrosion inhibitor for aluminium in hydrochloric acid solution, *Int. J. Electrochem. Sci.* 8 (2013) 11201-11214.
- [54] J. Halambek, K. Berković, Inhibitive action of *Anethum graveolens* L. oil on aluminium corrosion in acidic media, *Int. J. Electrochem. Sci.* 7 (2012) 8356-8368.
- [55] K. Dahmani, M. Galai, M. Cherkaoui, A. El Hasnaoui, A. El Hessni, Cinnamon essential oil as a novel eco-friendly corrosion inhibitor of copper in 0.5 M Sulfuric Acid medium, *J. Mater. Environ. Sci.* 8 (2017) 1676-1689.

- [56] L. Bammou, M. Mihit, R. Salghi, A. Bouyanzer, S.S. Al-Deyab, L. Bazzi, B. Hammouti, Inhibition effect of natural artemisia oils towards tinplate corrosion in HCl solution: Chemical characterization and electrochemical study, *Int. J. Electrochem. Sci.* 6 (2011) 1454-1467.
- [57] L. Bammou , B. Chebli , R. Salghi , L. Bazzi , B. Hammouti , M. Mihit, H. Idrissi, Thermodynamic properties of *Thymus satureioides* essential oils as corrosion inhibitor of tinplate in 0.5 M HCl: chemical characterization and electrochemical study, *Green Chem. Lett. Rev.* 3 (2010) 173-178. <https://doi.org/10.1080/17518251003660121>
- [58] J. Halambek, K. Berković, J. Vorkapić-Furač, The influence of *Lavandula angustifolia* L. oil on corrosion of Al-3Mg alloy, *Corros. Sci.* 52 (2010) 3978-3983. <https://doi.org/10.1016/j.corsci.2010.08.012>
- [59] J. Halambek, K. Berković, J. Vorkapić-Furač, *Laurus nobilis* L. oil as green corrosion inhibitor for aluminium and AA5754 aluminium alloy in 3 % NaCl solution, *Mater. Chem. Phys.* 137 (2013) 788-795. <https://doi.org/10.1016/j.matchemphys.2012.09.066>
- [60] R. Haldhar, D. Prasad, A. Saxena, *Armoracia rusticana* as sustainable and eco-friendly corrosion inhibitor for mild steel in 0.5M sulphuric acid: Experimental and theoretical investigations, *J. Environ. Chem. Eng.* 6 (2018) 5230-5238. <https://doi.org/10.1016/j.jece.2018.08.025>
- [61] P. C. Okafor, E. E. Ebenso, U.J. Ekpe, *Azadirachta Indica* Extracts as corrosion inhibitor for mild steel in acid medium, *Int. J. Electrochem. Sci.* 5 (2010) 978-993.
- [62] X. Li, S. Deng, H. Fu, Inhibition of the corrosion of steel in HCl, H₂SO₄ solutions by bamboo leaf extract, *Corros. Sci.* 62 (2012) 163-175. <https://doi.org/10.1016/j.corsci.2012.05.008>
- [63] S. Deng, X. Li, Inhibition by Ginkgo leaves extract of the corrosion of steel in HCl and H₂SO₄ solutions, *Corros. Sci.* 55 (2012) 407-415. <https://doi.org/10.1016/j.corsci.2011.11.005>
- [64] I.B. Obot, N.O. Obi-Egbedi, Ginseng Root: A new efficient and effective eco-friendly corrosion inhibitor for aluminium alloy of type aa 1060 in hydrochloric acid solution, *Int. J. Electrochem. Sci.* 4 (2009) 1277-1288.
- [65] M. Dahmani, A. Et-Touhami, S.S. Al-Deyab, B. Hammouti, A. Bouyanzer, Corrosion inhibition of C38 steel in 1 M HCl: A comparative study of black pepper extract and its isolated piperine, *Int. J. Electrochem. Sci.* 5 (2010) 1060-1069.
- [66] A. Dehghani , G. Bahlakeha, B. Ramezanzadehb, M. Ramezanzadeh, Potential of Borage flower aqueous extract as an environmentally sustainable corrosion inhibitor

- for acid corrosion of mild steel: Electrochemical and theoretical studies, *J. Mol. Liq.* 277 (2019) 895-911. <https://doi.org/10.1016/j.molliq.2019.01.008>
- [67] M. Faustin, A. Maciuk, P. Salvin, C. Roos, M. Lebrini, Corrosion inhibition of C38 steel by alkaloids extract of *Geissospermum laeve* in 1 M hydrochloric acid: Electrochemical and phytochemical studies, *Corros. Sci.* 92 (2015) 287-300. <https://doi.org/10.1016/j.corsci.2014.12.005>
- [68] I.B. Obot, E.E. Ebenso, Z.M. Gasem, Eco-friendly corrosion inhibitors: Adsorption and inhibitive action of ethanol extracts of *Chlomolaena Odorata* L. for the corrosion of mild steel in H_2SO_4 solutions, *Int. J. Electrochem. Sci.* 7 (2012) 1997-2008.
- [69] E.A. Noor, Potential of aqueous extract of *Hibiscus sabdariffa* leaves for inhibiting the corrosion of aluminum in alkaline solutions, *J. Appl. Electrochem.* 39 (2009) 1465-1475. <https://doi.org/10.1007/s10800-009-9826-1>
- [70] A. Saxena, D. Prasad, R. Haldhar, G. Singh, A. Kumar, Use of *Saraca ashoka* extract as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4 , *J. Mol. Liq.* 258 (2018) 89-97. <https://doi.org/10.1016/j.molliq.2018.02.104>
- [71] X.H. Li, S.H. Deng, H. Fu, Inhibition by *Jasminum nudiflorum* Lindl. leaves extract of the corrosion of cold rolled steel in hydrochloric acid solution, *J. Appl. Electrochem.* 40 (2010) 1641-1649. <https://doi.org/10.1007/s10800-010-0151-5>
- [72] Q. Wang, B. Tan, H. Bao, Y. Xie, Y. Moua, P. Li, D. Chena, Y. Shi, X. Li, W. Yang, Evaluation of *Ficus tikoua* leaves extract as an eco-friendly corrosion inhibitor for carbon steel in HCl media, *Bioelectrochemistry.* 128 (2019) 49-55. <https://doi.org/10.1016/j.bioelechem.2019.03.001>
- [73] A. Singh, E.E. Ebenso, M. A. Quraishi, Theoretical and electrochemical studies of cuminum cyminum (jeera) extract as green corrosion inhibitor for mild steel in hydrochloric acid solution, *Int. J. Electrochem. Sci.* 7 (2012) 8543-8559.
- [74] Z. Sanaeia, M. Ramezanzadeha, G. Bahlakehb, B. Ramezanzadeha, Use of *Rosa canina* fruit extract as a green corrosion inhibitor for mild steel in 1 M HCl solution: A complementary experimental, molecular dynamics and quantum mechanics investigation, *J. Ind. Eng. Chem.* 69 (2019) 18-31. <https://doi.org/10.1016/j.jiec.2018.09.013>
- [75] T. H. Ibrahim, M. A. Zour, Corrosion Inhibition of mild steel using fig leaves extract in hydrochloric acid solution, *Int. J. Electrochem. Sci.* 6 (2011) 6442-6455.