

Plant extracts as a natural corrosion inhibitors of metals and its alloys used in food preserving industry

A. Ninčević Grassino

Department of Chemistry and Biochemistry, Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

The protection of metals and its alloys against corrosion has attracted great attention, due to their various industrial application and economic importance. Pure metals and its alloys react chemically or electrochemically with corrosive medium to form stable corrosion compounds in which the loss of metals occurs and consequently metal surface becomes corroded. In order to prevent corrosion damage and eventual failure of components and systems both in processing and manufacturing industries, the use of corrosion inhibitors is very popular. Corrosion inhibitors are synthetic or natural substances when added in small concentrations to corrosive media inhibited the corrosion reaction and reduced corrosive attack on metals. Although, many synthetic compounds showed good anticorrosive properties, most of them are toxic for human and environmental. Due to the fact that increasing the awareness of health and ecological risks, new eco-friendly and harmless natural anticorrosive substances have drawn great attention. The various plants, such as aromatic herbs and spices have been used not only by human beings, e.g. food-stuffs, flavour, fragrance and medicine, but also as a rich source of anticorrosive inhibitors. Plants inhibition performance and efficiency are related to their chemical composition, which take the form of alkaloids, carbohydrates, polyphenols, proteins and tannins. These compounds usually have functional groups with oxygen, nitrogen and sulphur atoms, which can be easily adsorbed on metal surface due to range of functional group properties.

Therefore, this work reports application of plant extracts as anticorrosive agents for metals and its alloys used in food preserving industry. Furthermore, the methods used for extraction and characterization of plant materials, as well as methods for calculation of corrosion inhibition efficiency are described, too.

In conclusion, the proposed work points out that plants extract can be considered as a promising industrial resource for protection of metals and its alloys due to their environmental acceptability, ready availability and high inhibition efficiency properties.

Keywords: corrosion; natural inhibitors; plant extracts; chromatographic, spectroscopic and electrochemical techniques; surface analyses

1. Introduction

Steel, aluminium, tin and chromium are four metals commonly used for the food packaging. Tin and steel, chromium and steel are used as composite materials in the form of tinplate and electrolytic chromium-coated steel (ECCS), the latter being referred to as a tin free steel (TFS). Aluminium is used in the form of purified alloys containing small and carefully controlled amounts of magnesium and manganese. These metals are important materials for food packaging, due to several important qualities, i.e. good mechanical strength, toughness, ductility, solderability, weldability, nontoxicity, lubricity, lacquerability and impermeability. However, the chemical structure that gives them practical properties is also responsible for their main weakness, i.e. their susceptibility to corrosion. Corrosion is a term used to describe chemical/electrochemical reaction between metal and its environment to form corrosive compounds to some extent. When the metallic surface is not compact and continuous, the metal is exposed through the pores to aggressive food compounds or food additives and its corrosion is accelerated. The factors which may influence the corrosion are choice or damage of metallic surface, passivation level, type of food product, pH and acid content, presence of corrosion accelerators (nitrate, sulphur and phosphate compounds, plant pigments and synthetic colouring in the food), presence of oxygen within the sealed can, thermal processing (heat sterilization treatment) and storage temperature and time. The consequences are dissolution of high levels of metals, i.e. tin, iron, chromium and aluminium into food content [1-3]. For example, when tin and iron are in excess, they are toxic and may cause gastrointestinal symptoms provoking nausea, vomiting, diarrhea, fever and headache. The maximum limit for tin in canned solid food is 250 mg/kg and 150 mg/kg for beverages, while for iron the values are 50 mg/kg [4].

Due to the fact that corrosion reaction takes place at the metal surface, the rate of attack (corrosion rate) can be reduced and controlled by modifying the conditions at the surface. In this context, different corrosion inhibitors are recommended, nowadays particularly a new group of natural products is of interest, due to low toxicity, eco-friendliness and good corrosion efficiency. A number of papers reported in recent years the use of different natural products for corrosion inhibition of steel and aluminium, such as rosemary, lavender, ginkgo, laurel, thyme, zingiber, mentha and ruta [5-14]. However, a limited number of researches showed application of natural products as corrosion inhibitors of tinplate and tin free steel, commonly used material for food container manufacture. Ninčević Grassino *et al.* reported the use of essential onion oil (EOO) as a potential inhibitor of tin, chromium and iron from tinplate sheets [15,

16]. Head-space gases (H_2 , O_2 , N_2 and CO_2), as indicators of corrosion process were analysed by gas chromatography [16], whereas dissolution of iron and tin from tinplate can filled with tomato purée in presence of EOO and potassium nitrate were studied using atomic absorption spectroscopy and high performance liquid chromatography [17]. Furthermore, chemical composition, i.e. sugar, organic and amino acids content in canned tomato purée with EOO were analysed by high performance liquid chromatography [18].

Several studies have been shown that peels and seeds from various plant, as well as by-products or waste derived from food industry can be used for isolation and application of different value added compounds as a potential corrosion inhibitor. The extracts from orange, mango, passion fruit, cashew and tomato peel [19-21], *Garcinia Kola* and *Pongamia pinnata* seeds [22, 23] and grape pomace [24] have already shown promising and efficient corrosion inhibition properties.

In conclusion, the recent trend of reporting plant extracts as corrosion inhibitor of mild and carbon steel can be carried out on the tinplate, tin free steel and aluminium, due to the fact that these materials are not investigated enough. In addition, novel, economical and eco-friendly corrosion inhibitor derived from cheap and abundant renewable resources offer other enormous opportunities for further investigations.

2. Materials used for can production

Tinplate used for food packaging is formed of steel base, tin-iron alloy, free tin and passivated film with tin oxides, metallic chromium and chromium oxide. The steel base is a low carbon mild steel with 0.03-0.13 % of carbon. In general, its chemical composition has an important role in corrosion resistance of tinplate. The carbon steel base is coated with pure tin on both faces of sheets by hot dipping or anodic electrolytic processes in a molten tin.

In general, electroplating can be defined as an electrolytic metal deposition due to reduction reaction on the cathode electrode where the thin layer of metal adhered as a surface finishing processing. Thin metal films are plated on metals and alloys surface to enhance their appearance, corrosion and wear resistance. Such films must be adherent and uniform on regular or irregular metal surface, it must be cleaned prior to electro deposition in order to remove various foreign substances, e.g. oils, grease, dirt, oxides, etc. Otherwise, poor film adhesion and incomplete deposition will not protect the base steel and appearance will not be so satisfactory.

The main advantage of tin electrolytic deposition is the possibility of providing a higher coating weight, which will be in contact with aggressive food products [25]. Normally, this coating weight is used for the manufacture of internal surface of containers. It should be noted that application of heavier coating weight on internal and lighter coating weight on external surface of tinplate is the common practice in the food canning industry. This kind of material is called differentially coated tinplate with tin grades from 2.8 to 11.2 g/m². The tin-iron alloy ($FeSn_2$) is produced by diffusion of pure tin into the steel base during electrolytic process [26]. When the alloy layer is not compact and continuous, the steel is exposed through the pores to aggressive food compounds and its corrosion is accelerated.

During production of the tinplate, tin oxide films may be formed on its surface [27]. To prevent uncontrolled oxidation of the tin and protect metal against further oxidation, the tinplate is subjected to passivation treatment [28]. Also, it is applied to prevent appearance of sulphide stains by certain canned food (meat, fish and some vegetable products) and to improve lacquer adhesion to the metal substrate, i.e. the corrosion resistance towards food media. The most widely used passivation treatments are cathodic or a simple chemical dip treatment in a solution of sodium dichromate. Due to the fact that chromium compounds used in these procedures are toxic and carcinogenic, therefore diverse alternative passivation treatments were studied [29-31]. However, the conventional chromium passivation treatment is still used.

Besides tinplate, tin free steel (TFS) is also produced by electroplating, i.e. applying electrolytic chromic acid treatment over steel sheets. This type of material was developed to meet economic requirement and overcomes some tinplate properties. TFS shows great paint adhesion, excellent resistance to black sulphide stain and corrosion resistance after painting. Furthermore, no discoloration or deterioration causes by high temperature are the main properties of TFS.

It should be mentioned that some of non electrolytic finishing process include aluminium anodizing, i.e. chemical reaction between aluminium and oxygen to form a thin aluminium oxide film on an aluminium base metal. This process occurs as a natural phenomenon in air. Aluminium tendency to form passivation oxide layer, results in simple and ease manufacture of single piece aluminium cans, compared to laboriously constructed three pieces of steel. Besides single-serving containers, aluminium is the favoured material for shaped food cans, e.g. rectangular, oval, square, etc. Formable and versatile, aluminium offers opportunities for enhanced aesthetic appeal. Aluminium is less costly than tinplated steel, but offers the same resistance to corrosion. In addition, aluminium shows low density, good electrical and thermal conductivities and high ductility and good corrosion resistance.

3. Corrosion

Corrosion is defined as a destructive attack on metals and alloys through chemical or electrochemical reaction of metallic surface with corrosive medium. The consequence of its interactions is movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal. In other words, corrosion involves formation of stable compounds, i.e. corrosion products, between the compounds of corrosive solution and metals or its alloys. The tendency of a metal to corrode depends on different factors, such as structure of metal and its composition formed during alloying, damage of metal surface developed during fabrication, type of corrosion medium, pH and acid content, presence of corrosion accelerators (oxygen, nitrate, sulphur and phosphate compounds in corrosion medium), temperature and time of metal/metal alloys contacts with aggressive corrosion medium. According to work obtained by Chigondo and Chigondo [32], the different types of corrosion can be recognised, i.e. uniform, pitting, stress corrosion fatigue, intergranular crevice, filiform, erosion and fretting. The classification was done depending on environmental surrounding of metal, type of metal or metal alloys and possible chemical reactions occurred.

4. Corrosion prevention

Due to the fact that corrosion presents ubiquitous problem for a wide range of industrial applications and products, different strategies were employed to avoid possible metals dissolution and consequently contamination of foodstuffs. Corrosion progress can be prevented by lacquer coating application onto metallic surface or by addition of small amounts of corrosion inhibitor to corrosive medium.

4.1 Lacquer corrosion prevention

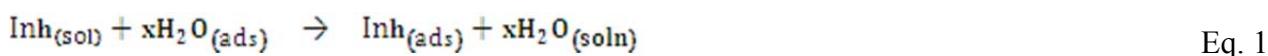
The use of organic coatings, i.e. lacquers on tinplate, tin free steel and aluminium has become a generalised procedure for cans manufacture. Lacquers should be chemically inert, resistant to mechanical or thermal stress and must adhere completely on metallic surface. Usually, one or two layers of lacquers are applied on metal surface to prevent interaction between the cans and its contents [33-35]. In some cases loss of adhesion may occur due to damage on the can surface during fabrication, but more often the detachment of the coating is due to breakdown processes taking place through or under the coating, due to the corrosion spreading from exposed metal. Therefore, the monitoring of lacquers [36, 37] is of major interest in industry practices in order to reduce the risk of loss of product properties and /or product contamination.

4.2 Synthetic organic corrosion inhibitors

Instead lacquers, there is a great interest of using different synthetic heterocyclic organic compounds, which are acting as a cathodic or anodic corrosion inhibitors. It has been found [38-41] that synthetic organic compounds could be used as effective corrosion inhibitors, due to the fact that they contained heteroatoms with high electron density and double or triple bonds in structure. Obviously, the compounds with both nitrogen and sulphur in their molecular structure have shown excellent corrosion ability, compared to those containing only nitrogen or sulphur. Moreover, the sulphur containing compounds possessed stronger corrosion inhibition efficiency, compared to nitrogen containing compounds. Inhibition function of organic compounds depends on its physicochemical properties, such as presence of functional groups, possible steric effects, electronic density of donor atoms and the possible interaction of p-orbitals of the inhibitor with d-orbitals of the metal surface atoms.

Generally, corrosion inhibitions protection is achieved by adsorption of ions or molecules of inhibitors onto metal surface. The absorption mechanism involves four possible types: *i*) electrostatic attraction between charged molecules of inhibitors and charged metal surface, *ii*) interaction of unshared electron pairs of the molecules with the metal surface, *iii*) interaction of the presence of conjugated bonds (π electron) in the compound with metal, and *iv*) adsorption occur by combination of *i*) and *iv*). As a results of adsorption, the corrosion rate is reduce by increasing or decreasing the anodic and/or cathodic reaction, decreasing the diffusion rate of aggressive components to the metal surface and decreasing the electrical resistance of the metal surface [42]

Adsorption mechanism of organic inhibitor at metal/solution interface, firstly involves replacement of one or more water molecules, initially adsorbed at the metal surface (Eq. 1).



$\text{Inh}_{(\text{soln})}$ and $\text{Inh}_{(\text{ads})}$ represent the inhibitors in the solution and adsorbed on the metal surface, respectively and x is the number of water molecules displaced by inhibitor.

Subsequently, the inhibitor may react with metal ions (M^{2+}), generated by oxidation or dissolution process (Eq. 2). Depending on relative solubility, the forming metal inhibitor complex (Eq. 3) may inhibit or catalyse further metal dissolution.



Although, synthetic organic compounds are efficient corrosion inhibitors, their synthesis is not always simple and cost-effective and many of them are toxic for humans and environment.

4.3 Natural organic corrosion inhibitors

Based on environmental and safety requests, the new class of non-toxic, natural corrosion inhibitors were developed. Natural products have potential to replace synthetic organic inhibitors due to follow main advantages, i.e. environmentally friendly and biodegradable in nature, readily available, synthesis by simple procedure with low cost. They are used for flavouring some food products, too, but their application in food canning industry as a corrosion inhibitor is not investigated enough. A number of natural products of plant origin, such as fruit, leaves, peel and seeds extracts have been reported as anticorrosive agents of various metals and alloy in acidic media, but their application as corrosion inhibitor for tinplate, tin free steel and aluminium used for production of food containers have not been studied yet. In addition, by-products or waste derived from food processing industry could be also used as a promising industrial resource for bio-compounds production and application as a non-toxic, cheap and effective green corrosion inhibitor, instead of ordinary chemical and toxic inhibitors.

As was previously mentioned, adsorption is main mechanism for most of the synthetic inhibitors. The inhibitive properties of natural, eco-friendly inhibitors are also based on two types of adsorption processes, i.e. physical (physisorption) and chemical (chemisorption) adsorptions. Physical adsorption occurred due to the electrostatic, dipole-dipole interactions between charged molecules of inhibitor and charged metal surface. Chemical adsorption involves the transfer or shearing of electrons from inhibitor to the metallic surface, resulting in formation of co-ordinate bond.

For example, the work obtained by Liu *et al.* [43] have shown that bamboo leaf extracts manifest both, physisorption and chemisorption mechanisms, at extract concentrations of 10 - 80 mg/L and 90 - 200 mg/L, respectively in hydrochloric and sulphuric acids. They have shown that bamboo leaf extract can be used as excellent natural inhibitor of cold rolled steel due to presence of O and N atoms in functional groups (O-H, N-H, C-C, C-O, C-N, C-N, C-O) and aromatic ring. Furthermore, the results of FTIR spectroscopy have also confirmed that *Ginkgo* leaves extracts contained oxygen and nitrogen atoms in mentioned functional groups [9]. Therefore, protection of metallic surface is done via O and N atoms presented in the flavonoids, ginkgolides and amino acids as main constituents of bamboo and *Ginkgo* leave extracts. Oxygen and nitrogen atoms found in the functional groups, such as C=O, N-H, O-H, C-O, C-N, C=C and aromatic ring of *Ilex kudingcha* C.J. Tseng are also responsible for the inhibition of the corrosion reaction on J55 steel [44]. Furthermore, FTIR and dispersive X-ray spectroscopy (EDX) results showed that *Piper longum* fruit extract contains oxygen and nitrogen atoms in functional groups (O-H, C=C, C=O, C-N, C-O) and aromatic ring, which meets the general consideration of typical corrosion inhibitors [23]. In addition, phenolic compounds, particularly flavonoids [20, 24, 45] have been shown to possess significant corrosion inhibition efficiency, which is primarily in relationship with their structural characteristics, such as number and position of phenolic hydroxyle or other groups and conjugation. Flavonoids are especially important antioxidants due to their high redox potential, which allows them to act as reducing agents, hydrogen donors, and singlet oxygen quenchers. They possessed metal chelating potential, forming bidentate metal chelates at the ortho-diphenolic groups of rings B and C [46, 47].

Phytochemical screening carried out on the extracts from *Phyllanthus fraternus* [48] and *Saccocalyx satureioides* [49] are constituent alkaloids, saponins, tannins, terpenoids, steroids, flavonoids and phenols. The corresponding chemical structures of these compound reveals that they contain O in functional groups, aromatic rings and O-heterocyclic rings, which encounter the general characteristics of typical corrosion inhibitors. Furthermore, analysis of *Ruta chalepensis* oil [14], using gas chromatography and gas chromatography/mass spectroscopy revealed that the major components responsible for corrosion inhibition were 2-Undecanone (67 %), 2-Decanone (9 %), 6-(3',5'-Benzodioxyl)-2-hexanone (6.3 %) and 2-Dodecanone (4 %).

5. Methods used for extraction of plant materials

Extraction of plant material can be done using various methods, divided into two main groups, i.e. conventional or unconventional (Fig. 1). All these techniques have shown some common objectives: *i*) to extract target compounds from complex plant material, *ii*) to convert the target compounds into a more suitable form for separation, detection and

application and *iii*) to provide strong and reproducible separation method that is independent of variations in the sample matrix. The extracting power of conventional (classical) techniques is based on application of heat and/or mixing of plant material with different solvents in use. Compare to conventional, non-conventional methods are more environmental friendly due to decreased use of organic chemical, reduced time of extraction, provided better yield and quality of extracts. It is important to mention that understanding of every aspect of used non-conventional techniques is crucial for successful isolation of target compound, due to the fact that most of these methods are based on different mechanism. However, to compare success of newly developed methods, the conventional ones are still considered as the reference method.

The majority of plant extracts for corrosion inhibition purposes were prepared by refluxing method [23, 43, 48, 50 - 52], such as *Piper longum* (distilled water, 5 h), bamboo (80 %, v/v ethanol, 75 °C, 2 h), *Phyllanthus fraternus* (1 M H₂SO₄, 5 h), *Gundelia tournefortii* (7:3 v/v, methanol/water mixture, 80 °C, 1 h), eggplant peel (distilled water, 2 h) and *Salvadora persica* (distilled water, 5 h). Furthermore, the peels of mango and orange [20] and seeds of *Garcinia kola* [22] were extracted in a Soxhlet extractor using ethanol, ethyl acetate, hexane and absolute ethanol, respectively. Other extracts, e.g. *Laurus nobilis*, *Ilex paraguariensis*, *Saccocalyx satureioides*, *Cola Acuminata*, *Camellia Sinensis*, *Ocimum gratissimum*, *Menta pulegium*, *Lavandula dentate*, *Matricaria recutita* and grape pomace were prepared by boiling, soaking, continuous agitation, hydro-distillation, ultrasonication and steam distillation [8, 10, 13, 26, 49, 53 - 55].

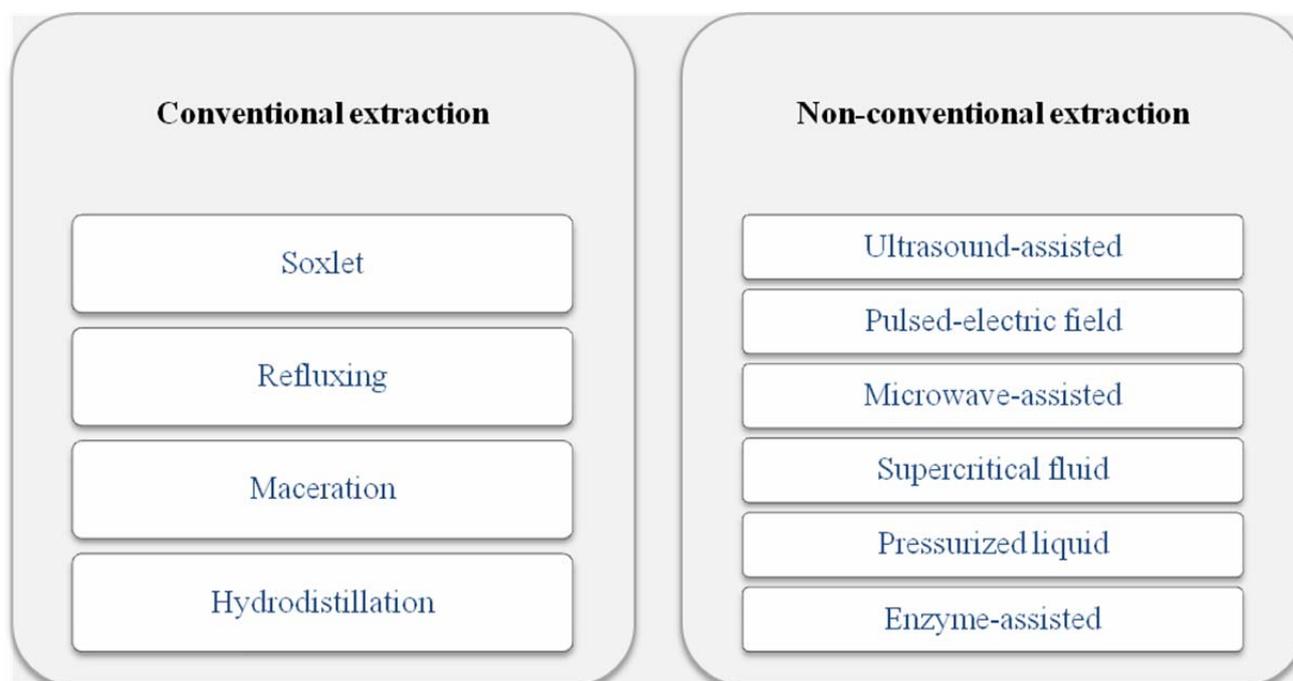


Fig. 1 Extraction method used for preparation of plant extracts.

6. Methods used for evaluation of corrosion inhibition efficiency

In order to investigate the inhibition efficiency of plant extracts in various corrosive medium, several methods have been employed. Frequently used are weight loss or gravimetric analysis and electrochemical methods. Weight loss test is based on sheets or specimens weight measurements before and after their immersion in corrosive medium during certain period. Subsequently, corrosion rate and efficiency can be calculated using specimen weight loss (Δm), specimen surface (A) and immersion time (t).

Electrochemical kinetics of a metal exposed to a corrosive medium (electrolyte) can be characterized by determining at least three polarization parameters, such as corrosion current density, (i_{corr}) corrosion potential (E_{corr}) and Tafel slopes (β_a and/or β_c). The rate of metal dissolution or corrosion can be calculated using follow polarization methods:

- Linear polarization which covers both anodic and cathodic portions of the potential (E) versus current density (i) curve for determination of polarization resistance (R_p).
- Tafel extrapolation technique which takes into account linear parts of the anodic and cathodic curves for determination of R_p . This method involves determination of the Tafel slopes β_a and/or β_c , as well as E_{corr} and i_{corr} from a single polarization curve.
- Electrochemical impedance spectroscopy requires alternating current and the output is Nyquist plot for charge transfer or diffusion control process, which can be used to determine R_p , which in turn is inversely proportional to the corrosion current density i_{corr} .

All mentioned electrochemical methods were used Li *et al.* [43] for determination of bamboo leaf extracts inhibition efficiency on cold rolled steel in two corrosion media, i.e. sulphuric (0.5 - 5.0 M) and hydrochloric (1.0 - 5.0 M) acids. They were found that inhibition efficiency increases due to increases of extracts concentration (5 - 200 mg/L) and immersion time (6 - 32 h). Maximum inhibition efficiency of 89 % and 79 % was obtained in 1.0 M hydrochloric and 0.5 M sulphuric acids, respectively. Deng and Li [9] were also investigated the inhibition effect of *Ginkgo* leaves extracts in hydrochloric (1.0 - 5.0 M) and sulfuric (0.5 - 2.5 M) acids using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The results showed that *Ginkgo* leaves extract act as a good corrosion inhibitor, particularly in 1.0 M hydrochloric compared to 0.5 M sulphuric acid. In addition, they were used atomic force microscope (AFM) and scanning electron microscopy (SEM) analyses as a two powerful methods to investigate the surface morphology at nano to microscale. These techniques have become a new choice to study the influence of inhibitors on the generation and progress of corrosion at the metal-solution interface. AFM and SEM techniques were also used Nasibi *et al.* [46] for mild steel surface examination after interaction with chamomile extracts. For determination of inhibition efficiency, they were applied electrochemical, i.e. potentiodynamic polarization and impedance spectroscopy techniques, which have shown that chamomile extracts acts as excellent inhibitor (93.3 %), at temperature of 22 °C and concentration of 7.2 g/L. Furthermore, corrosion inhibition efficiency of green tea extracts tested by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy has shown that all employed techniques are in good agreement with each other [45]. Maximum inhibition efficiency was 81.5 % (1 M HCl) and 71.7 % (0.5 M H₂SO₄), at extract concentration of 500 ppm. The inhibition efficiency of *Gundelia tournefortii* extract was found to be 93 % and 90 % in 2.0 M HCl and 1.0 M H₂SO₄, respectively, at concentration of 150 ppm [50]. Cathodic and anodic polarization curves show that *G. tournefortii* extract is a mixed-type inhibitor in both acidic media. In this context, the electrochemical Tafel polarization studies [56] revealed that *Eriobotrya japonica* (EB) leaf extract also acts as mixed type of inhibitor in hydrochloric (0.5 M), whereas in sulphuric (0.5 M) acid as anodic type. The impedance response of EB extracts consisted of characteristic depressed semicircles clarifying that the corrosion process of mild steel occurs under charge transfer control, while thermodynamic parameters indicated that the inhibition of corrosion occurred by physical adsorption mechanism. Furthermore, the work done by Bouammali *et al.* [8] showed that aqueous extract of *Lavandula dentata* in 1 M HCl also acts as mixed type with maximum inhibition efficiency of 95 % obtained at mass fraction of 2 %. Other aromatic herbs such as *Mentha pulegium* and *Ruta chalepensis* [13, 14] were proved as a efficient corrosion inhibitors on mild steel in acid media. The inhibitory effect of *Mentha pulegium* extract was found to increase with the concentration and reached 88 % at 33 % (v/v), whereas for *Ruta chalepensis* oil attained 77 % at 2.5 ml/L. In addition, *Thymus vulgaris*, *Xylopia aethiopica*, *Zingiber officinale*, *Piper longum*, *Saccocalyx satureioides*, *Cola acuminata* and *Camellia sinensis* leaves mix extracts, *Ocimum gratissimum*, *Larrea Tridentata*, *Eulychnia acida* Phil., *Khaya senegalensis*, punic plant and *Thapsia villosa* have been also successfully applied as a eco-friendly and non-toxic corrosion inhibitor of steel in acid media confirmed by already mentioned methods [23, 49, 54, 55, 57 - 61].

In the conspectus of using natural products as a corrosion inhibitor, various plant peels, seeds and pomace have been investigated as a cheap and effective corrosion inhibitor of mild and carbon steel. In this context, the extracts from mango, orange, passion fruit and cashew peels [19, 20], eggplant peel [51], *Cucurbita maxima* peel [62], *Musa acuminata* [63], have been tested, using electrochemical methods, weight loss measurements and SEM surface analysis. They have shown inhibition efficiencies in the range of 48 to 96 %, depending on peel type, extract concentrations, time and temperature of immersion and method used for corrosion assay. Furthermore, the grape pomace, as an industrial waste from wine and juice processing industry was also evaluated as corrosion inhibitor of steel. The maximum inhibition efficiency of 83 % and 93 % was obtained for 3%, crude and concentrated extracts.

7. Conclusion

Various plants extract are found to be effective, eco-friendly and non-toxic corrosion inhibitor due to presence of different organic compound, such as alkaloids, flavonoids, phenols, saponins, steroids, tannins, terpenoids, etc, whose attachment to adsorption sites on the metal surface is responsible for the inhibition process. Theirs excellent protection of steel in acidic medium was confirmed in different scientific work. However, its inhibition performance were not proved enough on tinplate, tin free steel and aluminium, commonly used materials in food canning industry. Moreover, theirs inhibition action were not investigated in other corrosive medium, except acidic, mostly hydrochloric and sulphuric. Therefore, it is certain that in the coming years usage of plant extracts can be promising, not yet fully exploring material for future scientific investigation. Furthermore, by-products or waste derived from food processing industry can be also propose as a new alternative natural resource for production of compounds with anticorrosive properties.

References

- [1] Perring, L, Basic-Dvorzak, M. Determination of total tin in canned food using inductively coupled plasma atomic emission spectroscopy. *Analytical and Bioanalytical Chemistry*. 2002;374:235-243.
- [2] Boogaard, PJ, Boisset, M, Blunden, S, Davies, S, Ong, TJ, Taverne, JP. Comparative assessment of gastrointestinal irritant potency in man of tin (II) chloride and tin migrated from packaging. *Food and Chemical Toxicology*. 2003;41:1663-1670.
- [3] Shimbo, S, Matsuda-Inoguchi, N, Watanabe, T, Sakurai, K, Date, C, Nishimura, A, Nakatsuka, H, Saito, H, Arisawa, K, Ikeda, M. Dietary intake of tin in Japan, and the effects on intake of canned food and beverage consumption. *Food Additives and Contaminants*. 2007;24:535-545.
- [4] European Commission. 2002. Commission Regulation (EC) No. 562/2002 of 2nd April 2002: setting maximum levels for certain contaminants in foodstuffs. *Official Journal of European Community*. L 86/5.
- [5] Kliškić, M, Radošević, J, Gudić, S, Katalinić, V. Aqueous extract of *Rosmarinus officinalis* L. as inhibitor of Al-Mg alloy corrosion in chloride solution. *Journal of Applied Electrochemistry*. 2000;30:823-830.
- [6] Vrsalović, L, Kliškić, M, Gudić, S. Application of Phenolic Acids in the Corrosion Protection of Al-0.8Mg Alloy in Chloride Solution. *International Journal of Electrochemical Science*. 2009;4:1568-1582.
- [7] Halambek, J, Berković, K, Vorkapić-Furač, J. The influence of *Lavandula angustifolia* L. oil on corrosion of Al-3Mg alloy. *Corrosion Science*. 2010;52:3978-3983.
- [8] Bouammali, H, Ousslim, A, Bekkouch, K, Bouammali, B, Aouniti, A, Al-Deyab, SS, Jama, C, Bentiss, F, Hammouti, B. The Anti-Corrosion Behavior of *Lavandula dentata* Aqueous Extract on Mild Steel in 1M HCl. *International Journal of Electrochemical Science*. 2013;8:6005-6013.
- [9] Deng, S, Li, X. Inhibition by *Ginkgo* leaves extract of the corrosion of steel in HCl and H₂SO₄ solutions. *Corrosion Science*. 2012;55:407-415.
- [10] Gülşen, A. Corrosion inhibition of mild steel by *Laurus nobilis* leaves extract as green inhibitor. *Research on Chemical Intermediates*. 2012;38:1311-1321.
- [11] Halambek, J, Cvjetko Bubalo, M, Radojčić Redovniković, I, Berković, K. Corrosion Behaviour of Aluminium and AA5754 Alloy in 1% Acetic Acid Solution in Presence of Laurel Oil. *International Journal of Electrochemical Science*. 2014;9:5496-5506.
- [12] Okafor PC, Apebende EA. Corrosion inhibition characteristics of *Thymus vulgaris*, *Xylopi aethiopica* and *Zingiber officinale* extracts on mild steel in H₂SO₄ solutions. *Pigment & Resin Technology*. 2014;43:357-364.
- [13] Khadraoui, A, Khelifa, A, Boutoumi, H, Belkheir, H. *Mentha pulegium* extract as a natural product for the inhibition of corrosion. Part I: electrochemical studies. *Natural Product Research*. 2014;28:1206-1209.
- [14] Khadraoui, A, Khelifa, A, Boutoumi, H, Hamitouche, H, Mehdaoui, R, Al-Deyab, SS. Adsorption and Inhibitive Properties of *Ruta chalepensis* L. Oil as a Green Inhibitor of Steel in 1 Hydrochloric Acid Medium. *International Journal of Electrochemical Science*. 2014;9:3334-3348.
- [15] Ninčević Grassino, A, Grabarić, Z, Pezzani, A, Fasanaro, G, Lo Voi, A. Influence of essential onion oil on tin and chromium dissolution from tinplate. *Food and Chemical Toxicology*. 2009;47:1556-1561.
- [16] Ninčević Grassino, A, Grabarić, Z, Pezzani, A, Squitieri, G, Berković, K. Corrosion inhibition with different protective layers in tinplate cans for food preserving. *Journal of the Science of Food and Agriculture*. 2010;90:2419-2426.
- [17] Ninčević Grassino, A, Grabarić, Z, Pezzani, A, Squitieri, G, Fasanaro, G, Impembo, M. Corrosion behaviour of tinplate cans in contact with tomato purée and protective (inhibiting) substances. *Food Additives and Contaminants*. 2009;26:1488-1494.
- [18] Ninčević Grassino, A, Grabarić, Z, De Sio, F, Cacace, D, Pezzani, A, Squitieri, G. Effect of storage time and natural corrosion inhibitor on carbohydrate and carboxylic acids content in canned tomato purée. *Food Science and Technology International*. 2012;18:219-22.
- [19] da Rocha, JC, da Cunha Ponciano Gomes, JA, D'Elia, E. Corrosion inhibition of carbon steel in hydrochloric acid solution by fruit peel aqueous extracts. *Corrosion Science*. 2010;52: 2341-2348.
- [20] da Rocha, JC, da Cunha Ponciano Gomes, JA, D'Elia, E. Aqueous Extracts of Mango and Orange Peel as Green Inhibitors for Carbon Steel in Hydrochloric Acid Solution. *Materials Research*. 2014; 17:1581-1587.
- [21] Ninčević Grassino, A, Halambek, J, Rimac-Brnčić, S, Djaković, S, Dent, Grabarić, Z. Utilization of tomato peel waste from canning factory as a potential source for pectin production and application as tin corrosion inhibitor. *Food Hydrocolloids*. 2016;52:265-274.
- [22] Ikeuba, AI, Okafor, PC, Ekpe, UJ, Ebenso, EE. Alkaloid and Non-Alkaloid Ethanolic Extracts from Seeds of *Garcinia Kola* as Green Corrosion Inhibitors of Mild Steel in H₂SO₄ Solution. *International Journal of Electrochemical Science*. 2013;8:7455-7467.
- [23] Singh, A, Singh, VK, Quraishi, MA. Inhibition of Mild Steel Corrosion in HCl Solution Using Pipali (*Piper longum*) Fruit Extract. *Arabian Journal of Science and Engineering*. 2013;38:85-97.
- [24] da Rocha, JC, Ponciano Gomes, JAC, D'Elia, E, Gil Cruz, AP, Cabral, LMC, Torres, AG, Monteiro, MVC. Grape Pomace Extracts as Green Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solutions. *International Journal of Electrochemical Science*. 2012;7:11941-11956.
- [25] Zhu, X, Sandenberg, RF. Corrosion of tinplate T54S and T61 in humid atmosphere and saline solution. *Material Corrosion*. 2001;52:685-690.
- [26] Elias, RA, Forder, SD, English, TH, Breen, C. ⁵⁷Fe conversion electron Mössbauer spectroscopy of factors influencing Fe-Sn intermetallic phase formation in tinplated steel. *Hyperfine Interaction*. 2002;141/142:447-451.
- [27] Zurlini, C, Gelati, S, Fragni, R, Montanari, A. Determination of tin oxides on the surface of electrolytic tinplate. *Industria Conserve*. 2003a;78: 313-318.
- [28] Zurlini, C, Fragni, R, Ferretti, C, Montanari, A, Chiodi, D. 2003b. Comparison of methods for chromium determinations in tinplate passivation film. *Industria Conserve*. 2003b;78:293-309.

- [29] Arenas, MA, Conde, A, de Damborenea, JJ. Cerium: a suitable green corrosion inhibitor for tinplate. *Corrosion Science*. 2002;44:511-520.
- [30] Mora, N, Cano, E, Polo, JL, Puente, JM. Corrosion protection properties of cerium layers formed on tinplate. *Corrosion Science*. 2004;46:563-578.
- [31] Catalá, R, Alonso, M, Gavara, R, Almeida, E, Bastidas, JM, Puente, JM, de Cristaforo, N. Titanium-passivated tinned for canning food. *Food Science and Technology International*. 2005;11:223-227.
- [32] Chigondo, M, Chigondo, F. Recent Natural Corrosion Inhibitors for Mild Steel: An Overview. *Journal of Chemistry*. 2016, Article ID 6208937:7 pages. <http://dx.doi.org/10.1155/2016/6208937>.
- [33] Barilli, F, Fragni, R, Gelati, S, Montanari A. Study on the adhesion of different types of lacquers used in food packaging. *Progress in Organic Coatings*. 2003;46:91-96.
- [34] Bernardo, PEM, dos Santos, JLC, Costa, NG, Influence of the lacquer and end lining compound on the shelf life of the steel beverage can. *Progress in Organic Coatings*. 2005; 54:34-42.
- [35] Manfredi, LB, Ginés, MJL, Benítez, GJ, Egli, WA, Rissone, H, Vázquez, A. Use of epoxy phenolic lacquers in food can coatings: characterization of lacquers and cured films. *Journal of Applied Polymer Science*. 2005;95:1448-1458.
- [36] Ninčević, A, Pezzani, A, Squitieri, G. Characterization of different types of lacquers used in food packaging: porosity, flexibility and IR reflectance spectroscopy tests. *Acta Alimentaria*. 2006;35:397-407.
- [37] Ninčević, A, Pezzani, A, Squitieri, G. Characterization of different types of lacquers used in food packaging: lacquer adhesion tests. *Acta Alimentaria*. 2007;36:27-37.
- [38] Bentiss, F, Traisne, M, Lagrenée, M. The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media. *Corrosion Science*. 2000;42:127-146.
- [39] Morad, MSS, Hermas, AAA, Influence of some amino acids and vitamin C on the anodic dissolution of tin in sodium chloride solution. *Journal of Chemical Technology and Biotechnology*. 2001;76:401-410.
- [40] Migahed, MA, Azzam, EMS, Al-Sabagh, AM, Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant. *Materials Chemistry and Physics*. 2004;85:273-279.
- [41] Mu, G, Li, X, Inhibition of cold rolled steel corrosion by Tween-20 in sulphuric acid: weight loss, electrochemical and AFM approaches. *Journal of Colloid and Interface Science*. 2005;289:184-192.
- [42] Khan, G, Newaz, KMS, Basirun, WJ, Ali, HBM, Faraj, FL, Khan, GM. Application of Natural Product Extracts as Green Corrosion Inhibitors for Metals and Alloys in Acid Pickling Processes - A review. *International Journal of Electrochemical Science*. 2015;10:6120-6134.
- [43] Li, X, Deng, S, Fu, H. Inhibition of the corrosion of steel in HCl, H₂SO₄ solutions by bamboo leaf extract. *Corrosion Science*. 2012;62:163-175.
- [44] Chen, S, Singh, A, Wang, Y, Liu, W, Deng, K, Lin, Y. Inhibition effect of Ilex kudingcha C.J. Tseng (Kudingcha) extract on J55 Steel in 3.5wt% NaCl Solution Saturated with CO₂. *International Journal of Electrochemical Science*. 2017;12:782-796.
- [45] Alsabagh, AM, Migahed, MA, Abdelraouf, M, Khamis, EA. Utilization of Green Tea a Environmentally Friendly Corrosion Inhibitor for Carbon Steel in acidic media. *International Journal of Electrochemical Science*. 2015;10:1855-1872.
- [46] Nasibi, M, Zaarei, D, Rashed, G, Ghasemi, E. Chamomile (*Matricaria recutita*) Extracts as a Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution. *Chemical Engineering Communications*. 2013;200:367-378.
- [47] Stalikas, CD. Extraction, separation and detection methods for phenolic acids and flavonoids. *Journal of Separation Science*. 2007;30:3268-3295.
- [48] Patel, NS, Hrdlicka, J, Beranek, P, Příbyl, M, Šnita, D, Hammouti, B, Al-Deyab, SS, Salghi, R. Extract of *Phyllanthus fraternus* Leaves as Corrosion Inhibitor for Mild Steel in H₂SO₄ Solutions. *International Journal of Electrochemical Science*. 2014;9:2805-2815.
- [49] Benahmed, M, Djeddi, N, Akkal, SH, Laouar S. Saccocalyx satreoides as corrosion inhibitor for carbon steel in acid solution. *International Journal of Industrial Chemistry*. 2016;7:109-120.
- [50] Soltani, N, Khayatkashan, M. *Gundelia tournefortii* as a Green Corrosion Inhibitor for Mild Steel in HCl and H₂SO₄ Solutions. *International Journal of Electrochemical Science*. 2015;10:46-62.
- [51] Ibrahi, T, Habbab, M. Corrosion Inhibition of Mild Steel in 2M HCl Using Aqueous Extract of Eggplant Peel. *International Journal of Electrochemical Science*. 2011;6:5357-5371.
- [52] Hassan, AAM, Abdel-Fatah, HTM. Aqueous Extract of *Salvadora Persica* as a Novel Green Corrosion Inhibitor for Low-Alloy Steel in Acidic Media - Part I. *International Journal of Electrochemical Science*. 2016;11:6959-6975.
- [53] Souza, TF, Magalhães, M, Torres, VV, D'Elia, E. Inhibitory Action of *Ilex paraguariensis* Extracts on the Corrosion of Carbon Steel in HCl Solution. *International Journal of Electrochemical Science*. 2015;10: 22-33.
- [54] Loto, CA, Popoola, API. Effect of Cola Acuminata and Camellia Sinensis Mixed Extracts on the Corrosion Inhibition of Mild Steel in 0.5M Sulphuric Acid. *International Journal of Electrochemical Science*. 2012;7:2983-2996.
- [55] Eddy, NO, Odoemelam, SA, Ama, IN. Ethanol extract of *Ocimum gratissimum* as a green corrosion inhibitor for the corrosion of mild steel in H₂SO₄. *Green Chemistry Letters and Reviews*. 2010;3:165-172.
- [56] Hijazi, KM, Abdel-Gaber, AM, Younes, GO. Electrochemical Corrosion Behavior of Mild Steel in HCl and H₂SO₄ Solutions in Presence of Loquat Leaf Extract. *International Journal of Electrochemical Science*. 2015;10:4366-4380.
- [57] Inzunza, RG, Valdez Salas, B, Schorr Wiener, M, Carrillo Beltran, M, Zlatev Koytchev, R, Stoytcheva Stilianova, M, Ramos Irigoyen, R, Vargas Osuna, L, Terrazas Gaynor, J. Aqueous Extract of Creosote Bush (*Larrea tridentata*) Leaves as Green Inhibitor for Carbon Steel in Hydrochloric Acid Solution. *International Journal of Electrochemical Science*. 2013;8:6433-6448.
- [58] Venegas, R, Figueredo, F, Carvallo, G, Molinari, A, Vera, R. Evaluation of *Eulychnia acida* Phil. (Cactaceae) Extracts as Corrosion Inhibitors for Carbon Steel in Acidic Media. *International Journal of Electrochemical Science*. 2016;11:3651-3663.
- [59] Ali, IH. Inhibitory Effect of Leaf Extract of *Khaya senegalensis* (Mahogany) on C-steel Corrosion in 1.0 M Hydrochloric Acid Solution. *International Journal of Electrochemical Science*. 2016;11:2130-2141.
- [60] Fouda, AS, Etai, SH, Elinggar, W. Punica Plant extract as Green Corrosion inhibitor for C-steel in Hydrochloric Acid Solutions. *International Journal of Electrochemical Science*. 2014;9: 4866-4883.

- [61] Kalla, A, Benahmed, M, Djeddi, N Akkal, S, Laouer, H. Corrosion inhibition of carbon steel in 1 M H₂SO₄ solution by *Thapsia villosa* extracts. *International Journal of Industrial Chemistry*. 2016; 7:419-429.
- [62] Anbarasi, K. Electrochemical and Corrosion Inhibition Studies of *Cucurbita maxima*. *Oriental Journal of Chemistry*. 2016;32:2139-2145.
- [63] Gunavathy, N, Murugavel, SC. Corrosion Inhibition Studies of Mild Steel in Acid Medium Using *Musa Acuminata* Fruit Peel Extract. *E-Journal of Chemistry*. 2012;9:487-495.