Chapter 8

Sustainable Corrosion Inhibitors for Copper and its Alloys

B. El Ibrahimi*

Department of Chemistry, Faculty of Sciences. IBN ZOHR University. Agadir. Morocco

* brahimhm@gmail.com

Abstract

The good properties of copper, as well as its alloys, make them a often used metallic materials in various industries. Regardless of their excellent corrosive resistance, the corrosion process of copper materials can occur under some specific conditions, hence, the need for corrosion inhibitors. Recently, due to many environmental agencies, the “green” aspect was introduced in many fields, including inhibition of corrosion. Keeping in mind economic and eco-friendly aspects, a wide range of compounds were employed as ecological inhibitors for copper materials. For this purpose, the current chapter aims to explore the application of numerous compounds as sustainable inhibitors to control the corrosion of copper materials in various media.

Keywords

Copper, Alloy, Corrosion, Sustainable Inhibitor, Biopolymer, Plant Extract, Ionic Liquids, Amino Acid, Acid, Alkaline, Ecological, Green

Contents

Sustainable Corrosion Inhibitors for Copper and its Alloys.....	175
1. Introduction.....	176
2. Amino acids as sustainable inhibitors against the corrosion of copper materials.....	178
3. Biopolymers as sustainable inhibitors against the corrosion of copper materials.....	183
4. Natural extracts as sustainable inhibitors against the corrosion of copper materials.....	186

5. Ionic liquids as sustainable inhibitors against the corrosion of copper materials.....189

References193

1. Introduction

Metal corrosion or metal degradation is a spontaneous and natural phenomenon that converts it into more stable forms (natural forms) like oxides, sulfide and so on. This natural conversion occurs via the electrochemical and/or chemical transformations caused by the adjacent environments. Metallic corrosion affects different fields such as railways bridges, industries, buildings, traffic and households [1]. In a recent study [2] performed by NACE¹, about 2.5 trillion \$ (USA) is the value of economic cost caused by the corrosion phenomena. Fig. 1 illustrates in detail the economic costs of corrosion. Nevertheless, this loss can be reduced up to 15–35%, if the corrosion protection approaches are applied.

Figure 1. The economic costs of corrosion [10].

¹ National Association of Corrosion Engineers.

To overcome such disadvantageous phenomena or reduce its impact, a variety of protection technologies were used, among them using a corrosion inhibitor is the most attractive method and practical one [3], because it is a rentable economic solution owing to its simplicity of application and its high efficiency. By definition, an inhibitor of corrosion is a chemical compound that introduced to aggressive medium to result in the decline of metal dissolution to an acceptable level [4,5].

Based on their chemical composition, the inhibitors of corrosion could be categorized into two major classes, i.e. organic inhibitors and inorganic inhibitors. The first set of inhibitors is widely applied in acidic and sometimes in near-neutral media, whereas the second inhibitors class is used for metal protection in alkaline environments. Since the first apparition of organic compounds to be used as corrosion inhibitors in 1945² [6], the developments in this field undergoing outstanding development. Several inhibitors with high anti-corrosion efficiencies were synthesized and reported, like chromates-based species. In this context, the effect of those compounds on human health and/or surrounding environment is missed and is not discussed. Recently, due to the activities of many environmental agencies worldwide, the “green” aspect was introduced in almost fields, in which the inhibition of corrosion is concerning [7]. Consequently, the improvement of new inhibitors of corrosion without or with negligible undesirable environmental impacts (i.e. sustainable corrosion inhibitors) is considered to be more desired [8,9].

Keeping in mind economic criteria and eco-friendly aspects together, a wide range of compounds were reported and used as potent sustainable inhibitors for several metallic materials in different corrosive environments. According to available literature, sustainable corrosion inhibitors can be subdivided into two different classes, the first one is the organic inhibitors, which regroups: amino acids, ionic liquids, biopolymers, plant extracts, surfactants, and pharmaceutical compounds. Concerning the second class, it contains the rare earth compounds, which are the inorganic inhibitors [10].

The attractive chemical and physical properties of copper, as well as its alloys, make them the largely used metals in various industrial fields, such as chemical industries, heating, electronics industries and cooling structures, other than in daily life [11-14]. Regardless of their excellent corrosive resistance, the corrosion process of copper materials can occur under some specific conditions, especially in aerated acidic media, which involves an enormous economic loss [15]. To resolve such problem, corrosion inhibitor was used as an efficient method to stop or reduce the degradation of copper materials [16].

² Before this year (i.e. the 1900s), used corrosion inhibitors are inorganic type.

In the aim to evaluate and quantify the prevention property of “green” inhibitors against the corrosion of copper materials, direct and indirect investigation methods were employed. Concerning direct methods are including weight loss, the volume of liberated H₂ gas (in acidic media) and temperature variation. Whereas indirect methods regroup several DC and AC electrochemical methods, especially potentiodynamic polarization measurements and electrochemical impedance spectroscopy. Furthermore, in recent works, some authors were used electrochemical frequency modulation (EFM). Due to their simplicity of performing, high precision, possibility to understand the action mechanism, low material and time consumption, electrochemical techniques are mostly used instead of direct methods.

In recent works, by using computational tools, corrosion scientists attempt to explain and understand more the action mechanism of those sustainable corrosion inhibitors under the atomic scale. Such interesting in using theoretical approaches related to the improvements of software and hardware performance of existing computers as well as the development of calculation algorithms in the last decade [17-22].

In the rest of this chapter, we will focus on the application of some biomolecules, namely amino acids and biopolymers, in addition to plant extracts and ionic liquids compounds as sustainable inhibitors toward the corrosion of copper and its based alloys in various corrosive media.

2. Amino acids as sustainable inhibitors against the corrosion of copper materials

The protection capacity of numerous amino acids or their derived compounds to behave as eco-friendly inhibitors toward copper materials corrosion was examined and reported in the literature by several researchers.

Those biomolecules showed a specific significance to consider them as good environmentally inhibitors of corrosion. This explains by their interesting intrinsic properties such as biodegradability property and nontoxicity effect. In addition, it can be produced at a high level of purity and has a higher solubility in aqueous solutions and economically rentable [23-25].

The structure of an amino acid molecule is shown in Fig. 2 (in the center of Fig. 2). It characterized by the presence of amine and carboxyl functional groups. Almost tested amino acid compounds as corrosion inhibitors were the alpha (α) type, in which amine and carboxyl groups are bonded to the same carbon atom as demonstrated in Fig. 2. For the rest of the molecule skeleton, it can be an H atom (i.e. *Glycine*, it is the simplest amino acid) or an organic side chain of different sizes and shapes. Fig. 2 summarized the

molecules of amino acid present in physiological media, which contributed to proteins building *in vivo* species starting from cell to human [24].

Figure 2. Molecular structure of amino acid and physiological amino acids [10].

The amino acid compounds are used in numerous applications like in the food industry, animal feed technology, pharmaceuticals, cosmetics, and human parenteral nutrition. All these applications and other ones have involved the progress of amino acid-based compounds market. With respect to their environmental aspect, the existence of heteroatoms, like oxygen, nitrogen and sulfur atoms, in addition to eventual π -electrons on their molecular skeleton has encouraged several researchers to study in depth their possible performance to act as the sustainable inhibitors for corrosion of copper materials in different corrosive mediums [26-29]. Mainly for brass and copper/nickel alloys.

The use of amino acid-based compounds as inhibitors for copper or its alloys³ was developed considerably throughout the latest years. In the first studies, the investigations were focused on the use of simple amino acids, i.e. physiological amino acids (Fig. 2). In

³ Mainly for CuZn and CuNi alloys.

this context, among tested biomolecules, *Cysteine* and *Methionine* have been studied extensively (as can be seen in Table 1), this particular attention is due to the presence of sulfur atoms, as well as nitrogen and oxygen atoms on their molecular structures, which can consist the active sites for adsorption on copper surface [10]. Table 1 resumes some obtained protection effectiveness of simple amino acids for copper or its alloys.

Table 1. Application of some simple amino acids as corrosion inhibitors toward the corrosion of copper materials.

Amino acids	Aggressive medium	Copper material	Inhibition efficiency (IE)	Ref
<i>Aspartic acid, Glutamic acid, Asparagine and Glutamine</i>	0.5 M HCl	Cu	IE(%): <i>Glutamine</i> (73%) > <i>Asparagine</i> > <i>Glutamic acid</i> > <i>Aspartic acid</i> at 10 mM.	[34]
<i>Methionine, Cysteine, Serene, Arginine, Glutamine and Asparagine</i>	0.1 M H ₂ SO ₄	Cu	IE(%): <i>Arginine</i> > <i>Glutamine</i> > <i>Asparagine</i> > <i>Methionine</i> > <i>Cysteine</i> > <i>Serene</i> at 10 mM	[92]
<i>Proline, Cysteine, Phenylalanine, Alanine, Histidine and Glycine</i>	8 M H ₃ PO ₄	Cu	<i>Histidine, Cysteine and Phenylalanine</i> give the maximum efficiency	[93]
<i>Cysteine and Methionine</i>	Neutral 3.5% NaCl	Cu10Al5Ni	IE(%): <i>Cysteine</i> (96%) > <i>Methionine</i> (77%) at 6 mM.	[94]
<i>Cysteine, Alanine and Phenylalanine</i>	0.2 g L ⁻¹ Na ₂ SO ₄ + 0.2 g L ⁻¹ NaHCO ₃ at pH 3	Bronze	IE(%): <i>Cysteine</i> (97% at 10mM) > <i>Alanine</i> (80% at 1 M) > <i>Phenylalanine</i> (52% at 10 mM)	[95]
<i>Glycine, Alanine, Leucine, Cysteine, Lysine, Histidine and Glutamic acid</i>	Neutral 0.06 M NaCl	CuNi5 and CuNi65	<i>Glycine</i> is an effective corrosion inhibitor	[96]

Despite that, the higher protection performance was judged by using high concentration levels of those amino acids. To overcome such deficiency and to enhance more their protection performance at lower concentrations, the corrosion scientists were carried out by applying the synergistic corrosion inhibiting effect. The synergism can be described as follow: the effect of combined substances is better as compared to the summation of separate actions of these substances [30,31]. In the field of corrosion inhibiting, the synergism effect can be reached by two different ways, the first one is by the interaction

between components of the inhibitor formulation, whereas the second way is by the interaction of one component and the species present in the aqueous solution.

The synergistic corrosion inhibiting effect with simple amino acids was attained via the addition of different compounds. The effect of cations and anions species on the effectiveness of simple amino acids have been widely examined, as well as, the action of mixing two inhibitors (i.e. amino acid + organic compound). Among tested cations, zinc (Zn^{2+}) and cerium (Ce^{4+}) cations have received significant consideration [32,33], whereas, in the case of anions, they were the halide species [34-37].

For instance, Zhang *et al.* [32] stated that the copper corrosion in acidic media was reduced significantly using *Methionine* (12 mM) + Zn^{2+} (0.5 mM) formulation. The authors explain that by the formation of *Methionine* – Zn^{2+} complex, which forms upon the copper surface a protective layer. In another study [33], utilizing PDP and EIS techniques and weight loss measurements, the formulation consisting of *L-phenylalanine* at 5 mM and Ce^{4+} at 2 mM was found as an effective inhibitor against copper corrosion in hydrochloride medium. In the first stage, *L-phenylalanine* had shown a limited inhibitive action, but by adding Ce^{4+} species in the second stage, it was enhanced. This effect was attributed to the formation of adsorbed *L-phenylalanine* – Ce^{4+} complex on the copper surface.

Concerning the synergistic effect caused by halide species, especially iodide anion, it has been reported that in the presence of this anion the prevention effectiveness of amino acids was improved. Nazeer *et al.* [36] have been reported an interesting synergistic corrosion inhibiting effect of iodide ions with *Glycine* for copper-nickel alloy immersed in sulfide polluted saline solution, which at 500 ppm of *Glycine* and 100 ppm of iodide anion, the obtained prevention efficiency reached 87.4 %. In acidic medium, the addition of KI was also shown a benefic effect on the protection performance of *Glutamine* for copper [34].

On another side, many investigations have been performed to examine the influence of amino acids/organic compounds mixtures on the corrosion inhibition process. Those organic mixtures were consisting of a melange of amino acid compounds themselves or amino acid with other organic compounds. For example, it has been reported [38] that *Glycine/Glutamic acid/Cysteine* amino acid mixture can be used as a potent corrosion inhibitor for copper in HCl medium. In similar aggressive media, it has been found [39] that *Methionine/Cetrimonium* bromide combination exhibits a good performance to reduce copper dissolution. These studies were performed employing PDP, EIS and cyclic voltammetry techniques.

Consequently, the synergism effect can be considered as a useful process to enhance the inhibition potency of simple amino acids, to decrease used concentrations and to expand the application of these biomolecules for copper materials in different aggressive environments.

The researches on using amino acid compounds as eco-friendly inhibitors against copper materials dissolution were not limited to employing known physiological amino acids or by applying the synergistic method, but it was extended to use amino acid derivatives. For this purpose, the new challenge for corrosion scientists was the synthesizing of new effective eco-friendly amino acid derivatives. According to corrosion literature, some derivatives were synthesized and examined as potential effective inhibitors to decline the copper materials corrosion in various environments. For instance, Khaled [40] have examined the inhibitive effect of *Methionine* and two corresponding derivatives, namely methionine sulfone and methionine sulfoxide (Fig. 3), on the dissolution rate of copper in 1 M HNO₃ solution. According to experimental findings, the inhibition performance increases as follow: *Methionine* sulfone (90.7 %) > *Methionine* sulfoxide > *Methionine* (81.6 %) at 5 mM. The observed comportment had been related to their structural parameters applying DFT and molecular dynamics calculations.

Figure 3. Molecular structures of *L*-methionine sulfoxide (left) and *L*-methionine sulfone (right).

On the subject of the application of amino acid-based derivatives as inhibitors toward copper materials corrosion, the number of carried studies are limited as compared to theirs in the case of iron and its alloys, which are received more attention by corrosion scientists. Such trend can be related to tremendous industrial applications of iron *Vis* copper materials [10].

3. Biopolymers as sustainable inhibitors against the corrosion of copper materials

Biopolymers products are commonly used as metal protective coatings. Due to their zero pollution impact, biodegradability and chemical stability, those compounds meet the requirements to be applied as efficient ecological inhibitors of corrosion for copper materials.

Those bio-macromolecules are extracted from natural sources (flora or fauna), which considered as renewable and low-cost alternatives of widely used corrosion inhibitors in industrial applications. Numerous carbohydrate macromolecules are reported in corrosion literature as potent inhibitors against metals dissolution in different media, such as chitosan, alginate, hydroxyethyl/carboxymethyl cellulose, starch, exudate gums, pectin, pectates, carrageenan, and dextrin/cyclodextrins biopolymers. Fig. 4 illustrates the molecular structures of some investigated biopolymers as corrosion inhibitors. Concerning their protective action, in most cases, it was attributed to the biopolymer chemical composition (i.e. type and number of presented heteroatoms) and their molecular weights, further to their electronic and molecular structures [41].

Figure 4. Molecular structure of some studied bio-macromolecules monomers

Among the above-listed biopolymers, chitosan and alginate biopolymers have been investigated for copper materials immersed in several aggressive environments [42-45], which showed a higher performance to reduce the corrosion rate of these materials. Chitosan is extracted mainly from two marine crustaceans, namely shrimp and crabs. This biopolymer is used in many applications, such as agriculture (e.g. fertilizer), food, packaging (i.e. bioplastic), water treatments and medical domains. It is well known that chitosan has a good complexing ability related to -NH_2 groups. Whereas, alginate is

extensively extracted from brown seaweed, like *Fucus* or *Laminaria*, which commonly used in textures, drink and food products [46].

For instance, in molar hydrochloric acid solution, chitosan was exhibited 86% as inhibition efficacy for copper at 0.1 mg L^{-1} [42]. The protective action of investigated bio-macromolecule was confirmed through visual observation as well as via SEM (Fig. 5) and AFM images. In recent work, El Mouaden *et al.* [43] have reported similar behaviors of chitosan in a sulfide-containing synthetic seawater environment, in which the inhibition effectiveness reached 89% at 800 ppm for copper. According to these studies, even at lower concentrations and higher temperatures levels as well as for long immersion times (from 7 to 90 days), chitosan was demonstrated a remarkable protection action against copper corrosion.

Figure 5. SEM images of polished copper sample before (a) and after its 24 h immersion (b) without and (c) with chitosan in molar HCl solution. Reprinted by permission from Springer [42] [4740431036855].

In saline solution (3 wt% NaCl), Oukhrib *et al.* [44] have been confirmed the protective action of chitosan against copper degradation that is 87% at 1 gL^{-1} . It is known that in solution, macromolecules can exist with different chain lengths (i.e. fragments). Under this consideration, the authors have been carried out theoretical studies on the interaction of different chitosan fragments with the copper surface. Based on *Monte Carlo* simulations, they were found that the length of the chitosan biopolymer was affected noticeably its mode of adsorption into the copper surface, indeed its adsorption energy. This shows the importance of employing theoretical tools to define and clarify the inhibition corrosion mechanism of those bio-macromolecules.

The obtained inhibition effect was attributed to the adsorption of chitosan fragments into copper surface via highest negative charges centers located on nitrogen and oxygen atoms or by complexing metal ions on the surface via lone pair electrons of amine and hydroxyl groups, which involves the establishment of protective layer upon the metallic surface.

These works confirmed the possibility to apply chitosan biopolymer as an effective sustainable anti-corrosion compound for copper materials under various conditions.

Concerning alginate biopolymer, it was exhibited a good performance against copper corrosion in acidic medium. According to Jmiais *et al.* [45], a maximum efficiency of 83% was achieved at a lower concentration of alginate (0.1 mg L^{-1}). The researchers have been reported that obtained experimental data are in good agreement with computational ones.

As it has been reported for amino acid-based compounds, studies were extended to synthesize new derivatives. Such trend attributes to the interest of corrosion scientists to improve more the anti-corrosion performance of exist biomolecules or to make them more soluble in aqueous media. For this purpose, several biopolymer derivatives were synthesized and tested as inhibitors of corrosion for numerous metals, especially iron-based metallic materials. However, the studies on copper materials are limited and need to be developed in future works. In the available literature, there is an alone study on copper conducted by Kumar *et al.* [47] in aqueous chloride solution. In this work, the authors have modified chemically an existing biopolymer (i.e. chitin) to produce a new derivative, namely phosphorylated chitin (PCT, Fig. 6). Maximum effectiveness of 92 % was attained by the addition of 200 ppm of modified biopolymer. The reduction of copper dissolution rate was attributed to the formation of a protective film involving Cu^{2+} – PCT complex.

Figure 6. Molecular structure of PCT monomer (where $R=H$ or COCH_3 and $n(-\text{COCH}_3) > n(-H)$).

The possibility to rise the inhibition efficiency of biopolymers via synergistic effect has not yet been explored for copper materials, which consists a new research axis that needs to be developed in future works. The same attention must be devoted to the ability of other biopolymers to act as sustainable inhibitors for copper-based metallic materials, e.g. hydroxyethyl/carboxymethyl cellulose, starch, exudate gums, pectin, pectate, carrageenan, and dextrin/cyclodextrins carbohydrate polymers. On the other hand, the application of biopolymers, or in general organic compounds with high molecular weight,

can be limited by their low solubility in the aqueous aggressive solutions [48]. For instance, poor solubility can overcome by chemical modification on the molecular structure of those compounds [49].

4. Natural extracts as sustainable inhibitors against the corrosion of copper materials

To face the degradation of copper materials and to replace environmentally unfriendly corrosion inhibitors compounds, the corrosion scientists reported the benefic action of natural origin compounds, which can be promising green anti-corrosion compounds. The trend to employ natural outcome substances as protective agents explained by their biodegradability, renewability and ecologically acceptability as well as economically advantageous [50].

Some research groups [51,52] have reported the good prevention property of some plant oils, like *Argan* oils. However, such trend is limited by the lower solubility of tested oils in used media, which involves the addition of supplementary organic solvents. Another deficiency that faces against the use of oils as sustainable inhibitors is not economically profitable. These weaknesses encourage more the evaluation of various plant extracts as sustainable corrosion inhibitors. The great interest in these natural extracts in recent years, also, due to the ability of most metabolites existing in the plant (i.e. flavonoids, catechins, organic acids, phenolic compounds, quinone, alkaloids, terpenoids) to be soluble in aqueous media [53]. Consequently, the obtained extract will contain numerous organic compounds with heteroatoms, aromatic heterocyclic and aliphatic rings, which can serve as actives adsorption sites. It is important to mention that the composition of these natural mixtures depends on several parameters like season, harvesting location and weather conditions.

Concerning, the prevention effect of an extract, it can be attained by the action of a specific extract component (i.e. molecule) or by a synergistic effect of many components. This (these) molecule(s) adsorbs upon the metal surface or complex metallic cations to form protecting organic layer, which separates metal surface from corrosive agents existing in aggressive environment [54].

On the other hand, the extraction effectiveness of a plant extract depends on many factors, mainly to used solvent for the extraction process and the fixed extraction temperature [55,56]. The solvent allows extracting the compounds present in plant materials by its diffusion into their tissues and then solubilized them. The available literature [57,58] reveals that water is widely used to perform the extraction process as compared to ethanol and methanol. This is due to its non-toxic nature, simplicity to use,

inflammable and readily availability. Relating to temperature, generally, the extract preparation is performed in 60-80 °C temperature range; because at lower levels, it limits the solubility of extract compounds, whereas, at higher levels, it can cause decomposition of these constituents.

The extracts of different parts of the same plant (e.g. seeds, leaves, root, and stem) were tested and reported to act as the green corrosion inhibitors in various electrolytic media. Generally, the leave extract was exhibited remarkable anti-corrosion activity as compared to other plant parts extracts. The noted difference in prevention activities is related to existing of different chemical components in extracts of each plant parts, in which, leaves are richer ones (due to photosynthesis process in leaves) [59].

According to corrosion literature, the researches concerning this topic has exponentially amplified over the past decade. In the rest of this section, we will cite the major findings of some collected works corresponding to the use of natural extracts as sustainable inhibitors for copper materials.

It has been reported that *vitex negundo* leaves extract can be served as an effective green anti-corrosion compound in 3 M nitric acid solution [60]. The electrochemical measurements confirm an inhibition percentage of over 90% using 0.1 gL⁻¹ of extract at 35 °C for four hours of immersion. In another investigation carried out on extract of leaves, Rahal *et al.* [61] underlined the benefic effect of *olive* leaves extract on the copper degradation in slain medium, in which the inhibition efficiency reached 86% at 2.42 mM of extract.

Serving the synergistic corrosion inhibiting effect, Fouda *et al.* [62] claimed a good inhibition effect of “aqueous extract of *lupine* seed + barium chloride” formulation in acidic medium for copper, which the inhibition effectiveness attained 90% (at 250 ppm + 10⁻³ M). The synergistic effect can be carried out also by combing two extracts as reported by Loto *et al.* [63]. In this work, the mixture of *Carica Papaya* and *Camellia Sinensis* leaves extracts was exhibited appreciable performance to control brass⁴ corrosion in molar HNO₃ solution.

The application of green extract was not focused on acidic and near-neutral media, but it was extended to alkaline solutions [64,65]. In this context, we cite the work carried out by Wedian *et al.* [65] on *Capparis spinose* extract in molar hydroxide aqueous solution. Under these conditions, a maximum of protection activity of 74% was obtained at 400 ppm of extract.

⁴ 65Cu³⁵Zn alloy.

In addition to all listed strongest features on using plant extract for copper protection, some extracts showed an excellent ability to be applied in different aggressive environments [64-68]. For example, the aqueous extract of *Jujube* (*Ziziphus lotus*) was exhibited an interesting reduction effect of copper dissolution in different media, namely acidic solution (93% at 1 gL⁻¹) [67] and natural seawater (83% at 1 gL⁻¹, see Fig. 7) [66]. Table 2 collects the inhibition effectiveness, IE(%), of some other plant extracts employed as sustainable anti-corrosion compounds for copper in different media.

Figure 7. SEM images of the copper surface after it immersion in natural seawater (A) without and (B) with aqueous extract of *Jujube* in natural seawater of Agadir, Morocco [66].

Table 2. IE(%) of some natural extracts employed as corrosion inhibitors for copper materials

Plant extract	Metal	Aggressive medium	Extract concentration	IE(%)	Ref
<i>Hyoscyamus Muticus</i>	Cu	1 M HNO ₃	0.5 g L ⁻¹	89	[97]
<i>Funugreek</i>	Cu	2 M H ₂ SO ₄	100 mL L ⁻¹	84	[98]
<i>Euphorbia helioscopia</i> linn	Cu	1 M HNO ₃	0.5 g L ⁻¹	91	[99]
<i>Capparis decidua</i>	Cu	0.5 M HCl	≈ 1 g L ⁻¹	51	[76]
<i>Egyptian licorice</i>	Cu	0.1 M HCl	8% (v/v)	90	[100]
<i>Veronica rosea</i>	Cu	1 M HNO ₃	0.3 g L ⁻¹	87	[74]
<i>Myrrh</i>	Cu-33Zn alloy	3.5% NaCl + 16 ppm S ⁻²	0.3 g L ⁻¹	67	[101]
<i>Emblica officinalis</i>	Cu and Cu-27Zn alloy	Natural seawater	1 g L ⁻¹	80	[102]

In recent years, the theoretical approach has been widely employed to discuss and understand the action mechanism of corrosion inhibitors under the atomic scale, as well

as to support obtained experimental results [19,69-71]. In the case of natural extract inhibitors, such depth approach was infrequently used for copper [72]. Taking it in the account and in the absence of further data support, probable interpretations (hypothesis) of observed protection behaviors were suggested. For instance, without a strong background and uncomplete vision on the studied inhibition system, some authors attributed the corrosion prevention of plant extract to complexes formation, whereas other ones to the adsorption mechanism [73]. In term of constituents, almost tested plant extracts remain “unidentified mixtures” that explains the origin of miss-understanding of the inhibition process. Despite that, recently, some efforts to characterize the main constituents of plant extracts, tested as corrosion inhibitors, were highlighted in the literature [62,74-77]. The main composition of some investigated green extracts for copper materials is shown in Table 3.

Table 3. Main constituents present in some plant extracts used as sustainable corrosion inhibitors for copper materials

Plant extract	Major constituents	Ref
<i>Euphorbia heterophylla</i>	Sterols; flavonoids; triterpenoids; saponins; alkaloids and tannins	[62]
<i>Propolis</i>	Luteolin; Prenylated coumarin; 7-O-prenylpinocembrin; cearoin; P-methoxycinnamic acid; 6-methoxy deriphyllin; linalool; 3-phenyl resveratrol and 3-prenyl-4-hydroxy-suberosin cinnamic acid	[75]
<i>Capparis decidua seeds</i>	Gluco-capparin; L-Stachydrine; β -sitosterol; L-3-Hydroxy stachydrine	[76]
<i>Garlic</i>	1-Oxa-4,6-diazacyclooctane-5-thione; 1,3-Dithiane; Propionic acid; Di-2-propenyl disulfide; 2-Methyltetrahydrothiophene; Diallyl trisulfide and 2-Prop-2-enylsulfanylacetonitrile	[77]

5. Ionic liquids as sustainable inhibitors against the corrosion of copper materials

By definition, ionic liquids are principally composed of ion species with a lower melting point ($< 100\text{ }^{\circ}\text{C}$). Following the required purpose, characteristics of these liquids can be changed by selecting the appropriate anion and cation species. Ionic liquids can be categorized into different groups. According to Hajipour and Refiee [78], there are 11 classes of ionic liquids, e.g. basic, acid, protic, supported and poly-ionic liquids. Another classification has been reported by Suresh and Sandhu [79], in which ionic liquids are subdivided into two major classes, namely anionic and cationic ionic liquids. Table 4 collects the molecular structure of some ionic liquids compounds belong to basic and acidic classes (according to Hajipour's and Refiee's classification).

Table 4. Molecular structure of some ionic liquids compounds.

Basic class	<p>(Common anions: Cl^-, CH_3OO^- ...)</p>
Acidic class	<p>(Common anions: H_2PO_4^-, HSO_4^- ...)</p>

Ionic liquids are characterized by several attractive properties such as their non-inflammability, negligible volatility, high thermal and chemical stability, as well as their high ability to dissolve almost organic and inorganic compounds and longtime stability. Furthermore, ionic liquids can be dissolved at a high level in aqueous solutions [80]. Taking into account the “green chemistry” aspect, ionic liquids are classified as green compounds due to their zero or little negative impact on health and environment [81].

All listed characteristics of this class of compounds make them potential candidates to substitute conventional organic solvents. This involves its utilization in many applications including solvent extraction, solvent for polymerization, synthesis of nanomaterials, separation of petrochemical relevance, chemical analysis, catalyst of chemical and biochemical transformations [81-83].

In recent years, the evaluation of ionic liquids as sustainable corrosion inhibitors to replace conventional inhibitors was the subject of many works and being an active topic around the “green corrosion inhibitors”.

Agreeing to the literature [84], ionic liquids were largely reported as efficient corrosion inhibitors for iron-based metallic materials as well as non-ferrous ones immersed in different aggressive media. The use of these liquids on ferrous metals or its alloys were received more attention from corrosion scientists as compared to non-ferrous ones, like copper and its alloys. Among existing ionic liquids, imidazole derivatives have been extensively employed [85,86].

Similar to tradition inhibitors, the anti-corrosion effect of ionic liquids is attributed to the formation of protecting film upon the surface of metal via their direct or indirect (via pre-

adsorbed species on the metal surface, like anions) adsorption. This process involves the isolation of metal from the corrosives species present in media.

In order to describe and understand their adsorption behaviors on the metallic substrate, generally, DFT/B3LYP⁵ computations and molecular mechanic simulations have been used. In most cases, a good agreement was outlined between observed inhibition effectiveness and the majority of obtained computational data (e.g. molecular dipole moment, HOMO⁶, LUMO⁷, ΔE and E_{ads} energies) [87-89].

At ambient temperature, Feng *et al.* [87] have been reported the excellent anti-corrosion action of thiazolyl blue (Fig. 8 (a)) ionic liquid for the copper in chloride solution. An efficiency of 92% was attained at 5 mM of tested organic inhibitor. Based on spectral (i.e. XPS and FT-IR) and contact angle techniques, this effect was explained by the formation of protective hydrophobic film (Fig. 9) on the metal surface by the adsorption of formed thiazolyl blue – metal complex (via nitrogen and sulfur atoms). The effective protection of tested ionic liquids against copper degradation is clear in Fig. 9.

Figure 8. Molecular structure of some tested ionic liquids for copper

⁵ Density Functional Theory at Lee–Yang–Parr correlation functional.

⁶ Highest Occupied Molecular Orbital.

⁷ Lowest Unoccupied Molecular Orbital.

Figure 9. SEM images and contact angle of the copper surface immersed in simulated seawater (a) without and (b) with thiazolyl blue ionic liquids [87].

The application of ionic liquids as corrosion inhibitor for copper was not limited to existing ones, but it was prolonged to develop new synthesized derivatives. For instance, in a bi-molar phosphoric acid solution containing chloride anions, Bousskri *et al.* [88, 89] revealed the good ability of three new synthesized Pyridazinium derivatives to act as eco-friendly inhibitors for copper corrosion. The evaluated compounds are [1-(2-(4-chlorophenyl)-2-oxoethyl)- (Fig. 8 (b), **CPEPB**), [1-(2-(4-nitrophenyl)-2-oxoethyl)- (Fig. 8 (c), **NPEPB**), and 1-pentyl-pyridazinium bromid (Fig. 8 (d), **PPB**) derivatives. The maximum effectiveness of 87, 88 and 93% were achieved at 1 mM of CPEPB, NPEPB and PPB, respectively. The authors affirmed the good agreement between obtained experimental and theoretical results.

Likewise, Qiang *et al.* [90] have been synthesized four allyl imidazolium compounds with different chain lengths (Fig. 8 (e)) and used them as inhibitor compounds against the corrosion of copper in 0.5 M H₂SO₄ medium. In the aim to investigate that, the authors were combined experimental and computational approaches. The developed molecular liquids were exhibited unfavorable action toward the dissolution rate of copper, which ascribed to the formation of protective adsorbed molecular layer of tested compounds on the copper surface. It was reported that the prevention effectiveness increases by raising chain length, which reaches 98% at 1 mM for the fourth allyl imidazolium derivative (i.e. with -C₈H₁₇). Such protection level shows the ability of ionic liquids to replace traditional toxic corrosion inhibitors (e.g. chromate, some organic inhibitors) to decline copper degradation in acidic media.

Similar work as previous ones, new ionic liquid-based compound was synthesized, namely 1-butyl-3-ethylimidazolium bromide (Fig. 8 (f)), then tested for copper

dissolution prevention in 0.1 M Na₂SO₄ (at pH = 3) [91]. According to obtained experimental data, high inhibition performance (over 90%) is recorded at low concentration (i.e. 1 mM). This reduction of the corrosion process was related to the isolation of almost copper surface from corrosives agents via a protecting film. The latest film was formed by the pre-adsorption of bromide ions on the copper surface followed by the interaction of carbon atoms of the tested molecule with it.

References

- [1] V.S. Sastri, E.Ghali, M. Elboudjaini, Corrosion Prevention and Protection Practical Solutions, first ed., John Wiley & Sons Ltd, 2007.
<https://doi.org/10.1002/9780470024546>
- [2] G.H. Koch, N.G. Thompson, O. Moghissi, J.H. Payer, J. Varney, IMPACT (International Measures of Prevention, Application, and Economics of Corrosion Technologies Study), NACE International, Houston, TX, 2016.
- [3] A.A. Olajire, Corrosion inhibition of offshore oil and gas production facilities using organic compound inhibitors - A review, J. Mol. Liq. 248 (2017) 775–808.
<https://doi.org/10.1016/j.molliq.2017.10.097>
- [4] Y. Kharbach, F.Z. Qachchachi, A. Haoudi, M. Tourabi, A. Zarrouk, C. Jama, L.O. Olasunkanmi, E.E. Ebenso, F. Bentiss, Anticorrosion performance of three newly synthesized isatin derivatives on carbon steel in hydrochloric acid pickling environment: Electrochemical, surface and theoretical studies, J. Mol. Liq. 246 (2017) 302–316. <https://doi.org/10.1016/j.molliq.2017.09.057>
- [5] E. Ech-chihbi, M.E. Belghiti, R. Salim, H. Oudda, M. Taleb, N. Benchat, B. Hammouti, F. El-Hajjaji, Experimental and computational studies on the inhibition performance of the organic compound “2-phenylimidazo [1,2-a]pyrimidine-3-carbaldehyde” against the corrosion of carbon steel in 1.0 M HCl solution, Surf. and Interfaces. 9 (2017) 206–217. <https://doi.org/10.1016/j.surfin.2017.09.012>
- [6] I. B. Obot, M. M. Solomon, S. A. Umoren, R. Suleiman, M. Elanany, N. M. Alanazi, A. A. Sorour, Progress in the development of sour corrosion inhibitors: Past, present, and future perspectives, Journal of Industrial and Engineering Chemistry 79 (2019) 1–18. <https://doi.org/10.1016/j.jiec.2019.06.046>
- [7] V.S. Sastri, Green corrosion inhibitors, Theory and Practice, John Wiley & Sons, Inc., New Jersey, 2011. <https://doi.org/10.1002/9781118015438>

- [8] P.B. Raja, M.G. 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>
- [9] V.S. Sastri, *Green Corrosion Inhibitors: Theory and Practice*, first ed., John Wiley & Sons Ltd, 2011. <https://doi.org/10.1002/9781118015438>
- [10] B. El Ibrahimi, A. Jmiai, L. Bazzi, S. El Issami, Amino acids and their derivatives as corrosion inhibitors for metals and alloys, *Arab. J. Chem.* 13 (2020) 740-771.
<https://doi.org/10.1016/j.arabjc.2017.07.013>
- [11] P. Zhang, Q. Zhu, Q. Su, B. Guo, S.-k. Cheng, Corrosion behavior of T2 copper in 3.5% sodium chloride solution treated by rotating electromagnetic field, *Trans. Nonferrous Met. Soc. China.* 26 (2016) 1439-1446.
[https://doi.org/10.1016/S1003-6326\(16\)64249-8](https://doi.org/10.1016/S1003-6326(16)64249-8)
- [12] L. Núñez, E. Reguera, F. Corvo, E. González, C. Vazquez, Corrosion of copper in seawater and its aerosols in a tropical island, *Corros. Sci.* 47 (2005) 461-484.
<https://doi.org/10.1016/j.corsci.2004.05.015>
- [13] S. Suzuki, N. Shibutani, K. Mimura, M. Isshiki, Y. Waseda, Improvement in strength and electrical conductivity of Cu–Ni–Si alloys by aging and cold rolling, *J. Alloys Compd.* 417 (2006) 116-120. <https://doi.org/10.1016/j.jallcom.2005.09.037>
- [14] H.-x. Wang, Y. Zhang, J.-l. Cheng, Y.-s. Li, High temperature oxidation resistance and microstructure change of aluminized coating on copper substrate, *Trans. Nonferrous Met. Soc. China.* 25 (2015) 184-190.
[https://doi.org/10.1016/S1003-6326\(15\)63594-4](https://doi.org/10.1016/S1003-6326(15)63594-4)
- [15] A.H. Moreira, A.V. Benedetti, P.L. Calot, P.T.A. Sumodjo, Electrochemical behaviour of copper electrode in concentrated sulfuric acid solutions, *Electrochim. Acta.* 38 (1993) 981–987. [https://doi.org/10.1016/0013-4686\(93\)87018-9](https://doi.org/10.1016/0013-4686(93)87018-9)
- [16] M.M. Antonijevic, M.B. Petrovic, Copper corrosion inhibitors. A review, *Int. J. Electrochem. Sci.* 3 (2008) 1–28.
- [17] G. Gece, The use of quantum chemical methods in corrosion inhibitor studies, *Corros. Sci.* 50 (2008) 2981-2992. <https://doi.org/10.1016/j.corsci.2008.08.043>
- [18] S. Kaya, L. Guo, C. Kaya, B. Tüzün, I.B. Obot, R. Touir, N. Islam, Quantum chemical and molecular dynamic simulation studies for the prediction of inhibition efficiencies of some piperidine derivatives on the corrosion of iron, *J. Taiwan Inst. Chem. Eng.* 65 (2016) 522-529. <https://doi.org/10.1016/j.jtice.2016.05.034>

- [19] B. El Ibrahimi, A. Soumoue, A. Jmiai, H. Bourzi, R. Oukhrib, K. El Mouaden, S. El Issami, L. Bazzi, Computational study of some triazole derivatives (un- and protonated forms) and their copper complexes in corrosion inhibition process, *J. Mol. Struct.* 1125 (2016) 93-102. <https://doi.org/10.1016/j.molstruc.2016.06.057>
- [20] M. K. Awad, M. R. Mustafa, M.M.A. Elnga, Computational simulation of the molecular structure of some triazoles as inhibitors for the corrosion of metal surface, *J. Mol. Struct. THEOCHEM.* 959 (2010) 66-74. <https://doi.org/10.1016/j.theochem.2010.08.008>
- [21] A. Aouniti, K. F. Khaled, B. Hammouti, Correlation Between Inhibition Efficiency and Chemical Structure of Some Amino Acids on the Corrosion of Armco Iron in Molar HCl, *Int. J. Electrochem. Sci.* 8 (2013) 5925-5943.
- [22] N.O. Eddy, U.J. Ibok, B.I. Ita, QSAR and quantum chemical studies on the inhibition potentials of some amino acids for the corrosion of mild steel in H₂SO₄, *J. Comput. Methods Sci. Eng.* 11 (2011) 25-43. <https://doi.org/10.3233/JCM-2011-0290>
- [23] D.Q. Zhang, B. Xie, L.X. Gao, Q.R. Cai, H.G. Joo, K.Y. Lee, Intramolecular synergistic effect of Glutamic acid, Cysteine and Glycine against copper corrosion in hydrochloric acid solution, *Thin Solid Films.* 520 (2011) 356–361. <https://doi.org/10.1016/j.tsf.2011.07.009>
- [24] M. S. Kilberg, D. Häussinger, *Mammalian Amino Acid Transport*, Springer Science & Business Media, 1992. <https://doi.org/10.1007/978-1-4899-1161-2>
- [25] B. El Ibrahimi, A. Jmiai, A. Somoue, R. Oukhrib, M. Chadili, S. El Issami, L. Bazzi, Cysteine Duality Effect on the Corrosion Inhibition and Acceleration of 3003 Aluminium Alloy in a 2% NaCl Solution, *Port. Electrochimica Acta.* 36(6) (2018) 403-422. <https://doi.org/10.4152/pea.201806403>
- [26] V.F. Wendisch, Microbial production of amino acids and derived chemicals: Synthetic biology approaches to strain development, *Curr. Opin. Biotechnol.* 30 (2014) 51-58. <https://doi.org/10.1016/j.copbio.2014.05.004>
- [27] J.-H. Lee, V.F. Wendisch, Production of amino acids – Genetic and metabolic engineering approaches, *Bioresour. Technol.* 245(B) (2017) 1575-1587. <https://doi.org/10.1016/j.biortech.2017.05.065>
- [28] S. Al-Dahir, N. Vithlani, A. Smith, J.F. Davis, S. Sirohi, *Side Effects of Drugs Annual*, Elsevier, 2017.

- [29] G. Deferrari, I. Mannucci, G. Garibotto, Amino Acid Biosynthesis, in: J.W. Sons (Ed.), Encyclopedia of Life Sciences, 2010.
<https://doi.org/10.1002/9780470015902.a0000628.pub2>
- [30] S.A. Umoren, M.M. Solomon, Synergistic corrosion inhibition effect of metal cations and mixtures of organic compounds: A Review, J. Environ. Chem. Eng. 5 (2017) 246-273. <https://doi.org/10.1016/j.jece.2016.12.001>
- [31] S.A. Umoren, M.M. Solomon, Effect of halide ions on the corrosion inhibition efficiency of different organic species – A review, J. Ind. Eng. Chem. 21 (2015) 81–100. <https://doi.org/10.1016/j.jiec.2014.09.033>
- [32] D.Q. Zhang, Q.R. Cai, X.M. He, L.X. Gao, G.S. Kim, Corrosion inhibition and adsorption behavior of methionine on copper in HCl and synergistic effect of zinc ions, Mater. Chem. Phys. 114 (2009) 612–617.
<https://doi.org/10.1016/j.matchemphys.2008.10.007>
- [33] D.Q. Zhang, H. Wu, L.X. Gao, Synergistic inhibition effect of L-phenylalanine and rare earth Ce(IV) ion on the corrosion of copper in hydrochloric acid solution, Mater. Chem. Phys. 133 (2012) 981–986.
<https://doi.org/10.1016/j.matchemphys.2012.02.001>
- [34] D.Q. Zhang, Q.R. Cai, X.M. He, L.X. Gao, G.D. Zhou, Inhibition effect of some amino acids on copper corrosion in HCl solution, Mater. Chem. Phys. 112 (2008) 353–358. <https://doi.org/10.1016/j.matchemphys.2008.05.060>
- [35] A.S. Fouda, A.A. Nazeer, E.A. Ashour, Amino acids as environmentally-friendly corrosion inhibitors for Cu10Ni alloy in sulfide-polluted salt water: Experimental and theoretical study, Mater. Prot. 52 (2011) 21-34.
- [36] A. A. Nazeer, K. Y. Nageh, I. A. Gehan, A. Elsayed, Effect of Glycine on the electrochemical and stress corrosion cracking behavior of Cu10Ni alloy in sulfide polluted salt water, Ind. Eng. Chem. Res. 50 (2011) 8796-8802.
<https://doi.org/10.1021/ie200763b>
- [37] D. Zhang, X. He, Q. Cai, L. Gao, G. Kim, Arginine self-assembled monolayers against copper corrosion and synergistic effect of iodide ion, J. Appl. Electrochem. 39 (2009) 1193-1198. <https://doi.org/10.1007/s10800-009-9784-7>
- [38] D.Q. Zhang, B. Xie, L.X. Gao, Q.R. Cai, H.G. Joo, K.Y. Lee, Intramolecular synergistic effect of glutamic acid, cysteine and glycine against copper corrosion in hydrochloric acid solution, Thin Solid Films. 520 (2011).
<https://doi.org/10.1016/j.tsf.2011.07.009>

- [39] D.Q. Zhang, B. Xie, L.X. Gao, H.G. Joo, K.Y. Lee, Inhibition of copper corrosion in acidic chloride solution by Methionine combined with cetrimonium bromide/cetylpyridinium bromide, *J. Appl. Electrochem.* 41 (2011) 491–498. <https://doi.org/10.1007/s10800-011-0259-2>
- [40] K.F. Khaled, Corrosion control of copper in nitric acid solutions using some amino acids – A combined experimental and theoretical study, *Corros. Sci.* 52 (2010) 3225–3234. <https://doi.org/10.1016/j.corsci.2010.05.039>
- [41] S.A. Umoren, U.M. Eduok, Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: A review, *Carbohydr. Polym.* 140 (2016) 314–341. <https://doi.org/10.1016/j.carbpol.2015.12.038>
- [42] A. Jmiai, B.E. Ibrahimi, A. Tara, R. Oukhrib, S.E. Issami, O. Jbara, L. Bazzi, M. Hilali, Chitosan as an eco-friendly inhibitor for copper corrosion in acidic medium: protocol and characterization, *Cellulose*. 24 (2017) 3843-3867. <https://doi.org/10.1007/s10570-017-1381-z>
- [43] K.E. Mouaden, B.E. Ibrahimi, R. Oukhrib, L. Bazzi, B. Hammouti, O. Jbara, A. Tara, D.S. Chauhan, M.A. Quraishi, Chitosan polymer as a green corrosion inhibitor for copper in sulfide-containing synthetic seawater, *Int. J. Biol. Macromol.* 119 (2018) 1311–1323. <https://doi.org/10.1016/j.ijbiomac.2018.07.182>
- [44] R. Oukhrib, B.E. Ibrahimi, H. Bourzi, K.E. Mouaden, A. Jmiai, S.E. Issami, L. Bammou, L. Bazzi, Quantum chemical calculations and corrosion inhibition efficiency of biopolymer “chitosan” on copper surface in 3%NaCl, *J. Mater. Environ. Sci.* 8 (2017) 195-208.
- [45] A. Jmiai, B. El Ibrahimi, A. Tara, S. El Issami, O. Jbara, L. Bazzi, Alginate biopolymer as green corrosion inhibitor for copper in 1 M hydrochloric acid: Experimental and theoretical approaches, *J. Mol. Struct.* 1157 (2018) 408-417. <https://doi.org/10.1016/j.molstruc.2017.12.060>
- [46] Y. Qin, J. Jiang, L. Zhao, J. Zhang, F. Wang, in: A.M. Grumezescu, A.M. Holban (Eds.), *Biopolymers for Food Design*, Academic Press, 2018, pp. 409-429. <https://doi.org/10.1016/B978-0-12-811449-0.00013-X>
- [47] K.V. Kumar, B.V.A. Rao, N.Y. Hebalkar, Phosphorylated chitin as a chemically modified polymer for ecofriendly corrosion inhibition of copper in aqueous chloride environment, *Res. Chem. Intermed.* 43 (2017) 5811–5828. <https://doi.org/10.1007/s11164-017-2964-x>

- [48] K. Wan, P. Feng, B. Hou, Y. Li, Enhanced corrosion inhibition properties of carboxymethyl hydroxypropyl chitosan for mild steel in 1.0 M HCl solution, *RSC Adv.* 6 (2016) 77515–77524. <https://doi.org/10.1039/C6RA12975G>
- [49] J. Haque, V. Srivastava, D.S. Chauhan, H. Lgaz, M.A. Quraishi, Microwave-induced synthesis of chitosan schiffbases and their application as novel and green corrosion inhibitors: experimental and theoretical approach, *ACS Omega.* 3 (2018) 5654–5668. <https://doi.org/10.1021/acsomega.8b00455>
- [50] P.B. Raja, M.G. 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>
- [51] 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.
- [52] F. Mounir, S. El Issami, L. Bazzi, R. Salghi, N. Abidi, S. Jodeh, L. Bazzi, A. Eddine, Green approach to corrosion inhibition of copper by two oils of *Argania Spinosa* (L.) in phosphoric acid, *J. Mater. Environ. Sci.* 6 (2015) 2066–2075.
- [53] L. Palou, A. Ali, E. Fallik, G. Romanazzi, GRAS, plant-and animal-derived compounds as alternatives to conventional fungicides for the control of postharvest diseases of fresh horticultural produce, *Postharvest Biol. Technol.* 122 (2016) 41–52. <https://doi.org/10.1016/j.postharvbio.2016.04.017>
- [54] 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>
- [55] M. Nasrollahzadeh, S.M. Sajadi, M. Khalaj, Green synthesis of copper nanoparticles using aqueous extract of the leaves of *Euphorbia esula* L and their catalytic activity for ligand-free Ullmann-coupling reaction and reduction of 4-nitrophenol, *RSC Adv.* 4 (2014) 47313–47318. <https://doi.org/10.1039/C4RA08863H>
- [56] J. Seo, S. Lee, M.L. Elam, S.A. Johnson, J. Kang, B.H. Arjmandi, Study to find the best extraction solvent for use with guava leaves (*Psidium guajava* L.) for high antioxidant efficacy, *Food Sci. Nutr.* 2 (2014) 174–180. <https://doi.org/10.1002/fsn3.91>
- [57] O. Nkuzinna, M. Menkiti, O. Onukwuli, Inhibition of copper corrosion by acid extracts of *Gnetum africana* and *Musa acuminata* peel, *Int. J. Multidiscip. Sci. Eng.* 2 (2011) 2045–2057.

- [58] 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>
- [59] B.E. A. Rani, B.B.J. Basu, Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview, *Int. J. Corros.* 2012 (2012) 1-15.
<https://doi.org/10.1155/2012/380217>
- [60] M.P. Savita, N. Chaubey, S. Kumar, V.K. Singh, M.M. Singh, *Strychnos nuxvomica*, *Piper longum* and *Mucuna pruriens*, seed extracts as eco-friendly corrosion inhibitors for copper in nitric acid, *RSC Adv.* 6 (2016) 95644–95655.
<https://doi.org/10.1039/C6RA16481A>
- [61] C. Rahal, M. Masmoudi, R. Abdelhedi, R. Sabot, M. Jeannin, M. Bouaziz, P. Refait, Olive leaf extract as natural corrosion inhibitor for pure copper in 0.5 M NaCl solution: a study by voltammetry around OCP, *J. Electroanal. Chem.* 769 (2016) 53–61. <https://doi.org/10.1016/j.jelechem.2016.03.010>
- [62] A.E.-A.S. Fouda, S.H. Etaiw, D.M.A. El-Azziz, O.A. Elbaz, Synergistic effect of barium chloride on corrosion inhibition of copper by aqueous extract of lupine seeds in nitric acid, *Int. J. Electrochem. Sci.* 12 (2017) 5934–5950.
<https://doi.org/10.20964/2017.07.08>
- [63] C.A. Loto, R.T. Loto, A.P.I. Popoola, Inhibition effect of extracts of carica papaya and camellia sinensis leaves on the corrosion of duplex (α β) brass in 1M nitric acid, *Int. J. Electrochem. Sci.* 6 (2011) 4900-4914.
- [64] N. Raghavendra, J.I. Bhat, Application of green products for industrially important materials protection: An amusing anticorrosive behavior of tender arecanut husk (green color) extract at metal-test solution interface, *Measurement.* 135 (2019) 625–639. <https://doi.org/10.1016/j.measurement.2018.12.021>
- [65] F. Wedian, M.A. Al-Qudah, A.N. Abu-Baker, The effect of *Capparis spinosa* L. Extract as a green inhibitor on the corrosion rate of copper in a strong alkaline solution, *Port. Electrochimica Acta.* 34 (2016) 39-51.
<https://doi.org/10.4152/pea.201601039>
- [66] R. Oukhrib, S. E. Issami, B. E. Ibrahimi, K. E. Mouaden, L. Bazzi, L. Bammou, A. Chaouay, R. Salghi, S. Jodeh, B. Hammouti, A. Amin-Alami, *Ziziphus lotus* as green inhibitor of copper corrosion in natural sea water, *Port. Electrochim Acta.* 35 (2017) 187–200. <https://doi.org/10.4152/pea.201704187>

- [67] A. Jmiai, B.E. Ibrahimi, A. Tara, M. Chadili, S.E. Issami, O. Jbara, A. Khallaayoun, L. Bazzi, Application of Zizyphus Lotuse- pulp of Jujube extract as green and promising corrosion inhibitor for copper in acidic medium, *J. Mol. Liq.* 268 (2018) 102–113. <https://doi.org/10.1016/j.molliq.2018.06.091>
- [68] F. Wedian, M.A. Al-Qudah, G.M. Al-Mazaideh, Corrosion inhibition of copper by Capparis spinosa L. extract in strong acidic medium: experimental and density functional theory, *Int. J. Electrochem. Sci.* 12 (2017) 4664–4676. <https://doi.org/10.20964/2017.06.47>
- [69] B. El Ibrahimi, K. El Mouaden, A. Jmiai, A. Baddouh, S. El Issami, L. Bazzi, M. Hilali, Understanding the influence of solution's pH on the corrosion of tin in saline solution containing functional amino acids using electrochemical techniques and molecular modeling, *Surf. Interfaces* 17 (2019) 100343. <https://doi.org/10.1016/j.surfin.2019.100343>
- [70] B. El Ibrahimi, A. Jmiai, K. El Mouaden, A. Baddouh, S. El Issami, L. Bazzi, M. Hilali, Effect of solution's pH and molecular structure of three linear α -amino acids on the corrosion of tin in salt solution: A combined experimental and theoretical approach, *J. Mol. Struct.* 1196 (2019) 105-118. <https://doi.org/10.1016/j.molstruc.2019.06.072>
- [71] B. El Ibrahimi, A. Jmiai, K. El Mouaden, R. Oukhrib, A. Soumoue, S. El Issami, L. Bazzi, Theoretical evaluation of some α -amino acids for corrosion inhibition of copper in acidic medium: DFT calculations, Monte Carlo simulations and QSPR studies, *J. King Saud Univ.* 32 (2020) 163-171. <https://doi.org/10.1016/j.jksus.2018.04.004>
- [72] M.P. Savita, N. Chaubey, V.K. Singh, M.M. Singh, Eco-friendly inhibitors for copper corrosion in nitric acid: theoretical and experimental evaluation, *Metall. Mater. Trans. B* 47 (2016) 47–57. <https://doi.org/10.1007/s11663-015-0488-6>
- [73] A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, Corrosion inhibition of some metals using lawsonia extract, *Corros. Sci.* 47 (2005) 385–395. <https://doi.org/10.1016/j.corsci.2004.06.006>
- [74] R. Ouache, H. Harkat, P. Pale, K. Oulmi, Phytochemical compounds and anti-corrosion activity of Veronica rosea, *Nat. Prod. Res.* 33 (9) (2019) 1374-1378. <https://doi.org/10.1080/14786419.2018.1474464>
- [75] L. Vrsalovic, S. Gudic, D. Gracic, I. Smoljko, I. Ivanic, M. Kliskic, E.E. Oguzie, Corrosion protection of copper in sodium chloride solution using propolis, *Int. J. Electrochem. Sci.* 13 (2018) 2102–2117. <https://doi.org/10.20964/2018.02.71>

- [76] P.S. Pratihari, M.P.S. Verma, A. Sharma, Capparis decidua seeds: potential green inhibitor to combat acid corrosion of copper, *Rasayan J. Chem.* 8 (2017) 411–421.
- [77] Z. Chen, H. Cen, L. Wei, Y. Cao, X. Guo, Inhibitory action of garlic extract in the corrosion of copper under thin electrolyte layers, *Surf. Rev. Lett.* 1850128 (2017) 1-9. <https://doi.org/10.1142/S0218625X18501287>
- [78] A.R. Hajipour, F. Refiee, Recent Progress in Ionic Liquids and their Applications in Organic Synthesis, *Org. Prep. Proced. Int.* 47 (2015) 249–308. <https://doi.org/10.1080/00304948.2015.1052317>
- [79] Suresh, J.S. Sandhu, Recent advances in ionic liquids: green unconventional solvents of this century: part I, *Green Chem. Lett. Rev.* 4 (2011) 289–310. <https://doi.org/10.1080/17518253.2011.572294>
- [80] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, Physical properties of ionic liquids: database and evaluation, *J. Phys. Chem. Ref. Data* 35 (2006) 1475–1517. <https://doi.org/10.1063/1.2204959>
- [81] H. Zhao, Innovative applications of ionic liquids as “green” engineering liquids, *Chem. Eng. Commun.* 193 (2006) 1660–1677. <https://doi.org/10.1080/00986440600586537>
- [82] A. Fernicola, B. Scrosati, H. Ohno, Potentialities of ionic liquids as new electrolyte media in advanced electrochemical devices, *Ionics* 12 (2006) 95–102. <https://doi.org/10.1007/s11581-006-0023-5>
- [83] T. Tsuda, C.L. Hussey, Electrochemical applications of room-temperature ionic liquids, *Electrochem. Soc. Interface* 16 (2007) 42–49. <https://doi.org/10.1149/2.F05071IF>
- [84] C. Verma, E.E. Ebenso, M.A. Quraishi, Ionic liquids as green and sustainable corrosion inhibitors for metals and alloys: An overview, *J. Mol. Liq.* 233 (2017) 403–414. <https://doi.org/10.1016/j.molliq.2017.02.111>
- [85] N.V. Likhanova, M.A. Domínguez-Aguilar, O. Olivares-Xometl, N. Nava-Entzana, E. Arce, H. Dorantes, The effect of ionic liquids with imidazolium and pyridinium cations on the corrosion inhibition of mild steel in acidic environment, *Corros. Sci.* 52 (2010) 2088–2097. <https://doi.org/10.1016/j.corsci.2010.02.030>
- [86] X. Zheng, S. Zhang, W. Li, M. Gong, L. Yin, Experimental and theoretical studies of two imidazolium-based ionic liquids as inhibitors for mild steel in sulfuric acid solution, *Corros. Sci.* 95 (2015) 168–179. <https://doi.org/10.1016/j.corsci.2015.03.012>

- [87] L. Feng, S. Zhang, Y. Qiang, Y. Xu, L. Guo, L. H. Madkour, S. Chen, Experimental and theoretical investigation of thiazolyl blue as a corrosion inhibitor for copper in neutral sodium chloride solution, *Materials* 11 (2018) 1042. <https://doi.org/10.3390/ma11061042>
- [88] A. Bousskri, R. Salghi, A. Anejjar, M. Messali, S. Jodeh, O. Benali, M. Larouj, I. Warad, O. Hamed, B. Hammouti, The inhibition effect of 1-pentyl pyridazinium bromide towards copper corrosion in phosphoric acid containing chloride, *Port. Electrochimica Acta* 34 (2016) 1-21. <https://doi.org/10.4152/pea.pea.201601001>
- [89] A. Bousskri, R. Salghi, A. Anejjar, S. Jodeh, M.A. Quraishi, M. Larouj, H. Lgaz, M. Messali, S. Samhan, M. Zougagh, Pyridazinium-based ionic liquids as corrosion inhibitors for copper in phosphoric acid containing chloride: electrochemical, surface and quantum chemical comparatives studies, *Der. Pharma. Chemica.* 8 (2016) 67-83.
- [90] Y. Qiang, S. Zhang, L. Guoc, X. Zheng, B. Xiang, S. Chen, Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid, *Corros. Sci.* 119 (2017) 68–78. <https://doi.org/10.1016/j.corsci.2017.02.021>
- [91] G. Vastag, A. Shaban, M. Vraneš, A. Tot, S. Belić, S. Gadžurić, Influence of the N-3 alkyl chain length on improving inhibition properties of imidazolium-based ionic liquids on copper corrosion, *J. Mol. Liq.* 264 (2018) 526–533. <https://doi.org/10.1016/j.molliq.2018.05.086>
- [92] G.L.F. Mendonça, S.N. Costa, V.N. Freire, P.N.S. Casciano, A.N. Correia, P.d. Lima-Neto, Understanding the corrosion inhibition of carbon steel and copper in sulphuric acid medium by amino acids using electrochemical techniques allied to molecular modelling methods, *Corros. Sci.* 115 (2017) 41-55. <https://doi.org/10.1016/j.corsci.2016.11.012>
- [93] H.H.A. Rahman, A.H.E. Moustafa, M.K. Awad, Potentiodynamic and quantum studies of some amino acids as corrosion inhibitors for copper, *Int. J. Electrochem. Sci.* 7 (2012) 1266–1287.
- [94] G.M.A. El-Hafez, W.A. Badawy, The use of Cysteine, N-acetyl cysteine and Methionine as environmentally friendly corrosion inhibitors for Cu–10Al–5Ni alloy in neutral chloride solutions, *Electrochim. Acta* 108 (2013) 860–866. <https://doi.org/10.1016/j.electacta.2013.06.079>
- [95] S. Varvara, I. Rotaru, M. Popa, R. Bostan, M. Glevitzky, L. Muresan, Environmentally-safe corrosion inhibitors for the protection of bronzes against

- corrosion in acidic media, Chem. Bull. "POLITEHNICA" Univ. (Timisoara) 55 (2010) 156-161.
- [96] W. A. Badawy, K. M. Ismail, A. M. Fathi, Corrosion control of Cu–Ni alloys in neutral chloride solutions by amino acids, Electrochim. Acta 51 (2006) 4182–4189. <https://doi.org/10.1016/j.electacta.2005.11.037>
- [97] A.S. Fouda, Y.M. Abdallah, G.Y. Elawady, R.M. Ahmed, Electrochemical study on the efectively of Hyoscyamus muticusextract as a green inhibitor for corrosion of copper in 1 M HNO₃, J. Mater. Environ. Sci. 5 (2015) 1519–1531.
- [98] S.M. Ali, H.A.A. lehaibi, The inhibitive performance of fenugreek for corrosion of copper and nickel in sulfuric acid, Int. J. Electrochem. Sci. 11 (2016) 953–966.
- [99] Y.M. Abdallah, K. Shalabi, Comprehensive study of the behavior of copper inhibition in 1 M HNO₃ by Euphorbia helioscopialinn. extract as green inhibitor, Prot. Met. Phys. Chem. 51 (2015) 275–284. <https://doi.org/10.1134/S2070205115020021>
- [100] M.A. Deyab, Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution, J. Ind. Eng. Chem. 22 (2015) 384–389. <https://doi.org/10.1016/j.jiec.2014.07.036>
- [101] H.S. Gadow, M.M. Motawea, H.M. Elabbasy, Investigation of myrrh extract as a new corrosion inhibitor for a-brass in 3.5% NaCl solution polluted by 16 ppm sulfde, RSC Adv. 7 (2017) 29883–29898. <https://doi.org/10.1039/C7RA04271J>
- [102] P.D. Rani, S. Selvaraj, Emblica officinalis (AMLA) leaves extract as corrosion inhibitor for copper and its alloy (Cu-27Zn) in natural sea water, Arch. Appl. Sci. Res. 2 (2010) 140–150.