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Chapter 19

Environmentally Friendly Corrosion Inhibitors

Rafael Martinez Palou, Octavio Olivares-Xomelt and Natalya V. Likhanova

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/57252

1. Introduction

In most industries whose facilities are constituted by metallic structures, the phenomenon of corrosion is invariably present. This problem originates very important material and economic losses due to partial or total replacement of equipment and structures, and plant-repairing shutdowns.

Material losses and corrosion consequences are priced so high that in some countries like the U.S. and England these factors have been estimated from 3 to 4% of the GDP.

Corrosion not only has economic implications, but also social and these engage the safety and health of people either working in industries or living in nearby towns. The oil industry in Mexico is one of the most affected by corrosion because this phenomenon exerts its effects from the very moment of oil extraction on, causing a constant struggle against it.

The use of corrosion inhibitors (CIs) constitutes one of the most economical ways to mitigate the corrosion rate, protect metal surfaces against corrosion and preserve industrial facilities [1, 2]. Inorganic CIs are those in which the active substance is an inorganic compound. This is one of the simplest ways to improve the passivity of a metal by adding electropositive metal salts to the medium. These metal ions must have a more positive redox potential more positive than the metal constituting the surface to be protected and also a more positive potential than that required for discharging a proton so that the electropositive metal to be reduced is deposited on the surface.

The deposited metal promotes the cathodic depolarization by overvoltage reduction and formation of an adherent deposit. Among the metals used for this purpose are: mercury (Hg), palladium (Pd), iridium (Ir), platinum (Pt), rhodium (Rh) and rhenium (Re).
Moreover, there are inorganic anions providing passivation protection to metal surfaces through their incorporation into the oxide layer; the most widely used of these are: chromate (CrO$_4^{2-}$), nitrate (NO$_2^-$), molybdate (MoO$_4^{2-}$), phosphate (H$_3$PO$_4$) and silicates [3].

Organic inhibitors have been the most widely used in petroleum refining processes because of their ability to form a protective layer on the metal surface in media with high hydrocarbons content. At present there are a number of organic inhibitors belonging to different chemical families i.e. fatty amides [4, 5], pyridines [6-8], imidazolines [9-12] and other 1,3-azoles [13-15] and polymers [16] have showed excellent performance as CIs (Table 1) [17].

<table>
<thead>
<tr>
<th>Chemical family</th>
<th>Structure</th>
<th>Main application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylamines (n = 2-12)</td>
<td>CH$_3$-(CH$_2$)$_n$-NH$_2$</td>
<td>CIs for acid media</td>
</tr>
<tr>
<td>Diamines (n = 2-8)</td>
<td>H$_2$N-(CH$_2$)$_n$-NH$_2$</td>
<td></td>
</tr>
<tr>
<td>Primary amines and diamines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycloalkyllic</td>
<td>Cyclcloalkyl</td>
<td>CIs for acid media</td>
</tr>
<tr>
<td>Aromatic (X = H, NO$_2^-$, CH$_3$, Cl, COOH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary amines</td>
<td>HN-CH$_2$-CH=CH$_2$</td>
<td>CIs for carbon steel in acid media</td>
</tr>
<tr>
<td>Etoxilated amines</td>
<td>CH$_3$-(CH$_2$)$_n$-NH-(OCH$_2$CH$_2$)$_n$</td>
<td></td>
</tr>
<tr>
<td>Alkyloximes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oximes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>CH$_3$-CH=NO-H</td>
<td>CIs for carbon steel in acid media</td>
</tr>
<tr>
<td>Chemical family</td>
<td>Structure</td>
<td>Main application</td>
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<tr>
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</tr>
<tr>
<td>Alkynitriles</td>
<td>$C_{17}H_{35}-CN$</td>
<td>Cls for carbon steel in acid media</td>
</tr>
<tr>
<td>Nitriles</td>
<td>$\text{MeO-}CN$</td>
<td>Cls for carbon steel in acid media</td>
</tr>
<tr>
<td>Aromatics</td>
<td>$\text{CNMeO}$</td>
<td>Cls for copper alloys and carbon steel in acid media</td>
</tr>
<tr>
<td>Ureas y thioureas</td>
<td>$\text{R-HN} - \text{NH-R}$</td>
<td>Cls for copper alloys and carbon steel in acid media</td>
</tr>
<tr>
<td>$X = \text{O, S, R = alkyl, aryl}$</td>
<td></td>
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</tr>
<tr>
<td>Amides</td>
<td>$\text{HX} - \text{NH} - \text{O}$</td>
<td>Cls for carbon steel in acid media</td>
</tr>
<tr>
<td>Amides y thioamides</td>
<td>$\text{R} - \text{SNH-R'}$</td>
<td>Cls for carbon steel in acid media</td>
</tr>
<tr>
<td>$\text{R, R'} = \text{alkyl}$</td>
<td></td>
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<tr>
<td>Imidazoles</td>
<td>$\text{N} - \text{N} - \text{R}$</td>
<td>Cls for copper alloys and carbon steel in basic media</td>
</tr>
<tr>
<td>$\text{R} = \text{alkyl, aryl}$</td>
<td></td>
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</tr>
<tr>
<td>Benzoazoles</td>
<td>$\text{N} - \text{X}$</td>
<td>Cls for copper alloys and carbon steel in basic media</td>
</tr>
<tr>
<td>$\text{X} = \text{N-R, S, O}$</td>
<td></td>
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</tr>
<tr>
<td>Imidazolines</td>
<td>$\text{N} - \text{NHR'}$</td>
<td>Cls for carbon steel in acid media</td>
</tr>
<tr>
<td>$\text{R} = \text{alkyl, aryl}; X = \text{NH}_2, \text{NHR, OH}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 1. Organic corrosion inhibitors widely used in petroleum refining processes

The aim of adding inhibitors in low concentrations to corrosive media is to delay the reaction between the metal and the corrosive species in the medium. CIs act by adsorbing either ions or molecules onto the metal surface, generally reducing the corrosion rate by blocking the anodic and/or cathodic reactions.

In spite of much inorganic, organic and polymeric compounds having showed good performances as CIs for different metals and alloys, many of these compounds are toxic and do not fulfill completely the requirements imposed by the environmental protection standards. The new generation of environmental regulations requires the replacement of toxic chemicals with the so-called “Green chemicals”. The final choice of the inhibitor for a particular application is restricted by several factors, including increased environmental awareness and the need

<table>
<thead>
<tr>
<th>Chemical family</th>
<th>Structure</th>
<th>Main application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridines</td>
<td><img src="N_X=CH_3,Br,OR" alt="Pyridines结构" /></td>
<td>CIs for carbon steel in acid media</td>
</tr>
<tr>
<td>Triazoles</td>
<td><img src="N_N=R" alt="Triazoles结构" /></td>
<td>CIs for copper alloys in basic media</td>
</tr>
<tr>
<td>Benzotriazoles</td>
<td><img src="N_N=R" alt="Benzotriazoles结构" /></td>
<td>CIs for copper alloys in basic media</td>
</tr>
<tr>
<td>Tetrazoles</td>
<td><img src="N_N=R" alt="Tetrazoles结构" /></td>
<td>CIs for copper alloys in basic media</td>
</tr>
<tr>
<td>Polyvinyls</td>
<td><img src="R-(CH=CH)_n" alt="Polyvinyls结构" /></td>
<td>CIs for carbon steel in acid media</td>
</tr>
<tr>
<td>Polysters</td>
<td><img src="R-(OCH_2CH_2)_n" alt="Polysters结构" /></td>
<td>CIs for carbon steel in acid media</td>
</tr>
</tbody>
</table>
to promote environmentally friendly processes, coupled with the specificity of action of most acid inhibitors, which often requires the combined action of compounds to achieve effective corrosion inhibition. This is the reason why in the last years big efforts have been made by researchers in this area to develop new environmentally friendly CIs (EFCIs).

In this chapter, generalities about the corrosion phenomena and CIs are presented and a review of research papers describing the development of novel EFCIs, both natural and synthetic, for several corrosive environments and different metals and alloys are discussed in detail, especially for the applications in the Oil Industry.

2. Generalities about corrosion [2]

The term corrosion can be defined as the interaction (electrochemical reaction) of a metal with the surrounding environment, causing a slow, steady, and irreversible deterioration in the metal, in both physical and chemical properties.

The corrosion causes very important material and economical losses due to partial or total replacement of equipment and structures, and plant-repairing shutdowns.

Corrosion not only has economic implications, but also social and these engage the safety and health of people either working in industries or living in nearby towns. The petroleum industry is one of the most affected by corrosion due to the presence of many corrosive substances in the crude oil, which affect equipments and pipelines from the extraction of crude oil to the transportation of final products.

The factors that can cause corrosion can be identified as:

- Physical
- Chemical
- Electrochemical
- Microbiological

Physical corrosion is caused by impact, stress or exhaustion of the material. Chemical corrosion is caused by oxygen, sulfur, fluorine, chlorine or other gases, which act directly on the metal under environmental conditions that facilitate this phenomenon. Electrochemical corrosion is a spontaneous process that denotes the existence of anodic and cathodic zones, and an electrolyte; electrical contact between the anodic and cathodic zones is also required (Figure 1).

Microbiological corrosion is the deterioration of a metal that occurs directly or indirectly as a result of the activity of microorganisms such as bacteria and algae. These microorganisms are deposited on the metal, creating a “live” area, using nitrogen, oxygen, hydrogen, and/or carbon from the environment for their metabolic activities, producing metabolites, which can be deposited on the metal promoting corrosion. Biological activity may cause corrosion in a variety of media such as natural water, sea water, petroleum products and oil emulsions.
According to the environment to which materials are exposed, there are various forms of corrosion: uniform or general, bite, erosion, stress, cavitation, galvanic and hydrogen embrittlement-blottering. Knowing how corrosion works helps to understand the phenomenon and provide possible solutions to counter the corrosive process.

a. Uniform or general corrosion is the most common, which is characterized by the fact that corrosion occurs uniformly over the metal surface and has a high corrosion rate; the loss of the metal surface occurs through an anodic site, and the appearance of the corroded surface is relatively uniform, but manifests roughness (Figure 2) [18].

![Figure 1. Representation of electrochemical corrosion.](image1)

b. Pitting corrosion: Is a localized attack, where some parts of the metal surface are free of corrosion, but small localized areas are corrode quickly; this occurs when any solid

![Figure 2. Uniform Corrosion](image2)
corrosion product or neutralization salts are located on the metal surface, causing deep holes, which is known as pitting (Figure 3); these areas are the most susceptible to the corrosion process [19].

c. Corrosion by erosion: This type of corrosion provokes uniform thinning of the metal surface, which is associated with the exposure to a high velocity fluid, which causes the corrosion product to be stripped from the metal surface, resulting in the exposure of the bare metal, which can be corroded again, causing an accelerated attack, (Figure 4). This type of corrosion is further exacerbated when fluids contain solid particles that are harder than the metal surface, which hit constantly the metal [20].
d. Stress corrosion cracking: This type of corrosion promotes the formation of a fracture in the metal structure due to mechanical stress and a chemically aggressive medium (Figure 5) [21].

![Stress corrosion cracking](image)

**Figure 5. Stress corrosion cracking**

e. Galvanic or bimetallic corrosion occurs when there is a potential difference between dissimilar metals immersed in a corrosive solution; the potential difference produces a flow of electrons between the metals, where the less resistant metal is the anode (metal active), and the most resistant is the cathode (noble metal). This attack can be extremely destructive, dramatically accelerating the corrosion rate of the most reactive metal, but the severity degree of galvanic corrosion depends not only on the potential difference between the two metals, but also on the involved surface area ratios, (Figure 6) [22].

![Galvanic corrosion](image)

**Figure 6. Galvanic corrosion**

f. Corrosion by cavitation is a form of erosion caused by the formation and rupture of vapor bubbles in the fluid near the metal surface, causing a sequence of pits in the form of small, but deep cracks (Figure 7) [23].
Corrosion via hydrogen embrittlement and blistering is associated with the hydrogen atoms that are produced on the metal surface in an aqueous medium; a reduction reaction when atomic hydrogen penetrates the metal takes place; the presence of defects allow the interaction between the hydrogen atoms and the metal, forming molecular hydrogen, which being trapped by the metal, provides enough pressure to form blisters, resulting in microcracks, (Figure 8). This type of failure occurs mainly in basic media, where there are compounds such as sulfides and/or cyanides; this corrosion process is also present in plants with catalytic refining processes.

In this kind of corrosion process, some hydrogen atoms diffuse through steel and become retained, where they recombine with each other, forming a very strong internal pressure that exceeds the strength of steel, forming blisters.

In most oil refining plants, the reactive metal is iron, which is the major component of the steel present in pipelines and equipment; the electrolyte is water and the corrosive or oxidizing agent is formed by acids, salts, bases, oxygen, etc. One of the most common methods used to
reduce corrosion in petroleum refining processes is the application of corrosion inhibitors, which are specific for each process phase, medium and corrosion type [24].

3. Corrosion control [25]

In order to control some of the corrosion problems, several preventive measures are taken:

a. Cathodic protection. This is an effective method to control corrosion on structures either buried or immersed in an electrolyte; according to the operation mode, anodes are classified as impressed current and sacrificial.

b. Protection with anticorrosive coating. This is mainly used to form a physical barrier between the corrosive environments to protect the structure. It is used mainly with metallic elements exposed to the atmosphere.

c. Corrosion Inhibitors. These are substances that added in small concentrations (parts per million, ppm) to a corrosive environment decrease the corrosion rate effectively. This method has its main application in the interiors of pipelines, vessels and equipments.

A corrosion inhibition program should be monitored continuously to ensure that it is achieving the desired protection.

The corrosion measurement is the quantitative method by which we know the effectiveness of the control that is being carried out, and provides feedback that makes possible to optimize the control and corrosion prevention methods.

Particularly in the Petroleum Industry, the monitoring can be done by using the following methods:

- Monitoring feedstocks by chemical analysis to find some of their features and corrosive contents.
- Monitoring corrosives by analysis of bitter waters of batteries (pH, chlorides, sulfides, ammonium thiocyanate and cyanide).
- Corrosion Monitoring: Be made in the following ways:
  a. Using gravimetric coupons located at places where corrosion is to be measured (Figure 9).
  b. With corrosimetric specimens. These probes are installed at the places to be monitored. A corrosometer connected to a probe detects a current amount and depending on it, it is known if there is corrosion and the communication speed.
  c. Analyzing the iron and copper contents in the bitter waters of accumulators.
  d. By placing hydrogen probes at the absorber tower.
4. Corrosion Inhibitors (CIs)

CIs are either organic or inorganic chemicals, or more commonly, formulations thereof that are added in small amounts (parts per million, ppm) to a corrosive environment in order to delay or decrease the corrosion process of the surface to be protected.

Due to the fact that equipment constructed with materials resistant to corrosion is very expensive, it is common to use corrosion inhibitors as a practical, economical and simple alternative.

A recent study in the United States indicated that their industries spent about $276 billion/year (on what?) and around 900 million/year on about 200 million tons of CIs. This market is shared by about 40% of inorganic inhibitors such as sulfonates and phosphonates (for cooling towers) and 60% of organic inhibitors, for example amines, cyclic amines, quaternary amidoamines, diethilamines, imidazoline and fatty acids, which are primarily used as CIs in the Petroleum Industry, in the production of gas, refineries, oil pipelines and products [26].

The CI formulations generally are made up of one or more active ingredients and suitable vehicles (other additives and solvents) that encourage compatibility with the environment and make viable the active transport to the area to be protected (metal surface).

The properties that must be met by a CI are [27, 28]:


b. The active principle of the CI must be in contact with the metal to be protected.

c. Must not have side effects.

Sometimes, two components or active ingredients in a formulation may have a higher efficiency when they are mixed than that obtained from the sum of the efficiencies that are
obtained when they are used individually at the same concentration. This effect is known as synergy or synergistic effect and is widely used in the formulation of CIs.

The CI can be classified in different ways [29, 30].

According to the specific application within the oil refining processes:

a. Embedding inhibitors.

b. Blistering inhibitors.

c. High temperature inhibitors.

d. Inhibitors for acidic media.

e. Inhibitors for basic media.

f. Inhibitors for cooling water.

The CI can also be classified according to the type of material to be protected. In the oil refining processes, CIs are of special interest for carbon steel, in which the major component is iron; and inhibitors for copper-zinc alloys (Admiralty), which are the most common materials used in the design of refineries.

CIs can be classified as anodic, which are those that inhibit oxidation of the metal; cathodic, which inhibit the reduction of oxygen; and mixed inhibitors, which inhibit both processes.

CIs can also be classified according to the type of compound that forms the active ingredient in the formulation as inorganic, organic and biocides.

5. Inhibitor mechanism

The action mechanisms of CIs are [31]:

• By adsorption, forming a film that is adsorbed onto the metal surface.

• By inducing the formation of corrosion products such as iron sulfide, which is a passivizing species.

• By changing media characteristics, producing precipitates that can be protective and eliminating or inactivating an aggressive constituent.

It is well known that organic molecules inhibit corrosion by adsorption, forming a barrier between the metal and the environment. Thus, the polar group of the molecule is directly attached to metal and the nonpolar end is oriented in a vertical direction to the metal surface, which repels corrosive species, thus establishing a barrier against chemical and electrochemical attack by fluids on the metallic surface (Figure 10).
An inhibitor may be effective in one system, while in another it is not, (Table 1); therefore, it is convenient to consider the following factors:

- Chemical structure of the inhibitor component.
- Chemical composition of the corrosive medium.
- Nature of the metal surface.
- Operating conditions (temperature, pressure, pH, etc.).
- Thermal stability of the inhibitor. - Corrosion inhibitors have temperature limits above which lose their effectiveness because they suffer degradation of the containing components.
- Solubility of the inhibitor in the system. - The solubility of the inhibitor in the system is required to achieve optimum results in the metal surface protection; this depends on the length of the hydrocarbon chain.
- The addition of surfactants to enhance the dispersibility or solubility of inhibitors.
- Modification of the molecular structure of the inhibitor by ethoxylation to increase the polarity, and thus reach its solubility in the aqueous medium.

The main features of an inhibitor are:

- Ability to protect the metal surface.
- High activity to be used in small quantities (ppm).
• Low cost compound(s).
• Inert characteristics to avoid altering a process.
• Easy handling and storage.
• Preferably with low toxicity.
• Non-contaminant.
• It should act as an emulsifier.
• It should act as a foaming agent.

6. Environmentally Friendly Corrosion Inhibitors (EFCIs)

In recent years, owing to the growing interest and attention of the world towards the protection of the environment and the hazardous effects of using chemicals on the ecological balance, the traditional approach on CIs has gradually changed. As mentioned before, for an inhibitor to be an effective protector against metal corrosion, it should be readily adsorbed on the metal surface through either physisorption or chemisorption processes. Either of these adsorption processes depends primarily on the physicochemical properties of the inhibitor group such as functional groups, electronic density at the donor atom, molecular structure, etc. For instance, organic molecules, which have had a wide applicability and that have been extensively studied and used as CIs, often contain nitrogen, oxygen, and sulfur atoms, as well as multiple bonds in their molecules.

6.1. Evaluating the toxicity of CIs

Aspects to be taken into account in the development of CIs are their toxicity and impact on environmental pollution of both the active and other components of the formulation.

The European Economic Community assigned the Paris Commission (PARCOM) the task of providing guidance for environmental pollution control, protection of the ecosystems and the evaluation of the toxicity of raw materials and industrial waste products.

The PARCOM Environmental has developed a standardized test that covers three aspects:

1. Toxicity: This must be determined for the formulation as a whole.

Toxicity should be measured by using either the 50 Lethal Concentration (LC50), which is the concentration at which 50% of the test organisms are killed, or the EC50, which is the concentration that can cause an adverse organism affection, e.g. the concentration decreases the emission intensity of luminescent bacteria by 50% or the concentration decreases the growth or average weight of certain microorganisms by 50%.

The toxicity degree may be classified according to the LC50 value, where these categories are described in Table 2 [32].
<table>
<thead>
<tr>
<th>CATEGORY</th>
<th>LC$_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supertoxic</td>
<td>5 mg/kg of weight or less</td>
</tr>
<tr>
<td>Extremely toxic</td>
<td>5-50 mg/kg</td>
</tr>
<tr>
<td>Highly toxic</td>
<td>50-500 mg/kg</td>
</tr>
<tr>
<td>Moderately toxic</td>
<td>0.5-5 g/kg</td>
</tr>
<tr>
<td>Slightly toxic</td>
<td>5-15 g/kg</td>
</tr>
<tr>
<td>Practically non-toxic</td>
<td>More than 15 g/kg</td>
</tr>
</tbody>
</table>

Table 2. Classification of the toxicity of chemical compounds according to the LC50.

Toxicity testing for corrosion inhibitors to be measured in at least three different species and for the optimum established time, (Table 3).

<table>
<thead>
<tr>
<th>Group</th>
<th>Preferred especies</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae</td>
<td>Skeletonema costatum</td>
<td>72-hour EC$_{50}$</td>
</tr>
<tr>
<td>Fish and crustaceans</td>
<td>Acartia tonsa</td>
<td>48-hour LC$_{50}$</td>
</tr>
<tr>
<td>Parasites</td>
<td>Coropium voluntaros</td>
<td>10-day LC$_{50}$</td>
</tr>
</tbody>
</table>

Table 3. Parameters for developing standardized toxicity tests.

2. Biodegradation: It must be determined for all the formulation components.

This test measures the persistence in the environment of the formulation components. The standard test that should be applied is the marine OECD. The allowable limit is more than 60% after 28 days.

3. Bioaccumulation: This test measures the level of product buildup in the body. Bioaccumulation is measured by the partition coefficient (eq. 1), as this parameter can be correlated with the cell interface/water ratio.

\[
P_{o} / w = \frac{\text{concentration in octanol}}{\text{concentration in water}}
\]

This means that the greater the partition coefficient, the more likely it is that the compound passes through the cell membrane, being bioaccumulated.

EFCIs can be arbitrarily divided into two categories: natural products and low toxicity synthetic products. In this last category, special attention has been paid to a new class of low toxicity organic compounds known as ionic liquids.

There are a few studies where CIs are evaluated according to the methodology described in this section and designed as low toxicity CIs or EFCIs. Most of the inhibitors that receive this
rating are based on products that are derived from natural sources that are considered as compatible, biodegradable or environmentally friendly, although strictly, their toxicity has not been assessed by following the testing protocol presented above.

In the next sections, a brief overview of recent research works on the study of EFCIs with particular interest in those with potential applications in the Petroleum Industry is given.

6.2. Natural products as EFCIs

Natural products have been studied extensively as corrosion inhibitors both in product mixtures extracted from natural sources such as plants or essentially pure products derived from animals or plants (i.e. vitamins and aminoacids).

From the economic and environmental view points, plant extracts are an excellent alternative as inhibitors because of their availability and biodegradability. These extracts can be obtained in a simple way and purification methods are not required. The extracts are generally obtained from cheap solvents that are widely available, at a low cost and with low toxicity; the aqueous extract is more relived, but due to the low solubility of many natural products in water, common ethanol extracts are also obtained. These extracts contain a variety of natural products such as essential oils, tannins, pigments, steroids, terpenes, flavones and flavonoids, among other well-known active substances used as CIs. In general, these compounds present conjugated aromatic structures, long aliphatic chains such as nitrogen, sulfur, and oxygen heteroatoms with free electron pairs that are available to form bonds with the metal surface; in most cases, they act synergistically to exhibit good efficiency regarding the corrosion protection. This can be demonstrated in the case of *Ginkgo biloba* in which the main components (flavonoids and terpenoids) have been identified (Figure 11). This extract has demonstrated excellent efficiency as CI with potential applications in the Oil Industry concerning the corrosion inhibition of Q235A steel. The antibacterial activity of the extracts against oil field microorganisms (SRB, IB and TGB) has also been proved [33].

The main disadvantage of using plant materials as CIs is their frequently low stability, they are readily biodegradable; however, this disadvantage can be minimized or avoided by adding biocides such as N-cetyl-N,N,N-trimethyl ammonium bromide.

In the last years, Umoren and Obot’s research group has published several papers about the evaluations of plant extracts as CIs, for example, *Phyllanthus amarus* [34], *Pachylobus edulis* [35], *Raphia hookeri* [36], *Ipomoea involcrata* [37] and *Spondias mombin L.* [38].

Recently, this group described the inhibitive action of Ethanolic extracts from leaves of *Chlomolaena Odorata L.* (LECO) as eco-friendly CI of acid corrosion of aluminum in 2 M HCl, using hydrogen evolution and thermometric techniques [39]; and more recently, for corrosion of mild steel in H2SO4 solutions [40]. In this last paper, the obtained results showed that LECO functioned as a CI and its efficacy increased with the extract concentration, but decreased with temperature. At a concentration as low as 5 %v/v of the extract, the inhibitory efficiency reached about 95% at 303 K, and 89% at 333 K.
In another interesting work, this group showed the excellent inhibitory properties of Coconut coir dust extract (CCDE) as corrosion inhibitor of aluminum in 1 M HCl, using weight loss and hydrogen evolution techniques at 30 and 60°C by monitoring the volume of evolved hydrogen gas at fixed time intervals (Figure 12). The representative plots of the volume of the evolved hydrogen gas as a function of the reaction time at 30 and 60°C for Al in 1 M HCl, in the absence and presence of different concentrations of the CCDE, showed a remarkable increase in the volume of evolved H$_2$ gas in the blank acid solution at both studied temperatures. As for the introduction of CCDE into the corrosive medium, it is seen that there is a considerable reduction in the volume of evolved hydrogen gas, suggesting that the CCDE components were adsorbed onto the metal surface, and blocked the electrochemical reaction efficiently by decreasing the available surface area [41].

**Figure 11.** Structures of flavonoids and terpenoids found in *Ginkgo biloba*. 
Table 4 summarizes examples of natural extracts that have been evaluated in recent years as CIs [42, 43].

In the category of natural isolated products, aminoacids and their derivatives are some of the most studied pure compounds as EFCI. These natural compounds and derivatives have been used as good CIs for mild steel [75-80], carbon steel [81-83], stainless steel [84], iron [85], nickel [86], copper [87-91], aluminum [92], and alloys [93] and [94] in different aggressive solutions.

Very recently, the inhibitory properties of l-histidine on the corrosion of carbon steel in weak acid media containing acetic acid/sodium acetat have been tested. The inhibition efficiencies obtained by weight loss measurements are in good agreement with values given by the Tafel method and electrochemical impedance spectroscopy. The adsorption of l-histidine obeys the Langmuir isotherm; the negative values of the Gibbs energy indicate the nature of the interactions between the inhibitor molecules and metal surface. Further, the inhibition effect was studied by using scanning electron microscopy and energy dispersive X-ray analysis [95].

Other low-toxicity natural products including natural polymers described as CIs are summarized in Table 5.

Figure 12. Plot of evolved hydrogen volume against time for Al in 1 M HCl with and without different CCDE concentrations at (a) 30°C and (b) 60°C. Reprinted from ref. [41].
<table>
<thead>
<tr>
<th>Reference</th>
<th>Natural product source</th>
<th>Metal or Alloy protected</th>
</tr>
</thead>
<tbody>
<tr>
<td>[44]</td>
<td>Polysaccharide (galactomannan) extracted from the endosperms of some leguminosae plants as coffee beans and chickpeas.</td>
<td>Concrete Armor Protection</td>
</tr>
<tr>
<td>[45]</td>
<td>Chenopodium ambrosioides extract</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[46]</td>
<td>Ethanolic Extracts from Seeds of Garcinia kola</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[47]</td>
<td>Musa acuminata flower extract</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[48]</td>
<td>Cannabis plant extract</td>
<td>Copper</td>
</tr>
<tr>
<td>[49]</td>
<td>Mexican Argemona plant extract</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[50]</td>
<td>Lavandula dentata aqueous extract</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[51]</td>
<td>Aframomum melegueta extracts</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[52]</td>
<td>Osmanthus fragrans leaves extract</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[53]</td>
<td>Neolamarckia cadamba extract (bark, leaves) and pure alkaloid (3 beta-isodihydrocadambine)</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[54]</td>
<td>Murraya koenigii leaves extract</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[55]</td>
<td>Berberine extracted from Coptis chinensis</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[56]</td>
<td>Hibiscus sabdariffa extract</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[57]</td>
<td>Artemisia oil</td>
<td>Steel</td>
</tr>
<tr>
<td>[58]</td>
<td>Ethanolic extract of Musa species</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[59]</td>
<td>Aqueous extract of Hibiscus rosa-sinensis Linn</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[60, 61]</td>
<td>Opuntia-Ficus-Indica (Nopal)</td>
<td>Aluminum and Steel</td>
</tr>
<tr>
<td>[62]</td>
<td>Tobacco extract</td>
<td>Steel and Aluminum</td>
</tr>
<tr>
<td>[63]</td>
<td>Aqueous extract of rhizome powder (Curcuma longa L)</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[64]</td>
<td>Onion juice</td>
<td>Zinc</td>
</tr>
<tr>
<td>[65]</td>
<td>Vernonia amygdalina</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[66]</td>
<td>Mangrove tannin</td>
<td>Copper</td>
</tr>
<tr>
<td>[67]</td>
<td>Punica granatum extract</td>
<td>Brass</td>
</tr>
<tr>
<td>[68]</td>
<td>Phoenix dactylifera L. fruit juice</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[69]</td>
<td>Rain water containing garlic extract</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[70]</td>
<td>Polyphenols extracted from olive mill wastewater</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[71]</td>
<td>Morinda tinctoria leaves extract</td>
<td>Mild steel</td>
</tr>
<tr>
<td>[72]</td>
<td>Aqueous extract of Creosote Bush (Larrea tridentata) leaves</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[73]</td>
<td>Prosopis laevigata</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[74]</td>
<td>Lavandula stoekas leaves extract</td>
<td>Stainless steel</td>
</tr>
</tbody>
</table>

Table 4. Extracts of natural products described as CIs.
Numerous inorganic and organic compounds have been reported as CIs for metals in different media, but the toxic nature of many of them limits their application. In the last decades, much attention has been focused on the need to design and develop synthetic non-toxic corrosion organic inhibitor to replace toxic ones for a sustainable development, for example, 12-aminododecanoic acid has been described as “green” CI for carbon steel [112], while imidazole derivatives [113] and guanidine [114] have been reported as non-toxic CIs for copper in acid media.

Several human drugs, including diuretics and barbiturates have shown good performance as CIs of metals in acid media [115-128]. In this sense, two well-known diuretics, Furosemide and Torsemide were recently evaluated as CIs of mild steel in hydrochloric acid medium. From the two inhibitors, Torsemide performance is superior to that of Furosemide due to its high electron density, which favors its adsorption on the metal surface. Polarization studies revealed that the inhibiting action of the compounds is under mixed control. The free adsorption energy and the temperature influence on the adsorption of inhibitors onto a mild steel surface have been reported. The adsorption of the compounds was found to obey the Langmuir adsorption isotherm. The inhibition and formation mechanisms of the Fe–inhibitor complex were confirmed by FT-IR and UV–visible absorption spectral analysis. The scanning electron microsco-

**Table 5.** Natural products, including natural polymers described as CIs.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Natural product</th>
<th>Metal or Alloy protected</th>
</tr>
</thead>
<tbody>
<tr>
<td>[96]</td>
<td>caffeine</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>[97]</td>
<td>caffeine</td>
<td>Copper</td>
</tr>
<tr>
<td>[98]</td>
<td>Purine and adenine</td>
<td>Copper</td>
</tr>
<tr>
<td>[99]</td>
<td>Vitamin B₁</td>
<td>AISI 4130 steel alloy</td>
</tr>
<tr>
<td>[100]</td>
<td>Vitamin B₁</td>
<td>Copper</td>
</tr>
<tr>
<td>[101, 102]</td>
<td>Vitamin C</td>
<td>Steel</td>
</tr>
<tr>
<td>[103]</td>
<td>Pteroyl-L-glutamic acid (Vitamin M)</td>
<td>Scale inhibitor for oil wells of carbonate reservoir</td>
</tr>
<tr>
<td>[104]</td>
<td>Citric acid</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[105]</td>
<td>Benzoic acid</td>
<td>Iron and aluminum</td>
</tr>
<tr>
<td>[106]</td>
<td>Vitamin B₁, B₂ and C</td>
<td>Nickel</td>
</tr>
<tr>
<td>[107]</td>
<td>Peptin</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[108]</td>
<td>lignin terpolymer</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[109]</td>
<td>cassava starches</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[110]</td>
<td>Carrageenan (polysacharide polymer)</td>
<td>Aluminum</td>
</tr>
<tr>
<td>[111]</td>
<td>Chitosan</td>
<td>Steel</td>
</tr>
</tbody>
</table>
py (SEM) and atomic force microscopy (AFM) results established the formation of a protective layer on the mild steel surface. Quantum chemical calculations were applied to correlate the inhibition performance of inhibitors with their electronic structural parameters [129].

In 2011 the application of drugs as promising novel EFCIs was reviewed [130]. Several synthetic polymers have also been designed as efficient EFCIs for carbon steel in alkaline solution [131] and for calcium carbonate scale inhibitor for cooling water [132, 133]. Ionic liquids (ILs) deserve particular attention due to the rapid grown in the number of applications in the Oil Industry [134], and particularly within the topic of synthetic EFCIs, these have shown an effective performance as inhibitors of various metals and alloys [135-151].

ILs are ionic compounds, showing anisotropic molecular shape; their structure contains both organic and inorganic type components with various functional groups. They offer novel physical and chemical properties like low toxicity, high chemical stability, low vapour pressure and high electrical conductivity [152-157].

Quite a number of ILs do behave not only as green solvents suitable for the electrochemical devices and methods but also as unique and robust electrolytes with high stability. Also, these compounds present structure properties suitable to be absorbed on metal surfaces and some derivatives of these families have proved that they can act as EFCIs in acid and basic corrosive environments.

Likhanova et al. have published a paper about the inhibitory action of 1,3-dioctadecylimidazolium bromide (ImDC$_{18}$Br), N-octadecylpyridinium bromide (PyC$_{18}$Br) in 1 M H$_2$SO$_4$ on mild steel at room temperature. The effect of the concentration of inhibitor compounds was investigated by electrochemical tests, whereas the surface analysis was performed at 100 ppm for both compounds. In the case of ImDC$_{18}$Br, corrosion products were additionally studied by X-ray diffraction and Mössbauer spectroscopy. The results revealed that ILs act as corrosion inhibitors with 82-88% at 100 ppm to protect the mild steel corrosion in the aqueous solution of sulfuric acid; their efficiencies are increased with the inhibitor concentration in the range 10–100 ppm range. SEM-EDX, XRD and Mössbauer analysis indicated the presence of carbon species and iron sulfates in the presence of ILs; whereas corrosion products such as iron oxyhydroxides were present in the absence of the ILs; this behavior was described by the proposed corrosion inhibition mechanism [158].

The same research group published a related paper in 2011 where five imidazolium-type ILs containing N1-vynil and N3-long alkyl saturated chains as cation and bromide as anion were synthesized under microwave irradiation and evaluated as CIs for acid environment. Weight loss and electrochemical polarization techniques were used to test the inhibitory properties of these compounds in AISI 1018 carbon steel immersed in 1.0 M H$_2$SO$_4$. All the studied ILs showed inhibitory properties dependent on the chain length linked to N3. The highest efficiency of IL4 was confirmed by Scanning Electron Microscopy (SEM)/Energy-Dispersive X-ray spectroscopy (EDX) and Atomic Force Microscopy (AFM) images of film formation. SEM revealed revealed that the surface morphology was strongly damaged in the CI absence, but in the presence of 100 ppm of CI, damage was considerably diminished, which confirmed the high efficiency of 1-Vinyl-3-octadecylimidazolium bromide at this concentration (Figure 13) [159].
ILs have also been employed to prepare a thin protective aluminum layer on carbon steel surface by electroreduction and electrodeposition of 1-butyl-3methyl-imidazolium chloroaluminate (AlCl₃/[BMIM]Cl) [160, 161].

Recently, the inhibition effect of 1-ethyl-3-methylimidazolium dicyanamide (EMID) against steel corrosion was investigated. In this study, EMID was evaluated as corrosion inhibitor for steel and then it was fixed in the polymer film. EMID is able to assemble a protective film on steel surface, under acidic conditions. The results of SEM analysis and potentiodynamic studies also showed that this inhibitor film is stable around corrosion potential. The steel surface becomes positively charged during inhibitor adsorption and the anionic part of EMID plays the major adsorption role. The inhibitor was fixed within polypyrrole coating on steel, and it was shown that this addition could improve the protection efficiency of the coating [162].

Junguroya et al. reported another recent interesting result. They found that water containing traces of hydrophobic ILs ([BMIM]Cl and [BMIM]NTf₂) exhibit unusual corrosion inhibiting behavior by protecting metal copper and nickel from electrochemical corrosion under aerobic conditions. The anodic dissolution of a copper electrode results in the formation of Cu(I) species. The simultaneous re-electrodeposition of nanocrystalline copper on the cathode occurred without additives to the resulting electrolyte [163]. Also, the high-temperature corrosion behavior of several metals (Ni, Cu, and alloys) in [BMIM]NTf₂ under aerobic conditions has been investigated by electrochemical methods [164].

The development of EFCIs based on organic rare earth compounds such as salycilates, phosphates, chromates and cinnamates was reviewed in 2011 [165].

7. Conclusions

As it has been seen through this chapter, corrosion inhibitors are economically feasible to mitigate the problems caused by corrosion. Environmental regulations in industrialized countries are increasing the pressure to eliminate, in the short term, a number of compounds
widely used in industrial to prevent corrosion. A number of alternatives of EFCIs are currently emerging, oriented towards minimizing environmental impact providing effective corrosion inhibition. EFCIs include natural products, extracts from plants, and synthetic low-toxicity compounds. We hope that these products will be able to replace, in the near future, the toxic commercial products that are still being used by many industries worldwide.

Author details

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