Arabian Journal of Chemical and Environmental Researches

Vol. 05 Issue 2 (2018) 101–123

Bibliographic review on the problem of corrosion and their protection by green inhibitors

I. Hamdani, O. Mokhtari, L. Lamri, S. Zaoui, D. Bouknana, A. Aouniti, M. Berrabah, A. Bouyanzer, B. Hammouti

[1] *Laboratory of Applied Chemistry and Environment (LCAE), Faculty of Science, Mohammed Premier University, 60000 Oujda, Morocco*

[2] *Centre Régional des Métiers d'Education et de formation CRMEF Oujda, 60000 Oujda, Morocco*

Received 29 July 2018, Revised 15 Aug 2018, Accepted 18 Aug 2018

Abstract

Corrosion can be defined as a phenomenon of Physico-chemical interaction of a metal and its environment, inducing degradation of the metal itself. This phenomenon provokes disturbing influences on the different economic and cultural fields at the environmental level: corrosion contributes to pollution. The last few years were the scene of intensified studies to combat corrosion, for this reason, several laboratories have sought to synthesize molecules that promote the inhibition of the corrosion often known corrosion inhibitors, the latter are compounds that inhibit corrosion with a heteroatom (O, S, N) in their composition, but at environmental considerations, recent research is tending towards the use of inhibitors based on plants, or' many natural products are widely used to combat corrosion.

Keywords : corrosion, physico-chemical interaction, inhibitors, natural products.

---

*Imad HAMDANI
E-mail address: *hamdani_imad@hotmail.fr*

1. Introduction

Corrosion, from the Latin "corrode", means to gnaw, to attack is generally the action of corrosive environments (atmospheric agents or chemical reagents). After the attack, metals tend to return to their original state of oxide, sulphide, carbonate, etc., which is more stable to the medium in question and thus suffer a deterioration in their properties [1]. This is a constant and persistent problem, often difficult to eliminate. Corrosion of mild steel and other metals is accentuated in the presence of an aggressive medium such as acid.

According to ISO 8044, corrosion is defined as "a Physico-chemical interaction between a metal and its environment that results in changes in the properties of the metal and can often lead to the weakening of the metal, the environment, or the technical system of which it is a part" [2]. However, the AFNOR standard (NFT30, 001) has defined the phenomenon of corrosion as the degradation of the initial metallic state which can go as far as its destruction under the action of the environment and by a process other than mechanical, whereas according to Bommersbach (2005), it is corrosion when the deterioration is irreversible of metal and has taken place by chemical or electrochemical reaction with the environment, which can be of different forms: uniform, localized, galvanic, etc., the properties of the metal are then altered [3].

Man has been facing corrosion problems since he has been using metals or alloys. The common use of iron made him immediately aware of rust and encouraged him to find a way to avoid its formation. The field of action of corrosion is certainly, nowadays, much wider since we have a large number of metals and alloys which are all attackable, in the surrounding environment, to a greater or lesser degree.

The consequences of corrosion are considerable from various points of view: industrial and economic, such as in most industrialized countries, the total cost of corrosion is estimated at between 2 and 4% of GNP (Gross National Product). However, of the total cost, 20 to 25% of the losses could be saved by a better knowledge of the causes of corrosion and a better application of protection techniques [4].

These losses could be higher without corrosion protection. Indeed, the corrosion problems faced by industry generate additional costs of industrial exploitation, not limited to steel, but affects all the achievements of the engineer, materials from the largest to the smallest; energy production, civil engineering, transport, machinery, medical equipment, microelectronic components, etc. [5]. The evaluation of losses due to corrosion must take into consideration :

- Direct losses: replacement of corroded materials and equipment.
- Indirect losses: repair, production losses.

As far as corrosion protection is concerned, it is possible to act on the material itself (judicious choice, adapted shapes, constraints according to the applications...), on the surface of the material (coating, painting, any type of surface treatment...) or on the environment with which the material is in contact (corrosion inhibitors).

Corrosion is not only a source of waste of raw materials and energy, but it can also cause accidents with serious consequences and, in some cases, contribute to the pollution of the natural environment. To remedy this problem, laboratory research has shown the great interest in using essential oils and extracts of aromatic and medicinal plants, which are natural, non-toxic and renewable products, as corrosion inhibitors.

2 General information on the use of corrosion inhibitors

2.1. Historical aspect

As a huge field, it is difficult to determine the exact temporal origin of corrosion inhibition also considered as a separate technology. During the first century AD, the great Roman naturalist and historian Pliny the Elder (23-79 AD) mentions methods of protection to prevent the corrosion of iron and bronze. The study of corrosion began around the 17th century, but it was not until the 19th century that the means of combating this phenomenon were scientifically studied, a few decades ago it was observed that the limestone deposit formed inside the pipes carrying certain natural waters protected the pipe. Rather than constantly improving the corrosion resistance of pipes by acting directly on them, it was then more practical to adjust the mineral concentrations of the solutions transported, which are at the origin of the "protective" limescale deposits. In a 1948 article [5], Waldrip referred to a 1943 report on oil well corrosion protection. Several articles concerning inhibition were written in the period 1945-1954: they dealt, among others, with inhibition in aviation, boilers, cooling systems, diesel engines, snow removal salts, oil refineries and oil tankers. Over the last fifty years, an increasing number of abstracts, articles and other works have been identified on this topic [6].

2.2. Definition :

The definition of a corrosion inhibitor by the National Association of Corrosion Engineers (NACE) is as follows: a corrosion inhibitor is "a chemical substance which, when added at low concentration to the corrosive medium, slows or stops the corrosion process of a metal in contact with that medium" [7].

I.2.3. Properties

The particular action of a corrosion inhibitor can be complex, as it depends on the corrosive medium-metal couple and the temperature and concentrations used. An inhibitor is effective if it meets several criteria. To do so, it must :

- Reduce the corrosion rate of the metal without affecting the Physico-chemical properties of the medium or the metal,
- Be stable at operating temperatures and in the presence of other constituents of the medium, especially oxidants,
- Be soluble and dispersible in the medium,
- Be effective at low concentrations,
- Respect the standards of non-toxicity, (be inexpensive).

2.3. Classes of inhibitors

There are several possibilities for classifying inhibitors, which differ from each other in various ways [8] :

The formulation of the products or chemical nature (organic inhibitor, inorganic inhibitor);
The inhibited electrochemical reaction (cathodic inhibitor, anodic or mixed inhibitor);
Reaction mechanism involved (adsorption and/or film formation) ;
Their field of application (acidic medium, neutral medium, gas-phase...) :

Nevertheless, this classification is not entirely adequate, as the same inhibitor can present at the same time characteristics specific to each classification group.

2.3.1. Classification according to the nature of the inhibitor

- Organic Inhibitors

Organic inhibitors are generally used in acidic environments. They comprise a non-polar, hydrophobic part consisting of one or more hydrocarbon chains and a polar, hydrophilic part consisting of one or more functional groups: amine (-NH), hydroxyl (-OH), mercapto (-SH), carboxyl (-COOH) and their derivatives enabling them to bind to the surface of the metal. Their use is currently preferred, despite inorganic inhibitors, mainly for reasons of ecotoxicity. According to Bommersbach, they have at least one heteroatom serving as an active centre for their fixation on the metal such as nitrogen (amines, amides, imidazolines, triazoles...), oxygen (acetylenic alcohols, carboxylates, oxadiazoles...), sulphur (derived from thiourea, mercaptans, sulfoxides, thiazoles...) or phosphorus (phosphonates) inhibitors that contain sulphur are more effective than those that contain nitrogen, because sulphur is a better electron donor than nitrogen. The main characteristic of these inhibitors is their high efficiency, even at low concentrations. The inhibitory effect often increases with the molecular weight of the inhibitor. The inhibitory action of these organic compounds, which is generally independent of the anodic and cathodic corrosion processes, is related to the formation (by adsorption) of a more or less continuous barrier, but of finite thickness, which prevents access of the solution to the metal. Unsaturated organic compounds are carriers of electrons capable of creating bonds with the metal atoms, therefore the inhibiting efficiency of these unsaturated compounds (double or triple bond) is very important. Organic inhibitors are generally made up of by-products of the petroleum industry [9]. One of the limitations in the use of these products may be the rise in temperature, as organic molecules are often unstable at high temperatures.

- Inorganic Inhibitors

Mineral molecules are most often used in a medium close to neutrality, or even in an alkaline medium, and more rarely in an acidic medium. The products dissociate in solution and it is their dissociation products that ensure the inhibition phenomena (anions or cations). The main inhibiting anions are oxo-anions of type XO^{4n-} such as chromates, molybdates, phosphates, silicates... The cations are essentially Ca^{2+} and Zn^{2+} and those which form insoluble salts with certain anions such as hydroxyl OH -. They improve the corrosion resistance of the metal either by limiting the diffusion of aggressive species towards the substrate by prior adsorption of the molecules (Chromate), or by forming a film on the surface and appear as effective inhibitors : (Molybdate and tungstate) and Phosphate, silicate and borate the number of molecules currently in use is becoming increasingly limited, as most effective products harm the environment. However, new organic complexes of chromium III and other cations (Zn^{2+}, Ca^{2+}, Mg^{2+}, Mg^{2+}, Mn^{2+}, Sr^{2+}, Al^{2+}, Zr^{2+}, Fe^{2+}...) effective against corrosion and non-toxic have been developed [10].

I.2.3.2. Classification according to the electrochemical mechanism of action.

In the classification by mechanism of electrochemical action, a distinction can be made between anodic, cathodic or mixed inhibitors (Figure 1).

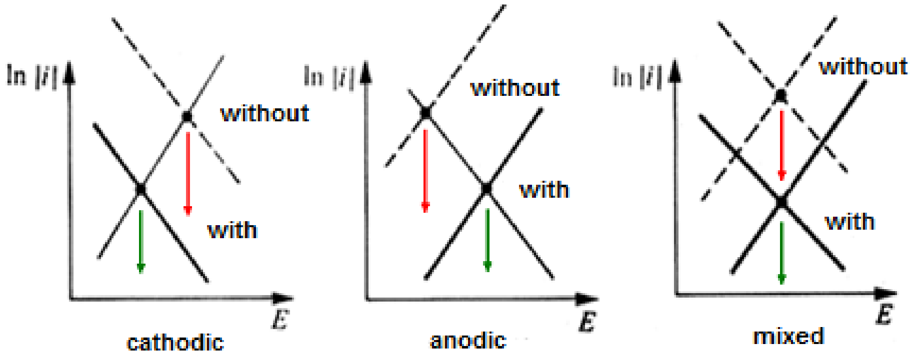

Figure 1: Evans diagrams showing the displacement of the corrosion potential due to the presence of a corrosion inhibitor [11].

The corrosion inhibitor forms a barrier layer on the metal surface, which modifies the electrochemical reactions (Figure 2).

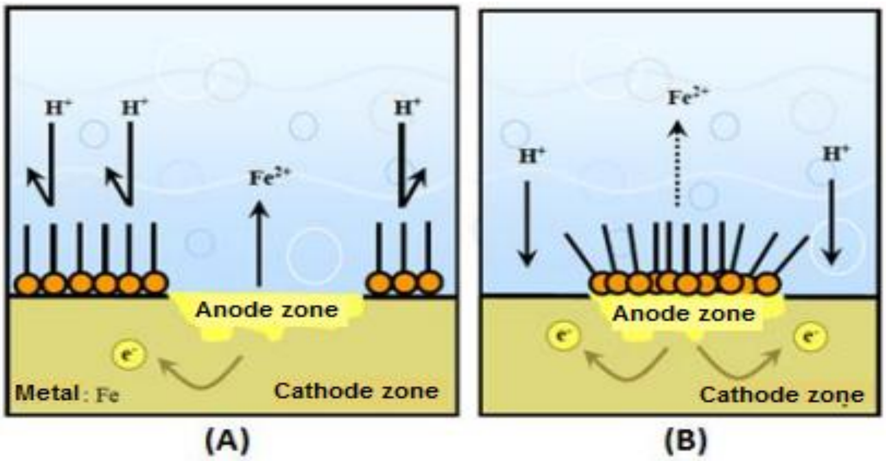

Figure 2: Formation of barrier layers in an acid environment interfering with electrochemical reactions A) Blocking of cathodic sites and B) Blocking of anodic sites [12]

This classification of inhibitors takes into account the electrochemical nature of liquid phase corrosion, which involves at least two reactions:

-An anodic metal dissolution reaction (oxidation reaction):

Example: Metal M $\rightarrow$ Mn^{n+} + n.e-

$Fe \rightarrow Fe^{2+} + 2.e-$

-A cathodic reaction of reduction of an oxidant from the solution :

$H^{+} + e- \rightarrow ½H_2\uparrow$ (gas) (in a non-aerated acidic medium)

This reaction is fairly fast in acids, but is slow in neutral or basic aqueous media.

Where

$O_2 + 4 H^{+} + 4 e^{-} = 2H_2O$ (aerated acid medium)

This reaction can be accelerated by dissolved oxygen (a process called depolarization).

The anodic inhibitor slows down the oxidation reaction, i.e. by blocking the anodic sites (seat of metal oxidation), which decrease the density of the metal dissolution current and shift the corrosion potential in the positive direction. This type of inhibitors should be used with care. If the inhibitor concentration is insufficient, the current density will be very high on these anodes and will cause deep pitting corrosion as the attack is limited to very localised holes, which can progress very rapidly in depth while keeping the rest of the surface unharmed (figure 67-b). In the same way, by blocking the cathodic sites (oxygen reduction site in aerated neutral environment or H+ proton reduction site in acidic environment) which decrease the density of the hydrogen reduction current and which displace the corrosion potential in the negative direction, it is called the cathodic inhibitor (figure 3-a).

Cathodic inhibitors are considered safer than anodic inhibitors because they are not likely to promote localized corrosion. Even if the amount of inhibitor added is insufficient to cover all the cathodes, the corrosion current intensity will decrease.

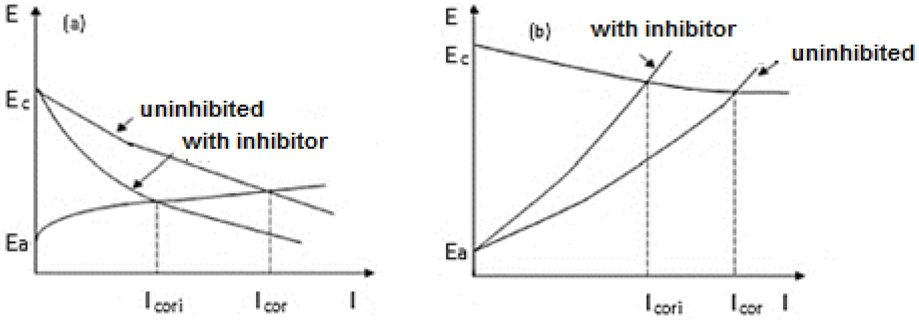

Figure 3: Mechanism of electrochemical action:(a) Cathodic corrosion control (b) Anodic corrosion control.

Finally, mixed inhibitors act on both cathodic and anodic reactions [13]. They decrease the speed of both partial reactions with little change in the corrosion potential [14]. By considering these general notions, it becomes clear that the mechanism of action of an inhibitor can be considered under two aspects: a "mechanism" aspect (intervention in the fundamental processes of corrosion (figure 4)) and a "morphology" aspect (intervention of the inhibitor molecule in the interfacial structure).

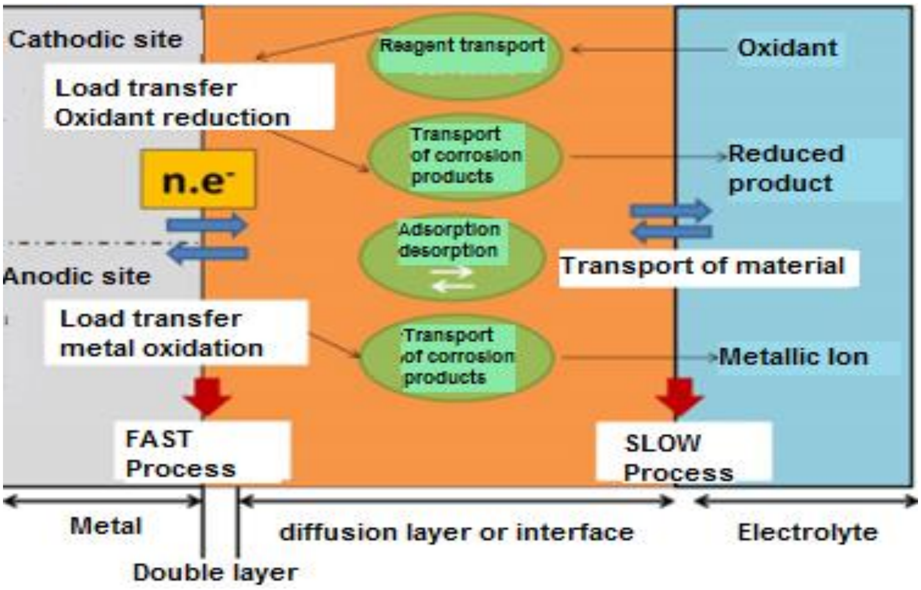

Figure 4: Different mechanisms taking place at the interface during the corrosion of a metal in a liquid medium.

I.2.3.3. Classifications according to interfacial action mechanisms

In the classification linked to the reaction mechanism involved according to their mode of action, different types of inhibitors can be distinguished: Adsorbent or "interface" inhibitors are generally organic inhibitors: They prevent the action of the aggressive medium by forming one- or twodimensional films of molecules by adsorption on the surface of the metal. Their fixation is mainly done by the active function of the inhibitor; however, the polar parts can also be adsorbed. Some inhibitors cause spontaneous passivation of the metal, which reduces the corrosion rate. In some cases, passivation can be promoted by buffer agents, which increase the pH near the metal surface [15], while other so-called "interphase" inhibitors are specific to neutral or alkaline media and cause the formation of surface films by precipitation of mineral salts or poorly soluble organic complexes, as these films reduce the accessibility of oxygen to the surface, In addition, they partially block anodic dissolution [15], e.g. polyphosphates $(NaPO_3)n$ and organophosphates belong to this category.

Adsorption is a universal surface phenomenon because any surface is made up of atoms that do not have all their chemical bonds satisfied, in fact between the metal surface and the adsorbed species there are two types of bonds: electrostatic bond and chemical bond, thus two distinct types of adsorption: physisorption and chemisorption, all the possible modes of adsorption are represented in figure 5.

- Physisorption (physical adsorption)

Physical adsorption retains the identity of the adsorbed molecules and involves weak bonds. Three types of bonds can be distinguished here:

Van der Waals bonds (are always present with very little energy and will lead to weak binding of the particle),

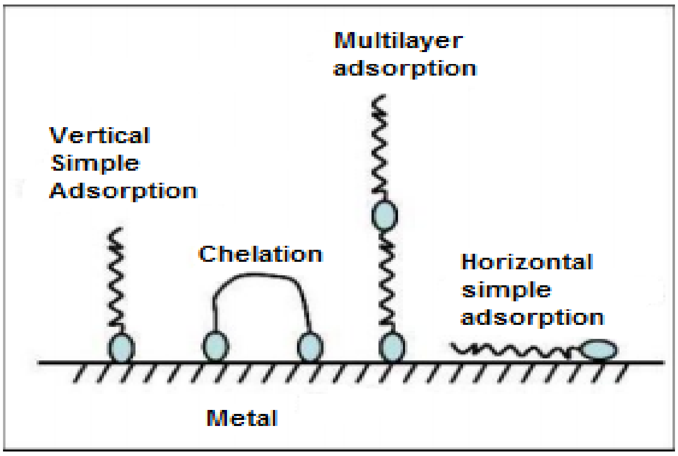

Figure 5: Schematic representation of the adsorption modes of inhibitory organic molecules on a metal surface.

Polar bonds (dependent on surface charges and inhibitor).

Hydrogen bonds (between a hydrogen bond donor and an acceptor, only N, O, P with free doublets [16]).

In terms of electrostatic interaction, an organic molecule can have the same adsorption behaviour with two metals of different nature, the charge of the metal is defined by the position of the corrosion potential of this metal in relation to its zero charge potential (E_0), this behaviour has been verified by

Antropov [17]. When the corrosion potential of this metal has a value lower than E_0, the adsorption of cations is favoured; whereas anions are adsorbed when the corrosion potential of the metal is in the region of positive potential with respect to E_0. Furthermore, physisorption is a relatively fast process characterized by its "quasi-reversibility", and by no change in the chemical bonds between atoms, and several layers of adsorbed atoms cannot superimpose. It is generally observed at low temperatures.

- Chemisorption

Chemisorption consists of the pooling of electrons between the polar part of the molecule and the unsaturated "d" orbitals of the metal surface, which leads to the formation of chemical bonds that are much more stable because they are based on higher bond energies.

Inhibition in an acidic medium involves chemisorption of the inhibitor, which is often an irreversible and metal-specific mechanism. Indeed, the electrons come mostly from the unpaired double bonds of inhibitor molecules such as O, N, S, P... (These atoms are characterized by their high electronegativity). The strength of the bond is determined by the electron density of the atom acting as the centre of the bond and by the polarity of the function, the more functional atoms tend to form bonds with the metal by giving electrons, the more effective the inhibitors are, in fact, the more electronegative the functional group of the organic molecule is, the greater the inhibitory effect of the molecule. Thus, the inhibitory efficacy increases in the following order:

$$O < N < S < Se < P$$

Chemical adsorption is accompanied by a profound modification of the electronic charge distribution of the adsorbed molecules.

The non-polar structure of the inhibitor molecule can increase the inhibitory efficacy by the inductive effect of methyl groups (electro-donor group), which influence the functional atoms to give electrons [18,19].

In addition, chemisorption is a slow, temperature-dependent process characterized by high activation energy.

Inhibitors acting by chemical adsorption are often more effective than those acting by physical adsorption because the sharing of electrons strengthens the bond between the metal and the inhibitor.

I.2.3.4. Classification by field of employment

In the classification relating to the field of application, a distinction can be made between corrosion inhibitors used in aqueous, organic or gaseous media.

- In aqueous media, the inhibitors used are chosen according to the pH of the corrosive medium: in acidic media, they are used to avoid a chemical attack of the metal during a pickling or descaling operation, whereas in neutral or alkaline media, they are often used to protect the pipes of cooling circuits.

- Those used in organic media are incorporated in engine lubricants, petrol or paints since these liquids often contain traces of water and ionic species that can cause corrosion.

- Gas-phase inhibitors are used to protect metal objects during transport and storage. For this purpose, organic compounds are often used as they have a high vapour pressure [20].

I.2.4 Adsorption isotherms

Corrosion can be slowed down by adsorption of an inhibitor on the metal surface. The degree of inhibition then depends on the equilibrium between the dissolved and adsorbed species, it is expressed by an adsorption isotherm. This mechanism is particularly important in acidic media.

The adsorption isotherm can be expressed as the relationship between the rate of recovery of an interface by the adsorbed species and the concentration of the species in solution [21,22]. This recovery can be described by the following relationship :

$$\theta = bCinh/1 + bCinh$$

where b is the adsorption coefficient and C_{inh} is the concentration of the inhibitor.

There are several models of adsorption isotherms, we can cite the three most frequently used models (Langmuir Isotherm, Temkin Isotherm and Frumkin Isotherm) and explain the conditions necessary for their validity in each case.

I.2.4.1 Langmuir Isothermal System

This model assumes that there is a fixed number of sites on the surface of the metal, each site can only adsorb a single particle, so the adsorption energy is constant. The rate of adsorption is proportional to the inhibitor concentration and the number of unoccupied sites.

The recovery rate is related to the concentration of the inhibitor by the Langmuir equation.

$$\frac{\theta}{1-\theta} = A.C.\exp(-\frac{\Delta Gads}{RT}) \qquad (1)$$

Where A is a constant independent of temperature, it is the concentration of the inhibitor in solution, ΔGads is the free energy of adsorption, θ is the fraction of sites occupied by the inhibitor ($0 < \theta < 1$) and (1-θ) is the fraction of unoccupied adsorption sites.

I.2.4.2 Temkin Isothermal

For this type of isotherm, the standard free adsorption energy decreases linearly with the recovery rate. It was observed mainly for average surface coverage rates ($0.2 < \theta < 0.8$). It is also assumed that there are interactions (attraction or repulsion) between the adsorbate and the adsorbent, resulting in multilayer coating [23].

The general equation for the Temkin isotherm is in the form :

$$e^{-2a\theta} = bC_{inh} \qquad (2)$$

Where a is an interaction constant between adsorbed particles, b is the absorption coefficient and C_{inh} is the concentration of the inhibitor in the electrolyte.

I.2.4.3 Frumkin Isotherm

It is characterized by the following general relationship:

$$(\theta/1-\theta)\ \exp\ (-f\theta)=K.C \qquad (3)$$

Where K is the equilibrium constant of adsorption and f is an energy parameter; given by :

$$K = \frac{1}{55.5}\exp(-\frac{\Delta G^{\circ}_{ads}}{\mathrm{RT}})$$

. The shape of the curve θ as a function of *log C* has the form of an "S". This type of isotherm is an extension of the Langmuir isotherm, it depends on the molecular interactions in the adsorption layer and the degree of heterogeneity of the surface.

I.2.5 Behaviour of inhibitors in acidic environments

The most frequently used inhibitors in acidic environments are organic molecules. In particular, aromatic molecules and macromolecules with linear or branched chains [24,25]. These inhibitors first act by adsorption on the surface of the metals, forming a mono- or multi-molecular layer with the metal which acts as an insulating mattress against the aggressive species in the solution, even before intervening in the corrosion reaction processes to reduce their speed. As previously mentioned, the organic compounds likely to function as corrosion inhibitors contain, in principle, an active centre capable of exchanging electrons with the metal: N, O, S, P.

In an aqueous medium because of their polar nature, water molecules adsorb on the surface of the metal. Indeed, effective organic inhibitors displace adsorbed water molecules (Figure 70). According to Bockris [26], the adsorption of an organic substance on the surface of the metal can be described by the following reaction:

$$Org_{(s)} + nH_2O_{ads} \longrightarrow Org_{ads} + n\,H_2O_{(s)}$$

Where n is the number of water molecules displaced from the surface for each organic molecule adsorbed. It is independent of the coating and charge of the metal, but depends on the geometric area of the organic molecule relative to that of the water.

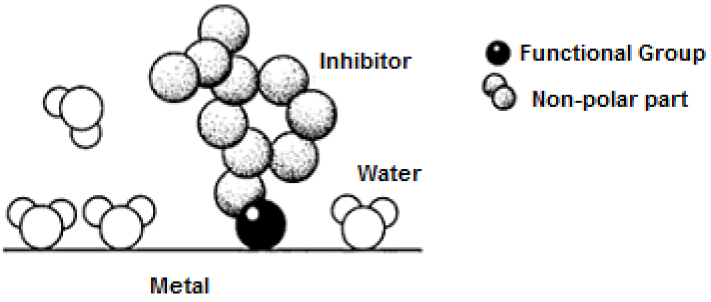

Figure 6: Adsorption of an organic inhibitor on a metal surface in an aqueous medium.

The adsorption of the organic molecule occurs because the interaction energy between the surface of the metal and the surface of the organic molecule is greater than the interaction energy between the metal and the water molecules.

I.2.6 Inhibitors specific to ferrous metals

Generally speaking, for each material, there is a family of inhibitors conducive to satisfactory corrosion protection. For example, for copper, nitrogen compounds are very often used as corrosion inhibitors and are remarkably effective under certain conditions [27]. In acid, neutral or alkaline media, corrosion inhibitors for ferrous metal studies are diverse and varied (**Table 1**).

Table 1: Examples of Inhibitors Used for the Protection of Ferrous Metals

Compounds	Examples	References
Nitrogenous	Hexamethylenetetramine or methenamine Diazoles: imidazole and its derivatives Triazoles and its derivatives such as benzotriazole Bipyrazole derivatives Oxadiazoles Quinoline derivatives Quinone derivatives such as Quinoxaline-2,3-dione Pyridine derivatives Mixed compounds such as Schiff bases resulting from the condensation of an amine with an aldehyde	[28-46]
Sulphur	Thiourea and its derivatives, Thiadiazole and its derivatives	[47-50]
Phosphorus	Phosphonates, phosphonic acids, phosphocarboxylic acid salts.	[51-53]
Oxygenated	Lactones, Carboxylic acids (succinic, β indolacetic ...), Carboxylates	[54-57]

All these inhibitor molecules contain atoms such as N, S, P or O which are capable of exchanging electrons with the metal to be protected and make it possible to obtain good performance in terms of inhibiting steel corrosion in an acid environment.

I.2.7 Alternatives to green corrosion inhibitors in acidic environments

Several studies have indicated that most organic and inorganic inhibitors are toxic and pose serious hazards to humans and the environment during their applications [58,59]. As a result, many researchers are focusing their efforts on replacing these toxic inhibitors with non-toxic ones. There is great interest in the use of green corrosion inhibitors, the latter are reported to be not only non-toxic and environmentally friendly, but also readily available and renewable, they can be safely extracted by simple low-cost procedures from natural products such as plants that show a very high inhibitory efficacy [60 - 63].

In 1930, "plant extracts of chelidoin and other plants were used as a corrosion inhibitor in an H_2SO_4 pickling bath [64]. In 1970 and 1980, the study of plant extracts became more extensive. While in the 1990s the publications and application of plant extracts as metal corrosion inhibitors increased. The bgugain is the first corrosion inhibitor that has been patented and its efficacy is of the order of 100% at $4\ 10^{-5}$M [65-67]. Over the last ten years, several published works have dealt with plant extracts as corrosion inhibitors. Among these plants, we cite for example :

The effect of Artemisia extract on the corrosion of steel in 0.5M H_2SO_4 media was studied by Bouklah et al [68]. The results obtained reveal that the extract reduces the corrosion rate quite significantly in the temperature range from 298 to 353 K and the inhibition efficiency increases with concentration and also increases with temperature, for 10 g/L the observed inhibition rate is 95% at 298 K and 99% at 353 K and it was found that the adsorption of Artemisia extract on the surface of steel also follows the Langmuir isotherm. Davanone (Figure 7), its major constituent [69] is a diketone, and the inhibitory action can be interpreted by the formation of a Fe(II)-davanone complex.

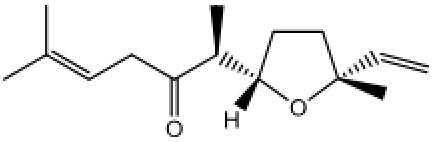

Figure 7: Molecular structure of davanone extracted from Artemisia

Bouyanzer et al evaluated the essential oil of Mentha pulegium is a steel corrosion inhibitor in 1M HCl [70], using mass loss measurements, potentiodynamic polarization and EIS measurements. The inhibition efficiency increases with oil content to reach 80% at 2.76 g/l. Mentha pulegiuma oil acts as a cathodic inhibitor.

El-Etre et al. conducted research on the effect of Olive Leaf Extract on corrosion inhibition of carbon steel in HCl (2M) medium. It is a mixed inhibitor and the maximum inhibition efficiency (93%) is obtained at 900 ppm, but it decreases if one passes from a temperature of 298 K to 343 K [71].

Faska et al. Used certain pure compounds derived from the majority constituents of EOs as an inhibitor of steel corrosion in acidic environments. Indeed, pulegone, the main component of the essential oil from the spearmint (Mentha pulegium), and pulegone oxide, prepared by oxidation of pulegone, were studied in 1M HCl medium. Inhibitory efficiencies increase with inhibitor content to reach 81% and 75% at 5 g dm-3, respectively for pulegone and pulegone oxide. Polarization curves revealed that both inhibitors have a cathodic character. The apparent activation energies decrease in the presence of these inhibitors, which explains the chemical adsorption of these two compounds on the surface of the steel [72].

Umoren et al. studied Hookeri raffia gum and Pachylobus edulis gum in the presence and absence of halides to inhibit corrosion of aluminium in HCl (2M) and HCl (0.1M) media respectively, the synergistic effects obtained by the presence of the halides namely KCl, KBr, KI increase the inhibiting efficiency. On the one hand Orubite-Okorosaye et al. [73,74], on the other hand, Orubite-Okorosaye et al. showed that Nypa Fruticans' Wurmb extract in the presence of KI showed good results against mild steel corrosion in HCl media (0.1 and 0.5 M) [75].

Kumar et al. mentioned that some EOs were tested on steel corrosion in HCl media using their vapours either in the solid-state (powder), as the case of Thymus vulgaris extract [76], while Poongothai et al. used other EOs in the liquid state (in a solvent) as in the case of plant essential oils: Jasminum grandiforum, Jasminum auriculatum, Oleum palmarosae, Ocimum basilicum, Vetiveria zizanioides [77].

Studies conducted by Satapathy et al. on the inhibition of mild steel in different HCl concentrations by the extract of Justicia gendarussa show a satisfactory inhibition capacity against corrosion [78].

El Ouariachi et al. tested essential oil from Rosmarinus officinalis as a steel corrosion inhibitor in 0.5M H2SO4 medium. The results obtained indicated that the corrosion rate decreases and the inhibitory efficiency increase with the oil concentration to reach 61% at 1 g/L [79].

Dahmani et al. conducted a comparative study on the corrosion inhibition of C38 steel in HCl (1M) media. They showed that black pepper extract and the Piperin compound isolated from the same plant showed high inhibition efficiency, 95.8% at 2g/L and 98.9% at 10-3 M at 35°C, respectively. In a temperature range of 40°C-70°C, the efficacy decreases for both types of inhibitors [80].

Several extracts have proven their ability to inhibit mild steel corrosion in different concentrations of HCl and H_2SO_4. We quote for example uncaria gambir extracts [81], alkaloids extracted from Guatteria ouregou , Simira Tinctoria, Siparuna guianensis, Aspidosperma album, Isertia coccinea , Palicourea guianensis [82-86], Neolamarckia cadamba [87], grain hull extract of Ecbolium virid [88], Brugmansia suaveolens and Cassia roxburghii [89], Argania Spinosa [90], Hibiscus sabdariffa calyx gum [91], Schinopsis lorentzii [92], extract from Acalypha torta Leaf [93], tannins extracted from Chamaerops humilis [94], Salvia officinalis and Pelargonium [95], Musa Paradisica Peel [96], Thymus algeriensis [97], Azadirachta indica [98], Garcinia cola, Kimbiolongo [99-100], Acacia tortilis [101], methanolic extracts from Pennyroyal and Mentha Suaveolens [102-103].

Conclusion

The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations are driving researchers to focus on the need to develop low-cost, non-toxic and environmentally friendly natural products as effective corrosion inhibitors for many metals and alloys in various aggressive environments.

These natural organic compounds are either synthesized or extracted from aromatic plants, spices and medicinal plants.

Plant extracts are considered to be an incredibly rich source of biosynthetic chemical compounds that can be extracted by simple, low-cost procedures and are water-soluble and biodegradable in nature.

References

[1] J. Benard, A. Michel, J. Philibert, J. Talbot, Métallurgie générale, Masson Editeurs (1969)

[2] DIN EN ISO 8044:" Corrosion of Metals and Alloys-Basic Terms and Dentitions" (ISO 8044: 1999) Trilingual version EN ISO 8044:1999.

[3] Bommersbach Pascal, (2005). Evolution des propriétés d'un film inhibiteur de corrosion sous l'influence de la température et des conditions hydrodynamique : caractérisation par techniques électrochmimiques. Thése. Villeurbanne: Institut National des Sciences Appliquées de Lyon.

[4] Corrosion Costs and Preventive Strategies in The United States, Report by CC Technologies Laboratories, Inc. to Federal Highway Administration (FHWA), Office of Infrastructure Research and Development, Report FHWA-RD-01-156 (2001)

[5] H.E. Waldrip, Present Day Aspects of Condensate Well Corrosion, *Corrosion*, 4(12): 611-618 (1948). https://doi.org/10.5006/0010-9312-4.12.611

[6] E. Hamner Norman, Scope and importance of inhibitor technology. in: Ed. By C.C. Nathan, Houston, NACE Corrosion Inhibitors. USA: National Association of Corrosion Engineers, (1973) 28.

[7] E. H. Norman, NACE Glossary of Corrosion Terms. *Materials Protection,* 4: 79-80 (1965).

[8] D. Landolt, Corrosion et Chimie de Surface des Métaux, 1st Edition, Alden Press, Oxford, (1993) 489.

[9] C. Fiaud, C. Lemaitre, N. Pébère. Inhibiteurs de corrosion. In : G. Béranger, H. Mazille, Corrosion et Anticorrosion (pratique industrielle), Hermès Science Publications, Paris, (2002) 245.

[10] S. Locquet, M. Lagrenée, J. Bonnans, F. Bentiss, Patent Wo, 10179 (2002).

[11] MILLET, J. P., - Durabilité et corrosion (cours Master Science et Technologie des Matériaux), Pitesti, (2008) ;

[12] E. Schaschl. NACE Corrosion Inhibitors, USA, National Association of Corrosion Engineers, (1973) 28.

[13] M. Dupart. Thèse de Doctorat d'état, INP Toulouse, France, (1981)

[14] D. Landolt., « Corrosion et chimie de surfaces des métaux ». Presses polytechniques et Universitaires Romandes, Vol. 12, Lausanne, 1997.

[15] E. McCafferty *; J. Electrochem. Soc.*, 12(3): 385 (1979).

[16] K. Khaed, M. M. Al-qahtani L, The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution : Chemical, electrochemical and theoretical studies, Materials Chemistry and Physics, 113, 1, 150-158, (2009)

[17] L.I. Antropov, 1st International Congress on Metallic Corrosion, Butterworths, London, (1962) 147.

[18] E. Mc.Cafferly, Corrosion control by coalin. Sciences press, Princeton, ISBN 978-0-471-73279-2 (1979)

[19] V. Carrassiti. *3th Europ. Corros. Inhibitor ferrara, Italy,* 525, (1970)

[20] D. Landolt., « Corrosion et chimie de surfaces des métaux ». Presses polytechniques et Universitaires Romandes, Vol. 12, Lausanne, (1997).

[21] A.G. BARD et L.R. Faulkner, Electrochimie, Edition Masson, ISBN : 9782225785955 (1983) 578.

[22] Z. GALIS, Fundamentals of electrochemical Analysis, Ellis Horwood limited. New York. (1976).

[23] R.I. Masel. Principles of adsorption and reaction on solid surfaces. NewYork: Willey, **ISBN**: 978-0-471-30392 (1996).

[24] B. Sathianandhan, K. Ralahrishnan, N. Subramyan, Triazoles As Inhibitors of Corrosion of Mild Steel In Acids, *Br. Corros. J.*, 5 : 270-273 (1970). https://doi.org/10.1179/bcj.1970.5.6.270

[25] A. Lgamri Thèse de doctorat, Faculté des Sciences de Rabat, N° d'ordre : 1877 (2000).

[26] J. O'M. Bockris et D.A.D. Swinkels, Adsorption of n - Decylamine on Solid Metal Electrodes, *J. Electrochem. Soc.*, 111 : 736 (1965). https://doi.org/10.1149/1.2426222

[27] B. Assouli, Thèse de doctorat, INSA de Lyon, N° :02ISAL0103 (2002) 164.

[28] E. Bayol, K. Kayakırılmaz, M. Erbil, The inhibitive effect of hexamethylenetetramine on the acid corrosion of steel, *Mater. Chem. Phys.* 104: 74-82 (2007). https://doi.org/10.1016/j.matchemphys.2007.02.073

[29] J. Aljourani, K. Raeissi, M. A. Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution, *Corros. Sci.* 51: 1836-1853 (2009). https://doi.org/10.1016/j.corsci.2009.05.011

[30] M. Duprat, F. Dabosi, F. Moran, S. Rocher, Inhibition of corrosion of a cabon steel by the aliphatic fatty polyamines in association with organic phosphorous compounds in 3% sodium chloride solution. *Corrosion-Nace*, 37: 262-266 (1981).

[31] N. Tsuji, K. Nazawa, Ultrathin proctective films prepared by modification of an N,N-dimethylalkylamine monolayer with chlorosilanes for preventing corrosion of iron. *Corrosion Science*, 42, 1523-1538 (2000).

[32] A. Shriri, M.Etman, F.Dabosi, Electro and physicochemical study of corrosion inhibition of carbon steel in 3% NaCL by alkymidazoles. Electrochimica Acta, 1996, vol.41, pp.429-437.

[33] S. Turgoose, In: Poroceeding of the 6th Europen Symposium of Corrosion inhibitors, Ann. Univ. Ferrara (Italie),1985, p.1041.

[34] D. A. Lopez, W. H. Schreiner, S.R. De Sancez, S.N. Simison, The influence of carbon steel microstructure on corrosion layers. An XPS and SEM characterization. *Applied Surface Science*, 207: 69-85 (2003).

[35] H. H. Hassan, Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part II: Time and temperature effects and thermodynamic treatments, *Electrochim. Acta*, 53: 1722-1730 (2007). https://doi.org/10.1016/j.electacta.2007.08.021

[36] H. H. Hassan, E. Abdelghani, M. A. Amina, Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part I. Polarization and EIS studies, *Electrochim. Acta*, 52: 6359-6366 (2007). https://doi.org/10.1016/j.electacta.2007.04.046

[37] M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. El Kadiri, B. Hammouti, M. Benkaddour,

Inhibitive action of some bipyrazolic compounds on the corrosion of steel in 1 M HCl -part I- Electrochemical study, *Mat. Chem. Phys.,* 105: 373-381 (2007).

[38] K. Tebbji, M. El kodadi, M. Benkaddour, H. Oudda, B. Hammouti, A. Ramdani, Inhibitive action of two bipyrazolic isomers towards corrosion of steel in 1 M HCl solution, *Appl. Surf. Sci.* 241: 326-334 (2005).

[39] Moha Outirite, M. Lagrenée, Monim Lebrini, Michel Traisnel, Charafeddine Jama, Hervin Vezin, Fouad Bentiss, AC impedance, X-ray photoelectron spectroscopy and density functional theory studies of 3,5-bis(n-pyridyl)-1,2,4-oxadiazoles as efficient corrosion inhibitors for carbon steel surface in hydrochloric acid solution, *Electrochim. Acta*, 55: 1670-1681 (2010). https://doi.org/10.1016/j.electacta.2009.10.048

[40] M.Z.A. Rafiquee, N. Saxena, S. Khan, M.A. Quraishi, Influence of surfactants on the corrosion inhibition behaviour of 2-aminophenyl-5-mercapto-1-oxa-3,4-diazole (AMOD) on mild steel, *Mater. Chem. Phys.* 107: 528-533 (2008). https://doi.org/10.1016/j.matchemphys.2007.08.022

[41] G. Achary, H.P. Sachin, Y. Arthoba Naik, T. V. Venkatesha, The corrosion inhibition of mild steel by 3-formyl-8-hydroxy quinoline in hydrochloric acid medium, *Mater. Chem. Phys.* 107: 44-50 (2008). https://doi.org/10.1016/j.matchemphys.2007.06.038

[42] V. R. Saliyan, A. V. Adhikari, Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propanohydrazide as an effective inhibitor of mild steel corrosion in HCl solution, *Corros. Sci.* 50: 55-61 (2008). https://doi.org/10.1016/j.corsci.2006.06.035

[43] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Al Himidi, H. Hannache, 2,3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1M HCl, *Mater Chem Phys* 105: 1-5 (2007). https://doi.org/10.1016/j.matchemphys.2007.03.037

[44] S.A. Abd El-Maksoud, A.S. Fouda, Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium, *Mater. Chem. Phys.* 93: 84-90 (2005). https://doi.org/10.1016/j.matchemphys.2005.02.020

[45] A.B. da Silva, E. D'Elia, J.A.C.P. Gomes, Carbon steel corrosion inhibition in hydrochloric acid solution using a reduced Schiff base of ethylenediamine, *Corros. Sci.* 52: 788-793 (2010). https://doi.org/10.1016/j.corsci.2009.10.038

[46] N. Soltani, M. Behpour, S.M. Ghoreishi, H. Naeimi, Corrosion inhibition of mild steel in hydrochloric acid solution by some double Schiff bases, *Corros. Sci.,* 52: 1351-1361 (2010). https://doi.org/10.1016/j.corsci.2009.11.045

[47] E. E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, U.J. Ibok, Effect of molecular structure on the efficiency of amides and thiosemicarbazones used for corrosion inhibition of mild steel in

hydrochloric acid, *Mater. Chem. Phys*, 60: 79-90 (1999). https://doi.org/10.1016/S0254-0584(99)00074-7

[48] S. D. Shetty, P. Shetty, H.V. Sudhaker Nayak, The inhibition action of N-(furfuryl)-N′ -phenyl thiourea on the corrosion of mild steel in hydrochloric acid medium, *Mater. Lett.* 61: 2347-2349 (2007). https://doi.org/10.1016/j.matlet.2006.09.009

[49] A.K. Singh, M.A. Quraishi, The effect of some bis-thiadiazole derivatives on the corrosion of mild steel in hydrochloric acid, *Corros. Sci.* 52: 1373-1385 (2010). https://doi.org/10.1016/j.corsci.2010.01.007

[50] F. Bentiss, M. Lebrini, M. Lagrenée, M. Traisnel, A. Elfarouk, H. Vezin, The influence of some new 2,5-disubstituted 1,3,4-thiadiazoles on the corrosion behaviour of mild steel in 1M HCl solution: AC impedance study and theoretical approach, *Electrochim. Acta,* 52: 6865-6872 (2007). https://doi.org/10.1016/j.electacta.2007.04.111

[51] S.H. Shim, D. A Johnson, B.E Moriarty. Characterization of localized and underdeposit corrosion in cooling water system. In: NACE Corrosion’88 Meeting, March 21-25, (1988), Saint-Louis, Missouri(USA).

[52] F. Mansfeld, M. W. Kendig, W.J. Lorenz, Inhibition in Neutral, Aerated Media. *Journal of Electrochemical Society,* 32: 290-296 (1985).

[53] N. Ochoa, G. Baril, F. Moran, N. Pebere, Study of the properties of a multi-component inhibitor used for water treatment. In cooling circuits. *Journal of Applied Electrochemistry,* 32: 497-504 (2002).

[54] K. Tebbji, N. Faska, A. Tounsi, H. Oudda, M. Benkaddour, B. Hammouti, The effect of some lactones as inhibitors for the corrosion of steel in 1 M hydrochloric acid, *Mater. Chem. Phys.* 106: 260-267 (2007).

[55] M.A. Amin, S.S. Abd El-Rehim, E.E.F. El-Sherbini, R.S. Bayoumi, *Electrochim. Acta,* 52: 3588 (2007).

[56] G. Avci, Corrosion inhibition of indole-3-acetic acid on mild steel in 0.5 M HCl, *Colloids Surf.*, A 317: 730-736 (2008). https://doi.org/10.1016/j.colsurfa.2007.12.009

[57] A.D. Mercier, in: Proceeding of the 5th European Sympsium of corrosion Inhibitors, Ann. Univ. Ferrara (Italie), (1980), p.553.

[58] S. Andreani, M. Znini, Paolini, L. Majidi, B. Hammouti, J. Costa, A. Muselli, Application of Senecio Inaequidens Essential Oil and Its Fractions as Eco-friendly Inhibitors of Mild Steel Corrosion in 1M HCl Solution, *Int. J. Electrochem. Sci.* 8: 11896-11915 (2013).

[59] E. Stupnišek-Lisac, A. Gazivoda, M. Madžarac, Evaluation of non-toxic corrosion inhibitors for copper in sulphuric acid, *Electrochim. Acta,* 47: 4189-4194 (2002). https://doi.org/10.1016/S0013-4686(02)00436-X

[60] C. A. Loto, O. O. Joseph, R. T. Loto, A. P. I. Popoola, Inhibition Effect of Vernonia amygdalina Extract on the Corrosion of Mild Steel Reinforcement in Concrete in 3.5M NaCl Environment, *Int. J. Electrochem. Sci.* 8: 11087-11100 (2013).

[61] A. S. Mahdi, S. K. Raheem, Corrosion inhibition of reinforced steel by thymus vulgarize (thyme) extract in simulated chloride contaminated concrete pore solution, *Journal of Advanced Research in Engineering and Technology (IJARET)* 5: 89-98 (2014).

[62] A.S. Mahdi, Amoxicillin as green corrosion inhibitor for concrete reinforced steel in simulated concrete pore solution containing chloride, *Journal of Advanced Research in Engineering and Technology (IJARET),* 5: 99-107 (2014).

[63] A. Singh, A. Kumar, T. Pramanik, A Theoretical Approach to the Study of Some Plant Extracts as Green Corrosion Inhibitor for Mild Steel in HCl Solution, *Orient. J. Chem.* 29: 277-283 (2013).

[64] P.B. Raja, M.G. Sethuraman, Natural Products as Corrosion Inhibitor for Metals in Corrosive Media A Review. *Mater. Lett.* 62: 113-16 (2008).

[65] S. Kertit, B. Hammouti et A. Melhaoui, Bgugaine (Bg) as excellent inhibitor of iron corrosion in HCl solution, *Moroccan Pattent* N° 23175 (1995).

[66] B. Hammouti, S. Kertit, A. Melhaoui. Electrochemical behaviour of bgugaine as corrosion inhibitor of iron in HCl medium. *Bulletin of Electrochemistry* 13: 97-98 (1997).

[67] S. Kertit, B. Hammouti, A. Melhaoui. a natural pyrolidine alkaloid product as corrosion inhibitor of iron in HCl medium. *Bulletin of Electrochemistry* 11: 553-555 (1995).

[68] M. Bouklah, B. Hammouti, Thermodynamic characterisation of steel corrosion for the corrosion inhibition of steel in sulphuric acid solutions by Artemisia, *Portug. Electrochim. Acta,* 24: 457-468 (2006).

[69] B. Benjilali, J. Sarris, H. Richard, Nouveaux chémotypes d'*Artemisia herba-alba*., *Sci. Aliment.* 2 : 515-527 (1982).

[70] A. Bouyanzer, B. Hammouti, L. Majidi. Pennyroyal oil from Mentha pulegium as corrosion inhibitor for steel in 1 M HCl. *Materials Letters.* 60: 2840-2843 (2006).

[71] A.Y. El-Etre, Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves, *Journal of Colloid and Interface Science,* 314: 578–583 (2007) https://doi.org/10.1016/j.jcis.2007.05.077

[72] Z. Faska, A. Bellioua, M. Bouklah, L. Majidi, R. Fihi, A. Bouyanzer, B. Hammouti, Effect of pulegone and pulegone oxide on the corrosion of steel in 1 M HCl, *Monatsh. Chem.* 139: 1417-1422 (2008).

[73] S.A. Umoren, E.E. Ebenso, *Pigment & Resin Technology*, 37: 173–182 (2008).

[74] S.A. Umoren, I.B. Obot, E.E. Ebenso, *E-Journal of Chemistry*, 5: 355-364 (2008).

[75] K. Orubite-Okorosaye, I. R. Jack, M. Ochei, O. Akaranta, *J. Appl. Sci. Environ. Manage.*, 11: 27 (2007)

[76] P.P. Kumar, K. Kannan, M. Natesan. *J. Metall. Mater. Sci.* 50 (4): 227 (2008).

[77] N. Poongothai, T. Ramachanderen, M. Natesan, S.C. Murugavel. *Mater. Perform. (NACE International).* 48 (9): 52-56 (2009).

[78] A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, P.V. Rodrigues, Corrosion inhibition by Justicia gendarussa plant extract in hydrochloric acid solution, *Corrosion Science*, 51: 2848–2856 (2009). https://doi.org/10.1016/j.corsci.2009.08.016

[79] E. El Ouariachi, J. Paolini, M. Bouklah, A. Elidrissi, A. Bouyanzer, B. Hammouti, J-M. Desjobert, J. Costa, Adsorption properties of Rosmarinus officinalis oil as green corrosion inhibitors on C38 steel in 0.5M H2SO4, *Acta Metall. Sin.* 23 (1): 13-21 (2010).

[80] M. Dahmani, A. Et-Touhami, S.S. Al-Deyab, B. Hammouti, A. Bouyanzer, Corrosion inhibition of C38 steel in 1 M HCl: A comparative study of black pepper extract and its isolated piperine, *Int. J. Electrochem. Sci.*, 5: 1060 – 1069 (2010).

[81] M.H. Hussin, M. J. Kassim, The corrosion inhibition and adsorption behavior of Uncaria gambir extract on mild steel in 1M HCl, *Mater. Chem. Phys.* 125: 461 (2011). https://doi.org/10.1016/j.matchemphys.2010.10.032

[82] A. Lecante, F. Robert, P.A. Blandinières, C. Roos, Anti-corrosive properties of S. tinctoria and G. ouregou alkaloid extracts on low carbon steel, *Current Applied Physics*, 11: 714-724 (2011). https://doi.org/10.1016/j.cap.2010.11.038

[83] A. Lecante, F. Robert, M., Lebrini, C. Roos, Inhibitive Effect of Siparuna Guianensis Extracts on the Corrosion of Low Carbon Steel in Acidic Media, *Int. J. Electrochem. Sci.*, 6: 5249 - 5264 (2011).

[84] M. Faustin, M. Lebrini, F. Robert, C. Roos, Corrosion Studies of C38 Steel by Alkaloids Extract of a Tropical Plant Type, *Int. J. Electrochem. Sci.*, 6: 4095 - 4113 (2011).

[85] M. Lebrini, F. Robert, P.A. Blandinières, C. Roos, Corrosion Inhibition by Isertia coccinea Plant Extract in Hydrochloric Acid Solution, *Int. J. Electrochem. Sci.*, 6: 2443 – 2460 (2011).

[86] M. Lebrini, F. Robert, C. Roos, Alkaloids Extract from Palicourea guianensis Plant as Corrosion Inhibitor for C38 Steel in 1 M Hydrochloric Acid Medium, *Int. J. Electrochem. Sci.*, 6: 847 – 859 (2011).

[87] P.B. Raja, A.K. Qureshi, A. A. Rahim, H. Osman, K. Awang, Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1M HCl media, *Corrosion Science,* 69: 292–301 (2013). https://doi.org/10.1016/j.corsci.2012.11.042

[88] S. L. A. Kumar, P. Iniyavan, M. S. Kumar, A. Sreekanth, A., Corrosion Inhibition Studies of Ecbolium Viride Extracts on Mild Steel in HCl, *J. Mater. Environ. Sci.*, 3: 461-468 (2012).

[89] M. Gopiraman, P. Sakunthala, D. Kesavan, V. Alexramani, I. S., Kim, N. Sulochana, An investigation of mild carbon steel corrosion inhibition in hydrochloric acid medium by environment friendly green inhibitors, *J. Coat. Technol. Res.*, 9: 15–26 (2012). https://doi.org/10.1007/s11998-011-9374-6

[90] L. Afia, R. Salghi, El. Bazzi, A. Zarrouk, B. Hammouti, M. Bouri, H. Zarrouk, L. Bazzi, L. Bammou, Argan hulls extract: green inhibitor of mild steel corrosion in 1 M HCl solution, *Res Chem Intermed,* 38: 1707- 1717 (2012). https://doi.org/10.1007/s11164-012-0496-y

[91] N. O. Eddy, B. I. Ita, S. N. Dodo, E. D. Paul, Inhibitive and adsorption properties of ethanol extract of Hibiscus sabdariffa calyx for the corrosion of mild steel in 0.1 M HCl, *Green Chemistry Letters and Reviews,* 5: 43-53 (2012). https://doi.org/10.1080/17518253.2011.578589

[92] H. Gerengi, H. I. Sahin, Schinopsis lorentzii Extract As a Green Corrosion Inhibitor for Low Carbon Steel in 1 M HCl Solution, *Ind. Eng. Chem. Res.*, 51: 780 –787 (2012). https://doi.org/10.1021/ie201776q

[93] P.M. Krishnegoda, V.T. Venkatesha, P.K.M. Krishnegowda, S.B. Shivayogiraju, *Ind. Eng. Chem. Res.* 52 : 722−728 (2013).

[94] O. Benali, H. Benmehdi, O. Hasnaoui, C. Selles, R. Salghi, Green corrosion inhibitor: inhibitive action of tannin extract of Chamaerops humilis plant for the corrosion of mild steel in 0.5 M H2SO4, *J. Mater. Environ. Sci.* 4 (1) : 127-138 (2013).

[95] Y. El ouadi, A. Bouyanzer, L. Majidi, J. Paolini, J. M. Desjobert, J. Costa, A. Chetouan, B. Hammouti, Salvia officinalis essential oil and the extract as green corrosion inhibitor of mild steel in hydrochloric acid, *J. Chem. Pharm. Res.* 6(7): 1401-1416 (2014)

[96] G. Ji, S. Anjum, S. Sundaram, R. Prakash, *Musa paradisica* peel extract as green corrosion inhibitor for mild steel in HCl solution, *Corros. Sci.* 10: 107-117 (2014) https://doi.org/10.1016/j.corsci.2014.10.002

[97] I. Hamdani, E. El Ouariachi, O. Mokhtari, A. Salhi, A. Bouyanzer, A. Zarrouk, B. Hammouti, J. Costa, An investigation of mild steel corrosion inhibition in hydrochloric acid medium by environment friendly green inhibitor, *Der Pharmacia Lettre,* 7 (9): 109-118 (2015)

[98] S. K. Sharma, A. Peter, I.B. Obot, Potential of Azadirachta indica as a green corrosion inhibitor against mild steel, aluminum, and tin: a review, *Journal of Analytical Science and Technology*, 6: article 26 (2015) https://doi.org/10.1186/s40543-015-0067-0

[99] A. Boujakhrout, I. Hamdani, N. Chahboun, A. Bouyanzer, R. V. Santana, A. Zarrouk, Antioxidant activity and corrosion inhibitive behavior of Garcinia cola seeds on mild steel in hydrochloric medium, *J. Mater. Environ. Sci.* 6 (12) : 3655-3666 (2015)

[100] A. Boujakhrout, I. Hamdani, O. Krim, A. Bouyanzer, R. V. Santana, A. Zarrouk, B. Hammouti, H. Oudda, Kimbiolongo extract as corrosion inhibitor for mild steel in 1.0 M HCl, *Der Pharmacia Lettre,* 8(2): 180-187 (2016)

[101] I.Y. Suleiman, M. Abdulwahab, F.E. Awe, A Study of The Green Corrosion Inhibition of Acacia tortilis Extract on Mild Steel in Sulphuric acid Environment. Acid Environment., *Journal of Advanced Electrochemistry* 2(1): 50–55 (2016)

[102] A. Salhi, A. Bouyanzer, I. El Mounsi, I. Hamdani, H. Bendaha, R. Rmili, H. Akichouh, M. Allali, A. Zarrouk, B. Hammouti, J. Costa, Inhibitive of methanol extract of Pennyroyal Mint (Mentha pulegium) on the corrosion of mild steel in HCl, *Der Pharmacia Lettre,* 8(2): 33-42 (2016)

[103] A. Salhi, A. Bouyanzer, I. El Mounsi, I. Hamdani, H. Bendaha, R. Rmili, H. Akichouh, A. Zarrouk, R. Touir, B. Hammouti, J. Costa, Natural product extract as eco-friendly corrosion inhibitor for mild steel in 1M HCl, *Der Pharmacia Lettre*, 8(2): 79-89 (2016)