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Electrochemical evaluation of natural extracts as effective corrosion inhibitors and surface treatments on metal substrates

ABSTRACT

Corrosion is a serious problem encountered in the industry, protection from it is more than necessary using inhibitors and treatments. These treatments can effectively ease the problem on the surface of the material substrate, particularly the metal substrate for being easily etched during usage and being unable to withstand abrasion. Experimental results showed that the extracts are effective inhibitors of corrosion. Polarization tests indicate that the inhibitors are of mixed nature and the corrosion mechanism does not change after their addition to the solution. The electrochemical impedance spectroscopy confirmed that inhibitory quality and surface treatments improved corrosion resistance. Surface analysis revealed that the surface of the sample for the control solution was covered and protected. However, for the inhibited solutions the presence of oxides was not observed.

Keywords: corrosion protection, inhibitor, surface treatments

1. INTRODUCTION

Corrosion is well known as the result of a chemical or electrochemical action of an environment on materials such as metals and alloys. It is a scourge that affects the materials used in many industrial fields: petroleum, electrical, chemical, nuclear industries, port facilities, environment, civil engineering, agrifood, and health. The ramifications are significant in many domains, but particularly in the industry: production halts, component replacements for corroded parts, pollution hazards, and accidents are common occurrences with occasionally severe financial repercussions. Corrosion causes significant economic losses, estimated at around US\$2.5 trillion per year globally (Koch et al., 2016) [1, 2], which is approximately 3.4% of the worldwide gross domestic product (GDP). In the United States alone, corrosion costs 875 billion dollars per year according to the National Association of Corrosion Engineers (NACE).

The reactivity of industrial materials to their environments is reflected in corrosion.

We distinguish two main processes of corrosion [3]:

- The electrochemical corrosion (or wet corrosion);
- The corrosion dryers. (or high-temperature gas corrosion).

The fundamental study of corrosion phenomena in the middle-wet falls primarily into electrochemistry, while their study is an applied field of science of materials that includes at the time the concepts of chemistry and physics. The corrosion phenomena take place on the surface of metallic materials exposed to an environment chemically aggressive. Not only is the priming of the corrosion but also its propagation; essentially a surface process both chemical and electrochemical.

Also, to study these mechanisms, electrochemical techniques are essential.

Thus, all this is likely to deteriorate: Corrosion is the permanent damage that a metal sustains from a chemical or electrochemical reaction with its surroundings. It can take many different forms, such as uniform, localized, etc., and it changes the properties of materials.

Regarding anti-corrosion measures, actions can be taken against the material itself (e.g.,

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selecting appropriate constraints based on application requirements, painting, coating, applying various surface treatments, etc.) or the environment that comes into contact with the material to be protected.

Today, protection against corrosion consists of a variety of treatments such as metallic coating or surface treatment, cathodic protection, or even the modification of the corrosive medium by adding inhibitors of corrosion. These latter ones constitute an original way to fight against corrosion. These are substances that, when added at low concentrations in corrosive media, reduce or even prevent the reaction of the metal within its environment. The trend today is the combination of two or more of these means of protection. The modified cerium seal PEO pretreatment significantly enhances the corrosion protection of 2A14 Al alloy by creating a robust duplex coating system. This system combines a cerium-based PEO coating with an epoxy layer, resulting in improved adhesion and long-term corrosion resistance. [3-5].

Among the methods, the most used one to protect the structural steel industry is coatings loaded with corrosion inhibitors. The paint additives known for their inhibitory effectiveness against corrosion are chromates, molybdates, tungstates, vanadates, phosphates, and polyphosphates [4]. However, these compounds are characterized by their significant toxicity (for chromates) and/or a detrimental effect on the environment. LDH (Layered double hydroxide) coatings contain a variety of inhibitors that are intercalated and may offer persistent corrosion protection. It illustrates the inhibitor release kinetics of LDHs as well as corrosion prevention mechanisms [6]. The inhibiting action of these pigment particles in paints relies on their dissolution in water, allowing inhibiting ions to diffuse to the metal surface and ions with the properties of inhibition must diffuse and reach the surface of the metal to repair and inhibit the phenomenon of corrosion. Corrosion inhibition performances of zinc were studied by potentiodynamic measurements and electrochemical impedance spectroscopy [7]. Several studies have shown that the salts soluble in the base of cerium, lanthanum, yttrium [8], and calcium [9] can be considered as inorganic inhibitors [10].

The materials capable of fulfilling the role of the corrosion inhibitor are of the lamellar type. Their structure consists of a stack of sheets, generally of inorganic nature. The latter can be either neutral such as metal sulphides MPS 3 ($M = \text{Mn, Zn, Cd}$), or anionic types of double lamellar hydroxides (HDL) or basic salts of hydroxides, or either cationic such as clay minerals of smectite types.

Heavy metals found in the water by industrial pollution and agricultural processing as well as the corrosion of the distribution piping, accumulate in food chains. Even at low concentrations, these heavy metals are very toxic.

For this, different electrode materials are studied and proposed by different researchers, as needed:

- To enhance the rate of electrochemical oxidation, various electro-catalytic metals, such as Pt and Au, as well as their alloys and compounds like Ti/Pt, have been utilized. Their main problem during oxidation at a constant potential, despite their high activity, is the loss of catalytic activity as a consequence of the formation of the species that block the surface of the anode. Also, these activated electrodes promote electrochemical conversion more than incineration and are very expensive, which limits their industrial applications.
- To reduce the costs of these processes, various anodes that are cheaper and available were proposed as steel or carbon materials such as carbon graphite or glassy carbon [11, 12]. In general, these electrodes have much lower catalytic activity and chemical and/or electrochemical corrosion problems.
- The boron-doped diamond anode (Boron-Doped-Diamond, BDD) has received a lot of attention in these recent years. Due to its great potential of Oxygen Evolution Reaction (OER) the reaction of oxygen release, it has a very high efficiency (100%) in the combustion of organic compounds in aqueous medium and its extreme stability (chemical and electrochemical). Therefore, the high costs of manufacture as well as their great fragility constitute negligible drawbacks.
- Scientific research is directed to the Metal Oxide Electrodes of Dimensionally Stable Anode (DSA) to try to solve all the problems associated with the previous electrodes. This is due to the enormous instability of metal oxides when optimizing electro-catalytic properties, the stability and the prices of the electrodes, by appropriate selection of various metallic elements, and the ability to prepare and file various media by simple and inexpensive techniques.

When the electrode is brought to a potential higher than that of the evolution of oxygen, competitive reactions that consume electrons, such as the formation of peroxide compounds, can limit the direct oxidation of the organic compounds present in the solution.

However, these oxidizing species can react with organic compounds to oxidize them in turn.

Not all electrode materials produce these oxidants, and in particular hydroxyl radicals, with the same efficiency. Much research has been devoted in recent years to the study of the treatment of wastewater polluted by organic compounds; the most efficient materials are those that have a high potential for the release of oxygen.

The comparison of the oxygen evolution potentials shows that the metal oxides and the boron-doped diamond have much larger electrochemical windows than platinum. This entails, under positive polarization in the region of the oxidation of water, the possibility of producing very oxidizing species that are very little adsorbed, and therefore particularly active for oxidation. Overall, this results in a remarkable electro-catalytic activity in organic compounds. In other words, the potential for oxygen evolution increases with the decrease in the adsorption force of hydroxyl radicals on the electrode; for example, the boron-doped diamond electrode has lower adsorption properties than the platinum.

The researchers worked in the field of Dimensionally Stable Anode (DSA) studied in depth, from the preparation to the characterization of these electrodes to understand and improve their electro-catalytic properties and their stability. Although the first RuO_2 -based DSA electrodes are emerging for their application in the Cl_2 -NaOH industry. The following years gave a step to the appearance of new electrode materials which are based on the original concept of DSA to find new applications.

Thus, in addition to the generation of Cl_2 , in most cases, the anodes of DSA are used against the electrode of a cathode of interest in several processes (production of hydrogen, electrodeposition of metals, electro galvanizing, protection against corrosion, etc.) wherein the anodic reaction in aqueous solution is mainly the OER. The most commonly used anode in these applications is Ti / IrO_2 [13].

However, over the past 20 years, DSA electrodes have experienced massive growth in the oxidation of organic and inorganic compounds. In particular, in the treatment of industrial water [14, 15], for which scientists have prepared and characterized other electrodes made of metal oxides.

RuO_2 and IrO_2 were the most studied metal oxides. These two oxides have some points in common, such as good conductivity (metal type) and a crystalline structure like rutile. However, this crystal structure is adopted by many dioxides of several metals, belonging to the p block (Sn, Pb, Ge, Te, and Si) as transition metals of the 3d, 4d,

and 5d series (Ti, Cr, Mn, Nb, Ru, Rh, Ta, Ir, Pt, and some others).

In practice, the big problem is centered on the loss of coating due to the dissolution of the active metal oxide. The chemical dissolution is favored when the ligands involved in the electrolyte (NH_3 , CN^- , OH^- and others that can form the complexes) or activators of the corrosion (Cl^- or F^- for example) [18]. The dissolution or the electrochemical corrosion can occur at potentials at which the coating is not stable, being oxidized and forming soluble species.

Erosion of the coating can occur, especially if the adhesion between the particles and the coating is not good and too porous, the evolution of gas can separate the particles and remove them. One deactivation mechanism occurs during the anodic process when chemical changes alter the electrode's conductive properties. For example, it has been proposed that the SnO_2 electrodes are deactivated by the formation of a passivating layer from the hydration of the outer layer.

The deactivation by passivation of the base metal is different from known mechanisms on all electrodes which operate at high current densities. It can happen in three ways:

- When the ions go through the pores and cracks of the coating, with the support, by reacting and/or the remover in a way that it causes a loss of adhesion and therefore local coating losses (stripping);
- With the formation of an insulating layer (for example TiO_2), added to the active material, formed during the heat treatment, due to the migration of ions and electrons at the support/oxide interface (the poorly adherent layer may also cause a coating loss);
- When the TiO_{2-x} oxide, is formed during heat treatment [15, 16], it loses its non-stoichiometric conductive conformation and changes to its insulating stoichiometric configuration (TiO_2), due to the migration of O_2 species through the coating.

Given the different deactivation mechanisms, several strategies have been proposed in the bibliography to extend the useful life of this type of electrode:

- Choice of support.
- Control of the coating thickness
- The use of the stable conductive interlayer.
- Doping of the coating with stabilizers (mixed oxide).

Regarding the choice of support, Vercesi et al. [17] carried out a detailed study on the corrosion of the different valve metals used as supports. For information, a "valve metal" is a metal that is

covered with a thin layer of protective oxide when it is oxidized (passivation) and which does not pass the current that is under a cathodic potential. They concluded that the best base metal was the tantalum, Ta. However, the Ti was the one used at an industrial scale because its properties, as a substrate, lower than Ta, are good enough and the price is much lower.

Another way to prevent or delay the formation of the insulating oxide is the addition of an oxide capable of creating solid solutions (interlayer) conductors with TiO_2 , such as iridium which forms mixed oxides of type of $\text{Ir}_x\text{Ti}_{(1-x)}\text{O}_2$. The deactivation of this type of mixed oxide electrodes occurs by the migration of the noble metal from the substrate/oxide layer interface to the outer oxide layer.

After much research, researchers found that the most stable electrode for OER in an acidic environment is Ti / IrO_2 (70%) - Ta_2O_5 (30%) [18]. So, to improve performance both in OER and in other electrochemical reactions, they studied the properties of several mixed oxides, with one active species (which provides catalytic activity) and other inactive species (which provides stability).

For the basic medium, the most stable and catalytic electrodes in the OER have been those based on cobalt spinel [19]. However, these electrodes do not exhibit strong activity in the oxidation of aromatic organic compounds. In this way, and since the vast majority of studies on electrode optimization have been designed for use in the acidic medium, it is necessary to further study the stability and deactivation in the basic medium with new electrodes that have good performance for their use in this medium.

2. MATERIALS AND METHODS

Corrosion resistance is not an intrinsic property of a given metal, but rather a property of the metal / medium interface. Hence, the characterization of the chemical composition of the microstructure of the metal as well as its electrochemical behavior is required. In addition, the corrosion behavior depends on the various stresses to which the material is subjected, whether they are physico chemical, thermal, or mechanical. One inferred that any means of action to prevent and/or fight against corrosion concerns one of the three elements of the system studied even its whole.

The inhibitors of corrosion constitute an original way of combating the corrosion of metals and alloys. The originality comes from that the anticorrosion treatment should not be done on the metal itself (choice of intrinsically corrosion-resistant material) but by the intermediary of the corrosive medium. It does this not, however, to

change the kind of the medium, but to add the inhibitor formulation (isolated molecule, mixture of molecules) in small amounts to the corrosive environment.

Natural extracts have emerged as an eco-friendly and sustainable solution for mitigating metal corrosion, offering a viable alternative to conventional synthetic inhibitors, which are often toxic and environmentally harmful. These extracts are typically derived from plant sources such as leaves, seeds, fruits, barks, and roots, and they contain a rich blend of organic compounds with diverse chemical structures. The primary constituents responsible for corrosion inhibition include alkaloids, flavonoids, tannins, saponins, terpenoids, and essential oils. These compounds possess functional groups like hydroxyl (-OH), carbonyl (C=O), carboxyl (-COOH), and nitrogen or sulfur-containing groups that can adsorb onto the metal surface, forming a protective barrier that isolates the metal from corrosive agents such as oxygen, chloride ions, and moisture. This adsorption process often follows Langmuir or Temkin isotherms, indicating the formation of a monolayer of inhibitor molecules on the metal surface.

For instance, the extract of *Lawsonia inermis* (henna), which is rich in lawsone and tannins, has demonstrated high corrosion inhibition efficiency on mild steel, often exceeding 90% under optimal conditions. Similarly, extracts from *Allium sativum* (garlic) containing sulfur-rich compounds like allicin have shown significant inhibition effects on copper corrosion. Another example is the use of green tea extract, derived from *Camellia sinensis*, which is abundant in catechins and polyphenols that exhibit strong antioxidant properties, thereby reducing the anodic and cathodic reactions responsible for metal dissolution and hydrogen evolution. The mechanism of action generally involves the adsorption of active compounds onto the metal surface, forming a physical and chemical barrier that decreases the metal's exposure to corrosive environments, thus reducing the corrosion current density and shifting the corrosion potential in electrochemical tests.

Electrochemical techniques such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) are widely used to evaluate the efficacy of natural extracts as corrosion inhibitors. Potentiodynamic polarization provides information on the reduction in corrosion current density and the nature of inhibition, whether predominantly anodic, cathodic, or mixed. EIS, on the other hand, measures the charge transfer resistance (R_{ct}) and the capacitance of the double layer, offering insights into the integrity and stability

of the protective film formed by the inhibitor. For instance, the impedance spectra of metals treated with pomegranate peel extract, rich in polyphenols and tannins, often reveal a significant increase in charge transfer resistance, indicating the formation of a robust protective layer.

Despite their numerous advantages, including biodegradability, non-toxicity, and cost-effectiveness, the use of natural extracts as corrosion inhibitors faces certain challenges. The complex and variable composition of plant extracts can lead to inconsistencies in inhibition performance, and their stability under harsh conditions may be limited. Moreover, the presence of multiple active components can make it difficult to pinpoint the exact compound responsible for the inhibition, complicating efforts to optimize and standardize their use. Nonetheless, ongoing research aims to address these limitations by exploring synergistic effects between different plant extracts, improving extraction techniques to enhance the concentration of active compounds, and developing formulations that improve their stability and efficiency in various corrosive environments. Overall, natural extracts hold significant promise as a green and sustainable approach to corrosion control, aligning with global efforts to reduce environmental impact and promote the use of renewable resources.

- In order to provide a unique form of protection, an inhibitor or a combination of inhibitors can be used. This can be done either permanently, allowing the use of metallic materials (unalloyed ferrous, for example) under acceptable conditions of corrosion resistance, though installation monitoring is necessary [20]. In this situation, it will be easier to predict the inhibitor's behavior in the short term, and, in theory, the system control will be more straightforward. Either as temporary protection during a period when the workpiece or the installation is particularly sensitive to corrosion (storage, stripping, and cleaning).
- An inhibitor or an inhibitor mixture may be combined with other means of protection: protection by adding a coating surface of paint, grease, oil, etc...

The inhibitor is a chemical substance added to the corrosion system at a concentration chosen for its effectiveness, which causes a decrease in the corrosion rate without changing significantly the concentration of the corrosive agent contained in the aggressive environment. Generally, an inhibitor should reduce the rate of corrosion of a metal, without affecting the physico-chemical characteristics, particularly the mechanical strength (e.g., risk of embrittlement by the hydrogen in an acid

medium). An inhibitor must be stable in the presence of the constituents of the medium, in particular, vis-à-vis the oxidants. An inhibitor must be stable at temperatures of use. An inhibitor should be effective at low concentrations. An inhibitor must be compatible with the standards for non-toxicity. An inhibitor should be inexpensive.

3. RESULTS

Corrosion is the irreversible deterioration of a metal caused by a chemical or electrochemical interaction within its surroundings. It can take many different forms, such as uniform, localized, etc., and changes the properties of the materials in question.

Regarding corrosion prevention, actions can be taken against the material itself (e.g., by applying corrosion inhibitors), on the material's surface (coating, painting, surface treatment of any kind), or on the environment the material comes into contact with (choice-wise, forms adapted constraints in the function of applications...) [20–22].

However, prevention against corrosion must be considered from the design phase of an installation. The preventative measures taken in good time allow to avoid many problems when it comes to ensuring a certain time of life for an object, especially for industries such as nuclear, chemical, or aeronautics, where the risk of accident can have particularly serious consequences for people and the environment.

Other researchers [21] show that alkylamines are strongly chemisorbed on the surface of iron, with the sharing of electrons between nitrogen and the atoms of the metal. This then results in a very good inhibition of the corrosion of iron in an acidic medium. It should be noted, however, that the alkylamines, classified as fairly strong bases, adsorb, preferentially, at the surface of ferrous and ferric oxides and hydroxides (considered as strong acids), which may explain the poor protection of the underlying metal.

There are more complex compounds such as aminobenzimidazole act as mixed inhibitors for the protection of brass (Cu / Zn alloy) where they inhibit corrosion by blocking the anodic and cathodic sites by the formation, on the surface of the brass, of a protective film consisting of complexes of Cu (II) and Zn (II). Aminobenzimidazole acts as a metal-coordinated bidentate ligand through nitrogen from the amino group ($>C=NH$) and nitrogen from the cyclic azole group ($=C-NH$) [22].

The amines that regulate the pH or the alkalization of the medium are intended to react chemically with the acidic species to neutralize

them. These properties tend to be operated to lower the activity of protons in the corrosive solution: neutral medium at temperature ordinarily the increase of the pH causes the metal in a region where the corrosion is slowing down (please revise the meaning of this sentence in red). Contrary to amine filaments, amine neutralizing will not protect against corrosion due to the presence of oxygen dissolved in the electrolyte [23].

Amines are considered to be a very efficient functional group against the corrosion of ferrous metals due to the combination of weak base properties with adsorption properties. In some cases, their inhibition can be further enhanced when combined with other types of molecules, such as carboxylic acids [24].

The hydrolysis of aluminum dihydrogen triphosphate (ATP), produces H^+ + protons [25], which could neutralize the hydroxyl ions resulting from the reduction of dissolved oxygen on the metal substrate, thus prolonging the life of the organic coatings [26]. The protective performance using ATP as a pigment was investigated by Dongdong Song [27], under full immersion conditions, of a water-based acrylic paint, applied to steel. The data obtained have permitted to provide the following protection mechanism: the specific pigments used in the paint formulation showed the release of phosphates that form a protective on the metal substrate, which interfere with the result, access of aggressive species on the surface of the substrate and will prevent the corrosion reaction thus protecting the substrate.

Moreover, it is only recently that the first successful implementation of nanocomposite orthophosphate of zirconium/polyurethane (α -ZrP / PU), for protection against corrosion, has been published [28]. α -ZrP / PU nanocomposite films are PU-based with different ZrP contents from 0.5 to 5% by weight. The results revealed that α -ZrP was dispersed very well in PU films with improved moisture barrier properties of α -ZrP / PU films and that no substantial agglomeration occurred, comparing a series of measures of electrochemical potential for corrosion (E_{corr}), the strength of polarization (R_p), the current of corrosion (i_{corr}) and of the spectroscopy impedance electrochemical performed on the coatings ZrP / PU and PU pure, applied on the electrodes in cold rolled steel. The inhibition of zinc corrosion in NaCl medium has been the subject of numerous studies in which different chemical compounds have been used. We cite here those whose results were more striking.

The use of other cationic type of inhibitors such as Ce^{3+} and La^{3+} could be put to the point [29]

and gave satisfaction with the efficiencies of the order of 91.2 % and 93.9 % respectively. The mode of protection in this case is provided by the formation, on the cathodic sites, of thick layers of $Ce(OH)_3$, Ce_2O_3 , or $La(OH)_3$ and La_2O_3 , which provide cathodic protection. Zinc, in addition to the formation of small amounts of $Zn(OH)_2$ and ZnO which have a barrier effect against the diffusion of oxygen as previously reported. Corrosion protection of bronze in a 3% NaCl solution. Potentiodynamic polarization curves were used to determine the anodic and cathodic behavior, indicating the effectiveness of the extract as a mixed-type inhibitor. The study also quantifies the phenolic content through HPLC analysis, which highlights the role of rutin, quercetin, and gallic acid in the inhibition process [30].

Recently, the inhibition by the organic molecules as the tricine [N- (Tri (hydroxymethyl) methyl) glycine (phrase incomplete, à revoir)]. It comes out that the latter can be considered as an inhibitor anode, of corrosion of zinc in the solutions of chloride neutral. An effective inhibitory of about 90.4 % has been registered in the presence of 10 mM. Tricine in a solution NaCl 0.5 M. This inhibition was the result of the adsorption of the inhibitor molecules through the atom of oxygen and/or an atom of nitrogen on the active centers in the area of the electrode, forming a barrier that blocks the process of anode corrosion [31].

In various fields, the production of coatings from nanostructures makes it possible to endow the surface with new functionalities in terms of appearance, hardness, adhesion, corrosion resistance, and wettability and permits to increase their performance and thermal or electrical conductivity. mechanical, chemical, or thermal resistance, etc ... while limiting production costs. Moreover, these materials are often multifunctional, making it possible to couple various functions at the same time.

In the field of optics, the structuring of the surface brings several functionalities to the surface. It reduces reflection and increases the absorption capacity of incident light [32, 33]. In addition, it also allows to provide coloration to a material without the use of dye [34]. Beyond its effects, the surface structuring can present very selective characteristics in wavelength and/or polarization. This property gives these devices the ability to behave like an optical filter [35] that can be adjusted by controlling the geometric parameters of the surface patterns.

In the field of tribology, one crucial factor that determines how well a mechanical contact performs is its surface structure. It affects not only the amount of lubricant transported but also the

quality of surface separation, which in turn affects wear and friction [36]. In the field of medical applications, the surface micro and nanostructuring of implants is a parameter to be taken into account in the cellular response. Positive bone reactions have been observed on dental implants, linked with their nanostructuring [37-39].

In the field of anti-corrosion coating applications, surface nanostructuring can provide other interesting properties to the material concerning protection against corrosion: mechanical properties such as flexibility and solidity, and therefore impact resistance. This is the case with the coating produced by Greer et al. with Caltech having on the surface nanopillars 100 nm in diameter of metallic glass rich in zirconium (Zr 35 Ti 30 Co 6 Be 29) [40].

In the field of self-cleaning coatings, neoculturation of the surface is essential. Corrosion and contamination of metallic structures can cause loss of their functionality as well as aesthetic values, self-cleaning, and anti-corrosion surfaces for metallic structures. [41-43]. Many works have tried to artificially reproduce the surface of the lotus leaf which is covered with micro/nano textures. Therefore, at this surface topography water does not fill the space between surface textures and relies on air. This configuration allows the drop of water to roll without adhering to the surface, which gives it the ability to wash away the dust present on the surface, hence the designation of a self-cleaning surface. Nanostructured materials at the surface constitute a class of nanomaterials that combine both properties at the nanometer scale as well as their synergy to either amplify existing ones or create new ones. The synergy between the properties of the patterns at the surface results both from the size of the patterns, from their organization, and the physical couplings between the patterns. According to the preparation methods mentioned in this chapter, a control of the size, the morphology and the spacing between the patterns is possible, and this is via the technical parameters of each of the methods. In the case of techniques using a mask, the properties (size, morphology, and spacing between patterns) of the textures prepared depend on those of the mask. On the other hand, for the techniques not using a mask, the properties of the textures are imposed by the parameters of the technique and the processing conditions. The hydrophobic systems can be prepared in one step by creating a surface roughness from a material having low surface energy such as perfluorinated compounds (tetrafluoroethylene...) [44,45], silicon [46-49], organic materials (polystyrene, alkylketene dimers,

polyamide, etc...) [50- 59], inorganic materials (ZnO , TiO_2 and SnO_2) [50-55]. According to the work of Ralph Hulseman of Hoowaki, nanostructured surfaces have been developed and were shaped in the form of small pillars of polymers such as silicone [56] on metal surfaces such as aluminum or steel. The first function is hydrophobicity with drop angles exceeding 150° (super-hydrophobic). This results in an anti-wetting effect, favorable against pathogens and atmospheric corrosion, but above all an oleophilic property resulting in reduced friction. In fact, on the one hand, a smaller quantity of oil is necessary, and on the other hand, in the event of a drop of oil falling on the substrate, it will be able to spread and thus reduce the risk of default.

Most hydrophobic systems are prepared in two stages: the first stage consists of forming a rough surface and the second of depositing on this surface a molecular film with low surface energy of the Teflon type [57]. The synergy of the two steps makes it possible to obtain optimal hydrophobicity. To obtain superhydrophobic surfaces, molecules of SiO_2 or silanes are chemically deposited by vapor phase (CVD) on various surfaces, the drop angles obtained are very high, greater than 170° and the deposition time is less than one minute. We can also cite examples of adsorption of Thiols on noble metals such as Ag [58].

Hydrophobic surfaces can be a solution against corrosion, as the wetting time is considerably reduced [59]. In this context, the work of GK Kannarpady et al. has shown that coatings composed of tungsten or aluminum nanorods from 25 to 75 nm provide the anti-icing property, which is highly sought after in aeronautics [60,61]. The functionalization of these nanostructured coatings by "Teflon-like" silanes brings to the surface a superhydrophobic behavior ($164^\circ \pm 3^\circ$). This protection can be used in drinking water pipes against corrosion.

Law and Zhao of the Xerox company [62] have shown that PTFE (Teflon) certainly has superhydrophobic but oleophilic properties. By adding super oleophobic character to surfaces, better performance is obtained. In addition, their work confirms that high hydrophobicity is not necessarily a sign of low adhesion and that the sliding angle of a drop of water can be high even for a surface with a high contact angle. To ensure the oleophobicity, tests were carried out on etched silicon to obtain pads 7 μm high, 3 μm in diameter, and with a spacing of 6 μm , on which is deposited by phase molecular deposition vapor (MVD: molecular vapor deposition).

TiO₂ also exhibits photo-induced super-hydrophobicity, that is to say, a contact angle θ between the surface and water of about zero degrees under UV exposure [63]. This property has been widely studied for anti-fog applications. The vapor easily blurs the view through a mirror or glass due to the many water droplets that condense on the solid surface. In the case of a TiO₂ coating exposed to UV, the water does not settle in the form of drops but is spread on the superhydrophobic surface. The opposite option aimed at eliminating water drops from the surface by playing on super-hydrophobic properties has also been proposed. However, this alternative does not make it possible to eliminate the mist deposited on the surface without the water drops being removed by an external intervention: the force of the wind, vibration, or manual intervention. Conversely, under practical conditions, vision is never disturbed by the spreading of water on a superhydrophilic surface [64].

It is interesting to note that the photoinduced super hydrophilicity enters into synergy with the photocatalytic activity of TiO₂ because the two phenomena occurred under UV irradiation. Thus, surface contamination can be totally or partially reduced (or made less toxic) by photocatalysis and the photodecomposition residues (partially mineralized elements) can be removed by a simple operation of rinsing with water, without the need for detergent. The combination of these two properties leads to the self-cleaning application. Over the past decade, self-cleaning devices have demonstrated their many benefits. In particular, they can be installed in outdoor or even indoor atmospheres, since UV rays do not only form part of the solar spectrum (typically 5%) but are also emitted by many indoor lighting devices, albeit in quantity much lower than solar radiation (typically 1 $\mu\text{W} / \text{cm}^2$, i.e. 10 times less). Because of these arguments, many self-cleaning products have been marketed in Japan, USA, Europe, and many other countries [65].

In a general manner, there is a variety of protective inhibitors that effectively addresses corrosion for every type of material. In neutral, alkaline, or acidic conditions, there are a wide range of corrosion inhibitors available for iron metal research. It has been established how carbon steel behaves electrochemically when alkyl imidazoles which are present in a NaCl solution [66]. It is observed that the number of atoms in the chain alkyl as well as the concentration of each organic substance examined both affect the effectiveness of corrosion inhibition. With 11 carbon atoms, the corrosion has been effectively and maximally

inhibited. The organic chemicals are adsorbed on the metal surface at low concentrations. An adsorption molecule is then "flat" on the electrode and acts on the process cathode as a result. An additional layer forms at high concentrations, enabling the inhibitor to cover the electrode's anode as well. The process anode and/or cathode mechanisms are altered in the two scenarios.

The behavior of mild steel in the presence of the triazole derivative 3,5-bis (4-methylthiophenyl) - 4H- 1,2,4-triazole) has been studied in acidic media, HCl (1 M) and H₂SO₄ (0.5 M). The results indicate that the inhibitory efficacy can reach values of the order of 99% and 80%, respectively [67]. The corrosion inhibition effect of *Calotropis procera* extract on 304 stainless steel in a 2 M HCl solution. Electrochemical methods such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PP), and electrochemical frequency modulation (EFM) were used to analyze the adsorption behavior, which followed the Langmuir adsorption isotherm. Surface morphology was also evaluated using various techniques [68]. The primary process of inhibition was caused by the molecules of triazole derivatives adhering to the steel surface. The latter turned out to be the Langmuir isotherm that was impacted by two modes: adsorption of the derivative of triazole with the doublets free of atoms of sulfur and/or of nitrogen or well of electrons the nucleus aromatic which act with orbital of vacancies of iron and adsorption of anions from the medium to the surface of the iron (Cl⁻ - SO₄²⁻ ...) which will attract the forms protonated derivative of triazole.

The characterizations of the corrosion products reveal the presence of a protective layer of iron III heptanoate on the metal surface while the impedance measurements indicate the great improvement in the corrosion protection of the steel in NaCl (0.1 M). This efficacy has been attributed to the release of progressive heptanoate clay on the one hand, and its fibrous morphology enhancing the barrier properties of the coating polymer on the other hand. In general, the molecules inhibiting the most commonly employed and the least toxic are the amines or even the salts of carboxylic acids, which are also present in the inhibitor zirconium orthophosphates, and are extensively studied because of their physico chemical properties. The main properties of these minerals are their ability to exchange their cations by exchange reactions thanks to their high cation exchange capacity; and their intercalation property of organic entities of different sizes. These qualities give them the name of the reservoir of cations or organic compounds.

The study of the cation exchange properties has also been completed with varying degrees of success by exchanging the labile protons of Zr orthophosphate by the Ca^{2+} , Mg^{2+} , and Zn^{2+} ions which present an interest in the field of inhibiting aqueous metallic corrosion. The conditions of ion exchange were explored by varying the temperature, by keeping in touch directly the dispersion of $\alpha\text{-ZrP}$ with the solutions of salts of metal corresponding ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) or by neutralizing them with the corresponding bases in the case of exchange by Ca^{2+} ($\text{Ca}(\text{OH})_2$) or by passing through the sodium form of $\alpha\text{-ZrP}$ ($\text{Na}^+ - \text{ZrP}$). The different characterizations of structural, microstructural, thermal, and spectroscopic performed on the compounds derived $\text{CaZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{Ca}^{2+} - \text{ZrP}$), $\text{MgZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{Mg}^{2+} - \text{ZrP}$), and $\text{ZnZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{Zn}^{2+} - \text{ZrP}$) agree to demonstrate the successful intercalation of the different cations within the interfoliar spaces of $\alpha\text{-ZrP}$ causing their expansion of 0.98 nm for $\text{Ca}^{2+} - \text{ZrP}$, and 0.96 nm for $\text{Mg}^{2+} - \text{ZrP}$, and $\text{Zn}^{2+} - \text{ZrP}$. However, it is important to note that less crystallized $\alpha\text{-ZrP}$ prepared under reflux ($\alpha\text{-ZrP-R}$) is ready better to exchange cation than the highly crystallized synthesized by the hydrothermal way $\alpha\text{-ZrP-H}$. Of more, intercalation of the cation metal into the compound $\alpha\text{-ZrP-R}$ is easy in the order given: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+}$. The study of inhibitory effect of corrosion zinc electrodes and mild steel has been extensively studied by different electrochemical techniques: measurement of corr, polarization, and spectroscopy impedance electrochemical for $\alpha\text{-ZrP}$ and $\text{Ca}^{2+} - \text{ZrP}$ because of the ease of intercalation Ca^{2+} into the interleaving space of $\alpha\text{-ZrP}$. Also, thanks to their properties of acid-base, the dispersions of materials to the base of $\alpha\text{-ZrP}$ alter the pH of a corrosive solution such as NaCl (0.1 M) exchange internal protons in the case of $\alpha\text{-ZrP}$ or exchange of protons of the area in the case of $\text{Ca}^{2+} - \text{ZrP}$. Thus, in the context of inhibition of the corrosion process, they act as inhibitors to corrosion by buffering the pH at the surface of the zinc and avoiding any increase of the pH due to the corrosion. In this sense, the best performance was achieved with $\text{Ca}^{2+} - \text{ZrP}$ which provides the terms chemically interesting to interface the electrochemical of zinc. The results of the analysis of metal surfaces by XRD and SEM, after the electrochemical tests, showed the formation of layers protective against corrosion. In fact, in the presence of $\text{Ca}^{2+} - \text{ZrP}$, a layer of zinc oxide (ZnO) and calcium phosphate was developed on bare zinc, while the presence of $\alpha\text{-ZrP}$ leads to the formation of zirconium, and zinc phosphates. For the corrosion inhibitor and the release of the latter

the second time, which was easily confirmed by obtaining, after the electrochemical test, from the stage sodium of $\alpha\text{-ZrP}$ after the replacement of entities organic by Na^+ cations, as well as by the formation of different protective layers as in the case of Cs-ZrP , where a very thin layer of zinc hydroxy heptanoate $[\text{Zn}_5(\text{OH})_8(\text{C}_7\text{H}_{13}\text{O}_2)_2]$ precipitated on bare zinc.

In addition, the products formed on the surface also have the effect of limiting the diffusion of oxygen and corrosive ions towards the metal surface, thus reducing the rates of corrosion. For the two parts, the orthophosphates of zirconium modified either by way of exchange cationic or by reactions acid-base have been used as fillers in the resin alkyd to test their electrochemical behavior on zinc and/or steel. The assessment of the inhibitory action of these loads (5 mass%) was achieved through spectroscopy electrochemical impedance (EIS) in a solution of NaCl (0.5 M).

As regards the corrosion of zinc, the sample RA-ZrP shows a performance of important protection that remains almost constant between 99 and 98 % during 768 hours of immersion of zinc. It should be noted that the organic coatings containing fillers based on $\alpha\text{-ZrP}$ and used as corrosion inhibitors exhibit an inhibitory efficiency that is better or at least comparable to that of ATP. This is explained by their laminated microstructure which improves the "barrier" properties of the coating. Also, these compounds act as mini tanks through their ability to release corrosion inhibitors over time and conferring the coating self-healing properties and ensuring the longevity of protection.

4. CONCLUSIONS

The fight against corrosion of materials, in a medium of hydrochloric acid of concentration 1M, by inhibitors of extracts. From the polarization tests, it appears that these three inhibitors are of mixed nature and the corrosion mechanism was not changed after their addition to the solution. Other analytical methods were used to further investigate the study, using the concentrations considered. The electrochemical impedance spectroscopy (EIS), allowed us to confirm the inhibitory quality and also to identify the corrosion mechanism, which takes place by charge transfer as well as the mode of inhibition by adsorption of the inhibiting molecules. This model assumes that the corrosion inhibition is due to the formation of a monolayer on the metal surface, reducing contact with the electrolyte, and that the interactions between the adsorbed particles are negligible. Tests on the influence of temperature, in the range of 25-60 °C, on the inhibitory power have shown that the increase in temperature decreases the

inhibitory effectiveness of the compounds considered. This suggests that their adsorption to the sample surface is electrostatic. Therefore, the determination of thermodynamic activation parameters confirmed this. Scanning electron microscopy showed the presence of a uniform protective layer covering the entire surface of the steel. Surface analysis revealed that the surface of the sample for the control solution was covered with iron oxide (Fe_2O_3). However, in the inhibited solutions, no presence of oxides was observed, which indicates that the steel surface is perfectly isolated from the solution by the adsorbed protective film.

Natural extracts serve as effective green corrosion inhibitors due to their rich composition of bioactive compounds capable of adsorbing onto metal surfaces and forming protective barriers against corrosive agents. Alkaloid-based inhibitors like quinine from *Cinchona* bark, nicotine from tobacco (*Nicotiana tabacum*), and berberine from *Berberis* species reduce corrosion by interacting with the metal surface through nitrogen atoms. Flavonoids such as quercetin from onions and tea, catechin from green tea (*Camellia sinensis*), and rutin from citrus fruits inhibit corrosion by chelating metal ions and forming stable complexes. Tannin-rich inhibitors like tannic acid from tea and oak bark, and ellagic acid from pomegranate, form insoluble layers that protect the metal. Terpenoids like limonene from citrus peels, thymol from thyme, and menthol from mint provide hydrophobic protection, while sulfur-containing compounds such as allicin from garlic and sulforaphane from broccoli disrupt corrosion reactions at the metal surface. Essential oil components like eugenol from clove, carvacrol from oregano, and cinnamaldehyde from cinnamon enhance corrosion resistance by forming antioxidant-rich films. Additionally, lawsone from henna (*Lawsonia inermis*), curcumin from turmeric (*Curcuma longa*), and azadirachtin from neem (*Azadirachta indica*) exhibit excellent inhibition efficiency through both physical and chemical adsorption, making natural extracts a promising, sustainable alternative to conventional synthetic inhibitors.

It has been demonstrated that the inhibitors function mostly as mixed inhibitors. The findings regarding the effect of concentration indicated that, at a concentration of 0.04 g/L, the highest efficiency was attained, with 96% of the saffron and 95% of the turmeric at that concentration. The anode and cathode current densities decreased as the concentration increased, according to the polarization curves. For all concentrations examined, impedance diagrams have demonstrated that this is a mechanism of charge transfer over a heterogeneous surface. A capacitive loop, which is typically thought to be a

representation of the charge transfer resistance at the metal/electrolyte contact, is included in the diagrams. Variations in concentration have an impact on the amplitude of the diagrams, as the concentration rises, so does the capacitive loop's size.

Future research in corrosion inhibition and surface treatments on metals is poised to focus on the development of green and sustainable inhibitors, particularly those derived from natural extracts, agricultural waste, and bio-based polymers, which offer eco-friendly alternatives to traditional toxic inhibitors. However, challenges remain in optimizing their chemical composition, improving their long-term stability, and understanding their adsorption mechanisms at the molecular level. The advancement of multifunctional surface treatments, such as nanostructured coatings, graphene-based films, and metal-organic frameworks (MOFs), is also a key area of exploration, with emphasis on enhancing properties like self-healing, antibacterial resistance, and mechanical robustness. Despite their potential, these advanced materials face challenges in scalability, cost-effectiveness, and durability under extreme conditions, such as high temperatures, salinity, and acidic environments, commonly encountered in industries like marine, oil and gas, and aerospace. Additionally, there is a critical need to deepen our understanding of corrosion mechanisms at the nanoscale through the use of advanced characterization techniques, such as atomic force microscopy and in situ transmission electron microscopy, to develop predictive models that link nanoscale behavior to macroscopic performance. The integration of machine learning and artificial intelligence offers a promising pathway for accelerating the discovery of new inhibitors and optimizing surface treatments, though the lack of standardized datasets and interpretable models remains a significant barrier. Moreover, research efforts must address the long-term performance and durability of corrosion inhibitors and coatings, emphasizing field testing and real-world applications to bridge the gap between laboratory results and practical use.

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Conflicts of Interest

The author declared no conflict of interest.

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IZVOD

ELEKTROHEMIJSKA PROCENA PRIRODNIH EKSTRAKATA KAO EFIKASNIH INHIBITORA KOROZIJE I POVRŠINSKIH TRETMANA NA METALNIM PODLOGAMA

Korozija je ozbiljan problem sa kojim se susrećemo u industriji i zaštita od nje je više nego neophodna upotrebom inhibitora i tretmana. Ovi tretmani mogu efikasno da ublaže problem na površini materijalne podloge, posebno metalne podloge jer se lako urezuje tokom upotrebe i ne može da izdrži abraziju. Eksperimentalni rezultati su pokazali da su ekstrakti efikasni inhibitori korozije. Polarizacioni testovi pokazuju da su inhibitori mešovite prirode i da se mehanizam korozije ne menja nakon njihovog dodavanja u rastvor. Spektroskopija elektrohemijske impedanse je potvrdila da su inhibitorni kvalitet i površinski tretmani poboljšali otpornost na koroziju. Površinskom analizom utvrđeno je da je površina uzorka za kontrolni rastvor pokrivena i zaštićena. Međutim, za inhibirane rastvore nije primećeno prisustvo oksida.

Ključne reči: zaštita od korozije, inhibitor, površinski tretmani.

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