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Plant extracts as green corrosion inhibitors for mild steel in corrosive media

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بسم الله الرحمن الرحيم

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Dedication

The journey was neither short nor easy; it was filled with challenges and moments of doubt. But I am here by the grace and guidance of God, completing this humble work.

I dedicate this work first and foremost to myself for enduring, for hoping, and for never giving up.

To my beloved parents, who gave me unconditional love and care, who were a guiding light in my life, and who gave me strength by believing in my abilities.

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I also dedicate this work to everyone who supported me in this project,

from my family and loved ones.

With all my gratitude

Sabrina Hamdi

Abstract:

Through this work, we aim to study the inhibitory effect of wild thyme leaf extracts on the corrosion of mild steel in two different media, one acidic and the other basic. We first conducted a chemical examination to identify the most important active components present in the plant extract.

The results obtained confirmed that the plant extracts have a good effect against steel corrosion. Using the gravimetric method, we obtained an inhibitory efficiency of up to 78.23% in acidic media, while it did not exceed 33.33% in basic media, due to the weak corrosion of steel.

We also achieved similar results using electrochemical methods (polarization and electrochemical impedance) in acidic media, where the inhibitory efficiency was 74.48% and good results in basic media 70.71 %.

Keywords: Steel corrosion, green inhibitor, wild thyme, gravimetric method, electrochemical method.

الملخص:

نهدف من خلال هذا العمل إلى دراسة التأثير التثبيطي لمستخلصات أوراق نبات الزعتر البري على تآكل الفولاذ اللين وسطين مختلفين أحدهما حامضي والثاني قاعدي، حيث قمنا في البداية بالفحص الكيميائي لمعرفة أهم العناصر الفعالة الموجودة في المستخلص النباتي.

أكدت النتائج المتحصل عليها أن للمستخلصات النباتية تأثيرا جيدا ضد تآكل الفولاذ، حيث تحصلنا باستخدام الطريقة الوزنية على كفاءة تثبيطية تصل إلى 78.23 % في الوسط الحمضي بينما لم تتجاوز 33.33 % في الوسط القاعدي وذلك بسبب ضعف تآكل الفولاذ.

كما توصلنا إلى نتائج مقاربة باستخدام الطرق الكهروكيميائية (الاستقطاب والمعاوقة الكهروكيميائية) في الوسط الحمضي حيث كانت الكفاءة التثبيطية 74.48 % ونتائج جيدة في الوسط القاعدي 70.71 %.

الكلمات المفتاحية: تآكل الفولاذ، المانع الأخضر، الزعتر البري، الطريقة الوزنية، الطريقة الكهروكيميائي.

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General Introduction

General Introduction

Metals are widely used in human activities due to their excellent mechanical and electrical properties. In order to preserve the desired state of these metals, their preventive maintenance is a priority. Corrosion is probably the most common undesired phenomenon that leads metals to become weaker . This natural process originates from the electrochemical interaction of metals with the corrosive environment. Sulfides, oxides, and others are generated through reactions between the metal surface and the corrosive medium [1].

Among metals, mild steel is the most widely used in the oil, food, energy, chemical, and construction industries due to its different applications, most of which are based on its excellent mechanical properties. This metal shows high mechanical resistance, durability, and toughness, among others,which makes it a highly available material and at a relatively low cost. Consequently, solutions to problems related to the degradation by the corrosion of steel, mostly mild steel, is a high-priority topic. to a lesser extent, copper and aluminum alloys are studied as well. The high cost associated with corrosion, due to the replacement of rusted metals, can be reduced by using corrosion inhibitors [2].

Significant investigative research has been focusing on the development of corrosion inhibitors for ferrous metal alloys. One of the most extensive investigations is the development of green corrosion inhibitors (GCIs). The GCIs from plant extract, which are the most widely investigated due to inexpensive, renewable, biodegradable and foremost aspect, are safe towards both the environment and human being. The performance of GCIs is evaluated by gravimetric analysis, electrochemical tests as well as theory and computational-based studies. A compilation of the inhibition performance calculated from these methods in various conditions is well reported. Plant extracts proved to be a good corrosion inhibitor where the result of inhibition efficiency is over 80%. This high efficiency is related to the high concentration of active constituent known as phytochemicals (flavonoids, alkaloids, tannins, etc) [3].

In this study, we used wild thyme (from the Oued Souf region) as a green corrosion inhibitor. Wild thyme is a perennial aromatic herb and shrub rich in natural antioxidants. It also contains essential vitamins and minerals important for optimal health. Its leaves are considered among the richest sources of potassium, iron, calcium, manganese, and magnesium [4].

The present investigation examined the corrosion behavior of mild steel over specific time intervals in both hydrochloric acid HCl 1M and sodium hydroxide NaOH 1M media, using wild thyme extract as a green corrosion inhibitor. The inhibitor's efficiency was evaluated through both gravimetric (loss of mass) and electrochemical techniques.

The work that we present in this manuscript is subdivided into four chapters and a conclusion:

- The first chapter presents a bibliographic study on metal corrosion and corrosion inhibitors.
- The second chapter provides general information about wild thyme.
- The third chapter describes the experimental procedures and the equipment used.
- The last chapter contains all the results and discussions.

Finally, a general conclusion summarizes the main findings of this dissertation.

Theoretical part

Chapter One

Metal corrosion and inhibitors

I- Generality on the Corrosion of metals

I-1. Introduction

Corrosion can compromise the safety of operating equipment by causing failure of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms. Safety is a critical consideration in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Loss of metal by corrosion is a waste not only of the metal, but also of the energy, the water, and the human effort that was used to produce and fabricate the metal structures in the first place. In addition, rebuilding corroded equipment requires further investment of all these resources metal, energy, water, and human.[5]

I-2. Corrosion definition

Several official definitions of the term corrosion exist. According to the International Union of Pure and Applied Chemistry (IUPAC), “corrosion is an irreversible interfacial reaction of a material (metal) with its environment which results in consumption of the material.[6]

In its simplest definition “corrosion is the deterioration of desired physicochemical properties of metals by the environment”“Metallic corrosion is a spontaneous phenomenon by which a metallic material returns to its stable state (metal oxides or metal sulfides),Most corrosion processes are electrochemical in nature”.[7]

I-3. Corrosion Types

Corrosion can develop according to different prosses that each define a type of corrosion [8]

a- Chemical Corrosion

This corrosion is due to a heterogeneous reaction between the metal and a gas or liquid phase. If the reagent is gas, corrosion is called "dry or oxidation"; on the other hand if the reagent is liquid, corrosion takes place with formation of a corrosion product on the surface of the metal.

There is no electric current in this type. We rarely meet this type of corrosion. It represents 3% of the total corrosion cases.[9]

b- Electrochemistry Corrosion

It occurs when there is heterogeneity, either in metal or in the surrounding environment. The existence of these heterogeneities determines the formation of a battery; An electric current then circulates between anode and cathode and the areas which constitute the anodes are the attacked centers. It manifests itself especially when one is in the presence of two redox couples, one donor, the other acceptor, justifying the appearance of an oxidation reaction of the metal.[8]

c- Biochemistry Corrosion

It is the bacterial attack on metals, especially in buried pipes. It is mainly due to the secrets of microorganisms present in the middle, in contact with metal.[8]

I-4. Corrosion forms

It is convenient to classify corrosion by the forms in which it manifests itself, the basic for classification being the appearance of corroded metal. Each form can be identified by mere visual observation. In most cases, the naked eye is sufficient but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable.

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are: [10]

I-4.1. Uniform corrosion

This is usually characterized by chemical or electrochemical reactions occurring on the reacting surface. The metal becomes thin and eventually there is a failure on the metal. Evenly corrosion is a very big deterioration of the material. However, this corrosion is bad observed because the age of the equipment can be accurately estimated with other simpler tests as shown in **Fig I.1**. [11]

Fig I.1: Uniform corrosion

I-4.2. Pitting corrosion

Pitting attacks exposed metal and forms pits (holes that go deep into the metal thickness). Contracted to uniform attack which occurs evenly all over the metal surface, pitting only forms holes in some areas. Holes resulted from pitting have various diameter measurements, which usually equal to their depth. Sometimes pits can be quite large, but in most of the case, they are relatively small. These small pits may form close together creating bigger pits and increase the damage.[12]

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Fig I.2 : Pitting corrosion

I-4.3. Galvanic corrosion

Also known as bimetallic corrosion, it is caused by the formation of an electrochemical between two metals. The degradation of the less resistant metal becomes intensive because it will behave like an anode. [9]

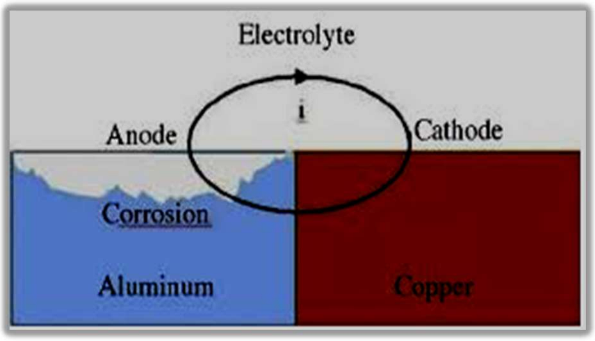


Fig I.3: Galvanic corrosion of aluminum

I-4.4. Stress corrosion cracking

The results from the combination of tensile stress, a susceptible material and a corrosive environment.[10]

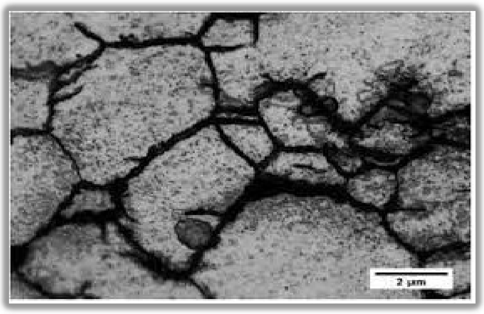


Fig I.4: Optical micrograph of Stress corrosion cracking

I-4.5. Crevice Corrosion

This form of corrosion is generally associated with the presence of small volumes of stagnant solution in deposits, joints or crevices.[12]

Fig I.5: Crevice Corrosion

I-4.6. Selective leaching

In this case, one element in an alloy dissolves preferentially. For example, zinc can leach out preferentially in a Cu--Zn brass.[13]

Fig I.6: Selective leaching

I-4.7. Erosion-Corrosion

This type of corrosion involves a combination of chemical attack and mechanical abrasion, which is worse than either alone.[13]

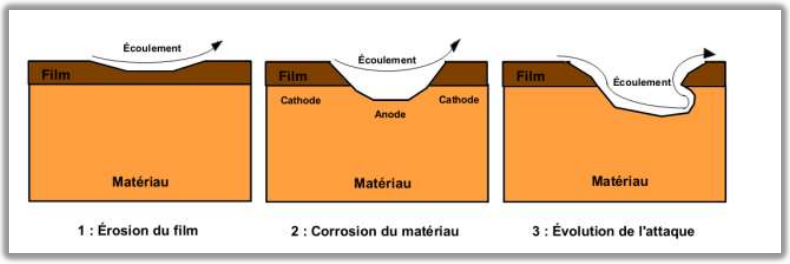


Fig I.7: Schematic representation of the corrosion-erosion phenomenon

I-4.8. Intergranular corrosion

IGC, also known as intergranular attack (IGA), is a type of corrosion in which the boundaries of crystalline materials are more susceptible to erosion than the interiors.[14]

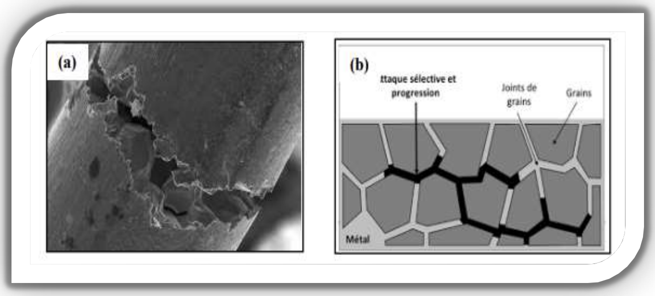


Fig I.8: Intergranular corrosion (a) and its mechanism(b)

I-5. Corrosion rate

The corrosion rate can be expressed in different ways depending on the application and personal preferences:[15]

- in the form of mass loss per unit area and per unit time.
- as the number of moles transformed per unit area per unit time.
- in corroded depth per unit time.
- as current density.

I-6. Factors Affecting Corrosion [16]

Corrosion behavior depends on a number of factors, which are classified into four groups:

1. **Environmental factors corrosive:**
    - Concertation of reagent.
    - Oxygen level
    - Medium pH
    - Temperature
    - Pressure
2. **Factors metallurgical**
    - Alloy composition
    - Production processes
    - Impurities

  - Heat treatment
  - Mechanical treatment

3. **Factors defining conditions of employment**
   - Surface finish
   - shape of parts
   - use of inhibitor
   - assembly processes
4. **Time-dependent factors**
   - ageing
   - mechanical stress
   - changes in protective coatings

I-7. Corrosion as a Chemical Reaction (Corrosion Mechanism)

The corrosion of metals is due to an irreversible oxidation-reduction reaction between the metal and an oxidising agent in the environment. The oxidation of the metal involves the reduction of the oxidising agent according to the reaction:[17]

Metal + oxidising agent → oxidised metal + reducing agent…………..Equ.1

Every redox reaction consists of two partial reactions: the partial oxidation reaction or anodic partial reaction, and the partial reduction reaction or cathodic partial reaction:

$Fe \rightarrow Fe^{+2} + 2e$ anodic ……………Equ.2

$2H^{+} + 2e \rightarrow H_2$ cathodic ……………..Equ.3

$Fe + 2H^{+} \rightarrow Fe^{2+} + H2$ global reaction ………………Equ.4

The corrosion process involves acid-base reactions as well as electrochemical reactions. It is the acid-base reactions that make metallic corrosion diversified depending not only on the electrode potential but also on the acid-base species present in the environment.[14]

I-7.1. Corrosion in Acids

One of the common ways of generating hydrogen in a laboratory is to place zinc into a dilute acid, such as hydrochloric or sulfuric. When this is done, there is a rapid reaction in which the zinc is attacked or “dissolved” and hydrogen is evolved as a gas:

$$Zn + 2\,HCl \rightarrow ZnCl_2 + H_{2\,(g)}$$

$$Zn + 2\,H^+ + 2Cl^- \rightarrow Zn^{2+} + 2\,Cl^- + H_{2\,(g)}$$

Many other metals are also corroded by acids, often yielding soluble salts and hydrogen gas, such as iron and aluminum. [14]

I-7.2 Corrosion in natural and alkaline solution

The corrosion of metals can also occur in fresh water, seawater, salt solutions, and alkaline or basic media. In almost all of these environments, corrosion occurs importantly only if dissolved oxygen is also present. Water solutions rapidly dissolve oxygen from the air, and this is the source of the oxygen required in the corrosion process.

The most familiar corrosion of this type is the rusting of iron when exposed to a moist atmosphere.

$$4\,Fe + 6\,H_2O + 3\,O_2 \rightarrow 4\,Fe\,(OH)_3 \downarrow \qquad [10]$$

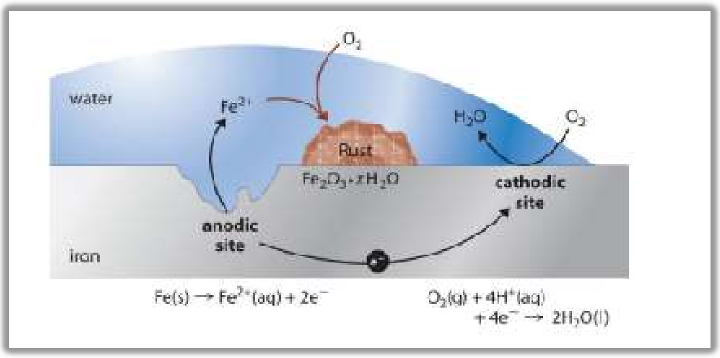


Fig I.9 Schematic illustration of corrosion mechanism

II. corrosion inhibitors

II-1. Definition

A corrosion inhibitor is a chemical substance that, when added in small quantities to a medium, effectively reduces the corrosion rate of the metal. They can act on the metal by modifying its surface state or by intervening on anodic or cathode reactions, they form a mono molecular layer on the metal by creating a barrier with the external medium.[18]

II-2. Inhibitor properties

For many objects, the strategy of applying a corrosion inhibitor is very interesting. This type of compound, added in low concentrations to the corrosive environments lows or stops the corrosion process of a metal. Generally speaking, an inhibitor formulation should**:**

- reduce the corrosion rate of a metal,

- be stable in the presence of other constituents of the medium,

- be stable at operating temperatures,

- be effective in low concentrations,

- be compatible with non-toxicity standards,

- be inexpensive.[19]

II-3. Use of inhibitors

- ✓ The oil industry: drilling, extraction, refining, storage and transportation.
- ✓ all stages of this industry, the use of corrosion inhibitors is essential to safeguarding installations. Water treatment (sanitary water, industrial process water, boiler water…etc).
- ✓ The temporary protection of metals, whether during acid pickling, plant cleaning or storage in the atmosphere (volatile inhibitors, incorporation into temporary protection oils and greases) or for the treatment of cutting oils.
- ✓ The metal paints industry, where inhibitors are additives that provide corrosion protection of metals.[20]

II-4. The mechanism of the inhibition process

There is no single general mechanism that can describe the behavior and mechanism of action of inhibitors because the mechanism of inhibition varies with several factors such as the concentration of the inhibitor, the pH of the solution, the nature of the ions in the solution, the presence of ions or foreign materials in the solution and the possibility of a reaction to form a secondary inhibitor, nature of the metal.

The mechanism of action of inhibitors is generally one or more of the three listed below:

1- Inhibitor chemisorption is chemically adsorbed on the metal surface and forms a thin protective film with a protective effect Inhibitor or by combining the inhibitor ions with the metal surface.
2- inhibitor leads to the formation of an oxide layer that protects the basic metal from corrosion.
3- The reaction of the inhibitor with the aqueous medium results in a complex medium that prevents metal corrosion.[21]

II-5. Classification of Corrosion Inhibitors

Inhibitors generally behave in two ways, either they form a protective shield on anodes or cathodes or they are directly adsorbed on the metal surface. Based on the mechanism, the inhibitors are divided into three groups: anodic, cathodic, and mixed, which are briefly discussed in Table 1.[22]

Table 1. A brief description of inhibitors based on mechanism.

Inhibitor	Corrosion Inhibition Method	The Most Common Inhibitor
Anodic	By forming a protective film along the anode, they increase their potential and reduce the corrosion reaction.	Chromates and tungstates
Cathodic	By blocking the cathode sites, they reduce the rate of the reduction reaction of the electrochemical corrosion cell, and as a result, the corrosion is reduced.	Elements arsenic and antimony
Mixed	By forming a film that causes deposits on the surface, they block the anodic and cathodic sites and delay corrosion.	Silicates and phosphates

II-6. Green inhibitors

Most of the commercially used inhibitors are synthetic and may have effective corrosion inhibition properties; however, they can lead to toxicity and environmental hazards. As a result, there is growing interest in alternative plant-based inhibitors that are cleaner and do not lead to environmental toxicity. Such environment-friendly inhibitors are commonly called as “green inhibitors”. Different extracts of natural products (e.g., plant roots, leaves, fruits, flower, etc.) are used as green inhibitors.[23]

green corrosion inhibitors are biodegradable, non-toxic, environmentally friendly, low in cost, and can be derived from renewable resources with minor health and safety risks.[24]

II-7. Factors affecting the efficiency of green inhibitors

green inhibitors efficiency in inhibiting corrosion is a function of their adsorption characteristics on the metal surface. Factors that have been considered by previous studies affecting green inhibitors inhibition efficiency depend majorly on their structure, concentration, temperature, and exposure time. An increase in green inhibitors concentration results in a simultaneous decrease in corrosion rate with an increase in inhibition efficiency, which approaches optimum level at a certain concentration value. This resulted from the formation of additional inhibitor molecules being adsorbed on the surface of the metal, which makes it complex for further corrosive attack to occur by the electrolyte solution. The dissolution of metal increases with corrosion exposure period in the presence of green inhibitors. This is linked to previously adsorbed inhibitor molecules from the metal surface resulting from partial desorption. Corrosion rate increases linearly as temperature increases such that an equilibrium exists between adsorption and green inhibitors molecule desorption at the surface of the metal at a particular temperature. An increase in temperature as a result of a higher desorption rate makes the equilibrium to shift until its reestablishment at various equilibrium constant values. Thus, green inhibitors inhibitive protectiveness decreases with increasing temperature.[25]

III. Common corrosion measurement techniques

Corrosion monitoring plays a vital role in noticing corrosion failure and studying the parameters that enhance corrosion. This helps in selecting the suitable prevention techniques, such as chemical inhibition. Furthermore, several inspection techniques are accomplished to identify corrosion damage according to pH, hydrogen ions that alter the corrosion resistance of a material, flow rate, pressure, and temperature. The most common inspection methods are ultrasonic testing, radiographic testing, and magnetic flux. Once corrosion is identified, corrosion measurement techniques using mechanical or electrical probes are used or analytical chemistry to determine the amount of dissolved gases [24]

III-1. Immersion tests (The lost mass method)

The advantage of this method is that it is easy to use and does not require a great deal of equipment, but it does not provide an approach to the mechanisms involved in corrosion. Its principle is based on the measurement of the weight loss **Δm** undergone by a surface sample **S**, during the immersion time **t** in a corrosive solution. The corrosion is given by the following relationship [26]:

$$\boxed{V_{corr} = \frac{\Delta m}{S.t}} \quad \text{mg/cm}^{-2}\text{.h}$$

$\Delta m = m_1 - m_2$

where:

- V_{corr}: corrosion rate (mg/cm^{-2}.h)
- m_1: initial mass of the sample before immersion (mg);
- m_2: final mass of the sample after immersion (mg);
- S: surface of the sample immersed in the corrosive medium (cm^2);

The inhibitory efficacy of a compound is given by the following relationship:

$$\boxed{\eta\% = \frac{\Delta m - \Delta m_{inh}}{\Delta m} \times 100}$$

III-2. Electrochemical methods

The electrochemical method is a method of measuring the corrosion rate by measuring the potential difference of the object to obtain the corrosion rate occurred, this method measures the corrosion rate at the time of measurement only which estimates the rate for a long time (estimating that although the results that occur between one time and another are different). The advantage of this method is we can directly know the rate of corrosion at the time of measuring, until the measurement time does not take a long time. The disadvantage of this method is that it cannot accurately describe the corrosion rate because it can only measure the corrosion rate only at certain times, until the usage life or the conditions to be tested.[11]

The electrochemical methods used to study the corrosion phenomenon can be divided into two categories:[14]

- ✓ Stationary methods,
- ✓ Transitional methods.

III-2.1. Stationary method: polarization curves

The polarization curve of the metal-solution interface is a fundamental characteristic of electrochemical kinetics, but only accounts for the slowest stage of the process global to the electrochemical interface.

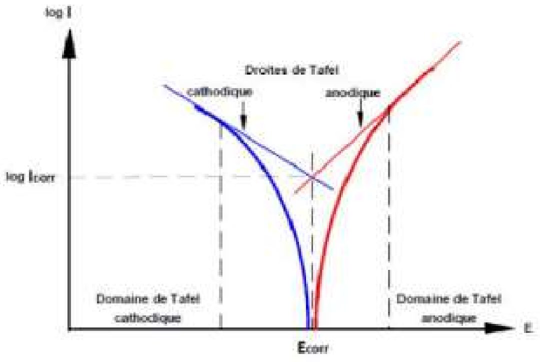
To determine a potentiostatic bias curve, we apply, using apotentiostat, different potentials between the working electrode and a reference electrode. We measure the stationary current that is established after a certain time in the electrical circuit between this working electrode and a counter-electrode.

This method makes it possible to determine in a precise way the electrochemical parameters of a metal in contact with an electrolyte namely : the instantaneous corrosion rate (V_{corr}), the corrosion potential (E_{corr}), the Tafel slopes, the polarization resistance(R_p), the diffusion limit currents.

It gives quick measurements and its implementation is relatively simple. The determination of the corrosion rate from the polarization curves is closely related to the kinetics governing the electrochemical process, there are three main types of kinetics :

- ✓ Charge transfer kinetics (activation).
- ✓ Mixed charge transfer - diffusion kinetics.
- ✓ Diffusion kinetics.

To experimentally determine these electrochemical parameters, a presentation logarithmic of the current density is in general preferable, since it highlights the linear relationship between the logarithm of the current density and the potential figure**I.**10 .

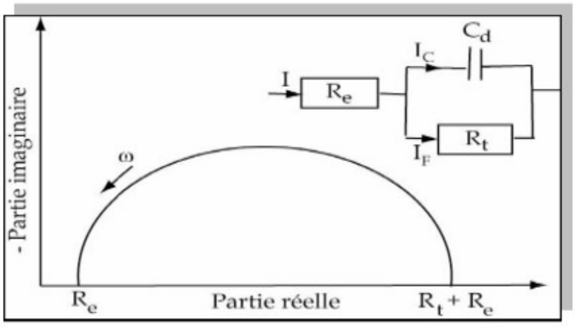


FigI.10: Determination of the electrochemical parameters from the Tafel lines.

The trace makes it possible to confirm the indications given by the evolution of the corrosion potential and to specify them by distinguishing the influence of the inhibitor on each of the reactions elementary, anodic and cathodic, to the electrode.[15]

III-2.2 Transient method: electrochemical impedance spectroscopy

Electrical impedance spectroscopy is sometimes called “Dielectric Spectroscopy” when the polarisation effect, as a result of an electric field, is expressed in terms of frequency-dependent complex permittivity and conductivity rather than impedance. Electrical impedance spectroscopy (EIS) is a powerful technique to investigate the electrokinetic properties of materials and their interfaces . The Experimental impedance spectroscopy data can be analysed using a suitable physical model (for example, the equivalent circuit model) to explain the physical or chemical processes in the material/interface. The EIS measurement can be achieved by applying an alternating voltage to the system and measuring the AC current response.[27].



FigI.11: Nyquist diagram and equivalent electrical circuit**.**

Chapter Two

General information of Wild thyme

(Thymus serpyllum L)

I. Thymus genus

Thymus is a Latin name of plant genus, which is considered to derive from the Greek word thyo (perfume) by some authors, while others consider the Greek word thymos (courage, strength). Thymus genus belongs to Lamiaceae family and includes about 350 aromatic species that are distributed around the world, being particularly abundant in the west Mediterranean region. These species are perennial and are characterized as being herbaceous subshrubs or shrubs with 10 to 30 cm tall, containing small and simple leaves, ramified and prostrated branches and big clusters of pink, white, cream or violet flowers.[28]

I-1. Spatial distribution

The genus Thymus is one of the 250 most diverse genera of the labiate family, there are almost 350 species of thyme distributed between Europe, West Asia and the Mediterranean. It is a very widespread plant in the west of North Africa (Morocco, Tunisia, Algeria and Libya), it also grows on the mountains of Ethiopia and south-west Arabia passing through the Sinai Peninsula in Egypt. It can also be found in Siberia and even in the Himalayas. According to a study conducted by Nickavar about 110 different species of the genus Thymus are concentrated in the Mediterranean basin. This is why we can consider the region Mediterranean as being the center of this kind.[30]

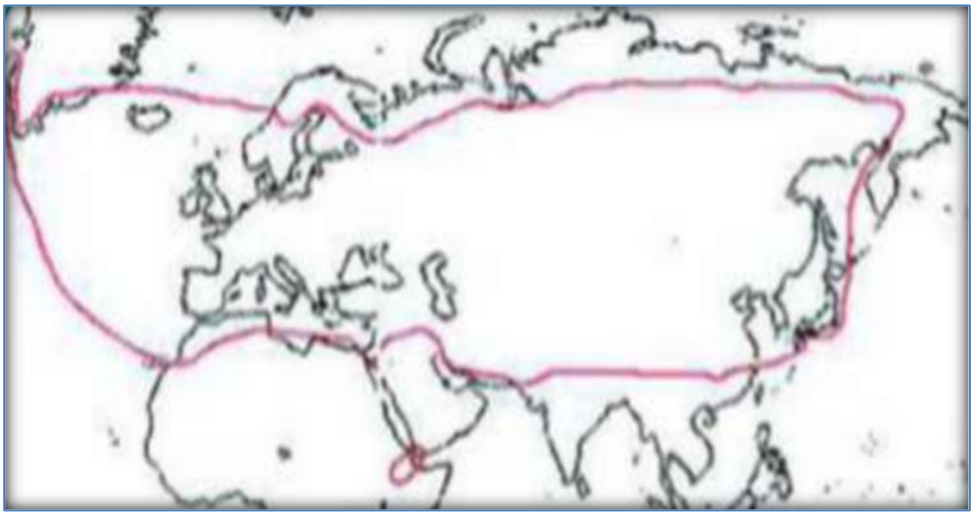


Fig II.12 : Distribution of the genus Thymus in the world

I-2. The difference among species of the genus Thymus

Species identification is usually based on the features of the habitus, leaf, stem, habitat, indumentum, inflorescences, bracts, bracteole, calyx, corolla, pollen along with some new features such as nutlet shape, distribution of trichomes and surface sculpture. [31]

Environmental conditions including soil fertility, moisture content of soil and growth temperature are the important factors that determine the nutritional content of plants grown in different geographical conditions. [32]

II-Wild thyme (*Thymus serpyllum L*)

Wild thyme is the common name of Thymus L., a wide genus of the Lamiaceae family, counting more than 500 species of an aromatic plantoriginally distributed in the Mediterranean area. It is a very polymorphicever green shrub, generally growing on dry, stony and sunny soils, up to1800 m above sea level Thyme of the Thymus Serpyllum is characterized by atrailing growth habit, hence the name “serpyllum”, meaning “to creep”.[33]

II-1. Botanical name, etymology of the plant name

The botanical binomial name of wild thyme is Thymus serpyllum L., with many botanical synonyms due to numerous descriptions of several authors depending on different regions and occurrences of the plant. Different literature sources give reasonable explanations for the etymology of plant names “thymus” and “serpyllum.” For the genus name “Thymus,” there seem to be two possible ancient Greek origins: 1.thúō, “to smoke” that which is burnt as incense or fumigation” for its fragrance, likely because of its use in religious celebrations or temple services. Secondly, the word could stem from thumos, which means “courage or strength” , where thyme symbolized bravery, perhaps due to the refreshing and powerful scent of wild thyme. The descriptive specific epithet (species name) “serpyllum” is also of Greek[34]

II-2. Botanical description and morphology

Serpyllum (wild thyme) is a perennial with creeping stems, woody at the base, with tendency to rooting, especially in the nodes. The stems are quadrangular, with a sparse pubescence. The leaves are small, usually rounded at the top and tapered at the base (3–10 mm long and 1–3 mm wide), glabrous on both sides. At the base along the edge they are covered with glandular trichomes containing essential oils. Flowers, with pink corolla, grows in clusters at the top of older stems, forming inflorescences. As other Thymus species, serpyllum presents gynodioecy, i.e. it produce two types of individuals, one with female flowers, and the other with hermaphrodite ones. It blooms from the end of May to September. The plant occurs mainly on dry, sandy soils especially at the edges of coniferous forest or on open spaced river banks as well as on poor grasslands.[35]

Fig II.13: Wild Thyme

Fig II.14: Wild thyme Leaves

Fig II.15: Wild thyme flower

FigII .16 : Botanical drawing

II-3. Classification [29]

Table 2. classification of wild thyme

Reign	Plantae (plant)
Branch Line	Spermaphytes (phanerogams)
Under branch line	Angiosperms
Class	Dicotyledons
Subclass	Metachlamydia (gamopetales)
Order	Tubiflorales
Under order	Verbeninae
Family	Lamiaceae (labiate)
Gender	Thymus

II-4. The medicinal properties of wild thyme

The medicinal properties of wild thyme have been extensively used in official and traditional medicine for many years and centuries, respectively. Fresh and dried herbs particularly the upper part of the above ground portion of wild thyme, collected when the plant is in bloom, possess certain healing properties due to the presence of significant amounts of essential oils. Recent years have seen increased interest in ethnobotanical, phytochemical, and pharmacological investigations into the medicinal properties of the species serpyllum which serves as a high-quality source for many different formulations in pharmaceutical and chemical industries. The herb is used in preparations of natural herbal remedies, such as syrups, tinctures, infusions, decoctions, tea, and oil.[36]

This aromatic plant possesses: antiseptic, diaphoretic, analgesic, carminative, expectorant and stimulant properties, and it has been also used in mouth washes and gargles and against cough and cold . Its essential oil contains various, powerful ingredients with proven disinfectant and immune stimulating features, capable to fight a range of infections. The oil relieves rheumatism, and is also used in hair loss treatments.[37]

During the Renaissance period (16th and 17th centuries), wild thyme was used internally to treat malaria and epilepsy. In the Western Balkans, this species has an important use as a sedative, or to improve blood circulation, and then as anticholesterolemic and immunostimulant. In alpine region of northeastern Italy, infusion or decoction of plant areal parts (in flowering stage) is used in treatment of rheumatism.

serpyllum is also used externally as an antiseptic, to treat wounds , to combat eczema , or to reduce swelling. In some areas of Italy, wild thyme is used as an important herb in cookery, mainly for flavouring meat or fish . In addition, ethnobotanical studies in Catalonia and Balearic Islands have proved usage of serpyllum in ethnoveterinary particularly as antidiarrheal . The British Herbal Pharmacopoeia classifies this species as a medicinal plant and among the indications for its use it mentions bronchitis, bronchial catarrh, whooping cough, and sore throats.[36]

III-Phytochemical study

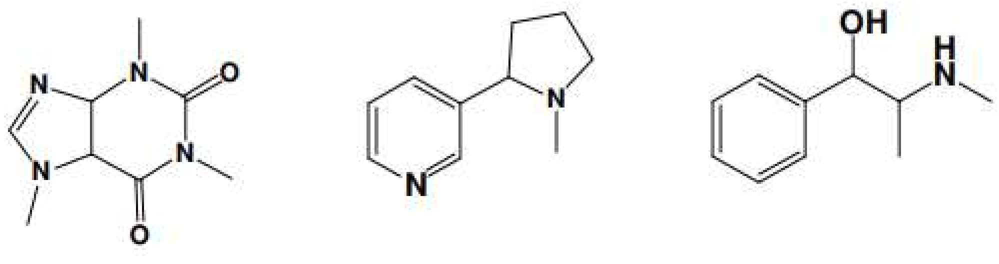
One of the major originalities of plants lies in their ability to produce very diverse natural substances. Indeed, next to the classic primary metabolites (carbohydrates, proteins, lipids and nucleic acids), they frequently accumulate a large number of compounds that are not directly derived from photosynthesis, but result subsequent chemical reactions. These compounds are called "secondary metabolites" whose physiological function is not always obvious but represents a source important number of bioactive molecules that can be used by humans in fields as different than pharmacology or agri-food.[38]

III-1. Phytochemical screening of the plant

III-1. 1. Alkaloids

They are basic nitrogen compounds, of natural origin, the nitrogen atom of which is inserted in a heterocyclic system.

Alkaloids have the property of reacting with salts of heavy metals. Most of the alkaloids have been exploited as drugs, stimulants or poisons. These are biologically active substances, their pharmacological activities are carried out in several domains. They act at the level of the central system as much as antidepressants (morphine, scopolamine), or stimulants (strychnine, caffeine), and at the level of the nervous system autonomous: sympathomimetics (ephedrine), sympatholytic (yohimbine). They can also play the role of antibiotics, such as: mytomycin and cycloserine. [29]



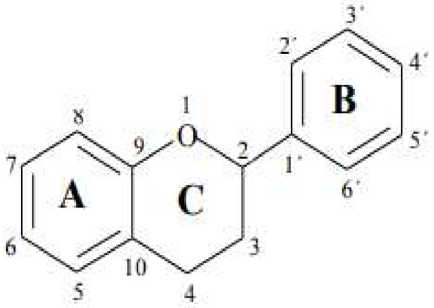
Caffeine Nicotine Ephedrine

Fig II . 17 : Structure of some alkaloids

III-1. 2. Flavonoids

deriving from the Latin term "flavus" meaning yellow, encompass a wide range of natural compounds that are part of the polyphenol family. They are considered as almost universal pigments of plants, responsible for the coloring of flowers, fruits and sometimes leaves. Their composition and quantity vary depending on the stage of development of the plant, which explains their interest commercial in the food and dyes industry, as well as their importance medicinal.[39]

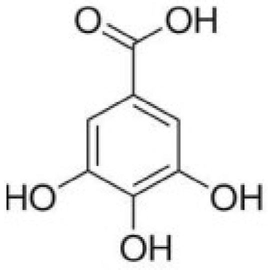
Flavonoids are characterized by a C15 structure (C6-C3-C6) with a heterocyclic benzopyran ring (C ring), an aromatic ring (A ring) and a phenyl constituent as the B ring, all of them with several structural variations.[28]



FigII .18: structure of flavonoids

III-1. 3. Tannins

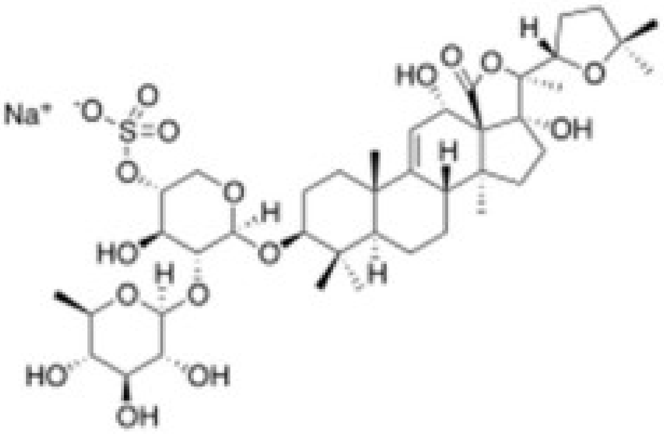
The term tannin comes from an ancient practice that used plant extracts to tan animal skins, in other words, to transform a skin into leather . The tannins are polyphenols that are found in many plants. Their structure complex is formed by repetitive monomeric units that vary by their center asymmetric, their degree of oxidation and their astringent flavor but having in common the property of tanning the skin. This ability is linked to their property of combining with proteins. Their molecular weight is between 500 and 3000 g/mol . These tannins are proton donors to lipid free radicals produced during the peroxidation. More stable tannic radicals are then formed, which has for consequence of stopping the chain reaction of lipid self-oxidation.[38]



FigII.19 : structure of tannins

III-1. 4. Saponins

The word saponin is derived from the Latin word "sapo". Saponins got their name from the factthat they produce a soap-like foam, They arehigh molecular weight glycosides, grouping together a complex and chemically verydiverse of triterpene or steroid molecules. They consist of a fractionhydrophobic aglycone (a steroidal or triterpene nucleus) linked to a mono- orHydrophilic polysaccharide.[40]



FigII.20 :structure of saponins

III.1.5. Anthocyanins

Anthocyanins (in Greek Anthos means flower, and kyanos means blue) arepigments, mainly in the form of stable and water-soluble glycosides, red inacidic medium, turning blue-violet in neutral or weakly alkaline medium. They are accumulatedin the cell vacuoles and they are responsible for the red, purple and blue colorsin fruits, vegetables, flowers and seeds, but also play an important role inplant physiology as insect attractors and in seed dispersal.[41]

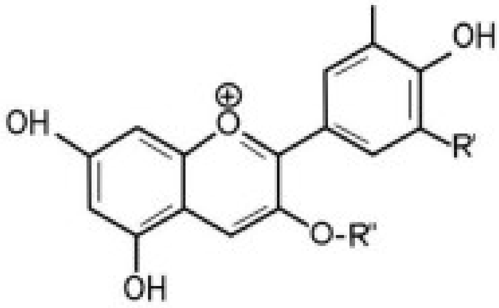
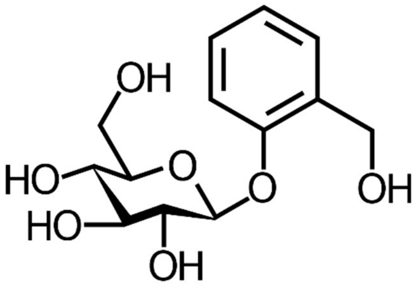


Fig II.21 : General structure of anthocyanins

III-1. 6. Glucosides

Glucosides are carbohydrate analogues resulting from condensation of oses and aglycones non-carbohydrate substances. Glucosides are molecules consisting of a carbohydrate function associated with various other types of molecules. Many plants store these glucosides in an inactive form. These molecules are made up of 2 distinct parts: the glycone, which corresponds to the carbohydrate group (consisting of one or more carbohydrate functions), and the aglycone, which is the non-carbohydrate part of the molecule. Glucosides can be classified according to the chemical function of the aglycone part.[42]



FigII.22 : General structure of glucosides

III-1. 7. Terpenes and sterols

Terpenes constitute an important group of natural products, comprising approximately 30000 compounds. Steroids constitute a group of lipids derived from triterpenoids (lipids with 30 carbon atoms). They are described as compounds that are essentially constituents of an oil essential and which contain carbon and hydrogen atoms with or without oxygen. They have received considerable interest in the dermal and transdermal administration of drugs with a wide range of physico-chemical properties.[42]

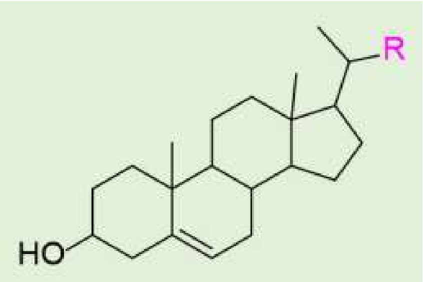
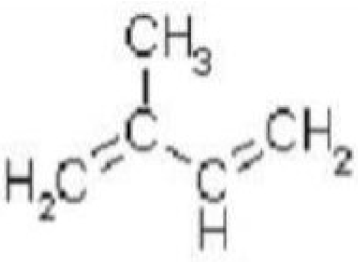


Fig II.23 : structure of sterol



FigII.24 : structure of Terpenes

III-2 Extraction methods

III-2.1. Definitions

Extraction is an operation that consists of separating certain compounds from an organism (animal or plant) according to various techniques [43]

Extraction consists in transferring a compound from one phase to another:

- From one liquid phase to another liquid phase.
- From a solid phase to a liquid phase.

III-2.2. Types of extraction

Since extraction is the first stage of scientific study, it has asignificant impact on the final result of the study. As a result of choosing the most suitable one among theextraction methods, it will be easier to obtain the best data. In choosing the most suitable method among the different extraction methods, many features such as the chemical structure of the plant we will study, the variability of the component amounts, and the polarities of the components are taken into consideration.

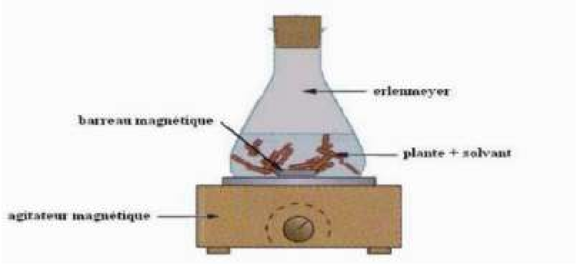
In order to carry out a good extraction process, it is necessary to choose a cheaper, easier, faster, and environmentally friendly method and to obtain the desired bioactive components with higher efficiency.[44]

III-2.3. Solvent extraction

The choice of extraction method is based on prior data on the physicochemical characteristics of the metabolites to be extracted. We distinguish numerous extraction methods (solid-liquid) of phytochemical compounds [14]:

III-2.3. 1. Maceration

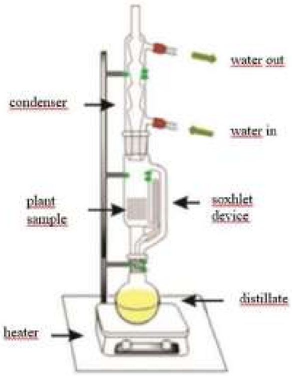
Maceration is the simplest solid-liquid extraction method. It consists of bringing the plant material into contact with the solvent without or with stirring, usually at room temperature. The operation although generally long and often high efficiency mediocre, is used in the case of extraction of heat-sensitive molecules. To be effective, a maceration without stirring, can last from about 4 to 10 days; this can present some disadvantages. In terms of fermentation, or contamination bacterial in particular if the solvent used is water. These phenomena can lead toa degradation of the active molecules. In order to avoid or reduce these disadvantages, themaceration can be carried out in a covered container, all protected from light and in some cases, kept in a refrigerator.[45]



FigII.25 : Diagram of the Maceration technique

III-2.3. 2. Soxhlet

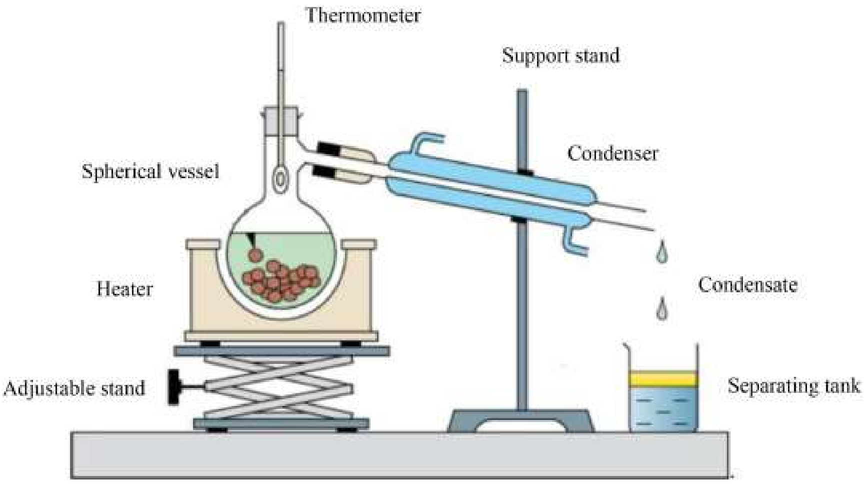
Among the main methods that have been applied for a long time, a technique so-called reference for evaluating the effectiveness of other solidliquid extraction methods. It was first used and described by Franz Von Soxhlet in 1879 by determining the amount of lipids in milk[46]



FigII.26 : Soxlet assembly

III-2.3. 3. Hydrodystillation

The principle of hydrodystillation (The Moritz method) is that of the distillation of immiscible binary mixtures. It consists in immersing the plant biomass in a still filled with water, which is then brought to a boil. The steam destroys the structure of the plant cells, releases the molecules contained and drives the most volatile ones by separating them of the cellulosic substrate. The steam, charged with the essence of the distilled raw material, is condenses in the coil of the still before being recovered in an essentiary (vase of decantation for essential oils). The parts insoluble in condensation water are decanted to give the essential oil supernatant. The part containing the compounds water-soluble is called distillation water (or hydrosol).[47]



FigII.27 : Extraction assembly by Hydrodistillation

Experimental part

Chapter Three

Materials and methods

I-Phytochemical evaluating for the plant

Phytochemical screening is a bunch of tests completed on the powder. These tests permit us to have a thought of the presence or nonattendance of specific essential metabolites also, auxiliary in the plant.

The phytochemical bunches are various, yet we can refer to the fundamental ones: alkaloids, polyphenols (flavonoids, anthocyanins, tannins, saponosides, coumarins, sterols, terpenes, natural ointments).

I-1. Sample preparation

After being sorted and cleaned, the leaves are left to dry in the open air; they are then crushed using an electric grinder. The powder obtained was then filtering to obtain a powder and stored in glass jars protected from light to avoid any deterioration.

I-2. Chemical composition of Wild thyme

I-2.1. Alkaloid Test [14]

5g of the dried and squashed plant are blended in with 50ml of 1% HCl in a container. After 30 minutes of maceration, the combination is sifted and added to the filtrate. a couple of drops of Mayer's reagent (25g of KI dissolved in 20ml of distilled water added to 13.5g of $HgCl_2$ dissolved in 20ml of distilled water then completed with distilled water up to 1L).

- The appearance of a yellowish-white precipitate shows the presence of alkaloids.

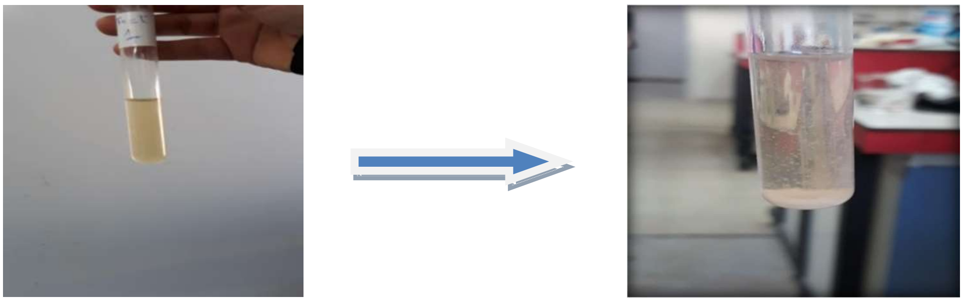


Fig III.28: Detection of alkaloids

I-2.2. Test of Flavonoids

10 g of plant material are macerated in 150 ml of 1% HCL for 24 hours. After filtering the mixture, a 10 ml aliquot of the filtrate is taken, to which a few drops of NH_4OH (to make it basic) are added.

- The appearance of a yellow color in the upper part of the test tube indicates the presence of flavonoids .

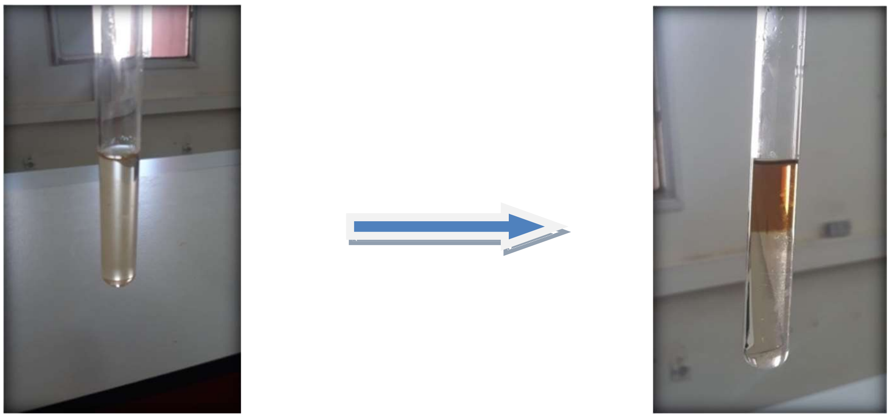


Fig III.29: Detection of Flavonoids

I-2.3. Test for Tannins

We take 5g of the powder, extract with 20 ml of ethyl alcohol C_2H_5OH, under agitation for 15 minutes, then filter. Then test the filtrate with a few drops of $FeCl_3$.

- The appearance of a green color indicates the presence of tannins.

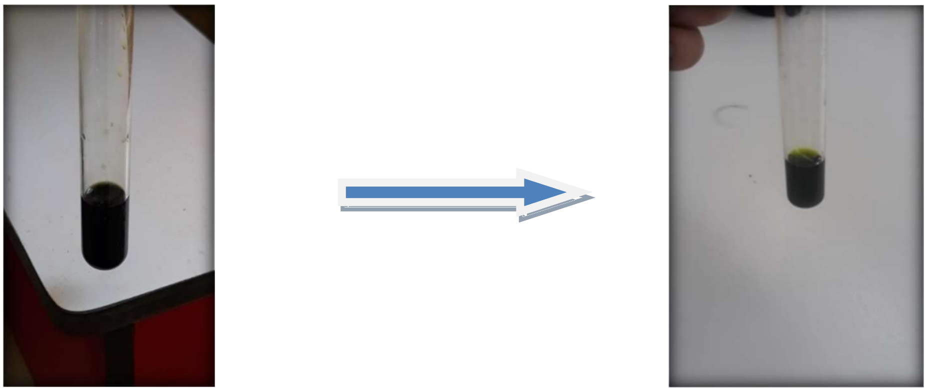


Fig III.30: Detection of Tannins

I-2.4. Test for Saponins

A mass of 2g of the plant powder was heated in 80ml of distilled water until boiling, after cooling, the mixture is filtered, and in a test tube, the tube is shaken lengthwise.

- The appearance of stable foam after 15 minutes indicates the presence of saponins.

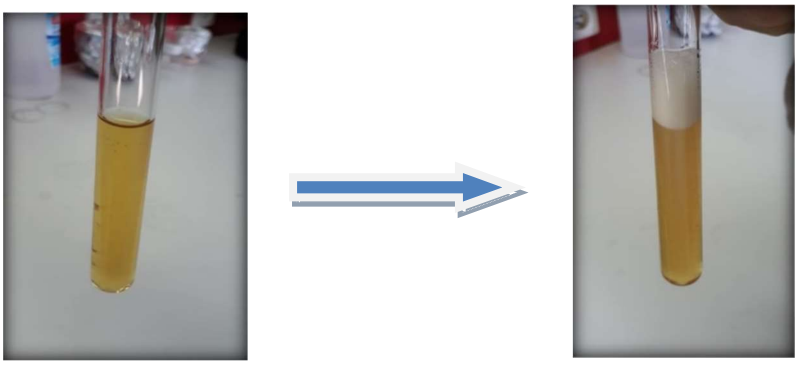


Fig III.31: Detection of Saponins

I-2.5. Test for Unsaturated Sterols and Terpenes

A 5g mass of powder was macerated in 20ml of chloroform. After filtration, 1ml of concentrated sulfuric acid (H_2SO_4) was added to the filtrate, carefully along the walls of the test tube. The point of contact between the two phases.

- The appearance of a violet or brown color turning towards gray indicates the presence of unsaturated sterols and terpenes.

FigIII32: Detection of unsaturated sterols and terpenes

I-2.6. Test for anthocyanins

1g of dry powder is macerated in 10ml of distilled water, brought to a boil for 15 minutes, then filtered. A few drops of HCl and (NH_4OH) are added.

- ➢ A change in color indicates the presence of anthocyanins.

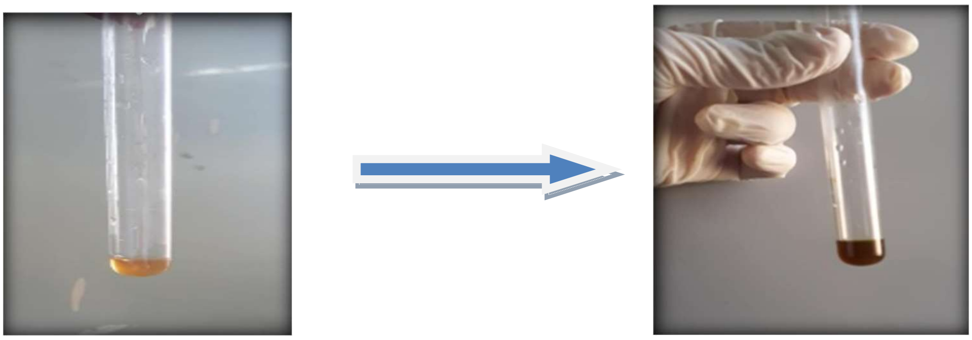


Fig III.33: Detection of anthocyanins

I-2.7. Test for leucoanthocyanins

First, 1g of powder is placed in 5 ml of propanol, then drops of concentrated HCl are added. The mixture is heated for 3 to 5 minutes in a water bath.

- ➢ After heating, the appearance of a red color indicates the presence of leucoanthocyanins.

Fig III.34: Detection of leucoanthocyanins

I-2.8. Starch Test

Take 1g of powder in a test tube, add a few drops of iodine (I_2) until a change in color to purple-blue indicates the presence of starch.

Fig III.35: Starch detection

I-2.9. Test for Glucosides

Put two drops of concentrated sulfuric acid on one gram of plant powder.

- The appearance of a brick-red color, then purple, indicates the presence of glucosides.

Fig III.36: Detection of glycosides

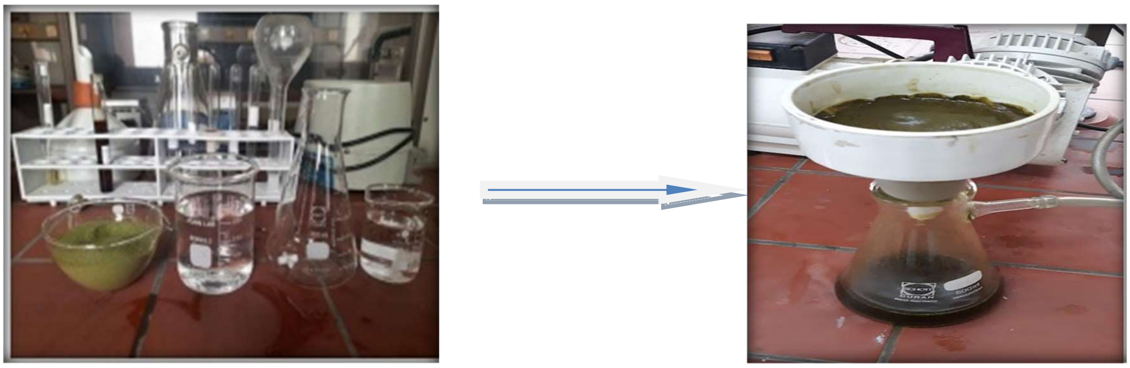
I-3. Green inhibitors use

In our study, we used green inhibitors, namely Wild thyme extract.

I-3.1 Preparation of the inhibitor

A quantity of 50 g of plant powder is macerated in 300 ml of 70% ethanol for 24 hours under agitation. The hydro-ethanolic filtrate obtained is filtered using a vacuum flask and filter paper, the precipitation is re-macerated in 200 mL of 70% ethanol for 24 hours. After filtering the latter, both filtrates are combined to obtain the maximum possible amount of extract. The separation of the solvent from the extract is done using a device called a Rotavapor.

In the Rotavapor, we perform vacuum evaporation using a vacuum pump with a control valve. During evaporation, the flask is rotated and immersed in a heated liquid bath. The device is equipped with a condensate collector flask with a refrigerant. The rotation of the flask creates a larger and renewed exchange surface, allowing for rapid evaporation. The reduction of pressure allows the solvent to evaporate at a reduced temperature, thus avoiding potential thermal degradation of the compounds. It's a simple, useful, gentle, and rapid evaporation method.



Maceration **filtration**

The extract obtained **Evaporation**

Fig III.37: The steps of preparing the inhibitor

II- Gravimetric study of corrosion inhibition

II-1. Studied material (Mild steel)

Mild steel, also known as low-carbon steel, is by far the most widely used and one of the world's cheapest and useful metals. It is essentially alloys of iron and carbon with small additions of elements such as manganese and silicon added to provide the requisite mechanical properties. The properties of mild steel depend primarily on the amount of carbon it contains. Mild steel contains carbon of up to 0.25% in constituent among other element. This made it useful to be turn into a wide range of products.[48]

Different grades of mild steel have varying carbon levels, influencing their strength and ductility. Higher carbon content increases strength but can reduce flexibility. Some grades also include additional alloying elements to improve specific properties like tensile strength, corrosion resistance.

Mild steel does not have a high resistance to corrosion in its untreated form, however, the corrosion resistance can be greatly improved by applying an appropriate surface protection product to the exposed parts.

1- Chemical composition of mild steel [49]

Mild steel is graded according to its chemical composition, how it is produced, and its properties, so you can easily choose the best product.

Table 3. Chemical composition of mild steel

Mild steel	**Fe %**	**C %**	**Mn %**	**S %**	**P %**	**N %**	**Cu %**
	98.81 – 99.26	0.14 – 0.25	0.30 – 0.90	≤ 0.05	≤ 0.04	≤ 0.01	≤ 0.5

2- Physical Properties of Mild Steel

Its impressive properties are responsible for growing use in a variety of industries. Some mild steel's physical properties are as follows:**[50]**

- High tensile strength
- High impact strength
- Good ductility and weldability
- A magnetic metal due to its ferrite content
- Good malleability with cold-forming possibilities
- Suitable for various heat treatment options to improve properties

3- Uses of Mild Steel

mild steel is a valuable material and generally use in most engineering applications for the production of some automobile components, structural shapes and sheets that are used in plants, Engineering facilities, pipelines, building bridges . The usage of carbon steel material is noticeable in various facets of human life such as in manufacturing, oil and gas, construction, medical, textile, transport and aviation industries to mention a few.[51]

II-2. Sample preparation

II-2.1. Cutting

We prepare two types of samples. The first type is square-shaped with a diameter of 3cm and a height of 0.76cm for gravimetric studies. The second type of samples has been cut into cylindrical shapes with a diameter of 1.40 cm and a height of 1 cm for electrochemical studies.

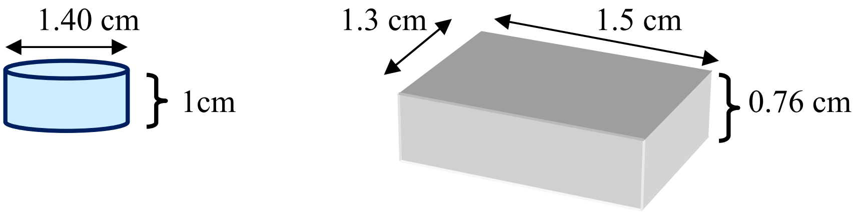


Fig III.38: Shape and dimensions of samples in cm

II-2.2 Polishing

The preparation of sample surfaces is carried out using abrasive papers of decreasing grain size: from 400 to 1200 mesh. Then, the piece is rinsed with distilled water and dried using an electric dryer to achieve a smooth surface, resembling a mirror finish. Subsequently, the samples are rinsed with acetone, washed with distilled water, dried for a few seconds, and immediately immersed in the corrosive solution.

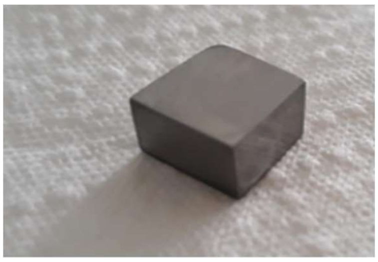


Fig III.39:sample after polishing

II-2.3. Preparation of corrosive environments

Four primary experimental media will be prepared:

- Acidic media: we prepare 1 M solution of hydrochloric acid HCl.
- Basic media: we have prepared 1 M solution of sodium hydroxide NaOH of concentration of 1 M, one with the inhibitor and the other without.

  In our study corrosive environments are divided into two categories one without inhibitor and the other with inhibitor.

II-3. Testing techniques (gravimetric study)

In this study, mass loss tests over time were conducted in four different environments: two involving 1 M hydrochloric acid, with and without an inhibitor, and two involving 1 M sodium hydroxide, also with and without an inhibitor.

A sufficient number of test environments will be prepared for each of the four media to measure mass loss at intervals of 24, 48, 72, and 96 hours. This will result in 12 test containers, into which the samples will be placed immediately after preparation and weighing.

After each specific period of time (mentioned above):

- Take out the sample is washed, dried and weighed again.
- The corrosion rate (or corrosion velocity) is calculated using equation (1).
- Each product's inhibitory is determined using equation (2)

The major drawback of this method lies in the difficulty of completely removing corrosion products without attacking the base metal.

The values of the corrosion rate V_{corr} are estimated by the following formulas:

$$\mathbf{V = \Delta M / S \cdot t \qquad (mg\ cm^{-2}\ h^{-1}) \quad \ldots\ldots\ldots (1)}$$

Where Δm = (mi - mf) being the mass loss expressed in mg, S being the surface of the substrate and t the residence time of the substrate in the solution.

$$\boldsymbol{\varepsilon\ (\%) = (V - V_{inh}) / V \times 100\ \% \qquad \ldots\ldots\ldots\ldots(2)}$$

where V and V_{inh} stand for the steel's corrosion rate values during immersion in the absence and presence of the inhibitor, respectively.[14]

III- Electrochemical Study

III-1. Electrochemical Setup

The electrochemical study of the behavior of steel in corrosive environments is based on plotting polarization curves i=f(E) and the Tafel line. The experimental setup used consists of a potentiostat-galvanostat of type PGZ 301 (Radiometer brand) and a microcomputer equipped with VOLTAMASTER 4 software, along with a three-electrode electrolysis cell.

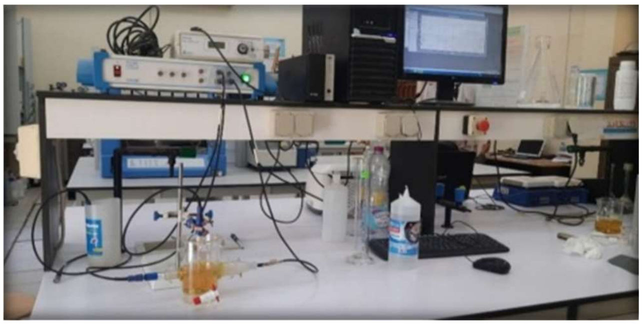


Fig III.40: Electrochemical Setup

III-2. Electrochemical Cell

Fig-41 shows the three-electrode electrochemical cell (Working electrode; Reference electrode; Auxiliary electrode).

1. Working electrode: This is an electrode made from a mild steel sample in cylindrical form, 1 cm in height and with a diameter of 1.4 cm (active surface).
2. Reference electrode: This is a saturated calomel electrode in potassium chloride. This reference electrode, noted as ECS, is unpolarizable, with a rigorously constant potential.
3. Auxiliary electrode or counter electrode: The auxiliary electrode is made of platinum (with a 1 cm active surface), intended to facilitate the passage of electrical current in the electrolysis cell.

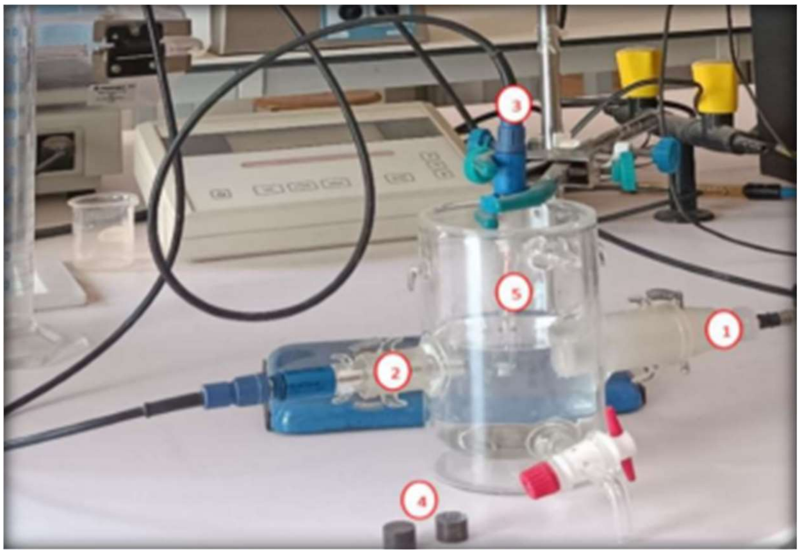


Fig III.41: Electrochemical Cell

1. Working electrode
2. Auxiliary electrode or counter electrode
3. Reference electrode
4. Samples
5. The cell containing 250 ml of 1M- HCl / 1M- NaOH.

Chapter Four

Results and discussions

I- Phytochemical Screening Results

In order to detect the presence of certain chemical constituents in the wild thyme plant, a series of phytochemical tests were performed. These analyses confirmed the presence of specific compounds, as presented in the table below.

Table4: results of phytochemical tests wild thyme

Phytochemicals	Result	
Alkaloid	+++	 Yellowish white precipitate
Flavonoids	+++	 yellow color
Tannins	+++	 Green color

Saponins	+++	 appearance of foam
Unsaturated Sterols and Terpenes	+++	 a violet or brown color towards gray
Anthocyanins	+++	 A change in color
Leucoanthocyanins	+	

		a red color
Starch	+	 a change in color to purple-blue
Glucosides	-	 No characteristic color was observed

- The sign (+): low presence.

- The sign (++): moderate presence.

- The sign (+++): strong presence.

. - The sign (-): absence.

We observe from the results in the previous table that wild thyme is rich in phytochemicals, especially flavonoids and alkaloids, which possess strong antioxidant activity. This suggests that wild thyme may be effectively used as a corrosion inhibitor.

II - Gravimetric study

II.1. Microscopic observation of steel

Observation by optical microscope of mild steel surfaces before and after immersion in corrosive medium. 1- (acidic medium of 1M HCl, without and with inhibitor) 2- (basic medium of 1M NaOH, without and with inhibitor) are shown in the following images:

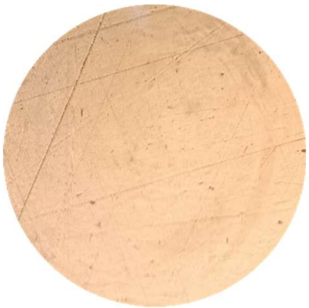
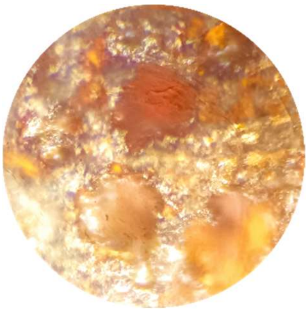
Before immersion in corrosive medium	After 4 days of immersion in corrosive medium	
	 1- HCl	 2- HCl + inh
	 3- NaOH	 4- NaOH + inh

Fig IV.42: Microscopic observation of steel

We can clearly observe in 2and 4 Figure IV.42 the formation of a thin layer that protects the steel surface from corrosion when using wild thyme plant extract as a corrosion inhibitor in both acidic and basic media, in contrast to the clear corrosion of the steel surface shown in 1 and 3 Figure IV.42 in corrosive media in which the plant extract was not used.

II.2. The effect of adding wild thyme extract on mass loss

In order to study the effect and effectiveness of wild thyme extract in protecting of mild steel from corrosion, we conducted weight measurements of mild steel in an acidic hydrochloric medium 1M HCl as well as in a basic sodium hydroxide medium 1M NaOH without using the extract, then by adding the extract at a concentration of 1%.

The following table shows the values of mass loss (Δm) and corrosion rate (V) of steel after (1, 2, 3 and 4 days) of immersion.

Table5: Variations in mass loss, corrosion rate and inhibitory efficiency

medium	**Time Hour**	**Δm (g)**	**V . 10^{-5} (g cm^{-2} h^{-1})**	**E %**
HCl	24 h	0.0168	8.583	**64.88**
	48 h	0.0262	6.692	**75.57**
	72 h	0.0267	4.547	**72.66**
	96 h	0.1061	13.551	**78.23**
HCl + inh	24 h	0.0059	3.014	/
	48 h	0.0064	1.635	/
	72 h	0.0073	1.243	/
	96 h	0.0231	2.950	/
NaOH	24 h	0.0048	2.452	**20.84**
	48 h	0.0060	1.533	**33.33**
	72 h	0.0200	3.406	**25.02**
	96 h	0.0434	5.543	**33.18**
NaOH + inh	24 h	0.0038	1.941	/
	48 h	0.0040	1.022	/
	72 h	0.0150	2.554	/
	96 h	0.0290	3.704	/

The data presented in the table and Figure IV.44 indicate that the inhibition efficiency of the inhibitor reaches 78.23 % in hydrochloric acid, which is significantly higher than its efficiency in sodium chloride, where it is only 33.33 %. This is maybe due to the stronger corrosive effect of acidic media compared to basic media, which makes studying mass loss in acidic media easier and the results of mass change clearer.

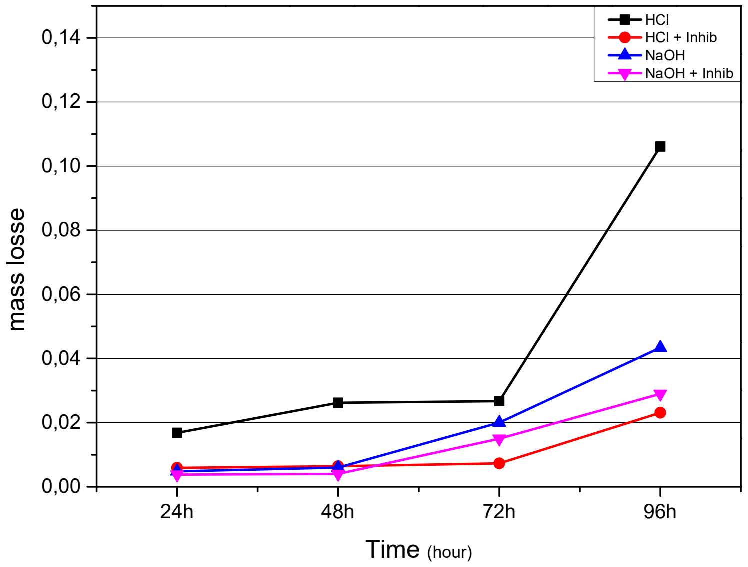


Fig IV.43: mass variation with immersion time

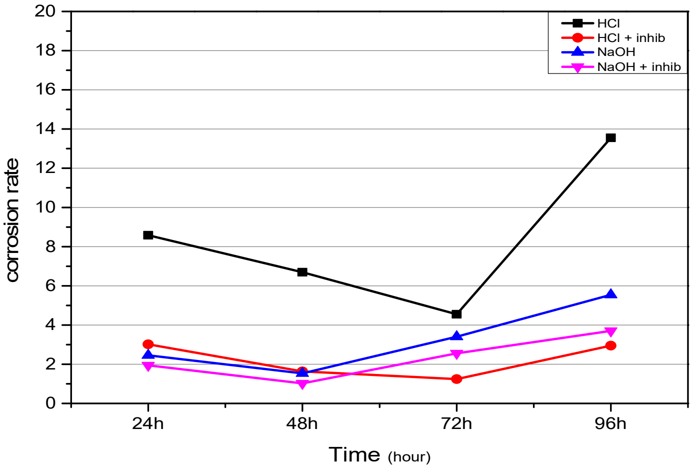
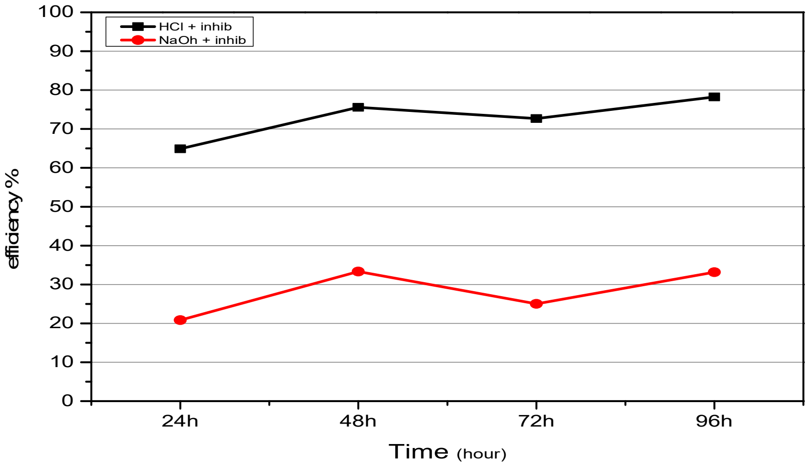


Fig IV.44: Variations of V corrosion with immersion time



FigIV.45: Variations of inhibitory efficiency with the time

Curve in (fig IV.43) represents the change in the lost mass with respect to time, clearly shows the effect of the plant extract in reducing the lost amount during the immersion period in the acidic medium, and to a lesser extent in the basic medium. This is due to the speed of corrosion in the acidic medium, which is clear in the curve in (fig IV.44) of change in the corrosion speed, which shows the decrease in the corrosion speed during the 2nd and 3rd days, which is due to the formation of a thin layer that reduces the effect of the medium on the steel surface and protects it from corrosion.

(fig IV.45) shows the inhibition efficiency of wild thyme extract in HCl acidic medium at an excellent rate compared to basic medium NaOH.

III. Electrochemical method

III.1. Free potential measurement

The polarization curves i =f(E) require knowledge of the free potential. After different tests, we opted for immersion of the sample for a period of 30 minutes. This time is sufficient to obtain satisfactory stabilization of the potential free. In acidic hydrochloric medium (HCl 1M) and in a basic sodium hydroxide medium (NaOH1M).

Before each manipulation the electrode work is polished with abrasive paper of different grain sizes.

III.2. Polarization curve

The polarization curve was drawn in a potential range corresponding to [-700 mV to -200mV], and we opted for a scanning speed equal to 30 mV/min. This speed allows us to obtain good reproducibility of the results without hiding the phenomena to be studied. The cathodic and anodic polarization curves of steel in HCl and NaOH medium at 25°C, in the absence and presence of inhibitor at 1% concentration are presented in Fig IV.46 and 47.

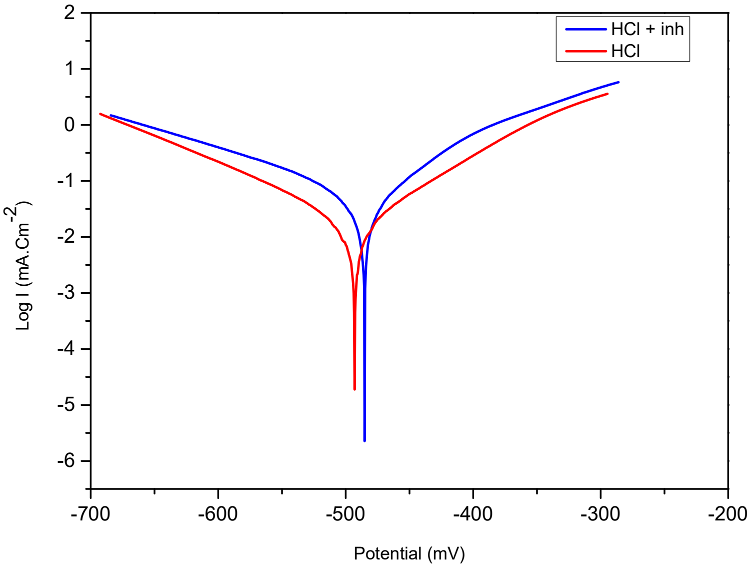


Fig IV.46: Tafel curve of mild steel in a acid environment without and with inhibitor

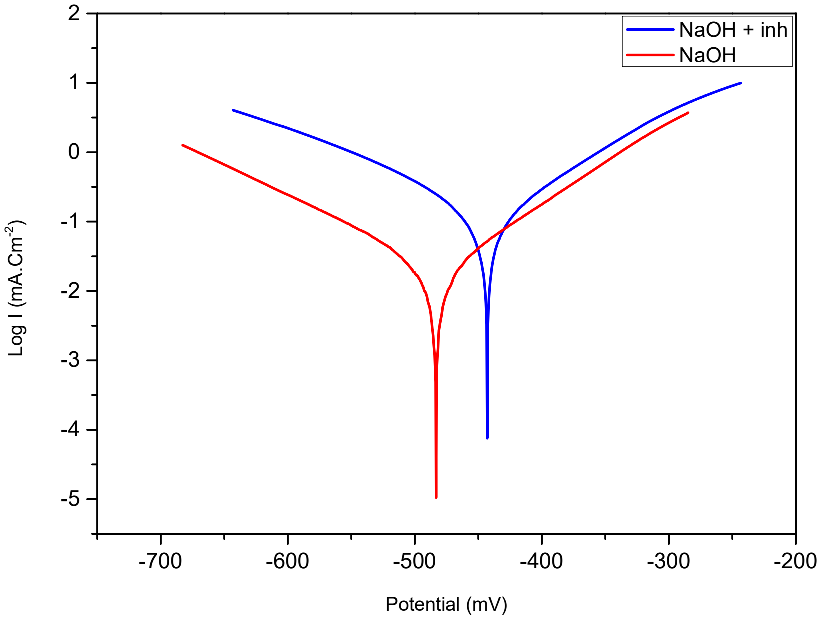


Fig IV.47: Tafel curve of mild steel in a basic environment without and with inhibitor

The figure presents the polarization curves obtained for the mild steel. The density of passivation current, corrosion potential and current, etc. are determined from these curves. Only the linearity domain of the cathode and anodic branches will be taken into consideration in the plot of the Tafel polarization curve. The corrosion rate is calculated by the *VOLTA MASTER4* software, using Tafel lines. The current density values corrosion (Icorr), the corrosion potential (Ecorr), the cathodic and anodic Tafel slopes (bc and ba) and the inhibition efficiency ε (%) for different medium acidic and basic with concentrations of 1% of wild thyme extract are reported in the following table:

Table 6: Values of electrochemical (polarization) parameters

medium	E (i=0) [mV]	Rp [ohm.cm2]	Icorr [mA/cm2]	Ba [mV]	Bc [mV]	Vcorrosion [g / Cm^2 D]	ε%
HCl	-492.3	417.33	0.0677	84.0	-137.8	851.7	**-**
HCl + inh	-481.7	897.45	0.0229	91.2	-105.1	273.3	**67.91**
NaOH	-292.3	607.11	0.0136	18.6	-135.2	401.8	**-**
NaOh + inh	-213.7	673.02	0.0105	63.2	-120.1	187.0	**53.46**

- **Rp**, Polarization resistance
- **Corrosion current**: obtained on the ordinate axis at the intersection of the tangents.
- **Ba and Bc**: Anodic and cathodic Tafel coefficient.
- **V Corrosion** (Corrosion or corrosion rate)

The analysis of these curves shows that there is an improvement in the corrosion potential when we use wild thyme extracts. we can deduce that the densities of the corrosion current (Icorr) decrease.

The same applies to corrosion rates, with inhibition efficiency increasing with the use of an inhibitor, reaching 67.91 % in acidic media, which is fully consistent with the results obtained using the mass loss method. In basic media, inhibition efficiency reaches 53.46 %, which is better than the result obtained using the mass loss method. This is due to the slower reaction of steel in basic solutions compared to acidic ones.

III.3. Electrochemical impedance curves

The Nyquist diagrams of the mild steel immersed in the corrosive solution without and with the addition of the inhibitor are shown in the FigureIV.48.

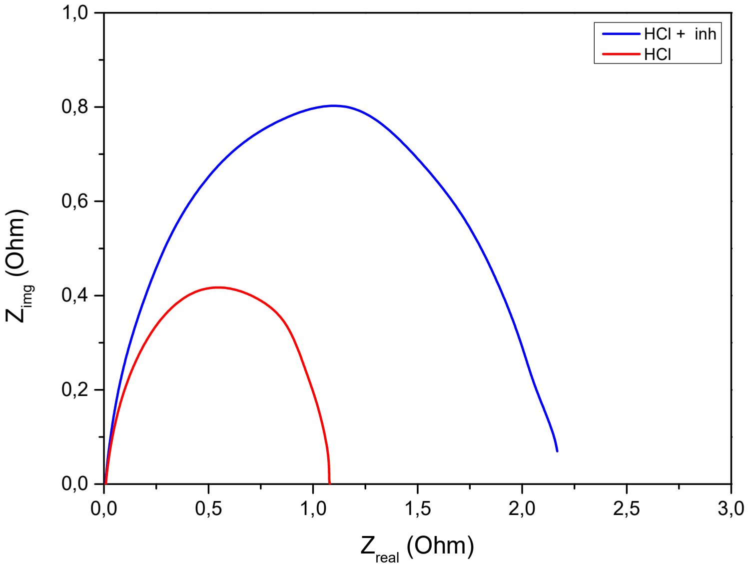


Fig IV.48: Diagrams of electrochemical impedance spectroscopy in an acidic medium without and with inhibitor.

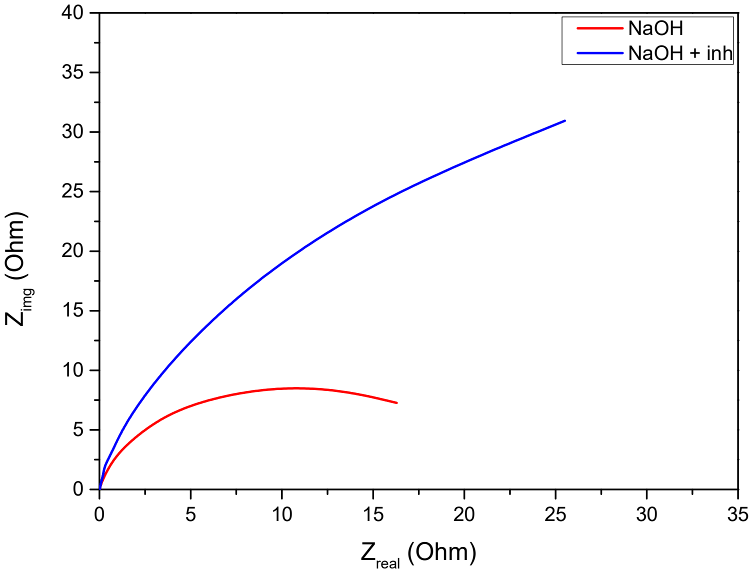


Fig IV.49: Diagrams of electrochemical impedance spectroscopy in a basic medium without and with inhibitor.

The resulting impedance patterns are not perfect semicircles, and this is attributed to the frequency dispersion of the interfacial impedance, generally due to the heterogeneity of the electrode surface.

The corrosion inhibitory effectiveness of steel is calculated from the load transfer resistance according to the relationship:

$$\varepsilon\% = \frac{R_{tinh} - R_t}{R_{tinh}} \times 100$$

where Rt and Rt (inh) are respectively the values of the load transfer resistances of the steel after immersion without and with addition of the inhibitor. The values of the electrochemical parameters and the inhibitory efficiency for deferent medium of our inhibitor for the corrosion of steel in 1M HCl and 1M NaOH medium are obtained by electrochemical impedance spectroscopy (ESI) are gathered in the following table.

Table 7: Values of the electrochemical parameters and the inhibitory efficiency for different medium

Medium	Rs ($\Omega.cm^2$)	C ($\mu F/cm^2$)	Rt ($\Omega.cm^2$)	ε %
HCl	7.418	553.06	402.11	-
HCl + inh	8.002	37.92	799.80	**74.48**
NaOH	5.973	18.46	89.35	**-**
NaOH + inh	6.813	16.53	305.07	**70.71**

From the results obtained in the table above, we note that the wild thyme extract has a good inhibitory efficiency in both acidic and basic media, and the value of the inhibitory efficiency is estimated at 74.48 % in HCl and 70.71 % in NaOH solution.

III.4. A comparative study of the influence of the inhibitor on the three analysis methods

we compare the results of the inhibitory efficiency of the inhibitor obtained using the three methods illustrated in (Fig IV.50), we note the following:

1. In acidic medium 1M HCl: The three results obtained were convergent (78.23% , 67.91% and 78.48), confirm that the effectiveness of the extract of wild thyme plant in protecting mild steel in acidic media.

2. In basic media 1M NaOH: The results of the electrochemical methods (polarization and electrochemical impedance) (53.46% and 70.71%) were better compared to the results obtained using the gravimetric method (33.33%). This is due to the low corrosion of steel in the basic solutions compared to strong acids solutions.

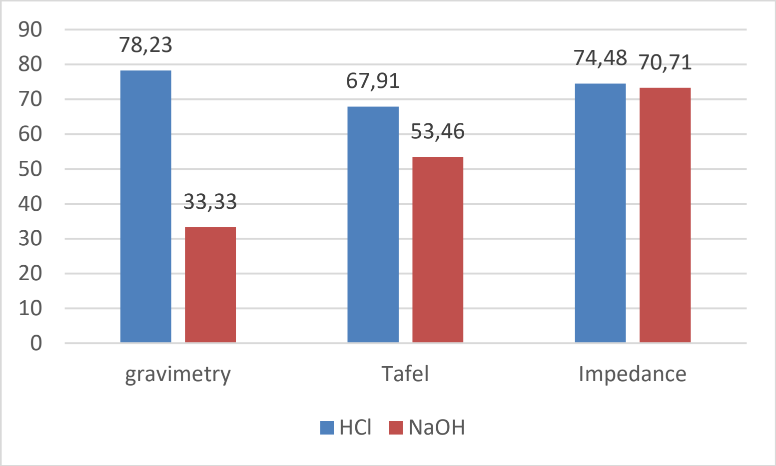


Fig IV.50: Comparison of inhibitory efficiency values in the three methods

General conclusion

General conclusion

The work presented in this dissertation is focused on the study of the corrosion inhibition of mild steel in aggressive medium of hydrochloric acid HCl 1M and sodium hydroxide NaOH 1M, using wild thyme extracts as a green inhibitor followed by a comparative study of the inhibitory efficiency using gravimetric method and electrochemical methods (polarization and impedance).

The workflow proceeded as follows: First, we confirmed the presence of the chemical compounds (tannins, saponicides, flavonoids, alkaloids, etc...) in the wild thyme extract.

After that, the plant extract was prepared by hydrodystillation in order to use it as an inhibitor in acidic and basic medium. We also prepared mild steel samples in square and cylindrical shapes. Finally, we tracked the corrosion process using an optical microscope and calculated the inhibitory efficiency using different measurement techniques (gravimetric method and electrochemical method).

The results that arise from this work are the following:

- Phytochemical screening of plants confirms the richness of the extract in large quantities of nitrogenous organic matter and sometimes oxygen. These are generally heterogeneous aromatic substances such as: tannins, saponisides, flavonoids and alkaloids, Therefore, it was chosen in this study to apply it as a corrosion inhibitor in aggressive environments.
- The mass loss of mild steel in hydrochloric acid is greater in acidic media than in basic media.
- The corrosion rate of steel decreases with the use of the inhibitor at a concentration of 1% in both acidic and basic medium, and we obtained values of 78.23% and 33.33%, respectively using gravimetric method.
- Examination using an optical microscope confirms the formation of a protective layer on the steel surface that protects it from corrosion.
- We also achieved similar results in acidic medium using electrochemical methods (polarization and electrochemical impedance), where the inhibitory efficiency was 74.48%, and 70.71% in the basic medium.

Finally, this work made it possible to highlight and promote green inhibitors (environmentally friendly materials) for use in the industry.

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خاص بالالتزام بقواعد النزاهة العلمية لإنجاز بحث

(ملحق القرار 1082 المؤرخ في 2021/12/27)

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الصفة: طالب سنة ثانية ماستر كيمياء تخصص: كيمياء المواد

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المسجل بكلية: العلوم الدقيقة قسم: علوم المادة والمكلف

بانجاز أعمال بحث : مذكرة ماستر في الكيمياء

عنوانها: Plant extracts as green corrosion inhibitors - for mild steel in corrosive media

أصرح بشرفي أني ألتزم بمراعات المعايير العلمية والمنهجية ومعايير الأخلاقيات المهنية والنزاهة الاكاديمية المطلوبة في انجاز البحث المذكور أعلاه وفق ما ينص عليه القرار رقم 1082 المؤرخ في 2021/12/27 المحدد للقواعد المتعلقة بالوقاية من السرقة العلمية ومكافحتها.

التاريخ: 2025/05/27

إمضاء المعني بالمر

SABRINA