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Presented by:
Nesrine Boughezala
Fatma Zohra Lourabi

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Inhibition of the corrosion of C45 steel in the middle of hydrochloric acid 0.5M HCl by a water extract of mint leaves

Jury:

Dr.	Ghania BENCHABANE	MCB	Mohamed Khider University of Biskra	President
Dr.	Saida MARMI	MCA	Mohamed Khider University of Biskra	Supervisor
Dr.	Malika NOUADJI	MCA	Mohamed Khider University of Biskra	Examiner

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بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

﴿ رَبِّ أَوْزِعْنِي أَنْ أَشْكُرَ نِعْمَتَكَ الَّتِي أَنْعَمْتَ عَلَيَّ وَعَلَىٰ وَالِدَيَّ وَأَنْ أَعْمَلَ صَالِحًا تَرْضَاهُ
وَأَدْخِلْنِي بِرَحْمَتِكَ فِي عِبَادِكَ الصَّالِحِينَ ﴾ (النمل: 19)

Dedications

*After thanking Allah, I dedicated my effort to study throughout these years to my great mother to the most valuable gift from God for me to my beloved mother, **Hind Hamza***

*I dedicate my success to the one I am proud of, my dear father, **Youcef***

*To my only sister, who has a pure heart and a smiling face, my kind sister, **Meriem***

*To my brothers who support me, and with them, life becomes beautiful, **Mohammed and Yacine***

*I do not forget to mention all my big family, all my friends, colleagues, and everyone who knows **Nesrine Boughezala**.*

*My friend who shared this work with me **Fatima Zohra**,*

Nesrine

DEDICATIONS

Oh, Allah, praise, and gratitude to you, until you are satisfied, and to you, praise is to you, thank you when satisfied, and praise is to you and thank you always and forever for your grace. We thank God that he helped us to accomplish this humble work, I dedicate this success:

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*To the hands that held me first are still the ones that hold me when I feel lost, and took care of me until I became old my loving mother **Saliha**.*

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*To who helped me with this job **Nesrine Boughezala**.*

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General nomenclature

Symbol	Meaning
CR	The corrosion rate.
CR ₀	The corrosion rate in the absence of inhibitor.
CR _{inh}	The corrosion rate in the presence of inhibitor.
S	Dipped surface area.
L	Length of the submerged part of the sample.
D	Width of the submerged part of the sample.
H	Height of the submerged part of the sample.
T	Dipping time.
m ₁	Sample weight before dipping.
m ₂	Sample weight after dipping.
Δm	Difference between weights.
El	Inhibition efficiency.
T	Absolute temperature.
F	Faraday constant (F=96500 C.mol ⁻¹).
R	The universal gas constant (R=8.31 J.mol ⁻¹ .k ⁻¹).
N _A	Avogadro's number (N _A =6.023×10 ²³).
h	Planck's constant (h=6.62×10 ⁻³⁴ m ² .Kg.s ⁻¹).
C _{solvent}	The molly concentration of solvent.
C _{inh}	The inhibitor equilibrium concentration.
K _{ads}	The equilibrium constant.
θ	The surface coverage.

General nomenclature

ΔH_{ads}	The standard adsorption enthalpy.
ΔS_{ads}	The standard adsorption entropy.
ΔG_{ads}	Free energy of adsorption.
E_a	The activation energy.

SUMMARY

SUMMARY

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General introduction

General introduction

Most people are familiar with corrosion in some form or another. The great majority of them have a personal feeling about the importance of corrosion. It has been there since the man succeeded in preparing metals that were not found in the native state in nature [1-3]. In addition, which is defined in general terms as the primary means by which metals deteriorate. Corrosion introduces itself into many parts of our lives, .for example, the outdoor rusting of steel, household [2], and the underground water, gas, and oil pipelines that crisscross our [1]. Where corrosion attacks mostly from the inside, causing its overall, partial, superficial or structural deterioration by an electrochemical, chemical or electrolytic attack. This corrosion can cause serious damage to the metal and degrade its properties [4], for example, steel, like most metals. It can be destroyed by corrosion, i.e., by chemical, electrochemical or biological reactions with the surrounding environment. Researchers have long been interested in studying steel corrosion in various corrosive environments. In particular, the acid environment [3]. Hydrochloric acid is among the most widely used products in the industrial sector. Indeed, this acid causes the degradation of metallic materials, either by electrochemical or chemical reactions. Currently, there are several methods available to protect metallic materials from corrosion in this medium, such as the use of a metallic coating, anodic protection, cathodic protection, galvanizing, the use of corrosion inhibitors, etc [4].

Corrosion inhibitors is an inhibitor that can be defined as a chemical compound added in small quantities to the medium to reduce the corrosion rate of materials. It can be intended either for permanent protection of the part (the installation then requires careful attention scrupulous), or temporary protection (especially when the part is particularly sensitive to corrosion or when it is exposed to a very aggressive environment) [5].

Inhibitory molecules can act according to different mechanisms, thus giving them inhibition performance depending on the study medium; the development of eco-compatible and biodegradable corrosion inhibitors is becoming an important issue nowadays. For this reason, and for their remarkable inhibitory properties, organic inhibitors have been widely acclaimed over the past decade [5] because they are environmentally friendly, nontoxic, and relatively less expensive [6]. Where these inhibitors act first by adsorption on the surface of metals before even intervening in the reaction process of corrosion to reduce its speed. Upon incorporating the inhibitors into the electric double layer found on the surface of the metal, the molecule polarized or the inhibiting ion modifies the charge distribution and consequently

potential. The majority of inhibitors capable of acting in an acid medium are organic compounds.

In our study, this kind of inhibitor was of interest, and we selected the water extract of mint leaves as a C45 steel inhibitor to study in the center of HCl hydrochloric acid in 0.5M concentration, intending to determine the effectiveness of this inhibitor under the influence of concentration, time and temperature using the weight loss method.

This work is divided into three chapters:

Chapter I: A theoretical study addressing general concepts of corrosion and inhibitions.

Chapter II: We described the experimental procedures, materials and devices used to study inhibitory effectiveness.

Chapter III: presents the results obtained from weight loss and analysis of photocopy optical microscope.

In the end, the most important results obtained were summarized in the conclusion.

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CHAPTER I

GENERAL CONCEPTS ABOUT CORROSION AND PROTECTION METHOD

I.1. Corrosion

I.1.1. Introduction

Corrosion is more than just an inevitable natural phenomenon; it is very important from the points of view of economics and tragic accidents involving loss of life. Corrosion can be very expensive as well as unsafe. Corrosion chemistry is changing at a rapid pace and every chemical process is viewed very critically from the points of view of safety, environmental impact, and economics. One of the methods of combating corrosion is the use of corrosion inhibitors that decrease the corrosion rates to the desired level with minimal environmental impact. The field of corrosion inhibitors is undergoing dramatic changes from the viewpoint of environmental compatibility [1].

In this chapter, we will talk about everything we need to know about corrosion and ways to prevent it, especially using natural inhibitors to reduce it as much as possible.

I.1.2. Definition

Corrosion is a natural process. Just like water, flows to the lowest level, all-natural processes tend toward the lowest possible energy [2]. The spontaneous oxidation of metal is termed corrosion. That is, Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. The medium in which the metal undergoes corrosion is termed a corrosive or aggressive medium. Corrosion products formed are chemical compounds containing the metal in the oxidized form except for gold and platinum, all other metals corrode and transform themselves into substances similar to the mineral ores from which they are extracted [3].



Fig. I.1. A picture that shows corrosion [4].

I.1.3. Mechanism of corrosion

The reason for the occurrence of corrosion is the instability of the metal and the corrosion arises as a result of the occurrence of oxidation and reduction reactions [5]. Corrosion of metals and alloys in aqueous environments or other ionically conducting liquids is almost always electrochemical in nature. It occurs when two or more electrochemical reactions take place on a metal surface. One of these reactions results in the change of the metal or some elements in the metal alloy from a metallic state into a non-metallic state. The products of corrosion may be dissolved species or solid corrosion products. Because electrochemical reactions are at the origin of corrosion, the corroding metal surface is considered an electrode [6].

The electrons are produced by a chemical reaction in one area, the anode area. The electrons travel through a metallic path, usually the parent metal, and are consumed through a different chemical reaction in another area, the cathodic area [4].

I.1.3.1. Anodic Reactions

The generic chemical reaction for this metal loss at anodic sites is [4]:



Where:

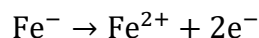
M: Is an uncharged metal atom at the metal surface.

M⁺: Is a positively charged metal ion in the electrolyte.

e⁻: An electron stays in the metal.

This type of chemical reaction is called metal oxidation, even though it does not directly involve oxygen, but only results in an increase in positive charge on the atom undergoing oxidation or loss of electrons. This resultant ion is dissolved into the water [4].

More than one electron can be lost in the reaction, as in the case of iron where the most common anodic reaction is [4]:

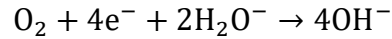


Where Fe is metallic iron. Fe²⁺ is a ferrous ion that carries a double positive charge.

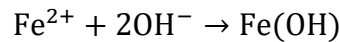
I.1.3.2. Cathodic Reactions

The electrons that are produced at anodic sites are consumed at cathodic sites. The type of chemical reaction that consumes electrons are called reduction [4]:

One of the most common cathodic reactions is the reduction of oxygen:



Further to this, the four OH^- ions are free in the water to combine with the Fe^{2+} ions to form $\text{Fe}(\text{OH})_2$ following the equation:



This whole process can be seen in the following diagram where the product is iron hydroxide, or what we commonly call rust [4].

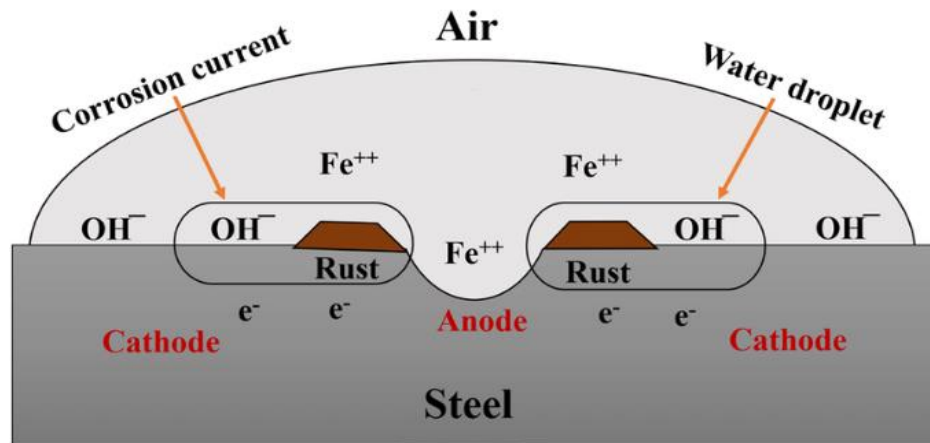


Fig.I.2. Corrosion mechanism of steel [7].

I.1.4. Metal corrosion in acidic medium

Acidic media are aggressive environments for metals and alloys, where the metal dissolves in the anode regions through the reaction of oxidation of the metal atoms to lose metal ions in the solution, and the reaction takes place at the cathode, in which hydrogen ions are released in the acid with the evolution of hydrogen, acidic solutions based on hydrochloric acid are used For chemical cleaning and pickling in general at low temperatures [8].

I.2. Types of corrosion

There are three main types of corrosion:

Table.I.1. Types of corrosion.

Chemical corrosion	<ul style="list-style-type: none">• It corresponds to the reaction of the metallic material with a gaseous phase or a liquid phase; in the first case, we speak of dry corrosion and a more or less protective solid deposit is formed. Cases of chemical corrosion by a liquid phase and not relating to electrochemical corrosion are extremely rare [9].
Electrochemical corrosion	<ul style="list-style-type: none">• Electrochemical corrosion, also called wet corrosion, is the most important and most frequent mode of corrosion. It resides essentially in the oxidation of the metal in the form of ions or oxides. The presence of dissolved salts (NaCl) increases the risks of corrosion by a greater difference in electrochemical potential [9].
Bacterial corrosion	<ul style="list-style-type: none">• This type of corrosion, also called bio-corrosion, brings together all the corrosion phenomena in which bacteria act directly or through their metabolism by playing a primordial role, either by accelerating an already established process, or by creating the conditions favorable to its establishment [9].

I.3. The causes of corrosion

The causes of corrosion are multiple and complex and result from chemical and/or physical interactions between the material and its environment [10].

Among them, we mention:

- Air humidity.
- Acidic medium.
- Do not forget the dangerous gases that corrode the surface of the metal.

I.4. Forms of corrosion

I.4.1. General (Uniform) attack

This is the most common form of corrosion. It occurs when a chemical or electrochemical attack occurs over a large area in a uniform manner. This is often referred to as a general wall loss or thinning. The uniform attack is the greatest destruction of metal on a tonnage basis [11].

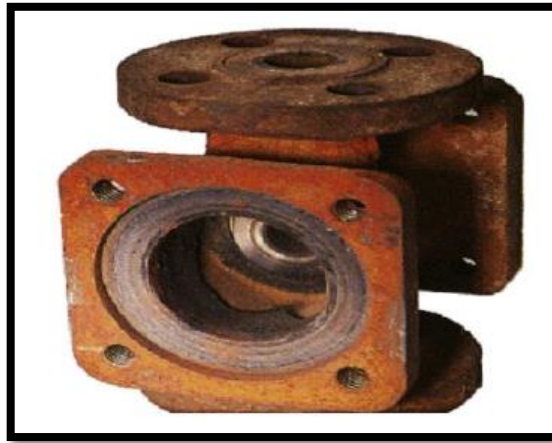


Fig.I.3. General corrosion (rust) of a steel part [12].

I.4.2. Localized corrosion

This phenomenon occurs, on the contrary, when the material is placed in the presence of an environment exhibiting a selective behavior to it.

This selectivity can have multiple origins both at the level of the material (heterophase alloy, presence of inclusions, locally defective surface protection, bimetallic material, etc.) and at the level of the environment (local variation in composition, pH, or temperature). This form of corrosion takes place at some surface point of a material [13].



Fig.I.4. Localized corrosion [14].

I.4.3. Crevice corrosion

Crevice corrosion is observed when there is infiltration of a solution between two parts of an assembly [13]. Depending on the cell configuration, the corrosion may be localized or uniform. Crevice corrosion is a highly localized attack occurring in a crevice or an otherwise shielded area when a material is exposed to a stagnant corrosive media. Common locations for crevice corrosion are Crevices (such as under bolt or rivet heads), Gasket surfaces, Holes, Lap joints, and Surface deposits. It is sometimes called deposit or gasket corrosion [11].



Fig.I.5. Crevice corrosion [15].

I.4.4. Pitting corrosion

Pitting corrosion is a form of extremely localized attack that results in holes in the metal. A highly localized corrosion attack that results in holes is referred to as pitting. Pits may be isolated or localized and of virtually any configuration. They occur at defects or

imperfections in a protective or passive film. It is a form of corrosion difficult or predict by laboratory tests [11].



Fig.I.6. Pitting corrosion [16].

I.4.5. Galvanic corrosion (bimetallic corrosion)

It is one of the most common forms of corrosion in an aqueous environment. Is due to the formation of an electrochemical cell between two materials in which one of the electrodes (the anode) is consumed to the benefit of the other (the cathode) which remains intact. This selectivity of the reactions is due to heterogeneity coming either from the material or from the environment or the Physicochemical conditions at the interface [13].



Fig.I.7. Galvanic corrosion [17].

I.4.8. Intergranular corrosion

This form of corrosion is manifested by the localized attack at the grain boundaries of the material. The heterogeneity at the level of the grain boundary and the existence of a corrosive medium playing the role of electrolyte represent two conditions for the development of this form of corrosion [13]. The only difference between this and uniform corrosion is that

the grains remain undamaged. The metallographic examination is usually the only way to identify this corrosion mechanism [11].

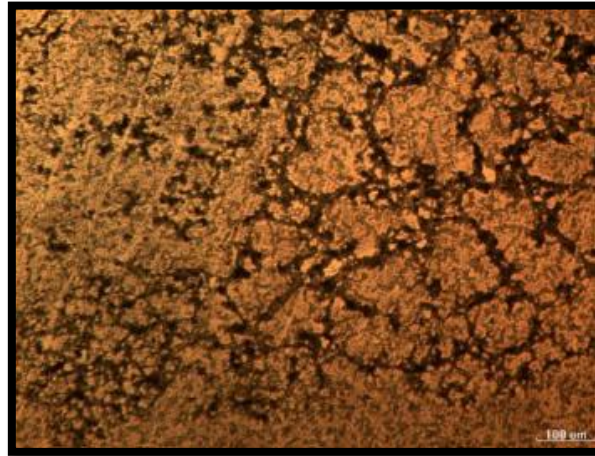


Fig.I.8. Intergranular corrosion [17].

I.4.9. Selective corrosion

It is also known as dealloying: This is the removal of one element from a solid alloy by corrosion processes. Most materials are made up of a combination of several elements. Dealloying occurs when one of the elements is removed from the metal matrix, leaving an altered residual structure. It is commonly identifiable by a color change or a drastic change in mechanical strength [11].

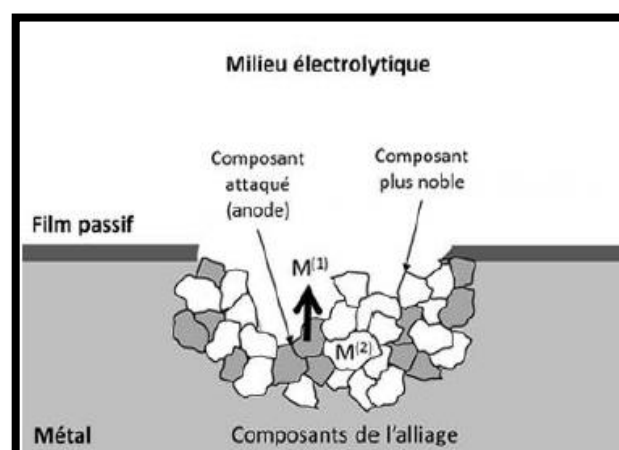


Fig.I.9. Selective leaching [17].

I.4.10. Erosion corrosion

Is used to describe the increased rate of attack caused by a combination of erosion and corrosion. If a fluid, stream contains suspended particles or where there is high velocity or turbulence, erosion will tend to remove the products of corrosion and any protective film and the rate of attack will be markedly increased. For example, plastic inserts are used to prevent erosion-corrosion at the inlet to heat-exchanger tubes [11].

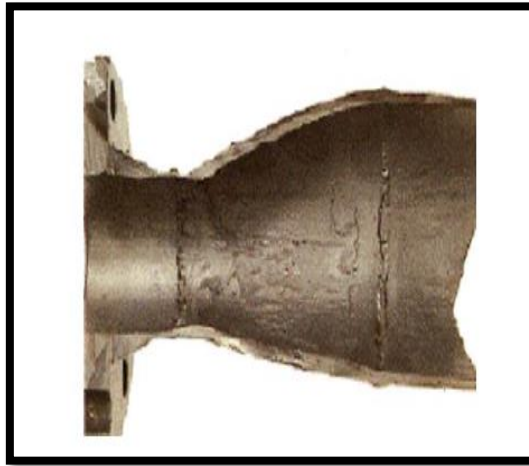


Fig.I.10. Erosion corrosion [13].

I.5. Corrosion reaction rate

Corrosion rate, the rate at which a material dissolves as a result of chemical action is an important parameter in this regard. It refers to the loss of thickness of a material per unit of time and area. The formula for the corrosion rate is [9]:

$$CR = \frac{KM}{S \rho t} \dots\dots\dots (I.1) [9]$$

Where M is the mass loss after the sample exposure time, and K is a constant ($K = 87.6$). Speed is expressed in millimeters per year (mm/year), M in milligrams, ρ in grams per cubic centimeter, S in square centimeters, and t in hours. In most applications, a corrosion rate of less than about 0.50 mm/year is acceptable. When an electric current is associated with electrochemical corrosion reactions, the corrosion rate can also be expressed as a function of this current or, more precisely, of the electric current density (J), the current per unit of corroded surface [9]. The corrosion rate CR, here in mol/dm².s, is calculated using the following equation:

$$CR = \frac{J}{nF} \dots\dots\dots (I.2) [9]$$

Where n is the number of electrons associated with the ionization of each metal atom and F is Faraday's constant.

I.6. Factors affecting corrosion

The phenomenon of corrosion depends on a large number of factors that always play a role in determining their development [18]:

I.6.1. Effect of temperature

Generally, the increase in temperature accelerates the phenomena of corrosion, because it decreases the field of stability of metals and accelerates the kinetics of the reactions [19].

I.6.2. Effect of acidity

The pH of the electrolyte is an agent, which negatively influences the electrochemical reactions of corrosion. Corrosion increases with decreasing PH of the medium [19].

I.6.3. Hydrodynamic regime

The transport of reactants to the interface and of reaction products to the electrolyte is likely to modify the kinetics of electrochemical reactions by changing the concentration of species and therefore the equilibrium potential. The hydrodynamic conditions fix the rates of reactions by controlling the transport of matter by the establishment of a species diffusion boundary layer, called the Nernst layer, which explains the importance of electrolyte agitation during laboratory corrosion tests [18].

I.6.4. Effect of salinity

Increasing the dissolved salts in the medium increases the speed of transmission of electric current and thus increases the rate of corrosion [5].

Table.I.2. Explain the factors affecting corrosion [5].

The middle	Nature of metal	Time factor	Conditions of use
<ul style="list-style-type: none"> • The composition of the gaseous or liquid medium. • The amount of dissolved salt and oxygen. • . PH nature of the medium • temperature. • thermodynamic conditions. • add damper 	<ul style="list-style-type: none"> • chemical composition. • thermal processing . • Mechanical treatment. • How to prepare. 	<ul style="list-style-type: none"> • Preservation conditions. • mechanical stress. 	<ul style="list-style-type: none"> • surface condition. • sample shape. • Mechanical agitation. • Welding. • Compilation terms.

I.7. Methods to control corrosion

There are five primary methods of corrosion control [2]:

- Material selection.
- Coatings.
- Inhibitors.
- Cathodic protection.
- Design.

I.7.1. Material selection

There is an ever-increasing variety of metals and alloys with each having its characteristics, applications, advantages, and limitations. For material specialists, it is important, when it comes to selecting a metal for an application, to understand the functional requirements including corrosion considerations. Several methodologies incorporating knowledge-based and intelligent database systems have been developed in the past to help address the issue of material selection. In addition, some researchers presented design models such as the graph theory and the matrix approach that involve calculations taking into consideration, among other factors, corrosion resistance [20].

I.7.2. Coatings

Coatings for corrosion protection can be divided into two broad groups—metallic and nonmetallic (organic and inorganic). With either type of coating, the intent is the same, that is, to isolate the underlying metal from the corrosive media [2].

I.7.3. Cathodic protection

Cathodic protection is one of the most important approaches to control corrosion. In essence, when a metal surface is cathodically protected, it can withstand corrosive environments without deterioration [20].

This type of protection is used to limit or prevent corrosion inside the electrolytic medium the method is to convert the cathode electrodes into anodized electrodes, so the metal is returned to the corrosion-immune region and corrosion is impossible [21].

In cathodic protection, an external current polarizes the entire surface of the metal to the thermodynamic potential of the anode; hence, the surface becomes equipotential. In other words, a net positive current [20].

I.7.4. Design

Where the tanks and containers are designed taking into account the condition of the medium flow and the absence of depressions, cracks, and closed corners [21].

I.7.5. Inhibitors

Corrosion inhibitors constitute an original means of combating the corrosion of metals. The originality comes from the fact that the anti-corrosion treatment is not done on the metal itself but through the corrosive medium [18].

I.8. Corrosion inhibition

I.8.1. Introduction

Another way to mitigate corrosion is by adding corrosion inhibitors to corrosive media. Corrosion inhibitors are organic or inorganic substances that when added in small quantities to corrosive media can to some extent protect the surface of metals [20].

I.8.2. Definition

An inhibitor is a substance that decreases corrosion when added to an environment in low concentration or as defined by the National Association of Corrosion Engineers (NACE) “An inhibitor is a substance that retards corrosion when added to an environment in low concentration” [22, 23].

Inhibition retards electrode reactions such as charge transfer or mass transport and especially the corrosion process. It consists in the use of chemical substances called corrosion inhibitors, which, by adding them in small quantities to the corrosive environment, reduce the speed of corrosion of the metal by acting on the medium or the surface of the metal [22].

I.8.3 Conditions of inhibitors

The inhibitor must meet several conditions, including the following [5]:

- Reduce the corrosion rate of metal without affecting its physical and chemical properties, especially resistance mechanical.
- To be stable in the presence of other components of the media, especially oxidants.
- To be stable at the temperatures used.
- It is effective at low concentrations.
- Be compliant with non-toxicity standards.
- Low cost and widely available.

I.9. Properties

Based on this definition, a corrosion inhibitor must therefore verify a certain number of fundamental properties [24]:

- ❖ Lower the rate of corrosion of the metal while preserving the Physico-chemical characteristics of the latter.
- ❖ Be stable in the presence of other constituents.

- ❖ Be stable in the temperature range used.
- ❖ Be effective at low concentration.
- ❖ Be effective under the conditions of use.
- ❖ Inexpensive about the savings it makes possible.
- ❖ Be compatible with current non-toxicity and environmental protection standards.

I.10. Classes of inhibitors

Corrosion inhibitors are classified according to several criteria [19] :

- 1) The nature of the products (organic or mineral inhibitors).
- 2) The electrochemical mechanism of action (cathodic, anodic, or mixed inhibitors).
- 3) Based on their interface mechanisms and principles of action (adsorption on the surface of the metal and formation of a protective film).

I.10.1. Nature of the molecules of the inhibitor

I.10.1.1. Organic inhibitors

Organic molecules are destined for more than certain development as corrosion inhibitors: their use is currently preferred to that of inorganic inhibitors mainly for reasons of ecotoxicity. The inhibiting action of these organic compounds is linked to the formation (by adsorption) of a more or less continuous barrier, but of finite thickness, which prevents access of the solution to the metal. The organic compounds used as inhibitors must have at least one heteroatom serving as an active center for their fixation on the metal such as nitrogen (amine, amides, etc.), oxygen (acetylenic alcohols, etc.), sulfur (derived from thiourea, mercaptans, sulfoxides, thiazoles...) or phosphorus (phosphonates). One of the limitations in the use of these products can be the rise in temperature, as organic molecules are often unstable at high temperatures [25].

I.10.2. Mineral inhibitors

These mineral inhibitors are used in alkaline environments and almost never in acidic environments. Mineral molecules dissociate in solution and anions and cations actually provide inhibition. Chromates, molybdates, silicates, and phosphates are the most important mineral inhibitors [26].

I.10.3. Green inhibitors

Currently, corrosion research is oriented toward the development of “green corrosion inhibitors” (also called “eco-friendly inhibitors”), compounds with good inhibition efficiency (IE), nontoxic and low risk of environmental pollution. The term “green inhibitor” or “eco-friendly inhibitor” refers to the readily available substances, renewable sources, that do not contain heavy metals or other poisonous compounds, and have biodegradability and biocompatibility with the natural environment [27].

Green inhibitors are often oils or extracts obtained by plants: bark, roots, leaves, and seeds, since it is made up of a mixture of compounds that belong to different product classes such as phenols, hydrocarbons, alcohols, aldehydes, ketones, etc. These inhibitors based on plant extracts have a non-toxic character [19].

I.11. Classification according to the mechanism of electrochemical action

I.11.1. Anodic inhibitors

The inhibiting effect is determined by plotting steel polarization curves in an appropriate medium. The addition in the medium of an anodic corrosion inhibitor modifies the initial polarization curve. Anodic inhibitors cause a large displacement of the corrosion potential in the positive direction. These types of inhibitors can be dangerous and should be used with great care. The addition of an inhibitor, by reducing the anodic surface without modifying the corrosion current density, leads to deep corrosion, which is, therefore, more dangerous. This is pitting corrosion [26].

I.11.2. Cathodic inhibitors

Cathodic inhibitors decrease the solvent reduction current density and shift the corrosion potential in the negative direction [23] by a displacement of the corrosion potential towards less noble values by increasing the cathodic overvoltage and by decreasing the concentration of O_2 in the corrosive medium [13].

Cathodic inhibitors are considered safer than anodic inhibitors because they are unlikely to promote localized corrosion [23].

I.11.3. Mixed inhibitors

The mixed inhibitor acts on both anodic and cathodic types, and reduces the rate of both reactions by forming a film on the metal surface by blocking both the anodic and cathodic sites,

when the film is deposited on the surface metal, the ohmic resistance of the electrolyte solution increases [19].

I.12. Reaction mechanisms

The mechanism of action of an inhibitor can be considered under two aspects:

- ✓ An aspect where the inhibitor intervenes in the fundamental processes of corrosion.
- ✓ An aspect where the inhibitor intervenes in the interfacial structure.

In addition, the mechanism of action of an inhibitor may undergo variations depending on Characteristics of the medium, in particular the PH. The mechanism of inhibition is very complex and could not be explained by a Single theory. Now, some would explain the action of inhibitors [24].

I.12.1. Formation of a protective film

When a metal electrode subjected to active dissolution in a particular medium is polarized in the positive potential direction using a potentiostat, the anodic dissolution current will decrease rapidly at a certain critical potential and the metal becomes passive. The passive state of metal reached either by the applied potential or by the addition of a strong oxidizing agent to the solution is due to the formation of a monatomic or a polyatomic oxide film on the surface of the metal [1].

I.12.2. Adsorption of inhibitor molecules to the metal surface

Adsorption is a universal surface phenomenon because any surface is made up of atoms that do not have all their chemical bonds satisfied. This surface, therefore, tends to fill this gap by capturing nearby atoms and molecules. Two types of adsorption can be distinguished: physisorption (formation of weak bonds) and chemisorption .The first also called physical adsorption, retains the identity of the adsorbed molecules. Three types of forces are to be distinguished [28].

I.13. Absorption mechanism

It is generally agreed that corrosion inhibition is due to the adsorption of the inhibitor molecule at the metal–solution interface, which is accompanied by a change in a potential difference between the metal electrode and the solution due to the non-uniform distribution of electric charges at the interface. The metal–electrolyte interface is characterized by an electrical double layer. The first layer is a sheet of charges at the metal surface caused by an excess or

deficiency of electrons. The second layer is formed on the solution side of the interface by specially adsorbed ions. These anions lose their coordinated water molecules or water sheaths, displace adsorbed water molecules from the metal surface, and in turn, are adsorbed on portions of the bare metal surface. These ions are known as potential-determining ions. The charges are balanced in part by hydrated ions of opposite charges in the outer Helmholtz plane called counterions. Outside this area is known as the Gouy–Chapman diffuse layer, where the concentrations of the counterions decrease toward that of bulk electrolyte and balance the net charge close to the metal surface [1].

The adsorption mechanism (the adsorption energy of the inhibitor) is determined according to the following equation [5]:

$$\Delta G_{ads} = -RT \ln K_{ads} C_{solvent} \dots \dots \dots (I.3) [5]$$

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \dots \dots \dots (I.4) [27]$$

ΔG_{ads} : Free energy of adsorption.

$C_{solvent}$: Is the molly concentration of solvent.

R: Is the universal gas constant.

T: Is the thermodynamic temperature.

K: The equilibrium adsorption constant.

I.14. Types of adsorption

I.14.1. Physical adsorption

Van der Waal's electrostatic forces that exist between the inhibitor (present in an electrolyte) and the metal surface cause this type of adsorption. It is commonly thought to be through the donation of an excess negative (or positive) charge to the metal surface [20]. Sometimes, physical adsorption is referred to as physisorption. During metal cathodic polarization, the metal surface becomes positively charged. In this case, the negatively charged anionic inhibitor will adsorb on the metal surface. Similarly, a positively charged cationic inhibitor will adsorb on the metal surface when it is negatively charged (i.e., during anodic polarization). Nunez summarizes the factors by which this phenomenon can occur. It can occur through [20]:

- 1) The electrostatic attraction between the charge on both the inhibitor and the metal.
- 2) The dipole interactions between the two materials when they are uncharged.
- 3) The p-electrons in the molecule and the orbitals in atoms of the metal.
- 4) A combination of those interactions.

Physisorbed inhibitor molecules have relatively weak electrostatic forces and can be detached from the surface by physical means such as increasing the temperature and/or velocity of the media (i.e., shear stress) [20].

I.14.2. Chemical adsorption

Chemical adsorption, also called chemisorption is an adsorption process that results in strong binding of the inhibitor with the metal surface. Actually, in chemisorption, a charge transfer or charge sharing takes place between the inhibitor molecule and the surface of the metal. An inhibitor that is chemisorbed usually interferes with the dissolving metal atoms by interacting with them, thus, blocking active surface sites. However, it has been noticed that chemisorbed molecules have a certain residence time. That is, they are in dynamic processes of adsorption/desorption steps. Chemisorption is known for its high heat of adsorption, persistence, and irreversibility [20].

I.15. Adsorption isotherm

Adsorption isotherms explain the degree of interaction of molecules of various inhibitors with the metal surface. Since corrosion inhibition, using organic inhibitor occurs with the development of protective films caused by the adsorbed extract molecules on metal surfaces. Isotherm equations were used to confirm that the inhibition mechanism is truly adsorption. Also, to establish the closest equation that relates the concentration of inhibitors to the adsorbed concentration at saturation, the empirical equations such as exponential, hyperbolic, logarithmic, and power are difficult to associate with the given mechanisms of the adsorption process. The Freundlich, Langmuir, and Temkin isotherms apart from their simplicity are easy to apply to derive complete information from their parameters to characterize the corrosion inhibition system [29].

$$f(\theta, x) * \exp(-\alpha\theta) = KC \dots \dots \dots (I.5) [29]$$

I.15.1. Van't Hoff equation

$$\ln K_{\text{ads}} = \frac{-\Delta H_{\text{ads}}}{RT} + \frac{\Delta S_{\text{ads}}}{R} + \ln \frac{1}{55.5} \dots \dots \dots (I.6) [30]$$

ΔS_{ads} : The standard adsorption entropy.

ΔH_{ads} : The standard adsorption enthalpy.

I.15.2. Thermodynamic equation

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \dots \dots \dots (I.7) [30]$$

I.16. Activation energy (Ea)

Activation energy is the minimum amount of energy required to initiate a reaction and is referred to as the kinetics of the reactions [20]. It is simply an indicator of how fast reaction proceeds, which is attributed to the formation of an inhibitor–metal complex insolvent, resulting in the higher energy barrier of, metal dissolution [30].

The activation energy (Ea) for the metal in the presence of inhibitors can be calculated by using the Arrhenius equation [30]:

$$CR = A \exp\left(\frac{-Ea}{RT}\right) \dots \dots \dots (I.8) [20]$$

Where CR is the reaction rate coefficient, A is the frequency factor for the reaction, e is the irrational number (approximately equal to 2.718), Ea is the activation energy, R is the universal gas constant, and T is the absolute temperature (Kelvin).

I.17. Factors affecting inhibitors

In the following, we present the most important information about the inhibitors represented in the factors controlling the performance and efficiency of the inhibitor.

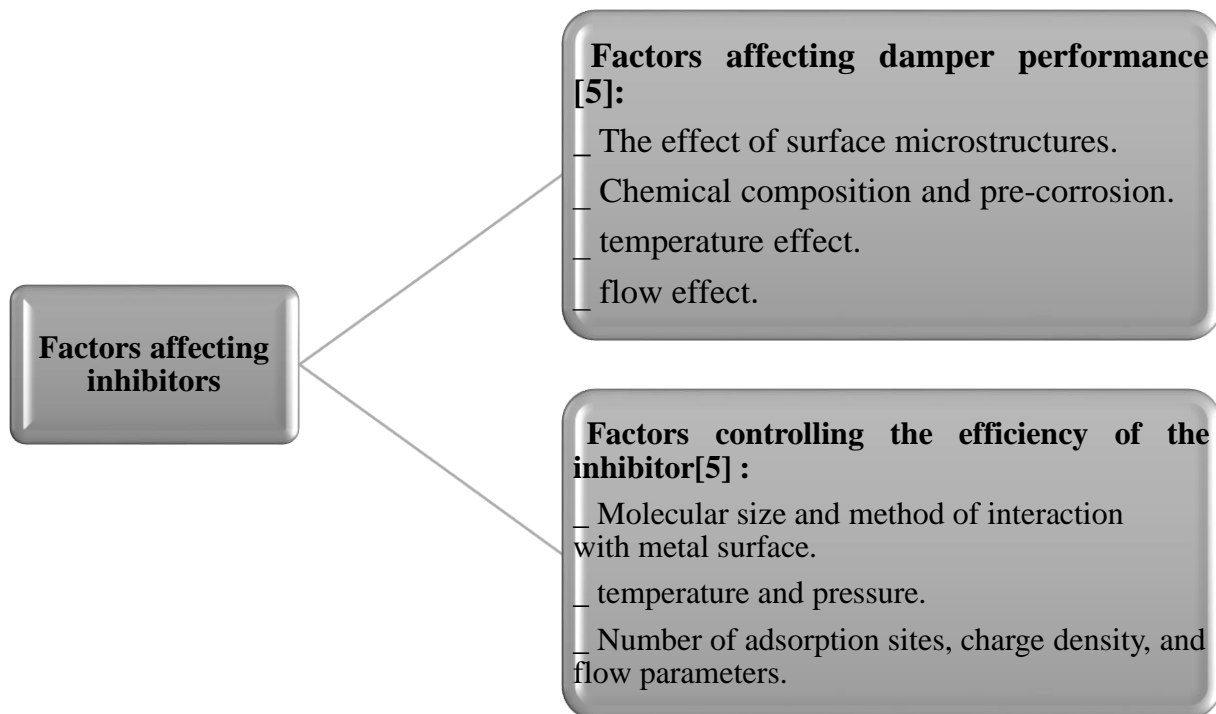


Fig.I.11. Diagram showing the factors controlling the performance of the damper and the factors affecting its efficiency.

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CHAPTER II

EXPERIMENTAL STUDY OF INHIBITOR EFFICACY

II.1. Introduction

In this chapter, we will address the preparation of samples of C45 steel metal and the preparation of an aqueous extract solution for mint leaves.

II.2. Instruments used

- Beaker (1000-200-30) ml.
- Measuring Flask (250-500) ml.
- Measuring Cylinder
- Vernier caliper.
- Abrasive papers.
- Basin.
- Spatula.
- Nomination papers.



Fig.II.1. Vernier caliper.

II.3. Equipment used

- A mechanical polisher.
- Precision electronic balance (0.0001g)...FA2004B.
- Hot plate Stirrer.
- Electronic thermometer.
- X-ray diffractometer.



Fig.II.2. Electrical Balance.

II.4. Samples Preparation

II.4.1. Steel C45

The material in this study is alloy steel C45 [1], which is a metal with excellent mechanical performance and consists of:

Table II.1. Chemical composition of the studied C45 steel (% by mass) [1].

Element	C%	Si%	Mn%	P%	S%	Cr%	Ni%	MO%
	0.45	0.40	0.80	0.045	0.045	0.40	0.40	0.10

II.4.2. Polishing process

Polishing is a surface machine that we use to remove the surface layer of the material and get a surface such as a mirror where there are no defects or visible scratches. The samples were polished using a mechanical polisher (Fig.II.3) .This machine works by turning a disc covered with changeable abrasive paper. In this machine, we use a water jet to cool the sample and rid it of surface particles.

We used abrasive papers of different grits from 80 to 1200, followed by rinsing with distilled water, then drying.



Fig.II.3. A mechanical polisher and samples after polishing.

II.5. Preparation of solutions

II.5.1. Preparation of the acid solution

The molar hydrochloric acid solution was prepared by dilution of a 37% grade stock solution in bi distilled water.

II.5.2. Preparation of inhibitor solution

To prepare the mint leaf solution we do the following:

- Just take the mint leaves, wash them thoroughly, and dry them out of the sun for 6 days.
- After it dries, we grind it in an electric blender until we get soft powder.
- In Beaker, we mix 300ml of distilled water with 10g of powder for 3 h at 60 ° C.
- After the mixing is over, we leave it for 24 h.
- We do the first filtering by filter paper.
- Then we take the remaining amount of the first filtration and add it to 300 ml of distilled water. We do the same steps to get the solution from the second filter.
- We mix the obtained solutions, and thus we get the original solution (the mother) and then we prepare the required concentrations (5ml, 7ml, 10ml, and 15ml).

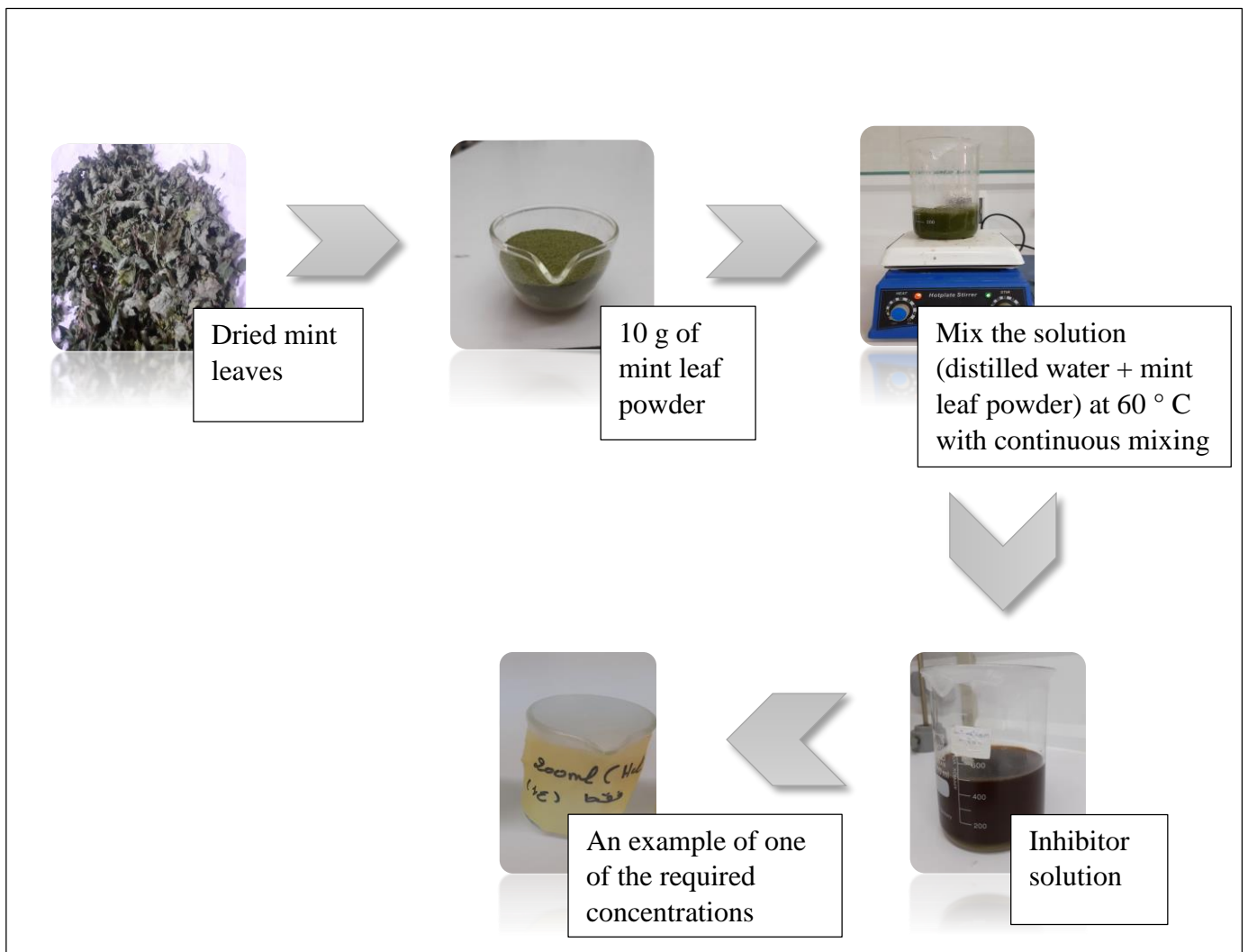


Fig.II.4. Outline showing the steps of work.

II.6. Experimental study of used methods

II.6.1. Weight loss method

II.6.1.1. Definition

The method of dipping or what is also called mass loss or weight loss is a classic manual method that requires you to be patient to get the right results that can be analyzed.

It is the weight of the samples to be calculated before being exposed to the corrosion environment, then exposed to the corrosion environment for some time, after which the corrosion environment is taken and the corrosion products are removed and then weighed, and the weight difference is expressed as the weight loss due to corrosion [2-4].

That occurred in a specified area S within a certain time t according to the following laws:

$$\Delta m = m_1 - m_2 \dots \dots \dots (II.1) [5]$$

Δm : Difference between weights.

m_1 : Sample weight before dipping.

m_2 : Sample weight after dipping.

$$CR = \frac{\Delta m}{St} \dots \dots \dots (II.2) [5]$$

CR: Corrosion rate.

t: Dipping time.

S: Dipped surface area.

$$S = 2(L \times D + L \times H) + (H \times D) \dots \dots \dots (II.3)$$

L: Length of the submerged part of the sample.

D: Width of the submerged part of the sample.

H: Height of the submerged part of the sample.

$$EI\% = \frac{CR_0 - CR_{inh}}{CR_0} \times 100 \dots \dots \dots (II.4) [5]$$

EI: Inhibition efficiency.

CR_0 : Corrosion rate without inhibitor.

CR: Corrosion rate in the presence of an inhibitor.

II.7. The principle of work

II.7.1. Effect of concentrations

- We weigh the samples until we get their initial weight of m_1 .
- Preparing the required receptacles for solutions (200 ml HCl, with the rest of the concentrations of the inhibitor solution).
- We define the dimension to be dipped and cover the rest with plastic tape.
- Dipping samples into solutions and leaving them for 24 h.

- After the end of the time, we take the samples out of the solutions and clean them thoroughly with distilled water.
- We weigh them back while taking their dimensions to calculate to get the right focus.

II.7.2. Effect of dipping time

After choosing the right focus with the highest inhibition efficiency, we did the following:

- We bring new samples (polishing) and determine the dimension we want to submerge.
- We take a set of 30ml beakers and fill it with the specific focus solution and then dip the samples for 3, 7, 10 and 15 days.
- After the specified period, we remove the samples, wash them, and dry them.
- We calculate the weight of the samples again and take the dimensions of the submerged surface.

II.7.3. Effect of temperature

In this experiment, the sample preparation is slightly different where:

- After polishing the samples, we determine the part we want to dip and cover the remaining part, and then leave the samples to dry.
- We weigh the samples and record the initial weight value.
- We fill the four barriers with the solution with the appropriate concentration and then dip the samples, but we put the face where we want to study the corrosion higher.
- Put the hot plate at 35 ° C, 45 ° C, and 55 ° C and leave the carpet in for 2 h.
- We leave one of the samples at room temperature 25° C for 2h.
- After the specified period, we remove the samples, then wash, and dry them.
- We weight the samples again and then measure the dimensions of the submerged surface.

II.8. Surface investigation

II.8.1. Analysis techniques

The purpose of analytical techniques is to determine the composition of a sample and to determine the components of the sample. They have been in existence for a long time but have made considerable progress since the development of computers and electronics [6].

II.8.1.1. Optical Microscope

The polished sections of the material are observed using an optical microscope, equipped with Normaski contrast, the images are acquired digitally. Its interest is twofold, according to the magnification of the chosen optics (from 100 to 400 times) on the one hand, the structural defects (cracks) are observed at low and medium magnification, on the other hand, the morphology and texture of the reinforcements and precipitates and second phases of the matrix are revealed by a strong enlargement [7].



Fig.II.5. Optical microscopy type UNITRON model A6-1588.

II.8.1.2. X-ray diffraction (XRD)

The study of the structural characterization of protective layers requires the use of the technique of X-ray diffraction [1].

X-ray diffraction is a coherent and elastic scattering phenomenon that occurs when an X-ray beam (electromagnetic wave) falls on a material [1].

The principle is that the X-ray beams produced by the tube are sent to the sample into which they are deflected by the atoms. These diffracted beams interfere with each other, leading to the production of an intense signal in certain specific areas of space. This signal is collected by the detector, and drawn as a curve (diffractogram) that has peaked at very specific diffraction

angles. The position of these peaks is a real signature of the arrangement of atoms inside a crystal (distance between atoms, between intracrystalline planes). The empirical relationship between the angles at which peaks are observed and the distances between atomic planes are Bragg's law [6].

$$n\lambda = 2d\sin\theta_n \dots\dots\dots (II.5) [8]$$

λ : Wavelength of the X-ray beam.

d : Distance of two reticular planes.

θ : The angle of incidence of the X-rays.

n : The diffraction order.

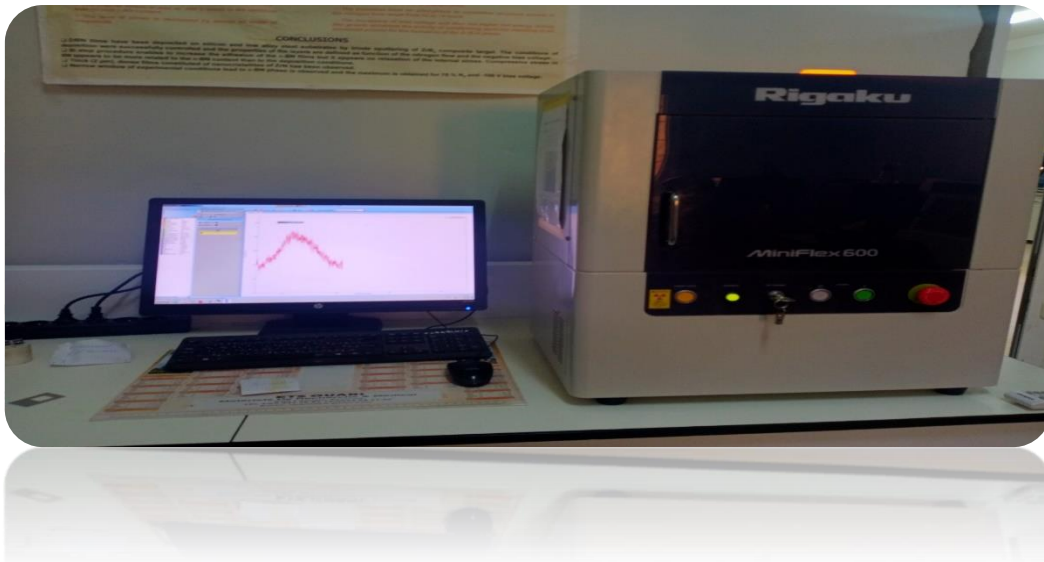


Fig.II.6. X-ray diffraction (XRD) machine.

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CHAPTER III

RESULTS AND DISCUSSION

III.1. Introduction

In this chapter, we will discuss and explain the results obtained from the experimental study of the C45 steel metal inhibition process by water extract from mint leaves under the effect of concentration, dipping time, and temperature using the weight loss method.

III.2. Study of weight loss measurements

III.2.1. Effect of concentration

To study this effect we change the concentration of the inhibitor and calculate the corrosion rate and inhibition efficiency and our results were as follows:

Table.III.1. Represents corrosion rate values and inhibition efficiency of C45 steel at 0.5 M HCl as a function of inhibitor concentration.

C (g.l ⁻¹)	S(cm ²)	Δm(g)	t(h)	CR(g.cm ⁻² .h ⁻¹)	E (%)
0	1.7799	0.0113	24	2.6453E-04	/
0.7	1.1800	0.0029	24	1.0240E-04	61.2891
1	1.3979	0.0023	24	6.8555E-05	74.0839
1.5	2.5067	0.0018	24	2.9920E-05	88.6894

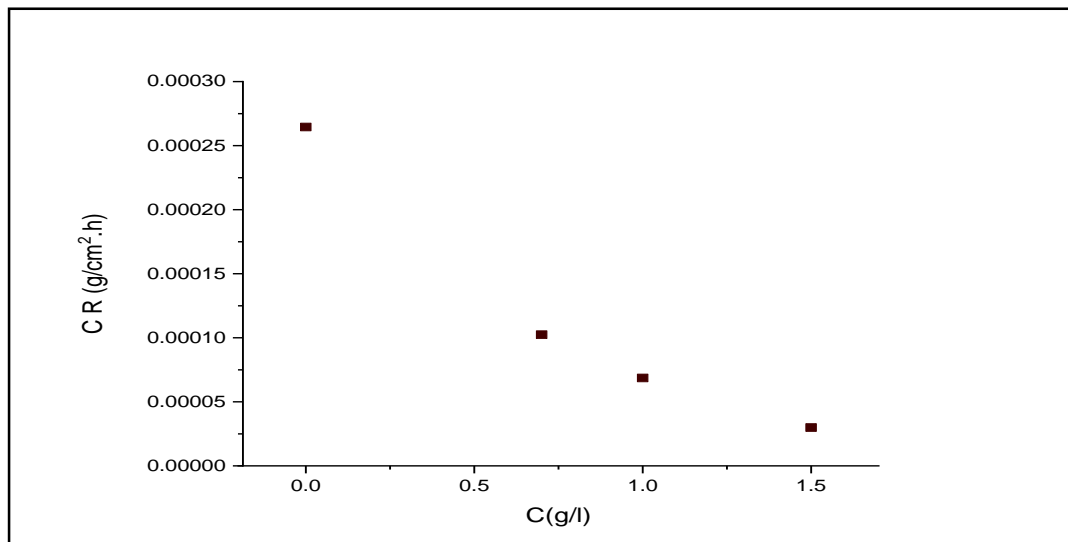


Fig.III.1. A curve represents the variation of the corrosion rate as a function of concentration in the absence and presence of inhibitor.

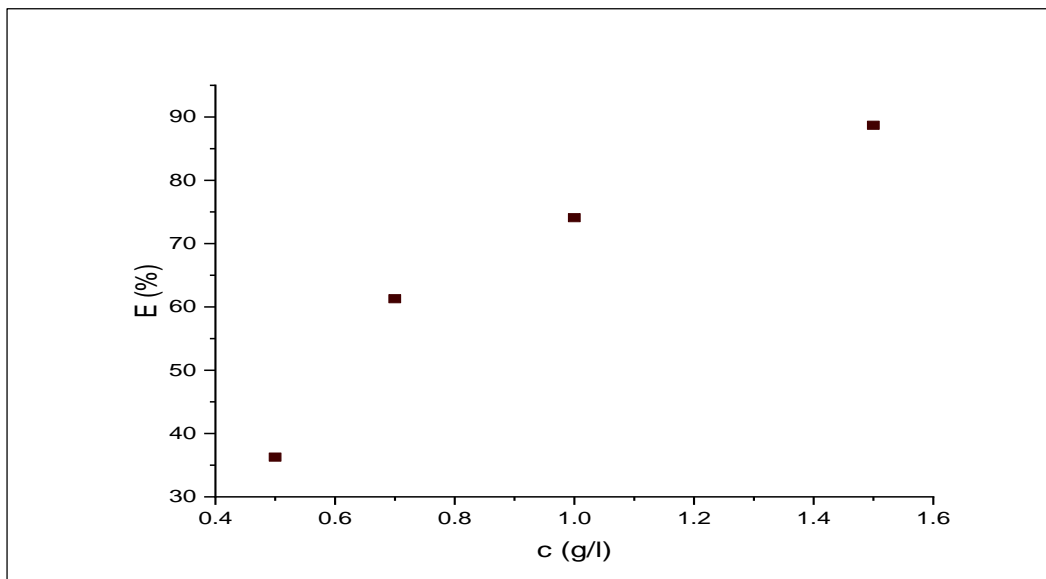


Fig.III.2. A curve represents variation of inhibition efficiency as a function of concentration.

Through the curve (Fig.III.1), which represents a change in the corrosion rate as a function of concentration, we observed that the value of the corrosion rate peaked at 2.64533×10^{-4} ($\text{g.cm}^{-2}.\text{h}^{-1}$) in the absence of an inhibitor. Then you start decreasing when you add the inhibitor that showed moderate effectiveness in the case of small concentrations, such as when you focus 0.7 (g.l^{-1}) The corrosion rate value was 1.0240×10^{-4} ($\text{g.cm}^{-2}.\text{h}^{-1}$) and then this value increases with the concentration increasing to 2.9920×10^{-5} ($\text{g.cm}^{-2}.\text{h}^{-1}$) at 1.5 (g.l^{-1}).

The curve (Fig.III.2) represents the change in inhibition efficiency as a function of concentration, as we observed a proportional relationship between inhibition efficiency and concentration where the inhibition efficiency in weak concentration was 61.28% at 0.7 (g.l^{-1}) and then increased to 88.68% at 1.5 (g.l^{-1}).

The inverse correlation between the corrosion rate and the concentrations is interpreted as a layer that protects the metal surface by the inhibitor that impedes the corrosion process [1].

The inhibition process is known as inhibitor adsorption on the surface of the metal, whose activity is initially weak in the aggressive medium (solution), which means that the corrosion rate is high, and then decreases.

The increased efficiency of inhibitors returns to the increase in adsorption of inhibitors with a pronounced coverage of protection on the mild steel surface with increased inhibitor

Concentration. This adsorption can be ascribed to the presence of various heteroatoms, and multiple bonds [2].

Researcher Helen Lee Yensen said that increased inhibition efficiency and lower corrosion rate are due to the steel surface absorption of the inhibitor molecules from which active sites are covered and blocked on the surface and forming a barrier layer that reduces the interaction between the metal and the corrosion solution [3].

III.2.2. Effect of dipping time

The effect of dipping time is one of the most important effects to be studied on the work of the inhibitor (water extract from mint leaves) by dipping samples of C45 steel in 0.5 M HCl and leaving them for different periods in an appropriate concentration of 1.5 (g.l⁻¹), where we get the results shown in the tables (Table.III.2) and (Table.III.3):

Table.III.2. The table shows corrosion rate values and inhibition efficiency values for steel metal C45 in 0.5 M HCl as a function of dipping time in the absence of an inhibitor.

t(h)	s(cm ²)	Δm(g)	CR(g.cm ⁻² .h ⁻¹)
24	1.7799	0.0113	2.6453E-04
72	1.3775	0.3753	3.7840E-03
168	1.0856	1.3753	7.5408E-03
240	1.0034	1.942	8.0642E-03
360	1.002	1.9947	5.5298E-03

Table.III.3. The table shows the corrosion rate values and inhibition efficiency values of C45 steel in 0.5 M HCl as a function of dipping time in the presence of an inhibitor.

t(h)	S(cm ²)	Δm(g)	CR(g.cm ⁻² .h ⁻¹)	E (%)
24	2.5067	0.0018	2.9920E-05	88.68
72	1.0836	0.0053	6.7932E-05	98.20
168	1.1954	0.0389	1.9370E-04	97.43
240	1.6056	0.0915	2.3745E-04	97.05
360	0.5854	0.0877	4.1614E-04	92.47

The curve (Fig.III.3) expresses the change in the corrosion rate of steel metal C45 in 0.5M HCl as a function of time in the absence and presence of inhibitor where we observed:

In the absence of an inhibitor, there is an increase in corrosion rate values from 2.6453×10^{-4} ($\text{g. cm}^{-2} \cdot \text{h}^{-1}$) 24 h to 8.0642×10^{-3} ($\text{g. cm}^{-2} \cdot \text{h}^{-1}$) after 240 h and then decreased to 5.5298×10^{-3} ($\text{g. cm}^{-2} \cdot \text{h}^{-1}$) after 360 h. In case of inhibitor, the corrosion rate values gradually increase starting with the value of 2.9920×10^{-5} ($\text{g. cm}^{-2} \cdot \text{h}^{-1}$) after 20 h to reaching the value of 4.1614×10^{-4} ($\text{g. cm}^{-2} \cdot \text{h}^{-1}$) after the duration of 360 h.

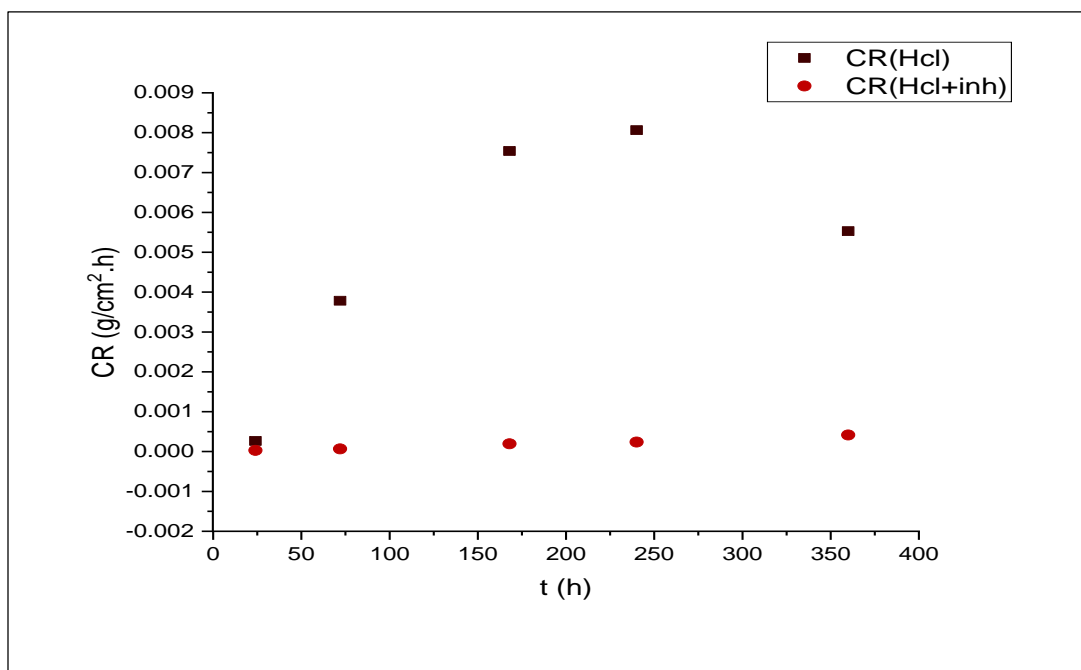


Fig.III.3. A curve represents the variation of the corrosion rate as a function of time in the absence and presence of inhibitor.

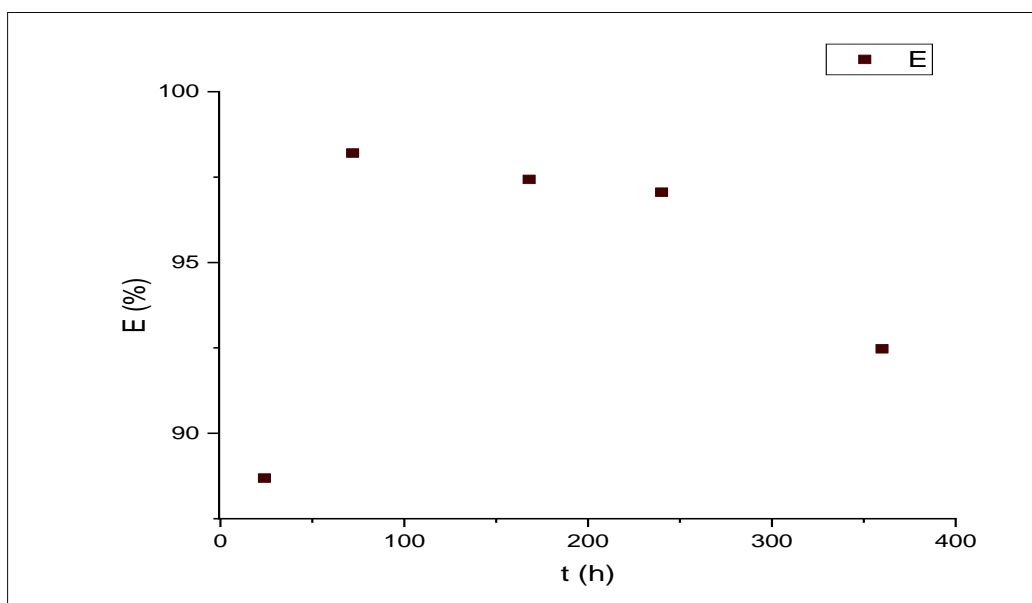


Fig.III.4. Curve represents variation of inhibition efficiency as a function of dipping time.

The curve (Fig.III.4) that studies the inhibition efficiency as a function of time, where we observed a good efficacy of the inhibitor from the first 24 h where the inhibition efficiency was 88.6894% and then this value increased to 98.2048% after 72 h of dipping time. It then drops to 92.4745% after 360 h.

We explain the increasing rate of corrosion in the absence of the inhibitor to the interaction between the metal surface and the corrosion solution where aggressive activity increases with increased time resulting in the sabotage of the metal surface.

We explain the decrease in the value of the corrosion rate after rising to a decrease in the speed of the electrochemical reaction over time, where they form layers of corrosion waste on the surface of the carbon steel that hampers the continuation of the corrosion process and this phenomenon is known as a recession [1] the protective film was formed more effectively against the acid corrosion attack [4].

The value of the inhibition efficiency increases with the partial absorption of the inhibitor molecules on the metal surface and Stango and Vijayalakshmi added that the number of vacant sites on the metal surface being occupied by the inhibitor molecules increased as a long time was allowed for the contact and in this study, we conclude that the immersion time for 72 h is the optimal period to achieve high inhibition efficiency [4].

The reason for the low inhibition efficiency thereafter is the reaction of the loss of the inhibitor molecules over time, from which the inhibitor molecules benefit in the system and form coordination links between the metal and inhibitor atoms [3].

III.2.3. Effect of temperature

Temperature is one of the most important external physical factors affecting the corrosion rate of steel metal C45 and the efficiency of water-extracted inhibition of mint leaves. We studied the effect of temperature on C45 steel metal in 0.5M HCl in the absence and presence of the inhibitor. The results were as shown in (Table.III.4) and (Table.III.5).

Table.III.4. The table shows the values of steel metal corrosion rate C45 in 0.5 M HCl as a function of temperature in the absence of an inhibitor.

T(K)	S(cm ²)	Δm (g)	t(h)	CR (g.cm ⁻² .h ⁻¹)
298	16.3250	0.1625	2	4.9770E-03
308	15.2660	0.1814	2	5.9413E-03
318	19.4828	0.2351	2	6.0335E-03
328	1.7731	0.011	2	3.1019E-03

Table.III.5. The table shows corrosion rate values and inhibition efficiency of C45 steel metal at 0.5 M HCl as a function of temperature in the presence of an inhibitor.

T(K)	S(cm ²)	Δm (g)	CR (g.cm ⁻² .h ⁻¹)	E%
298	1.14990	0.0014	6.0875E-04	87.76
308	1.13097	0.0017	7.5157E-04	87.35
318	1.21677	0.0021	8.6294E-04	85.69
328	1.14932	0.0021	9.1358E-04	70.54

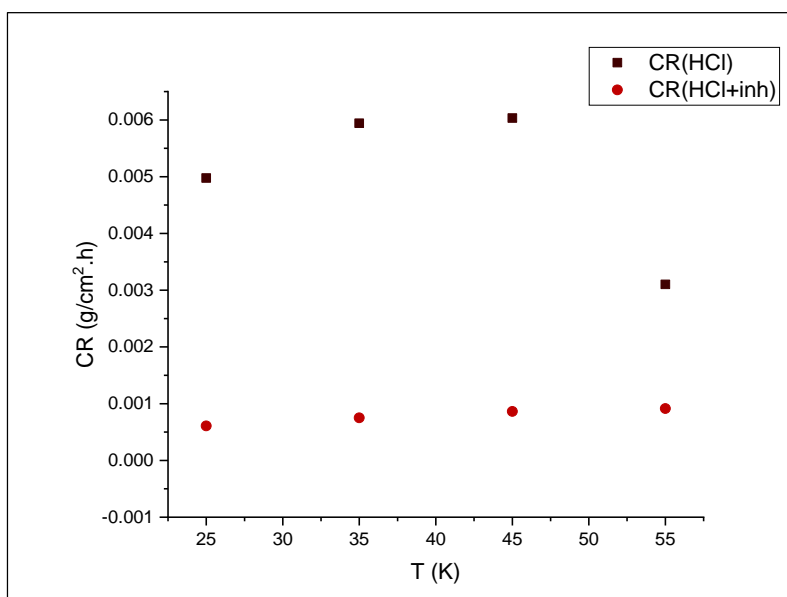


Fig.III.5. A curve represents the variation of the corrosion rate as a function of the temperature in the absence and presence of the inhibitor.

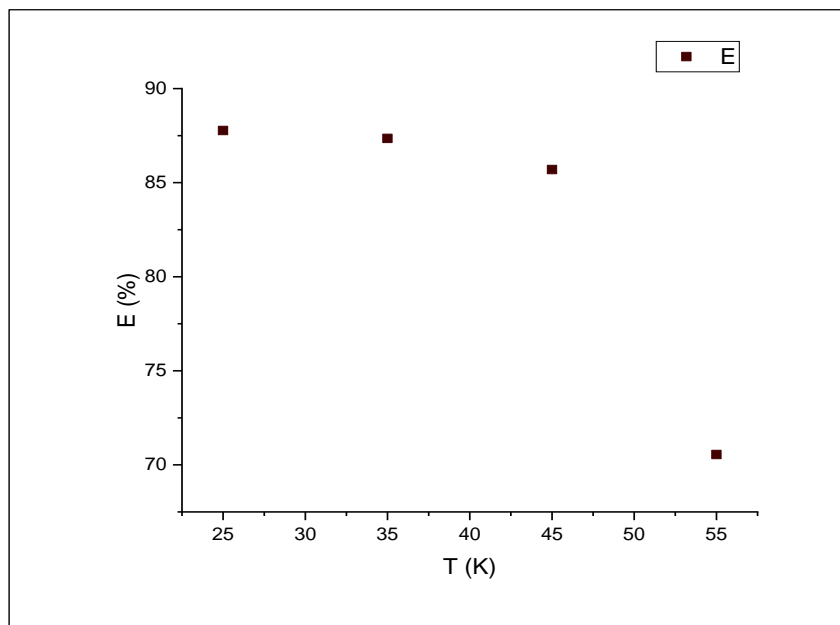


Fig.III.6. A curve represents the variation of inhibition efficiency as a function of temperature.

The first curve (Fig.III.5) shows the experimental results obtained for the corrosion rate of C45 steel metal in 0.5M HCl in the case of absence and presence of inhibitor at 1.5 (g.l⁻¹) where we observed:

In the absence of an inhibitor, the corrosion rate increases gradually from 4.4977×10^{-4} (g.cm⁻².h⁻¹) at 298K temperature to 6.0335×10^{-3} (g.cm⁻².h⁻¹) at 318K.

In the case of the inhibitor, the corrosion rate was at its lowest value, estimated at 6.0875×10^{-4} (g.cm⁻².h⁻¹) at room temperature 298K, and then increased to 9.1358×10^{-4} (g.cm⁻².h⁻¹) at the 328K temperature.

In the curve (Fig.III.6) which represents the inhibition efficiency as a function of the temperature in the presence of the inhibitor, we observed that at high temperature the inhibition efficiency decreases, for example at 298 K the inhibition efficiency was 87.76 % and at 328 K became 70.5 %.

Generally, increasing temperature accelerates corrosion events by decreasing the stability domains of metals and accelerating the kinetics of reactions and transport. The extent of its influence differs, however, depending on the corrosive medium in which the material is found [5].

The decrease in the rate of corrosion after an increase in temperature is due to the formation of a layer of deposits of the corrosion process on the surface of the metal.

The lower damping efficiency explains the increase in the compatibility of the damper with the metal surface in general. The higher the temperature, the faster the corrosion process and the solubility of the metal protective films, which increases the susceptibility of each metal [2].

III.3. Kinetics of corrosion reactions

We have previously stated that the temperature factor affects the corrosion of the C45 steel 0.5M HCl. To know the strength of the effect of this factor on the inhibition ratio, the values of the kinetic corrosion reactions must be determined E_a , ΔH_{ads} , ΔS_{ads} after we select the appropriate concentration of 1.5 (g.l⁻¹) and when changing the temperature from 298 to 328 K in the absence and presence of the inhibitor.

The molar activation energy of corrosion steel C45 at 0.5 M HCl is calculated by the presence and absence of the inhibitor from the Arrhenius relationship where there is a correlation between corrosion rate and temperature and is expressed by the following equation:

$$CR = A \exp\left(\frac{-E_a}{RT}\right) \dots \dots \dots (III.1) [6]$$

The formula becomes after taking the decimal logarithm:

$$\log CR = \log A - \frac{E_a}{2.303RT} \dots \dots \dots (III.2) [7]$$

Where: 2.303 Represents the conversion value from the natural logarithm (Ln) to the decimal logarithm (Log).

Table.III.6. The table shows the level of logarithmic corrosion (absent and extant inhibitor) and the inverted temperature corresponding to a concentration of 1.5 (g.l⁻¹).

1/T (K ⁻¹)	Log(CR) HCl	Log(CR) HCl+inh
0.0034	-2.3030	-3.2156
0.0032	-2.2261	-3.1241
0.0031	-2.2194	-3.0640
0.0030	-2.5084	-3.0393

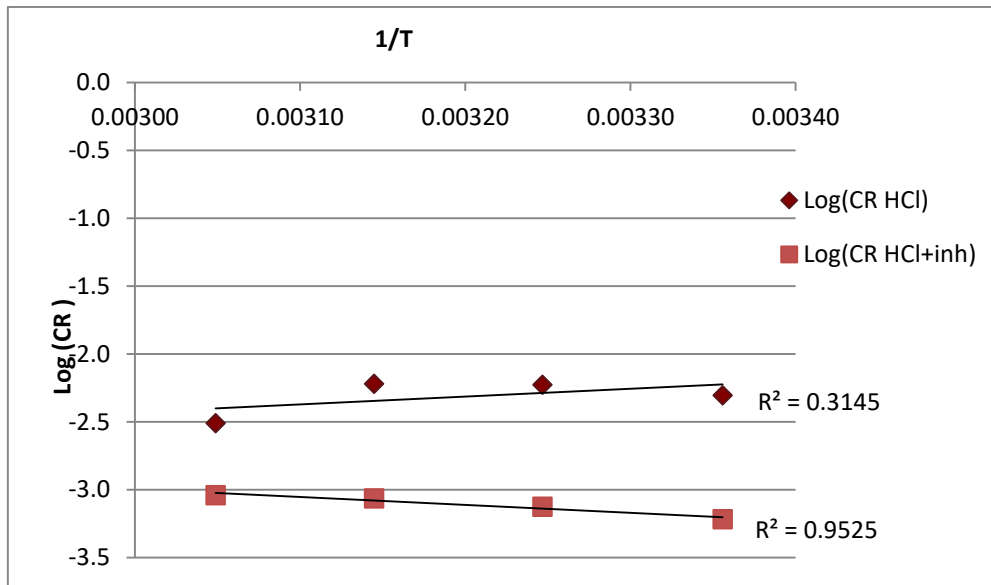


Fig.III.7. The curve represents variation the level of logarithmic corrosion as a function of the inverted temperature in the absence and presence of inhibitor.

E_a is calculated graphically when drawing values (Log CR) as a function (1/T).

Where we get a straight line equated from the shape: $y = ax + b$

Where: $a = \frac{-E_a}{2.303R}$ and $b = \log(A)$ as shown in the curve (Fig.III.7).

Table.III.7. The table shows the values Log (CR/T) of steel metal C45 in 0.5 M HCl as a function of the inverse of the temperature in the absence and presence of the inhibitor.

1/T (K ⁻¹)	Log (CR/T) HCl	Log (CR/T) HCl+inh
0.0034	-3.7010	-4.6135
0.0032	-3.7702	-4.6681
0.0031	-3.8726	-4.7172
0.0030	-4.2487	-4.7796

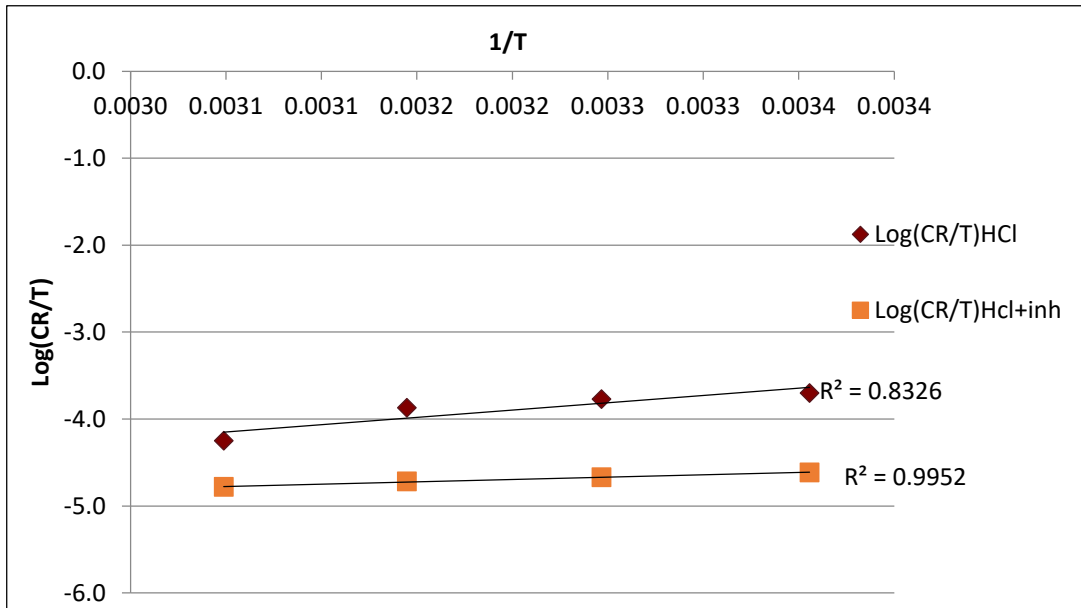


Fig.III.8. The curve represents values Log (CR/T) of steel metal C45 in 0.5 M HCl as a function of temperature inverter in the absence and presence of inhibitor.

In the previous chart, we see that we have two curves, one in the absence of the inhibitor and the other in its existence, which are straight lines that do not cut zero and their equation is:

$$\text{Log}\left(\frac{CR}{T}\right) = f\left(\frac{1}{T}\right) \dots\dots\dots (III.3)$$

Since ΔH_{ads} , ΔS_{ads} is calculated graphically by the equation:

$$\text{Log}\frac{CR}{T} = \frac{-\Delta H_{ads}}{2.303R} \left(\frac{1}{T}\right) + \left(\text{Log}\frac{R}{Nh} + \left(\frac{\Delta S_{ads}}{2.303R}\right)\right) \dots\dots\dots (III.4) [2]$$

Where:

ΔH_{ads} : Is the standard adsorption enthalpy.

R: Is the universal gas constant.

h: Is Planck's constant.

N: Is the Avogadro's number.

ΔS_{ads} : Is the standard adsorption entropy.

From the two previous equations, the slope of the curve equal to $\frac{-\Delta H_{ads}}{2.303R}$ and from it, we can calculate the value of ΔH_{ads} , ΔS_{ads} was evaluated from the intercept

$\left(\text{Log} \frac{R}{N_h} + \left(\frac{\Delta S_{ads}}{2.303R}\right)\right)$ of the same plot [2].

Table.III.8. Kinetics results from corrosion reactions in the absence and presence of an inhibitor.

	HCl	HCl+inh
Ea (kJ.mol ⁻¹)	-10.9567	11.0904
ΔH_{ads} (kJ.mol ⁻¹)	-32.2723	-10.2252
ΔS_{ads} (J.mol ⁻¹ .k ⁻¹)	-375.313773	-320.0300347

Through the table (Table.III.8) we note an increase in the value of activation energy with the presence of the inhibitor and its decrease in its absence, which explains this if an inhibitor causes a rise in Ea value when compared to the uninhibited solution, this could be frequently explicated as a suggestion for the formation of an adsorptive film by physisorption mechanism. While a decrease in Ea, value when compared to the uninhibited solution is often interpreted as an indication of chemisorption [8].

Generally, the increase in activation energy in the presence of an inhibitor compared to the blank is due to the physical adsorption on the metal surface. The unchanged or lowered value of Ea suggests chemical adsorption. On the other hand, it is accepted that mixed adsorption is characterized by lower or no change in Ea values [9].

Through the values of each of the ΔH_{ads} and ΔS_{ads} found in the table, we note:

First, we note that ΔH_{ads} values are negative in both cases in the presence and absence of an inhibitor and since we know that when the change of ΔH_{ads} is positive, the reaction absorbs heat (the endothermic reaction) and when the change of ΔH_{ads} is negative, it is an exothermic reaction and in our study, we found the reaction is a diffuser the heat.

The adsorption entropy ΔS_{ads} in the absence and presence of the inhibitor is largely negative the sign is negative. It means that the adsorption process is accompanied by a decrease in entropy. This can be explained as follows: before the inhibitor was adsorbed on the surface, the degree of disorder was high, but when the inhibitor molecules were characterized in an

organized manner on the surface, the result was a decrease in entropy [10]. Also, negative values of ΔS_{ads} indicate that the degree of the disorder increased when moving from a reactant

To a product [2]. That is, the adsorption of one inhibitor molecule on the metal surface causes more water molecules to be absorbed, which in turn causes an increase in disorder [11].

III.4. Adsorption isotherm results

Generally, the ability of the investigated inhibitor molecules to be adsorbed on the metallic surface determines their protective efficacy. As a result, it is critical to comprehend the adsorption isotherm, which offers crucial information on the inhibitor molecules' interactions with the surface of the metal. The nature and chemical structure of the inhibitor molecules, and how they are adsorbed on the metal surface (physisorption or chemisorption), influence the corrosion inhibitory mechanism of the metallic surface. The inhibitory concentrations and surface coverage (θ) were studied using several adsorption techniques to determine the best adsorption behavior [12]. The recovery rate (θ) values for different inhibitor concentrations obtained from weight loss measurements in the studied temperature range, (25°C) were used to determine the isotherm corresponding to the inhibitor adsorption process. Thus, different isotherms comprising Langmuir, Temkin, Frumkin, El-Alwado, Freundlich, and Flory-Huggins were tested for suitable adsorption isotherms [13]

Table III.9. The different linearized isotherm models were undertaken in the present study [8].

Isotherm	Linearized form	Equation
Langmuir	$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$	(III.5)
Frumkin	$\ln\theta = \ln K_{ads} + x \ln C_{inh}$	(III.6)
Temkin	$\theta = -\frac{1}{2 \times \alpha} \ln K_{ads} - \frac{1}{2 \times \alpha} \ln C_{inh}$	(III.7)
El-Alwado	$\log\left(\frac{\theta}{1-\theta}\right) = \log K_{ads} + n \log C_{inh}$	(III.8)
Freundlich	$\ln\theta = \ln K_{ads} + n \ln C_{inh}$	(III.9)
Flory-Huggins	$\log\left(\frac{\theta}{C_{inh}}\right) = \log x K_{ads} + x \log(1-\theta)$	(III.10)

Where θ is the surface coverage, K_{ads} is the equilibrium constant of the adsorption, C_{inh} is the inhibitor equilibrium concentration.

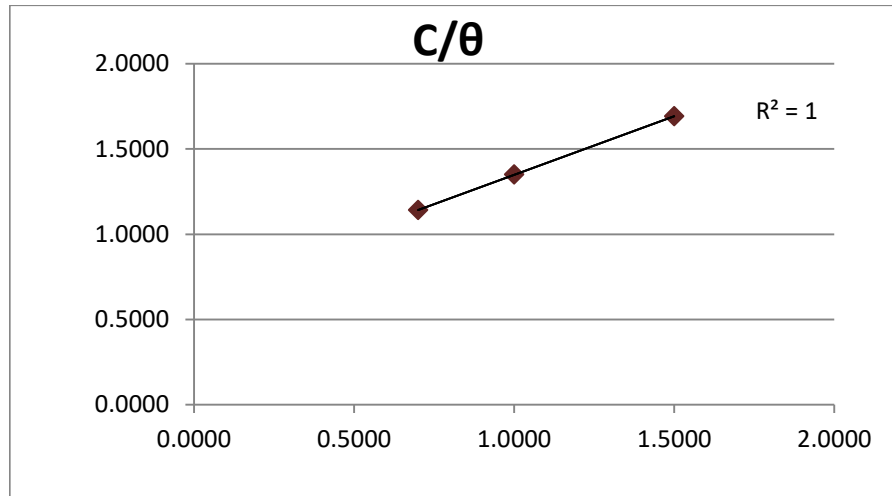


Fig.III.9. Langmuir.

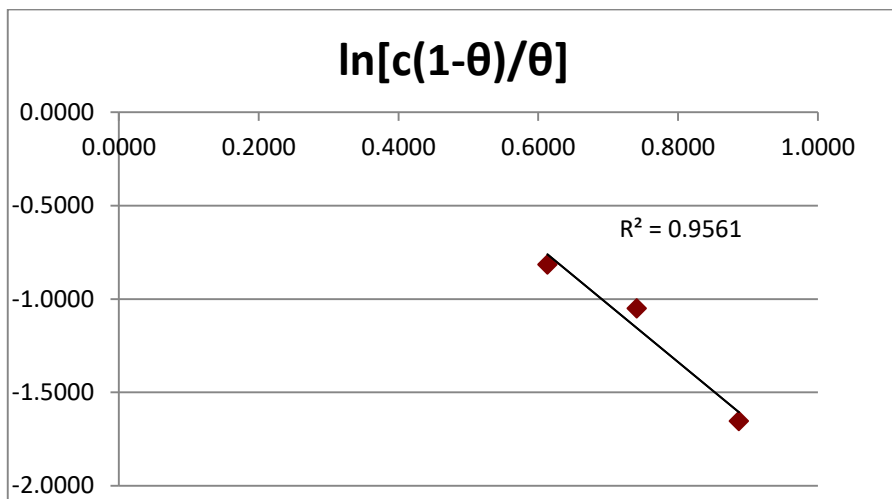


Fig.III.10. Frumkin.

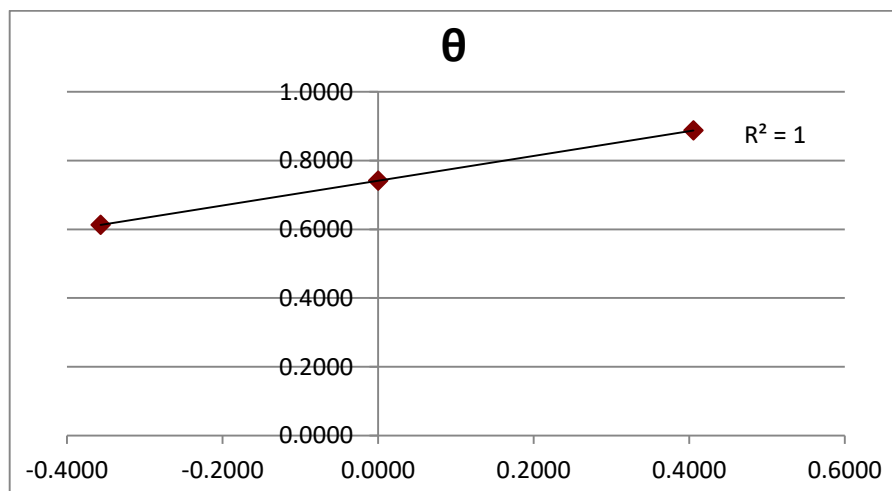


Fig.III.11. Temkin.

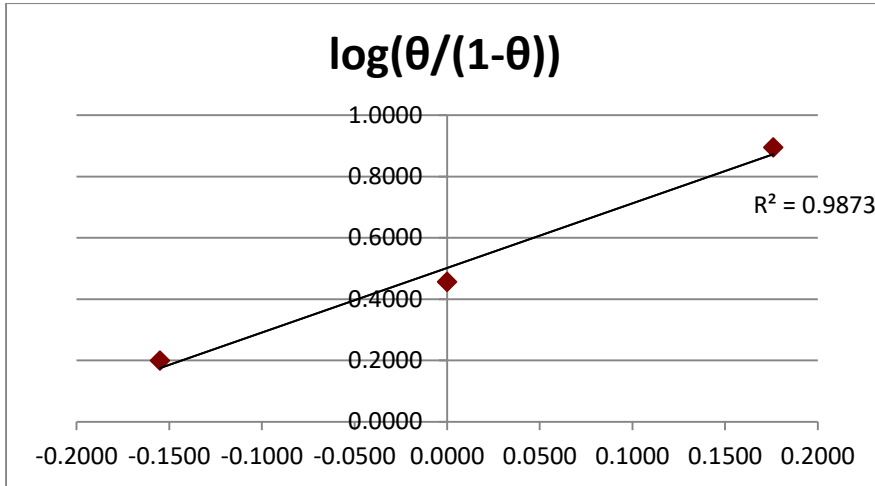


Fig.III.12. El-Alwado.

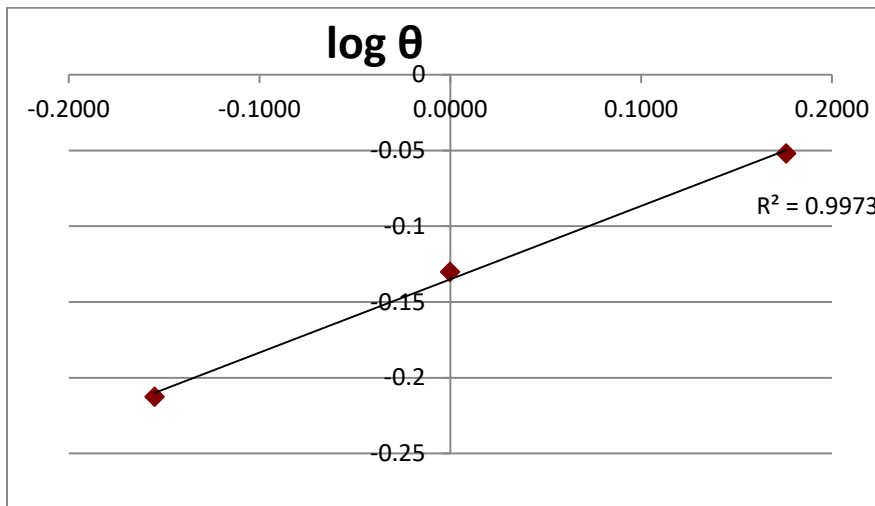


Fig.III.13. Freundlich.

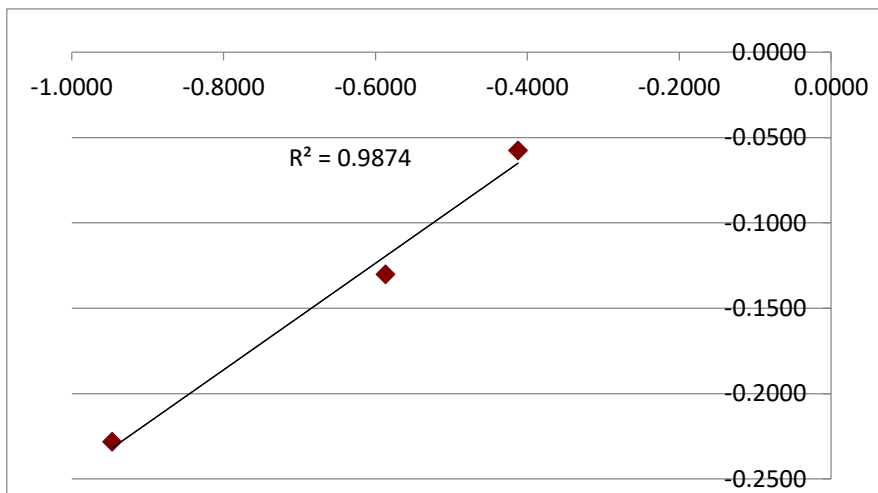


Fig.III.14. Flory-Huggins.

Table III.10. The table showing the correlation coefficient values of all isothermal equations.

Isotherm	R ²
Langmuir	1
Frumkin	0.9561
Temkin	1
El-Alwado	0.9873
Freundlich	0.9973
Flory-Huggins	0.9874

Notes that the graphic curves of straight lines and the table that all R² values approach the unit except Langmuir and Temkin values are equal to the unit (R²=1). This result confirms that adsorption, in this case, is subject to Langmuir and Temkin relations. This means that the inhibitor performs the adsorption process and forms a single layer on the surface of the metal and occupies the most effective positions [14].

The experimental observations led the researchers to develop several theoretical models to describe adsorption isotherms. The best known is Langmuir, which assumes a fixed number of sites on the surface. Each of these sites can only adsorb one particle [10]. Based on the article of the researcher Fatima Bouhlal who confirmed that the Langmuir model is done by the interaction of inhibitor molecules on the metal surface by dissonance where they absorb and condense these molecules on the metal surface [3], Langmuir model assumes the following[15]:

- The surface of the adsorbent (metal) is uniform.
- Adsorption sites are equivalent.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism assuming that the metal surface is uniform.

The Langmuir equation where Langmuir isotherm refers to the adsorption of molecules on the surface at a concentration of a medium at a fixed temperature. The equation was developed by Irving Langmuir the equation is [10] (III.5).

The Temkin model was based on the influence of indirect adsorbent/adsorbent interactions on adsorption isotherms. Temkin's isothermal model assumes that the adsorption heat of all molecules decreases linearly with increased coverage of the adsorbent surface.

So that the adsorption of these organic inhibitors prevents the dissolution or return of metal as well as a uniform distribution of the binding energies, up to maximum binding energy [10].

III.4.1. Gibbs Adsorption Energy

Gibbs energy is a quantity whose change in the course of a chemical reaction is equal to a change in the internal energy of the system and its equation [16]:

$$\Delta G_{\text{ads}} = -RT \ln K_{\text{ads}} \quad \text{..... (III.11)}$$

Table III.11. Table showing values of K_{ads} and ΔG .

Isotherm	K_{ads}	ΔG_{ads} (KJ.mol ⁻¹)
Langmuir	2.2618	-11.9672
	2.8586	-12.5471
	5.2275	-14.0419
Temkin	7.8579	-15.0511
	7.8519	-15.0492
	7.8582	-15.0512

According to the results shown in the table, we were able to calculate the value of the equilibrium constant for the adsorption rate from the equations of Langmuir and Temkin, according to their equations:

$$\text{Langmuir} \quad k_{\text{ads}} = \frac{1}{C_{\text{inh}}} \frac{\theta}{(1-\theta)} \quad \text{..... (III.12)}$$

$$\text{Temkin} \quad K_{\text{ads}} = \frac{1}{C_{\text{inh}}} \exp(-2\alpha\theta) \quad \text{..... (III.13)}$$

Where α is a slope, and from it calculates the value of the Gibbs energy.

It is believed that high negative values of the Gibbs energy indicate the spontaneity of the adsorption processes and the stability of the adsorption layer on the metal surface [13]. is due to the strong adsorption of the inhibitor on the steel surface, which also is related to electrostatic interactions between charged molecules and metal (physical adsorption) while the values of ΔG_{ads} up to (-20 kJ/mol) refer to the process of physical adsorption, values of about

(-40 kJ/mol) or more to chemisorption due to shared use or transfer of electrons from a molecule to a metal surface and values in the range from (-20 to -40 kJ/mol) correspond to a joint mechanism consisted of physical and chemical adsorption [16].

From the table, we note that d_g values for both Langmuir and Temkin are confined between (-11.96 to -14.04 kJ/mol) and (-15 kJ/mol). This indicates that ΔG_{ads} values are associated with electrostatic interactions between charged molecules and metal [13]. This confirms that the adsorption type is automatic physical adsorption.

Finally, from our study to inhibit the corrosion of C45 steel in 0.5M HCl by water extract from mint leaves using the weight loss method and the values of corrosion reaction movements, we conclude that the type of thoughtful adsorption is automatic physical adsorption of the nature of the heat distributor and is characterized by reduced chaos.

III.5. Results of the surface study

III.5.1. Optical Microscope

Imaging the microstructure by Optical Microscope optical microscope at Mohamed Khider University of Biskra / Physics and Chemistry Laboratory, and the microstructure images are shown in (Fig.III.14):

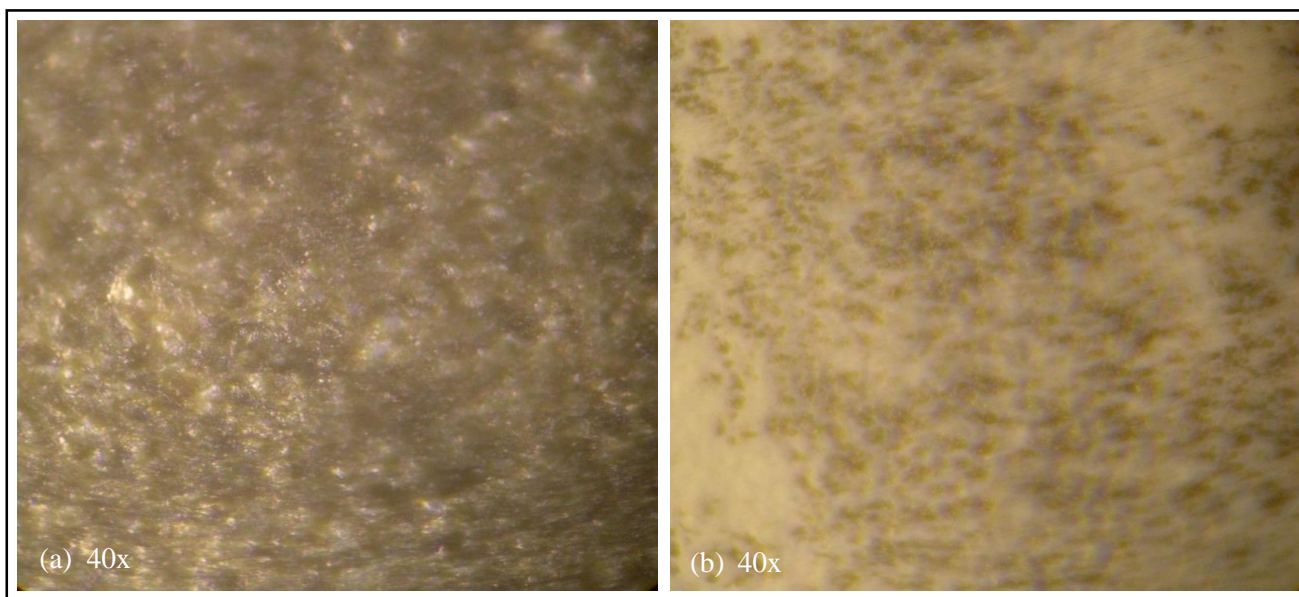


Fig.III.15. Optical microscopy images of a sample immersed in HCl solution for 24h in:

(a) The absence of the inhibitor, (b) The presence of the inhibitor .

Scanning microscopy is used to make micrographs of the surface of the samples, to characterize the different deposits and corrosion of surfaces.

Images (a) and (b) are images by optical microscope of C45 steel in 0.5 M HCl sample surface in the presence and absence of inhibitor (water extract from mint leaves) after submerging the sample for 24 h at a constant temperature of 25°C.

We note in the picture (a) the change in the color of the sample and the presence of illuminated white areas, which are observable drilling with the naked eye resulting from damage to the surface of the steel because solution HCl and its corrosion greatly due to the presence of defects and impurities on the surface resulting from the improper polishing process.

Microscopic image (b): In the presence of the inhibitor we observe the great disappearance of white areas and the deposition of a layer that can be seen with the naked eye and the formation of a protective membrane of the inhibitor particles on the surface of the metal and cover the holes, but not entirely because of the presence of defects that obstructed the process of forming the protective layer and also can be due to the failure to leave the sample for a sufficient period or even because of the concentration of the inhibitor can be insufficient. All these factors affect the work of the inhibitor and its protection of steel.

III.5.2. X-ray diffraction results

To ensure that the water extract of effective inhibitor mint leaves an immersion test was performed for samples of steel C45 in an acid medium 0.5 M HCl for 24h in the presence and absence of organic inhibitor. The X-ray examination was performed. The results were as follows:

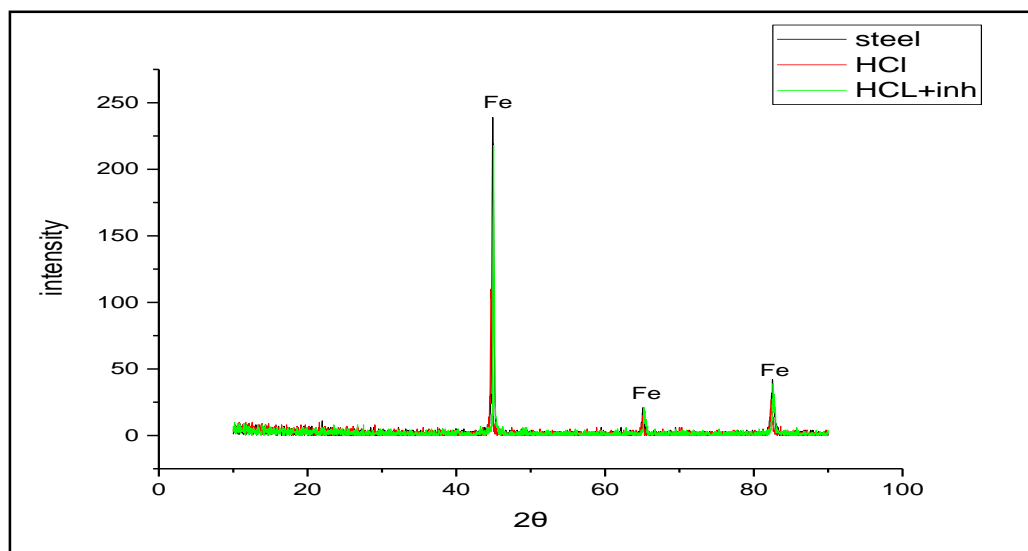


Fig.III.16. A set of XRD curves of steel in 0.5 M HCl medium without and with inhibitor addition.

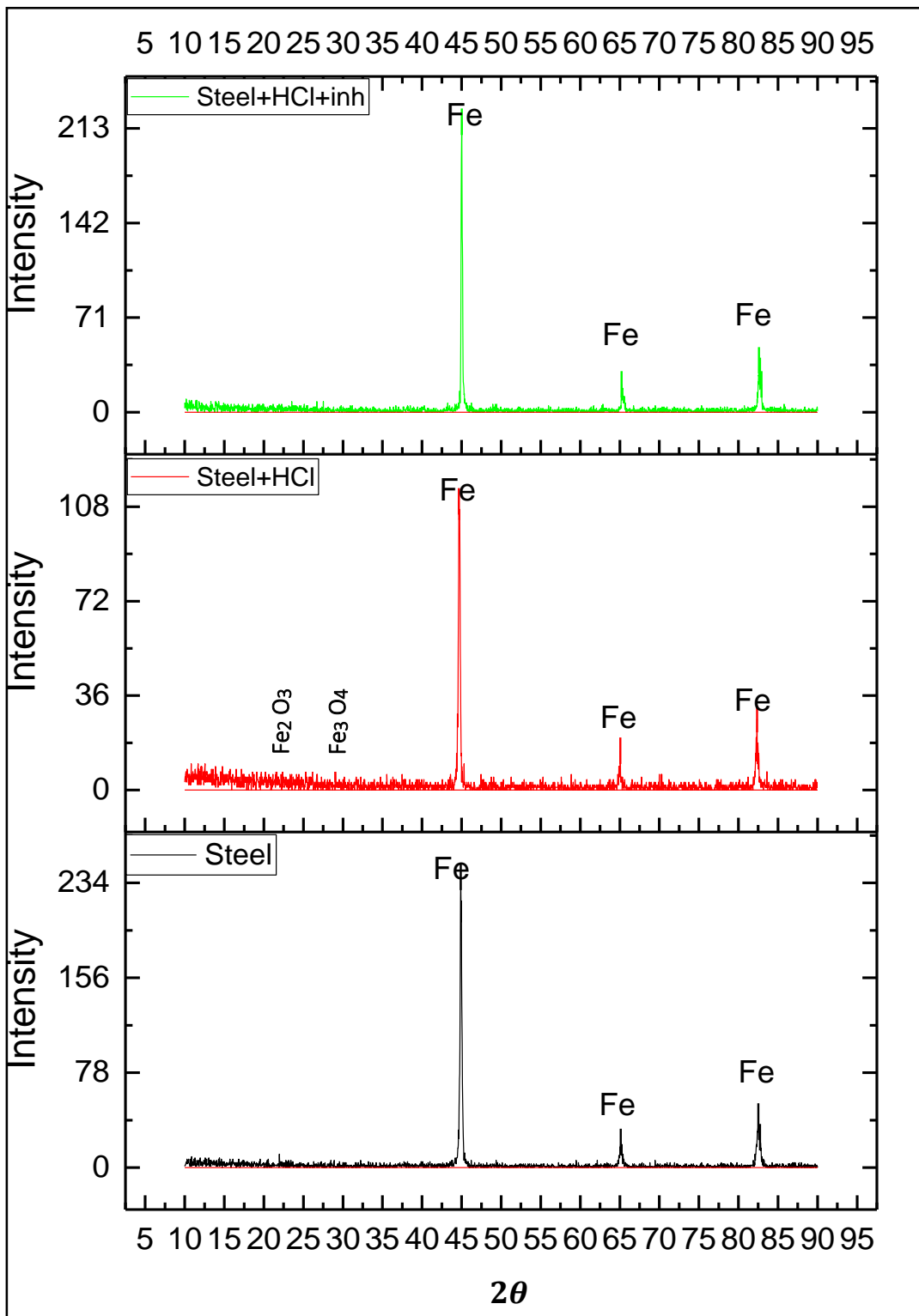


Fig.III.17. XRD of steel in 0.5 M HCl medium without and with inhibitor addition.

In the absence of the inhibitor, we notice a noticeable decrease in the iron peaks compared to the case of steel only, due to corrosion and due to the absence of a protective layer for the surface, but with that, we note the formation of both Fe_2O_3 and Fe_3O_4 .

In the case of the presence of the inhibitor, we notice a slight decrease in the iron peaks compared to the case of the steel surface only, noting the disappearance of both peaks, Fe_2O_3 , Fe_3O_4 , and this is due to the formation of a protective layer that protects the surface, but this protection is not total because the formation of the layer was local and not total due to the presence of defects.

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General conclusion

General conclusion

Plant extracts are excellent corrosion inhibitors, as they should be exploited especially because they are natural, environmentally friendly, non-toxic, available as well as cheap. This is why we made a water extract from mint leaves with the aim of using it as a corrosion inhibitor C45 steel in the middle of 0.5M of hydrochloric acid.

To conduct this study, we used weight loss method by playing on both concentration, dipping time and temperature and the surface was studied through Optical microscope, and X-ray deviation. The results of this study are summarized as follows:

The value of inhibitory effectiveness increase with the concentration of inhibitor increasing to 88.68% at 1.5 (g.l⁻¹).

Studying the effect of dipping time provided us with information on the formation of protective layer on the metal surface, where the highest value for the inhibition efficiency was 98.20% after 72 h at the ideal concentration 1.5 (g.l⁻¹).

Temperature tests were carried out, at the ideal concentration of 1.5 (g.ml⁻¹) as results showed that the temperature increase had a negative impact on the inhibition efficiency, with 87.76% at 298K and dropping to 70.54% at 328K.

The isothermal adsorption equations also shown that organic inhibitor molecules are absorbed according to the Langmuir and Temkin model.

The values of the different energies of activation also show the following:

Activation energy (Ea) in the presence of inhibitor is greater the activation energy (Ea) in the absence of inhibitor $E_a(\text{HCl}) > E_a(\text{HCl} + \text{inh})$.

Negative values of ΔH_{ads} and ΔS_{ads} in case of the presence and absence of the inhibitor, respectively, show us that this inhibitor is an exothermic reaction and that the accident reaction is random.

Gibbs free energy values ΔG_{ads} below (-20 KJ.mol⁻¹) reveal that the adsorption mechanism is an automatic physical mechanism.

Observations resulting from the study of the sample surface using Optical microscope confirm the existence of a protective layer formed on the surface of the C45 steel, demonstrating the strong effect of the inhibitor's effectiveness in protecting the metal surface from corrosion,

General conclusion

as a dense layer appeared on the metal surface led to the disappearance of eroded areas (drilling),

As for X-ray diffraction, we noticed that if the steel dipped into the centre of HCl acid, the corrosion outputs Fe_2O_3 and Fe_3O_4 appeared and disappeared if an inhibitor was added to the middle.

Hence, we conclude that there is a compatibility between the results obtained from the weight loss method and the analytical methods.

Finally, this work enabled us to achieve the following specific objectives:

1. Study the effectiveness of organic inhibitor (water extract for mint leaves).
2. Use weight loss method to test the inhibitor.
3. Sample surface inspection with analytical techniques.

Perspectives

To develop this scientific research, we offer you some suggestions and ideas that can be considered in future work:

- The same study can be re-examined with the change or addition of new conditions.
- The acid medium used in this work can change like using H_2SO_4 or NaCl .
- Use other methods of corrosion study such as polarization method and impedance method.
- The inhibitor used can be mixed with other materials such as tea to increase inhibitive effectiveness.

Abstract

In this work we studied the effectiveness of the organic inhibitor of the water extract of mint leaves in the center of hydrochloric acid 0.5M HCl and the experimental study was conducted using the lost mass method. The effect of both concentration and dipping time as well as temperature has been taken into account in the presence and absence of inhibitor, we conclude from the foregoing that the type of adsorption studied is automatic physical adsorption as well as exothermic reaction. To inspect the surface of the samples, we used analytical techniques for both the light microscope and the X-ray diffraction (XRD) from which we observed the appearance and disappearance of corrosion results Fe_2O_3 Fe_3O_4 after adding an inhibitor to the medium.

Keywords: Corrosion, Inhibitor, Adsorption, Aqueous extract of mint leaves, Steel, Deposition.

Résumé

Dans ce travail, nous avons étudié l'efficacité de l'inhibiteur organique de l'extrait d'eau de feuilles de menthe dans le centre de l'acide chlorhydrique 0.5M HCl et l'étude expérimentale a été menée en utilisant la méthode de masse perdue. L'effet de la concentration et du temps de trempage ainsi que de la température a été pris en compte en présence et en absence d'inhibiteur, nous concluons de ce qui précède que le type d'adsorption étudié est l'adsorption physique automatique ainsi que la réaction exothermique. Pour inspecter la surface des échantillons, nous avons utilisé des techniques analytiques pour le microscope optique et la diffraction des rayons X (DRX). À partir desquelles nous avons observé l'apparition et la disparition des résultats de corrosion Fe_2O_3 Fe_3O_4 après avoir ajouté un inhibiteur au milieu.

Mots clés : Corrosion, Inhibiteur, Adsorption, Extrait aqueux de feuilles de menthe, Acier, Dépôt.

الملخص

قمنا في هذا العمل بدراسة فعالية المثبط العضوي من المستخلص المائي لأوراق النعناع في وسط حمض الهيدروكلوريك 0.5M HCl وأجريت الدراسة التجريبية باستخدام طريقة الكتلة الضائعة. تم الأخذ بعين الاعتبار تأثير كل من التركيز ووقت الغمس وكذلك درجة الحرارة وذلك في وجود وغياب المثبط، نستنتج مما سبق أن نوع الامتزاز المدروس هو امتزاز فيزيائي تلقائي وكذلك هو تفاعل ناشر للحرارة . ولمعاينة سطح العينات قمنا بالاستعانة بتقنيات التحليل لكل من المجهر الضوئي وايضا حيود الاشعة السينية التي لاحظنا من خلالها ظهور نتائج التآكل Fe_2O_3 و Fe_3O_4 واختفائها بعد إضافة مثبط إلى الوسط.

الكلمات المفتاحية: التآكل، المثبط، الامصاص، المستخلص المائي لأوراق النعناع، الفولاذ، الترسيب.