

وزارة التعليم العالي و البحث العلمي

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH



MOHAMED KHEIDER University BISKRA

Faculty of Sciences and Technology

Chemical Engineering Department

Field: Process Engineering

Option: Chemical engineering

Réf:.....

**A Dissertation for the Fulfillment of the
Requirement of a Master's Degree**

Theme

The inhibition effect of Gum Arabic (GA)

On the corrosion of carbon steel in HCl

medium.

Presented by:

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Presented on: 02 June 2016

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Favorable opinion of the supervisor:

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ملخص

التآكل هي ظاهرة لا تمس فقط الجانب الاقتصادي والمالي ولكنها تعدت ذلك إلى ما هو أهم و هو الجانب الصحي للأفراد سواء الذين يشغلون مناصب على مستوى الشركات الصناعية المعنية أو الأفراد الذين يقطنون بجوار الشركات و العنصر البشري عموماً. في العقود الأخيرة، تم استخدام وبشكل واسع عنصر الكرومات (عامل مسرطن) كمثبط للتآكل. لكن، و بسبب سميته العالية توجهت الأبحاث نحو مركبات طبيعية مقبولة و جيدة من الناحية الصحية والبيئية. من الأكيد أن المركبات العضوية الطبيعية سوف تظهر كمثبطات فعالة للتآكل في السنوات القادمة بسبب توفرها على خصائص ممتازة كتحللها البيولوجي الممتاز وتوفرها بشكل واسع ويتميزها بعدم السمية. الأبحاث المنشورة حول استخدام المركبات الطبيعية كمثبطات للتآكل تثبت و بشكل واضح و جلي أن عصر ما يسمى بالمثبطات الخضراء قد بدأ فعلاً. في هذه الدراسة تم دراسة فاعلية تثبيط الصمغ العربي على عينات مختارة من أنابيب نقل البترول في وسط حمض كلور الماء في وجود مؤكسد يتمثل في حديد نو درجة أكسدة تساوي ثلاثة. النتائج أثبتت على أن الصمغ العربي مثبط جيد في وسط حمض كلور الماء بتركيز 1مول/لتر. القيمة العظمى للفاعلية قدرت بـ 92% في تركيز 2 غ/ل .

الكلمات المفتاحية : التآكل، الكرومات، السمية، مثبط، المثبطات الخضراء، الصمغ العربي.

ABSTRACT

Corrosion not only has economic implications, but also social and these engage the safety and health of people either working in industries or living in nearby towns. In the past, chromates were the most commonly used inhibitive pigments. However, due to their high toxicity, many studies have been devoted to the development of more environmentally acceptable organic coatings. It is certain that natural compounds emerge out as effective inhibitors of corrosion in the coming years due to their biodegradability, easy availability and non-toxic nature. Careful perusal of the literature clearly reveals that the era of green inhibitors has already begun. In our study, we focus on the effectiveness of Gum Arabic on the corrosion of pipeline transport of oil in the center of hydrochloric acid in the presence of an oxidizing iron is to a degree of oxidation equal to three. The results show that GA is a good inhibitor in 1 M HCl. The maximum percentage inhibition efficiency was found to be 92% at 2 g/L .

Keywords: Corrosion, chromates, toxicity, inhibitors, biodegradability, green inhibitors, Gum Arabic.

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Symbols & Acronyms

GA : Gum Arabic

η_a : Anodic overvoltage

η_c : Cathodic overvoltage

m : Weight loss (Faraday's law)

A : Atomic mass of metal (g)

i_{corr} : Intensity of the corrosion current (Ampere)

n : the number of valence electrons

F : Faraday's constant (96500 C/mole)

A : Pre-exponential factor

E_a : Activation energy

R : Universal gas constant

T : The absolute temperature.

AISI : American Iron and Steel Institute

API : American Petroleum Institute

ISO : International Organization for Standardization

FAO : Food and Agriculture Organization

WHO : World Health Organization

CEN : The European Committee for Standardization; French: Comité Européen de Normalisation.

XRD : X-Ray Diffraction

psi : Pound per Square Inch

CR : Corrosion rate (weight loss experiments)

ML : Metal loss

\hat{i} : The intensity of the current

i : The electrode current density,

i_0 : The exchange current density,

η : Activation overpotential ($E - E_{\text{corr}}$)

E : Electrode potential.

R_p : Polarization resistance ($\Omega \text{ cm}^2$)

b_a : The anodic Tafel constant

b_c : The cathodic Tafel constant

E_{corr} : Corrosion potential.

η_{POL} : Inhibition efficiency (polarization method)

I_{corr} : The values of current density without inhibitor (GA)

$I_{\text{corr(inh)}}$: The values of current density with inhibitor (GA)

I% : The inhibition efficiency of GA (weight loss experiments)

m_1 : The weight (mg) before immersion test

m_2 : The weight (mg) after immersion test

A : The surface area of the specimens (cm^2)

t : Time (Day)

I% : Inhibition efficiency (Weight loss measurements)

$E_{q=0}$: The potential of zero charge

General Introduction

The corrosion-related costs to the transmission pipeline industry are very expensive. It can occur on the internal or external surfaces of the pipe and usually appears as either general corrosion or localised (pitting) corrosion [1]. Crude oil may contain significant levels of carbon dioxide, hydrogen sulfides, organic acids and chlorides, which in combination with free water make the pipeline environment. The refining of crude oil results in a variety of corrosive conditions. Refinery corrosion is generally caused by a strong acid attacking the equipment surface. The other important fields of application are acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes. Among the acid solutions, hydrochloric acid is one of the most widely used agents [2].

In the past, chromates were the most commonly used inhibitive pigments. However, due to their high toxicity, many studies have been devoted to the development of more environmentally acceptable organic coatings [3]. It is certain that natural compounds emerge out as effective inhibitors of corrosion in the coming years due to their biodegradability, easy availability and non-toxic nature. Careful literature reveals that the era of green inhibitors has already begun [4].

Several studies have been published on the use of natural products as corrosion inhibitors in acid solutions, Okra mucilage [5], aqueous garlic peel extract [6], the extract of *Salvia officinalis* leaves [7], alkaloids extract from *Oxandra asbeckii* plant [8], *Osmanthus fragrans* leaves extract [9], aqueous coffee ground extracts [10], *Azadirachta indica* extract [11], *Phyllanthus amarus* extracts [12], bamboo leaf extract [13], *Justicia gendarussa* plant extract [14]. Polymers may be a better choice as they possess long chain molecules and show high inhibition efficiency at very low concentration in most aggressive media [5]. However, study on the inhibition efficiency of natural compounds for pipeline steel in HCl medium is still lacking. Assessment of corrosion inhibitors for metals in aggressive media is important for some industrial facilities. While choosing an inhibitor, several factors such as its cost, toxicity, availability and environment friendliness need to be taken into account. In spite of the high efficiency of many commonly used

General Introduction

synthetic compounds, they are often toxic, carcinogenic or even allergenic, green inhibitors are used as corrosion inhibitors. In the present review, attention has been focused on the corrosion inhibiting properties of various parts of plant extracts for metals in different media.

To replace the toxic-synthetic corrosion inhibitors with environmentally friendly types, several observational studies had been suggested about the applications of these materials in the corrosive environments which were found mostly among the class of natural products. Plants have been recognized as sources of naturally occurring compounds, some with rather complex molecular structures and having varying of physical, chemical and biological properties. All these compounds are non-toxic from plant origin or non-toxic synthetic compounds as dyes and drug compounds had been classified as environmentally friendly and / or ecologically acceptable materials. The scientific communities were taken an effort to develop cost-effective corrosion inhibitors from plant origin and were readily biodegrade and have low mobility for minimum environmental impact. To investigate the efficiency of these inhibitors, there are different experimental techniques like weight loss, polarization, electrochemical impedance spectroscopy, hydrogen evaluation and energy disperse spectroscopy were used.

Commercial Gum Arabic was selected for the present study. The plant is easily biodegradable; readily available from the renewable sources. GA is a branched-chain, complex polysaccharide, either neutral or slightly acidic, found as a mixed calcium, magnesium and potassium salt of a polysaccharidic acid [15]. GA is used primarily in the food industry as a stabilizer, and as bio-gooley simulacrum to paint on the surface to test its ease to be removed from our anti-fouling coating [16].

The first ever reports on corrosion inhibition of metals involving Gum Arabic was reported by Umoren et al. [17,18], but the maximum inhibition efficiency (%) was 21.9–43.7 at 30°C, with 0.5 g L⁻¹ of Gum Arabic as the maximum concentration of inhibitor. We will prove that the Gum Arabic is good inhibitor in acidic medium with inhibitor concentrations higher than 0.5 g L⁻¹.

The work presented in this memory focus on the inhibitory efficacy of the Gum Arabi on steel API 5L (X60 and X42) (pipeline) under acidic medium (hydrochloric acid) by surface analysis and electrochemical methods. Thus, the goal is to first better understand the steel corrosion mechanism API 5L (X60 and X42) in acid environments, and then evaluate the

General Introduction

inhibitory properties of the inhibitor. The structure of this study subdivided into three Chapters :

Chapter I: The first part is devoted to the literature review about the corrosion mechanism of carbon steel and influencing factors and focussed on the inhibitory properties of organic inhibitors, inhibiting mode.

Chapter II: as brief description of all the experimental techniques used in this study and the experimental conditions used and adopted.

Chapter III: This part is related to the effect of immersion time, concentration of Gum Arabic, the oxidant Fe^{3+} , this chapter is devoted to optimizing the concentrations of GA to fight against corrosion in acidic environments.

Chapter I :

Approach

*Overview of Corrosion
and Protection Strategies
(Literature Review)*

I.1. Problem statement

The corrosion of metals in many industries, constructions, installations is a serious problem. In order to prevent or minimize corrosion, inhibitors are usually used. Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by using chemisorption and/or physisorption mechanism on the metal surface or reacting with metal ions and forming a barrier-type precipitate on its surface [19].

However, most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environment. Therefore, it is desirable to source for environmentally safe inhibitors [20 – 25]. It has been shown that natural products of plant origin contain different organic compounds (e.g. alkaloids, tannins, pigments, organic and amino acids, and most are known to have inhibitive action [26 –33]. Other authors have also shown that the inhibitive effect of some plants solution extract is due to the adsorption of molecules of phytochemical present in the plant on the surface of the metal [34 – 37]. The review including a plant extract “ Gum Arabic” as corrosion inhibitor has recently been published [38].

Corrosion control of metals is of technical, economical, and environmental importance. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce.



Figure I-1: The cross section of the "scale" of a pipe

I.2. Background

Corrosion is one of the most common, costly and widespread industrial problems in today's modern world. Corrosion comes from the Latin word "**corrodere**" which means "**to gnaw away**". It is defined as the degradation or breaking of bonds between the atoms in a metal and the formation of thermodynamically more stable compounds.

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes, and electrochemical potential. The study of corrosion of steel and iron is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest. Acid solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing, require the use of corrosion inhibitors in order to restrain their corrosion attack

Chapter I : Literature Review

on metallic materials [39].

I.3. The Study of Corrosion

There are *four main reasons* to study corrosion. Three of these reasons are based on societal issues regarding

- Human life and safety,
- The cost of corrosion,
- Conservation of materials (Pipeline),
- The fourth reason is that corrosion is inherently a difficult phenomenon to understand, and its study is in itself a challenging and interesting pursuit.

In addition to the lines discussed above, corrosion science is an interdisciplinary area embracing *chemistry, materials science, and mechanics*.

Corrosion is a commonplace occurrence, like the rusting and flaking of an old iron yard piece. Here we will explore the process by which corrosion takes place and the different ways unwanted corrosion can be controlled. Energy, often large amounts, are poured into winning the desired metals from their natural ores; manufacturing some metal products can be very costly. Corrosion causes deterioration of manufactured products, damaging their structure and ultimately rendering the product useless. Allowing corrosion is not cost efficient and can inhibit productivity; understanding and preventing corrosion is important for maintaining infrastructures and machinery or any products that face corrosion.

I.3.1. Corrosion Science vs. Corrosion Engineering

❖ **Corrosion science** is directed toward gaining basic scientific knowledge so as to understand corrosion mechanisms.

❖ **Corrosion engineering** involves accumulated scientific knowledge and its application to corrosion protection. Ideally, corrosion science and corrosion engineering complement and reinforce each other, but it has been the author's observation that most workers in the field of corrosion settle into one camp or the other. The most effective corrosionists are those who

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understand both the science and the engineering of corrosion.

Corrosion Engineering is the field dedicated to controlling and stopping corrosion.

I.3.2. Challenges for Today's Corrosion Scientist

Several important timely challenges to the corrosion scientist can be listed.

These are the following:

1. The development of protective surface treatments and corrosion inhibitors to replace inorganic chromates, which are environmentally objectionable.
2. An improved conservation of materials through the development of corrosion-resistant surface alloys which confine alloying elements to the surface rather than employing conventional bulk alloying.
3. The formulation of a new generation of stainless steels containing replacements for chromium and other critical metals.
4. An improved understanding of passivity so as to use our fundamental knowledge to guide the development of alloys having improved corrosion resistance.
5. Understanding the mechanism of the breakdown of passive oxide films by chloride ions and subsequent pitting of the underlying metal.
6. The development of organic coatings which can detect a break in the coating and automatically dispatch an organic molecule to the required site to both heal the coating and inhibit corrosion.
7. The ability to predict the lifetime of metals and components from short-term experimental corrosion data.
8. It is suggested that the reader refer back to these challenges as he or she proceeds through this text. Perhaps the reader can provide additions to this list.

I.4. Corrosion process

Corrosion is a process through which metals in manufactured states return to their natural oxidation states. This process is a reduction-oxidation reaction in which the metal is being oxidized by its surroundings, often the oxygen in air. This reaction is both spontaneous and electrochemically favored.

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Corrosion is a natural process, which converts a refined metal to a more stable form, such as its oxide or hydroxide. It is the gradual destruction of materials (usually metals) by chemical reaction with their environment.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen.

Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal, and results in a distinctive orange colouration. [40]

I.4.1. Conditions for Corrosion of Metals

There are *three main components necessary* for corrosion to occur:

- 1) Metal (example: iron , steel)
- 2) Oxygen (usually from the atmosphere)
- 3) An electrolyte (usually water)

Many metals used in production occur naturally in an ore and therefore must be separated out, leading to reduced stability.

These metals, such as iron, will spontaneously return to their natural states.

The products of corrosion often reflect the metal's natural state.

I.4.2. Representation of Corrosion Processes and How Corrosion Occurs

Corrosion can occur in two general ways; over the entire surface of the metal (Generalized Corrosion), or in local spots or areas (Localized Corrosion).

- **Generalized Corrosion:** Typically never happens, aside from in acidic conditions. This uniform corrosion over the entire surface of the metal is rare and leads to overall thinning which has little effect outside of fatigue and stress conditions.
- **Localized Corrosion:** The most common, and most detrimental, form of localized corrosion is pitting. Pitting is when the attack happens in one single location on the surface and creates a pit, or small cavity, in the metal. This type of corrosion attack is

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hard to prevent, engineer against, and often times difficult to detect before structural failure is met due to cracking. Pipes are often compromised due to pitting.

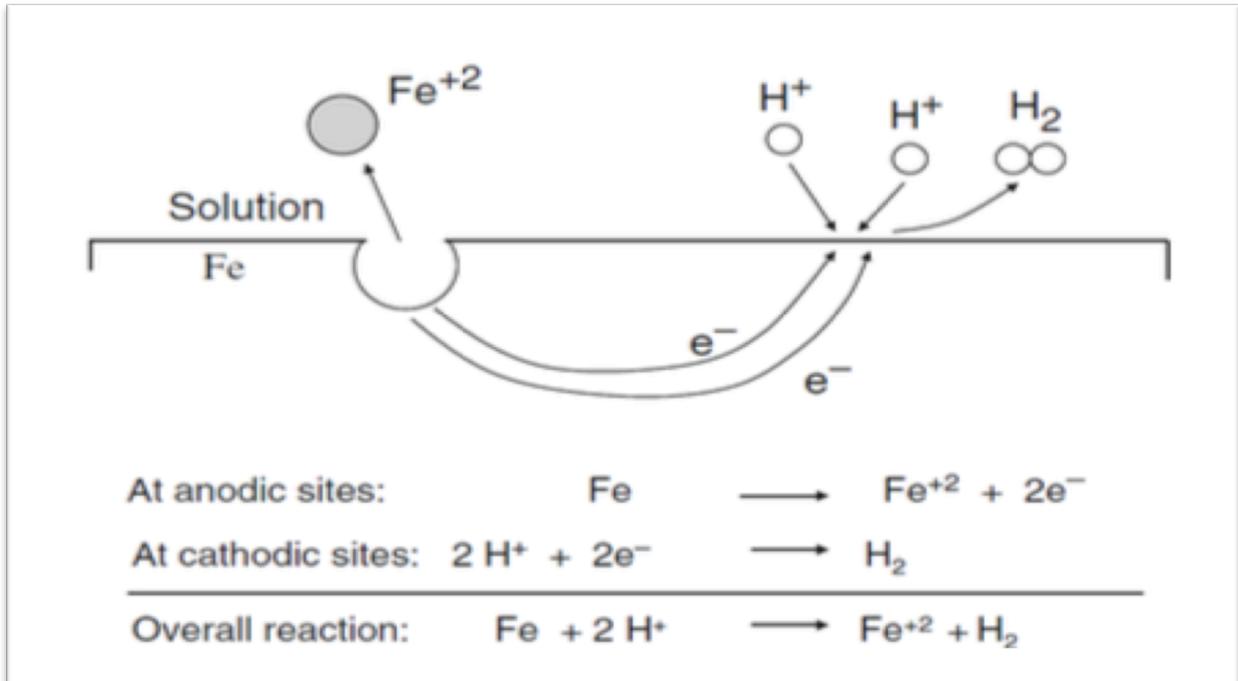


Figure I-2: Coupled electrochemical reactions

I.4.3. The Eight Forms of Corrosion

Fontana and Greene [11] have conveniently classified the various types of corrosion into eight forms. The eight forms of corrosion are as follows:

1. Uniform attack (or general corrosion)
2. Galvanic corrosion (two metal corrosion)
3. Crevice corrosion
4. Intergranular corrosion
5. Pitting
6. Selective leaching (dealloying)
7. Stress-corrosion cracking
8. Erosion corrosion

I.5. Steel review

The term ‘steel’ is used to describe alloys composed primarily of iron and carbon. Steel is the most widely used engineering material in the world due to its low price and favourable material properties, which include high strength and ductility . The World Steel Association estimates that the global production of steel in 2012 exceeded 1,5 billion tonnes , which was over 30 times greater than aluminium production, the next second most used metal in the world .

A classification of steel is presented in Table I.1 on the basis of carbon composition with typical applications of the types of steel given .

Table I.1: Classification of steel based on carbon composition

Name of steel	Carbon composition (wt. %)	Example of application
Ultra low carbon steel	0.03 <	
Low carbon steel	0.04 – 0.15	Wire, tubing, car bodies
Mild	0.15 – 0.30	Buildings, bridges, piping
Medium	0.30 – 0.60	Machinery, tractors, mining equipment
High	0.60 – 0.99	Springs, railroad car wheels
Ultra high carbon steel	1.0 – 2.0	Ball bearings, drills, metal cutting tools
Cast iron	2.0 – 4.0	Engine cylinder blocks,

I.6. Corrosion of carbon steel in acidic medium

Carbon steel is one of the most versatile, least expensive and most widely applied of the engineering metals (Example: oil and gas industry [71]). It is unequalled in the range of mechanical and physical properties with which they can be endowed by alloying and heat-treatment. The main disadvantage is that carbon steel has poor resistance to corrosion in even relatively mild service environments and usually need the protection of coatings or environment conditioning. This generalization excludes stainless irons and steels that are formulated with high chromium contents to change their surface chemistry. According to a report by NACE and CC Technologies appropriately titled “ Corrosion Costs US Transmission Pipelines as much as 8.6 Billion Dollar/Year ”. [72]

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I.6.1. The mechanism of corrosion of carbon steel in an acidic medium

When an acid comes into contact with carbon steel, an immediate attack on the metal occurs with the formation of hydrogen gas and the ferrous ion, as shown in the reactions (Eq I-1) ; (Eq I-2).

- a) The Anodic reaction (oxidation)



- b) The cathodic reaction (reduction)



Therefore the corrosion of carbon steel is due to a reaction of irreversible oxidation-reduction between the metal (Fe) and an oxidizing agent (H⁺) as shown in the overall an global reaction (Eq I-3).



➤ **Pourbaix diagrams :**

The Principle of POTENTIAL-PH Diagrams was established in the 1940s in Belgium by Pr.Marcel Pourbaix. A potential- pH diagram is a graphical representation of the relations, derived from the Nernst equation, between the pH and the equilibrium potentials (E) of the most probable electrochemical reactions occurring in a solution containing a specific element.

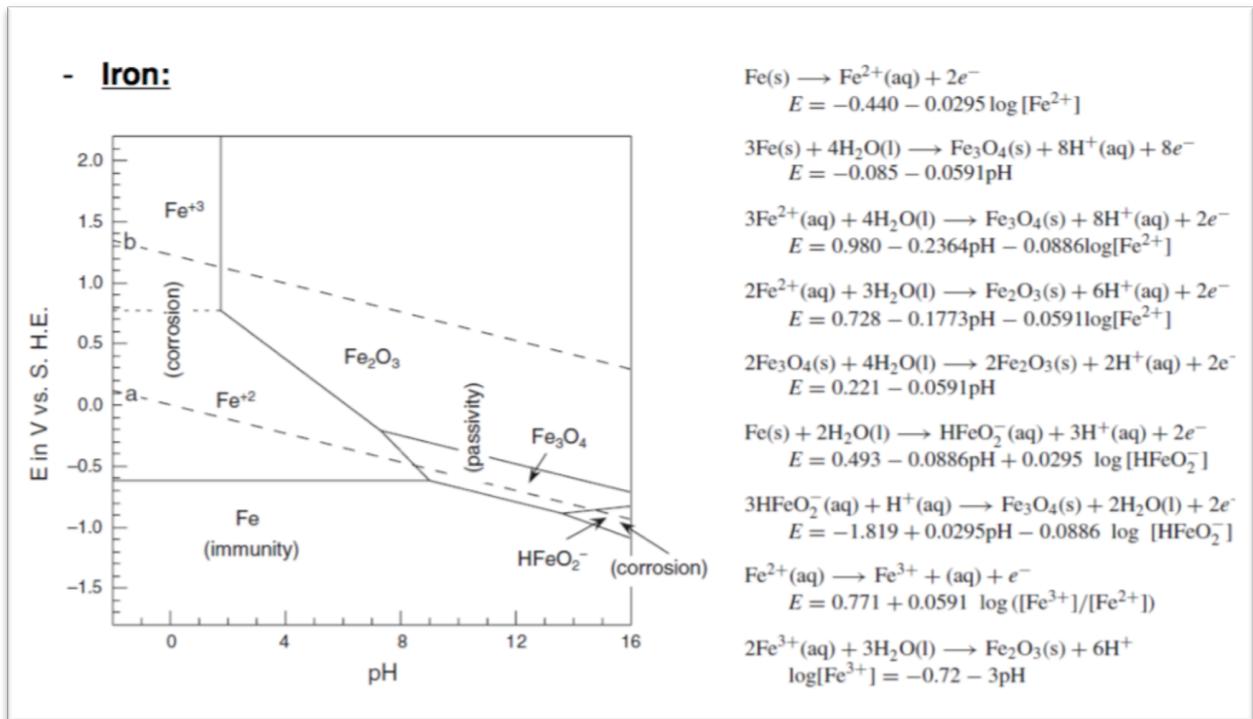


Figure I-3: Pourbaix diagram for iron at ionic concentrations.

Pourbaix Diagrams plot electrochemical stability for different redox states of an element as a function of pH, these diagrams are essentially phase diagrams that map the conditions of potential and pH (most typically in aqueous solutions) where different redox species are stable. The lines in Pourbaix diagrams represent redox and acid-base reactions, and are the parts of the diagram where two species can exist in equilibrium. For example, in the Pourbaix diagram for Fe below, the horizontal line between the Fe³⁺ and Fe²⁺ regions represents the reaction Fe³⁺(aq) + e(-) = Fe²⁺(aq), which has a standard potential of +0.77 V. While we could use standard potentials for all these lines, but in practice Pourbaix diagrams are usually plotted for lower ion concentrations that are more relevant to corrosion and electrochemical experiments.

- Example: Iron Pourbaix diagram

Areas in the Pourbaix diagram mark regions where a single species (Fe²⁺(aq), Fe₃O₄(s), etc.) is stable. More stable species tend to occupy larger areas.

Lines mark places where two species exist in equilibrium.

- **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent
- **Pure acid-base** reactions are **vertical** lines - these do not depend on potential

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Examples of equilibria in the iron Pourbaix diagram (numbered on the plot):

- ✓ $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$ (pure redox reaction - no pH dependence)
- ✓ $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ (pure redox reaction - no pH dependence)
- ✓ $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+$ (pure acid-base, no redox)
- ✓ $2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 2\text{e}^-$ (slope = $-59.2 \times 6/2 = -178$ mV/pH)
- ✓ $2\text{Fe}_3\text{O}_4(\text{s}) + \text{H}_2\text{O} \rightarrow 3\text{Fe}_2\text{O}_3(\text{s}) + 2\text{H}^+ + 2\text{e}^-$ (slope = $-59.2 \times 2/2 = -59.2$ mV/pH)

I.6.2. Kinetics of Corrosion - the Tafel Equation

I.6.2.1. Tafel straight lines :

If there is a big difference between the potential E and E^0 this is called overvoltage η , the anodic reaction or cathodic reaction becomes negligible compared with each other.

- ❖ For the anodic overvoltage η_a :

$$i = i_a = i^\circ \exp\left(\alpha \frac{nF}{RT} \eta_a\right) \quad \text{Eq I-4}$$

- ❖ For the cathodic overvoltage η_c :

$$i = i_c = i^\circ \exp\left(-\left(1 - \alpha\right) \frac{nF}{RT} \eta_c\right) \quad \text{Eq I-5}$$

In these relationships, we can define the the anodic and cathodic Tafel coefficients by:

$$b_a = \frac{RT}{\alpha nF} \quad \text{Eq I-6}$$

$$b_c = \frac{RT}{(1 - \alpha)nF} \quad \text{Eq I-7}$$

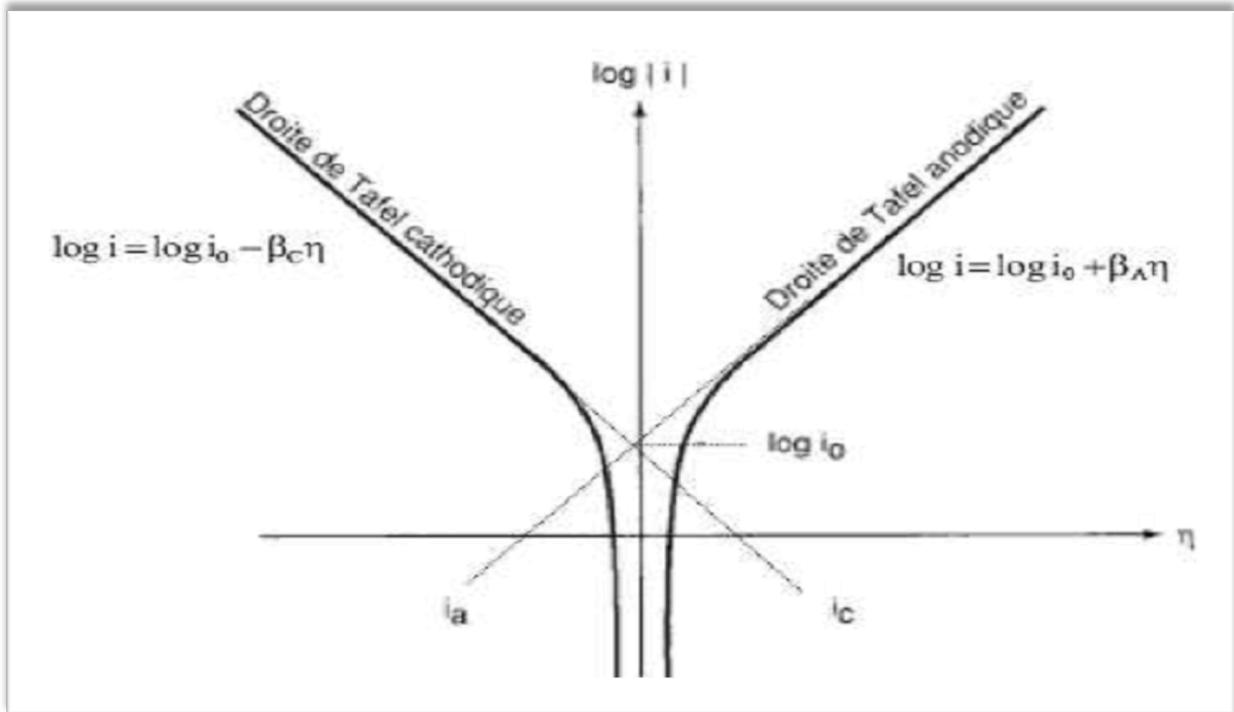


Figure I-4: Polarization curves and Tafel line(s).

I.6.2.2. Faraday's Law: Quantitative survey

Corrosion of a metal is reflected in a weight loss. To determine the lifetime of a structure subjected to electrochemical attack, it is necessary to evaluate the amount of metal transferred to solution according to time.

Faraday's law allows us to assess the weight loss m (g):

$$m = \frac{A \cdot i_{corr} \cdot t}{nF} \quad \text{Eq I-8}$$

A : atomic mass of metal (g) ,

i_{corr} : intensity of the corrosion current (Ampere),

t : time (s),

n : the number of valence electrons,

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F : Faraday's constant (96500 C/mole).

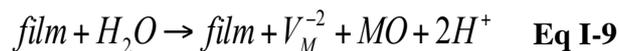
This relationship shows that for any given metal, the weight loss is proportional to the corrosion current. On classe les métaux en quatre catégories :

I.6.3. Passivation of carbon steel

Passivity is defined as a condition of corrosion resistance due to formation of thin surface film under oxidizing conditions, some metals and alloys having simple barrier films with reduced corrosion of active potential ; and it is a state of the metals or alloys in which their corrosion rate is significantly slowed by the presence of natural or artificial passive film, compared with the absence of this film.

I.6.3.1. Passive film Development

Let us consider a completely passive metal surface, which is covered by an oxide film MO. As on the surface of bare metal, water dipoles can adsorb at the interface between the film and the aqueous solution (Figure I-5 (a)), and the deprotonation process reproduced, with formation of a complex MO then the oxide MO (Figure I-5 (b)). The cation M did not come from the metal but from the oxide, resulting the formation of a cation vacancy in the oxide, according to a global reaction :



V_M^{-2} is a cationic « vacancy », negatively charged, which migrates to the metallic substrate under the action of surface's electric field F. The result is a film schematically shown in (Figure I-5), It has an "internal" interface with the metal and an "external" interface with the aqueous solution.

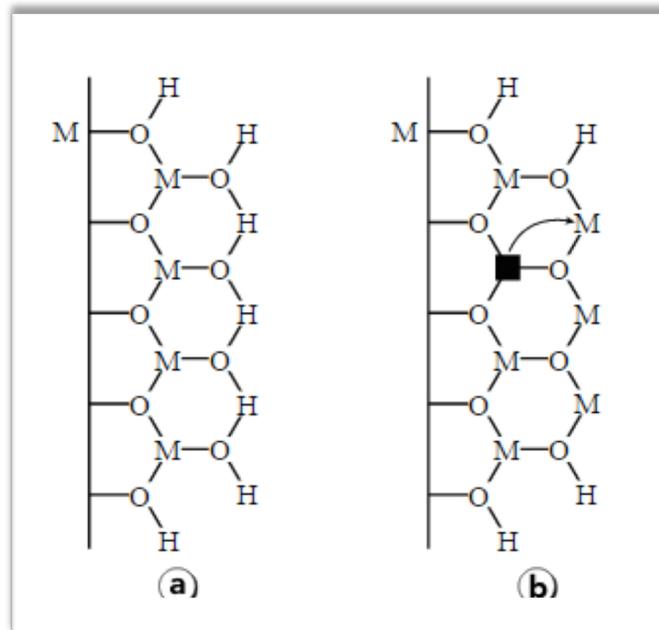


Figure I-5: Formation of a passive film.

When the first oxide layer formed, the water molecules can again adsorbed (a) and we get the continuation of the deprotonation process. The only difference being with the first layer is the cation forming the complex MOH will not come from the metal but the oxide already formed (b) (vacancy ■) or a gap.

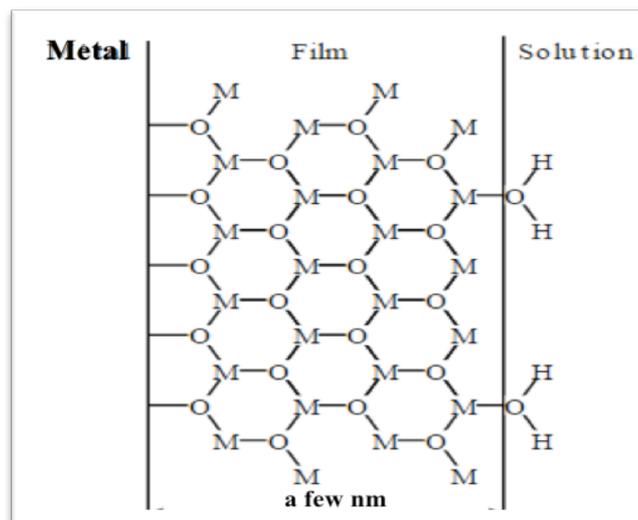
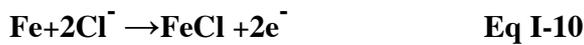


Figure I-6: Formation of a passive film.

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I.6.4. Corrosion product of carbon steels in hydrochloric acid

Under certain conditions, particularly in neutral and alkaline medium, also in Acid medium, the corrosion products are sparingly soluble and precipitate at the metal surface as hydroxides or salts. Superficial film little compact or porous form. So they do not protect the metal against corrosion, but cause a slowdown reaction [73]. Generally under acidic conditions, the ion Cl^- can accelerate the corrosion probably by the anodic dissolution. The mechanism may be expressed as follow:



The equations (Eq I-10) is corresponding to the equation (Eq I-1).

It is noted that FeCl_2 is an unstable product, it would be oxidized to FeOOH .

FeOOH may hardly turn into Fe_2O_3 (hematite) because of its low free energy, when exposed to dry air, the FeOOH can turn into Fe_2O_3 . When oxygen is insufficient, FeOOH can transform to Fe_3O_4 (magnetite). In general, in acidic medium, carbon steel experienced widespread corrosion induced by the solvated protons H^+ and forms a corrosion product layer composed mainly of Fe_2O_3 [74].

I.6.5. Type of corrosion of carbon steel in an acidic medium

In acidic medium, the *general corrosion* is the most common form for carbon steels. But in the presence of metal oxidants such as Fe^{3+} and Fe^{2+} , *localized corrosion by pitting* can be occurs.

The ferric iron (Fe^{3+}) is the responsible for general corrosion and pitting corrosion of carbon steels [75], the effect is worse with hydrochloric acid (presence of Cl^- ions). The Corrosion occurs when there is a precipitation of iron oxides with aeration during the acid cleaning process, which produces ferric ions that corrode the carbon steel as shown in the equation

(Eq I-11).



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Figure I-7 illustrates the corrosion of carbon steel in an acidic medium. [76]

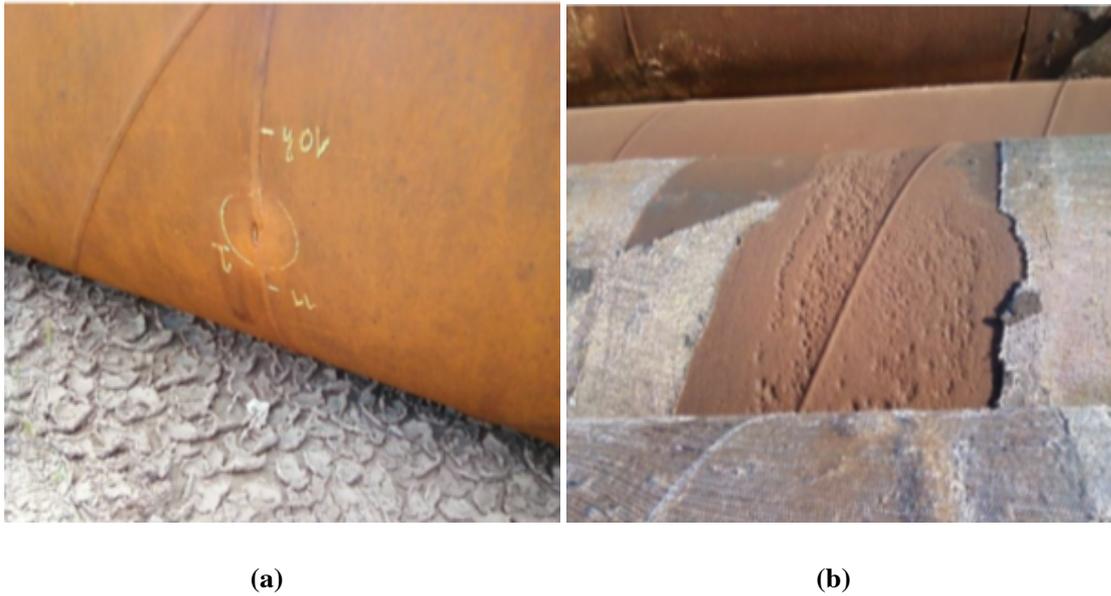


Figure I-7: (a) Localized corrosion by pitting. (b) General corrosion .

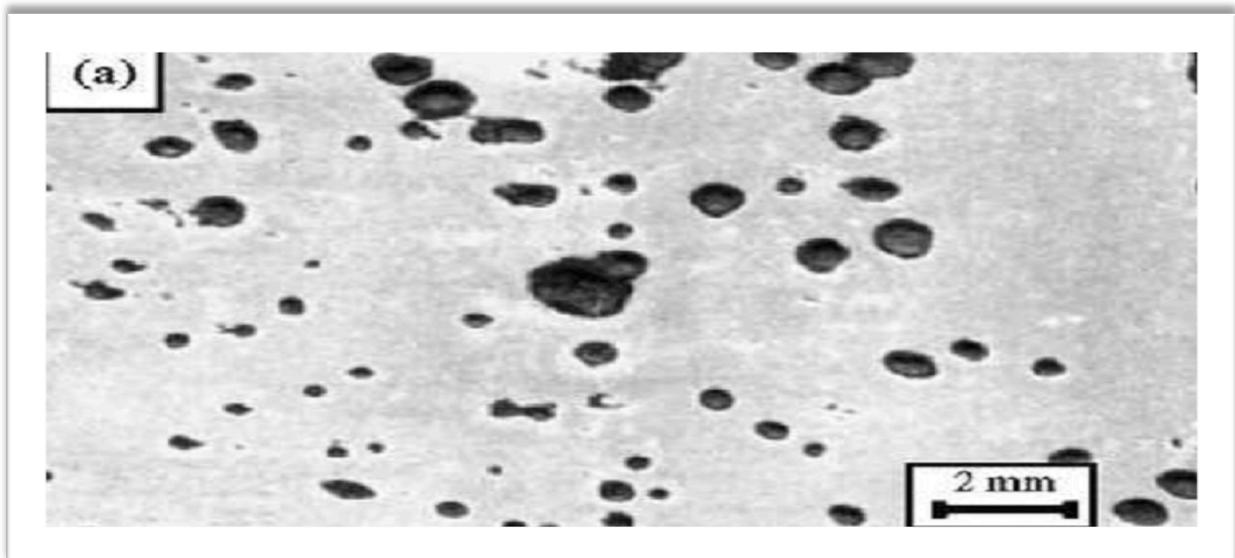
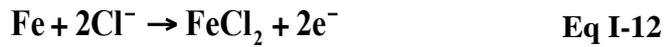


Figure I-8: Localized corrosion (Pitting) morphological view after pitting corrosion of steel in a chloride medium.

I.6.6. Influence of Cl^- on corrosion

Generally in an acidic medium, the ions as Cl^- can accelerate corrosion process would probably by favoring the anodic dissolution. The mechanism may be expressed as :

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Equation (Equ. I.12) is corresponding and to be similar to the equation (Equ I-13).



FeCl_2 is an unstable product, it would be oxidized to FeOOH , and Cl^- is released again then restart a new cycle

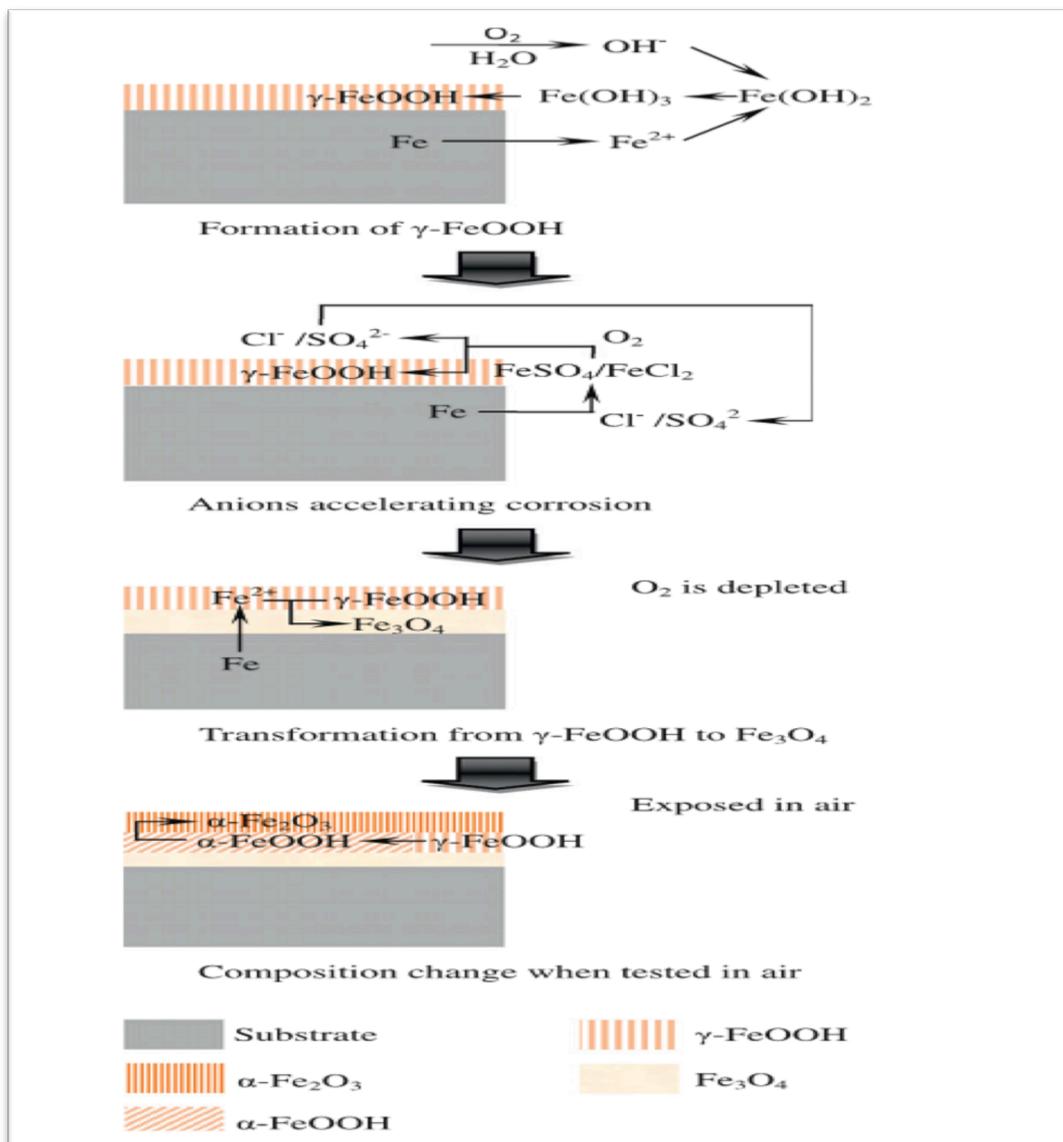


Figure I-9: Evolution of rust layers on carbon steel sample immersed in a simulated solution.

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I.6.7. pH effect

In aqueous medium, corrosion of carbon steel depends on the pH (Figure I-10). [73] At low pH, there is a reduction of protons and corrosion is higher when the medium is acidic.

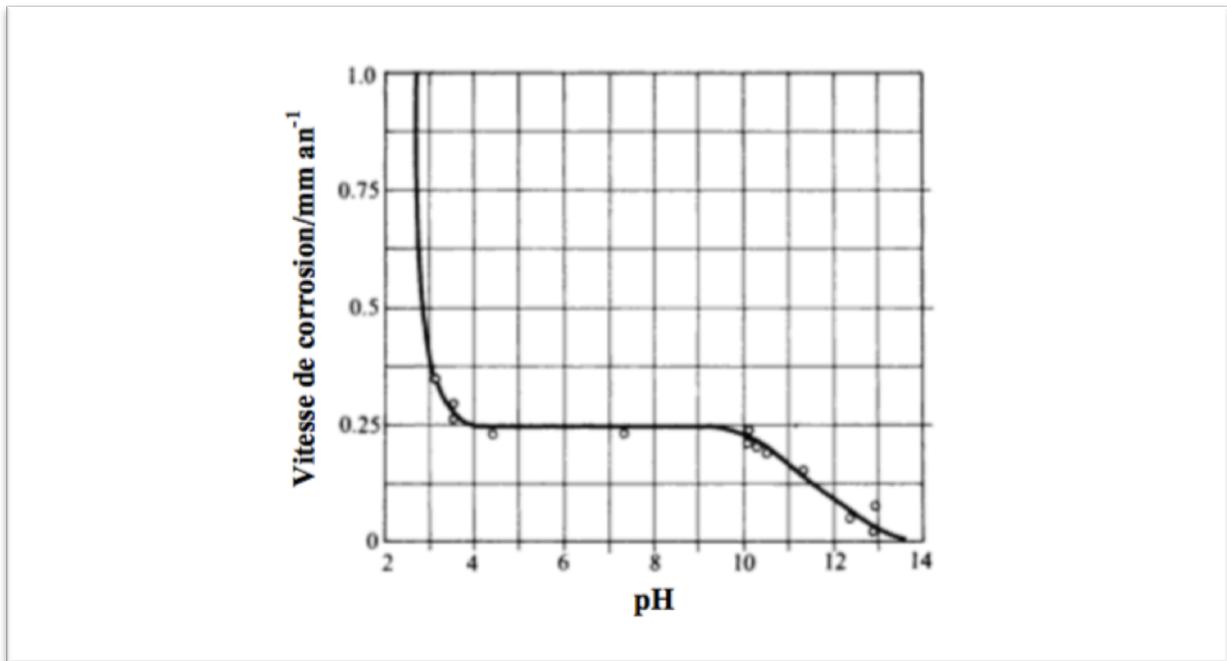


Figure I-10: Change in the corrosion rate of the steel on function of pH.

I.6.8. Influence of temperature on the corrosion

Temperature can affect on the corrosion in several ways. If the corrosion rate is completely directed by the elementary process of oxidation of the metal, the corrosion rate increases exponentially with temperature increasing. This relation is expressed by Arrhenius expression [77]:

$$I_{\text{corr}} = A \cdot \exp\left(\frac{-E_a}{RT}\right) \quad \text{Eq I-14}$$

Where I_{corr} is the corrosion rate, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature.

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The effect of temperature on the rate of corrosion is represented by the equation (Eq I-14) at two temperatures on taking the report of corrosion rate [78]:

$$\text{Log}\left(\frac{I_{\text{corr2}}}{I_{\text{corr1}}}\right) = \frac{Ea}{2,303R} \left(\frac{1}{T1} - \frac{1}{T2}\right) \quad \text{Eq I-15}$$

Where I_{corr1} and I_{corr2} are the corrosion rates at two different temperatures $T1$ and $T2$ respectively. Equation (Eq I-15) can be used to evaluate the effect of a temperature change on the corrosion rate for this simple speed or rate process. Examples of corrosion after this rate law are iron in hydrochloric acid and iron in sodium sulphate (Na_2SO_4) at a pH equal to 2. This is most common for the corrosion in acidic conditions. [77]

I.6.9. Influence of carbon steel microstructure

According to Dean and Grab [79], the corrosion rate of carbon steel in acidic media strongly depends on the chemical composition of the steel, Particularly the carbon content. Accordingly, the anodic oxidation reaction of iron (Eq I-1) occurs on the ferrite phase, and the cathodic reduction reaction of hydrogen (Eq I-2) occurs on the cementite phase (pearlite) [56]. These reactions explain the important role of carbon content on the steel corrosion rate.

I.7. Corrosion Inhibitors

A corrosion inhibitor is a substance which reduces the rate of corrosion when added to the corrosive environment in a suitable concentration, without the concentrations of the corrosive species present being changed significantly. An inhibitor is, as a rule, effective when present in small concentrations.

The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts have become important as an environmentally acceptable, readily available and

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renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency and the use of inhibitors is one of the most practical methods to protect steel from corrosion, especially in acidic solutions where it is critical to prevent unexpected metal dissolution and acid consumption . Inhibitors containing double or triple bonds play an important role in facilitating the adsorption of these compounds onto metal surfaces. A bond can be formed between the electron pair and/or the p electron cloud of the donor atoms and the metal surface, there by reducing corrosive attack in an acidic medium .

In recent years, interest has increased in the development and use of low-cost and eco-friendly compounds as corrosion inhibitors for steel. Plant extracts are generally inexpensive and can be obtained through simple extraction processes. In our work, the effect of aqueous extracts of Gum Arabic on the corrosion of carbon steel in 1 mol.L⁻¹ HCl was studied .

The objective of this study was to investigate the inhibitory effects of GA extract as a corrosion inhibitor for carbon steel in a 1 mol.L⁻¹ solution of hydrochloric acid.

I.7. 1. The corrosion inhibition of carbon steel in an acidic medium

Corrosion inhibitors are an original way to fight against corrosion of metals and alloys. The originality comes from the anti corrosion treatment is not done on the metal itself (coating, choice of inherently corrosion resistant material) but by or through the corrosive medium. However, it is not to change the nature of this medium, but adding the inhibitor formulation (isolated molecule, mixture of molecules) in small quantities in the corrosive middle as indicated by the definition of an inhibitor according to ISO 8044: *"A chemical substance added to the corrosion system at a concentration chosen for its effectiveness, and that causes a decrease in the corrosion rate without significantly changing the concentration of any corrosive agent in the aggressive environment"*. This definition implies a difference between something called *"corrosion inhibitor"*, which concerns only the use of anti-corrosion additive, and something named *"inhibition of corrosion"* terminology which can be extended to any means to reduce the corrosion rate.

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I.7.2. The essential properties of a corrosion inhibitor

Corrosion can be prevented through using multiple products and techniques or can combat corrosion in many different ways, e.g.:

- Controlling the electrode potential so that the metal becomes immune or passive.
- Applying cathodic or anodic protection.
- Reducing the rate of corrosion with the aid of corrosion inhibitors added to the environment.
- Applying an organic or inorganic protective coating.

Outside any mechanism of action, a corrosion inhibitor should check a number of fundamental properties:

- A decrease on the metal corrosion rate and should maintain and conserve the physicochemical characteristics .
- Must be stable in the presence of any other component on the environment, particularly oxidants, such as some biocides.
- Being inexpensive.
- Being non-toxic.
- Being effective at low concentrations.
- Being steady in the temperature of use.
- Do not modify the stability of the species contained in the medium,

I.7.3. Mechanisms of actions of inhibitors

Inhibitors are substances or mixtures that in low concentration and in aggressive environment inhibit, prevent or minimize the corrosion. [41]

Generally the mechanism of the inhibitor is one or more of three that are cited below:

- ✓ The inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface;

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- ✓ The inhibitor leads a formation of a film by oxide protection of the base metal;
- ✓ The inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex. [42 - 44].

I.7.4. Inhibitors classifications

The corrosion inhibitors can be chemicals either synthetic or natural and could be classified by:

- The chemical nature as organic or inorganic;
- The mechanism of action as anodic, cathodic or a anodic-cathodic mix
- Adsorption action,
- Oxidants or not oxidants. [42]

In general, the inorganic inhibitors have cathodic actions or anodic. The organics inhibitors have both actions, cathodic and anodic and the protective by a film adsorption.

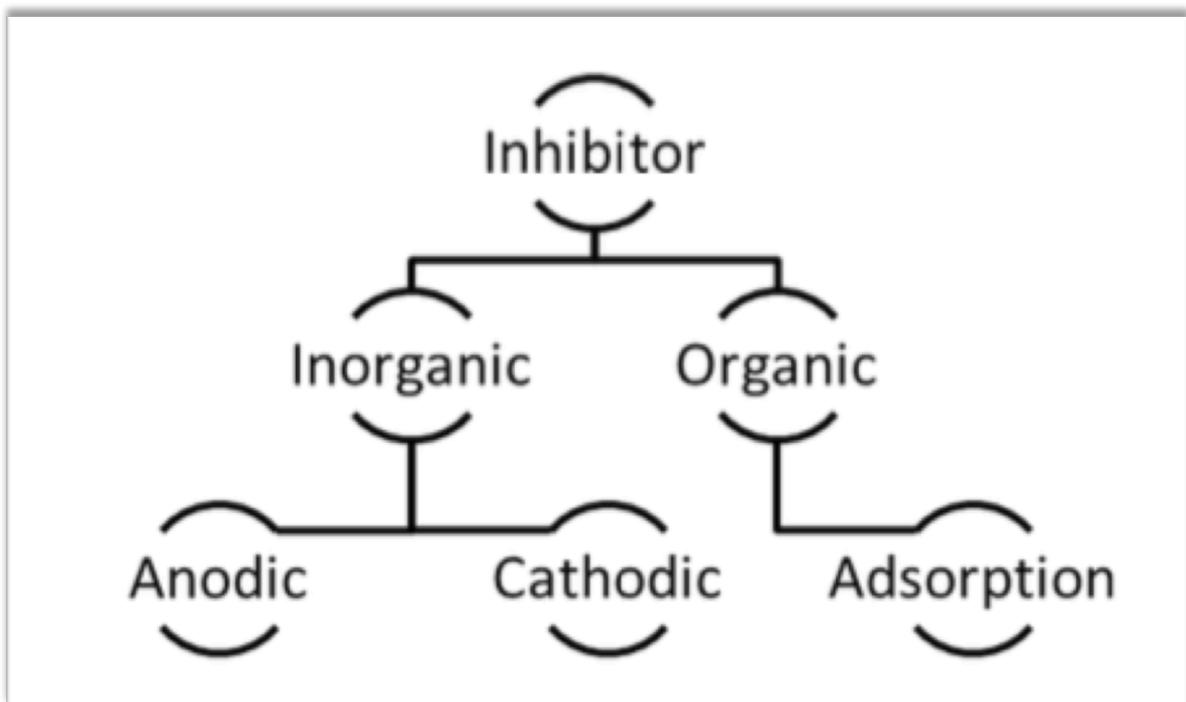


Figure I-11 : Classification of inhibitors

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I.7.4.1. Inorganic inhibitors

A. Anodic inhibitors

Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction, that is blocks the anode reaction and supports the natural reaction of passivation metal surface, also due to the forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface. [42] [45] (Figure I-12) shows a potentiostatic polarization diagram of a solution with behavior inhibitor anodic. The anodic reaction is affected by the corrosion inhibitors and the corrosion potential of the metal is shifted to more positive values. As well, the value of the current in the curve decreases with the presence of the corrosion inhibitor.

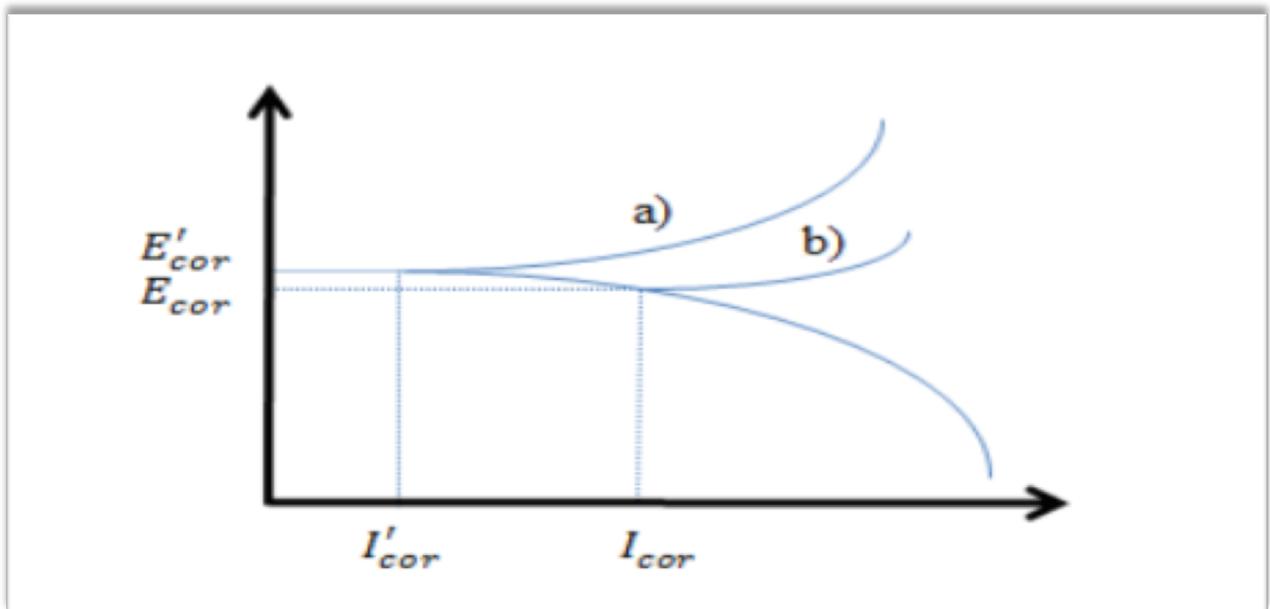


Figure I-12 : Potentiostatic polarization diagram: electrochemical behavior of a metal in a solution with anodic inhibitor (a) versus without inhibitor (b).

The anodic inhibitors reacts with metallic ions Me^{n+} produced on the anode, forming generally, insoluble hydroxides which are deposited on the metal surface as insoluble film and impermeable to metallic ion. From the hydrolysis of inhibitors results in OH^- ions. [42] (Figure I-13) shows how is the mechanism of the anodic inhibitory effect.

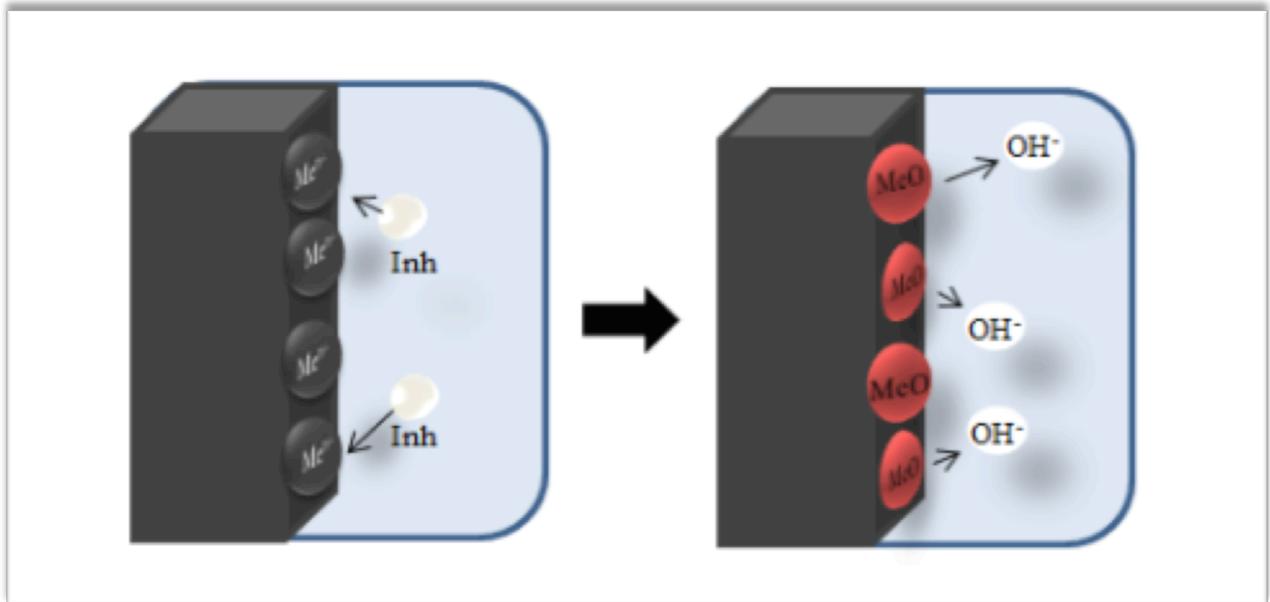


Figure I-13 : Illustration of anodic inorganic inhibitors effect and their mechanism of action.

B. Cathodic inhibitors

During the corrosion process, the cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. These inhibitors have metal ions able to produce a cathodic reaction due to alkalinity, thus producing insoluble compounds that precipitate selectively on cathodic sites. Deposit over the metal a compact and adherent film, restricting the diffusion of reducible species in these areas. Thus, increasing the impedance of the surface and the diffusion restriction of the reducible species, that is, the oxygen diffusion and electrons conductive in these areas. These inhibitors cause high cathodic inhibition.[46]

The (Figure I-14) shows an example of a polarization curve of the metal on the solution with a cathodic inhibitor. When the cathodic reaction is affected the corrosion potential is shifted to more negative values.

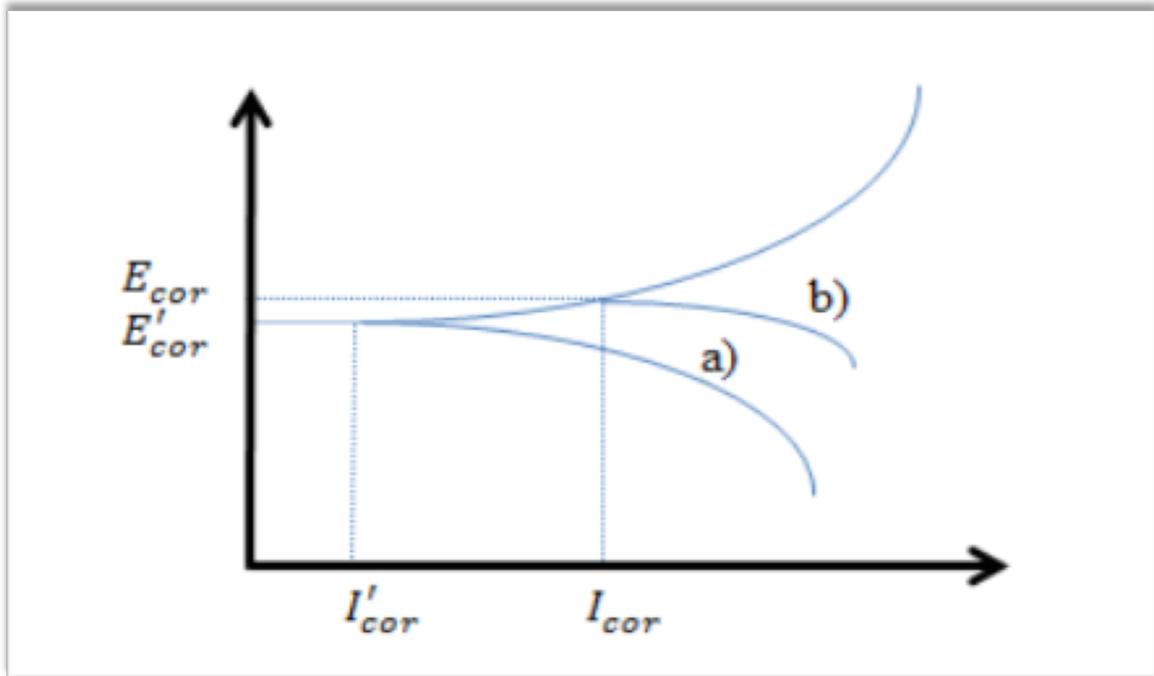


Figure I-14 : Potentiostatic polarization diagram: electrochemical behavior of the metal in a cathodic inhibitors solution (a), as compared to the same solution, without inhibitor (b).

The cathodic inhibitors form a barrier of insoluble precipitates over the metal, covering it. Thus, restricts the metal contact with the environment, even if it is completely immersed, preventing the occurrence of the corrosion reaction. Due to this, the cathodic inhibitor is independent of concentration, thus, they are considerably more secure than anodic inhibitor. The (Figure I-15) shows the illustration of mechanical effect of cathodic inhibitors to restrain the corrosion process.

[42]

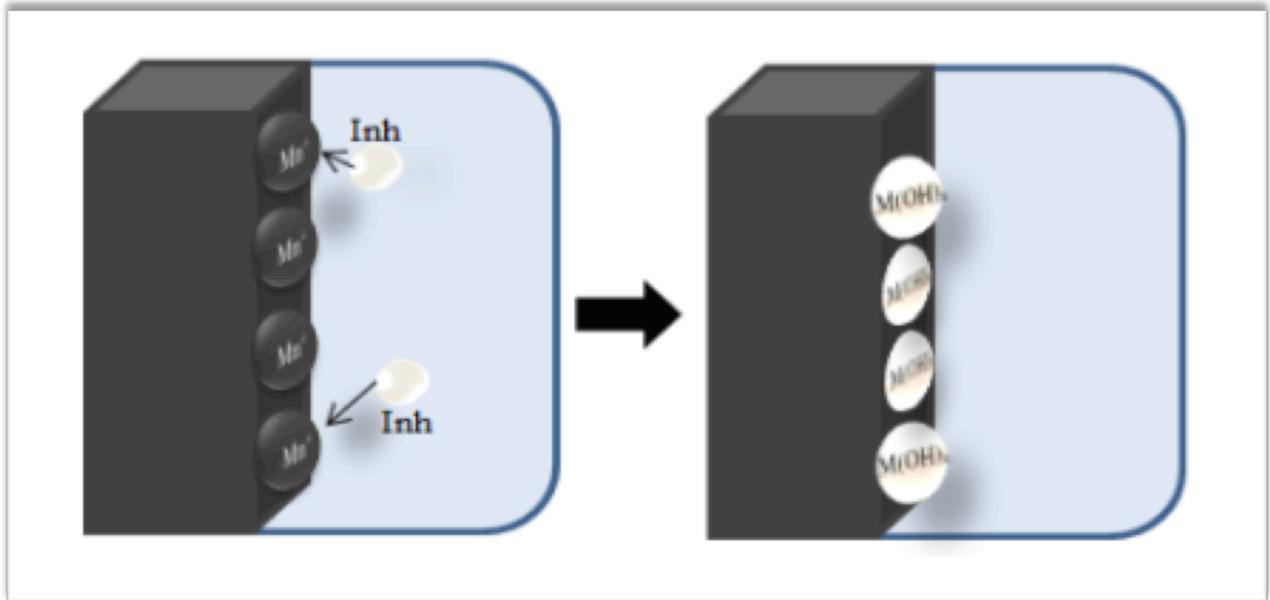


Figure I-15 : Illustration has shown the mechanism of actuation of the cathodic inhibitors.

I.7.4.2. Organic inhibitors

Organic compounds used as inhibitors, occasionally, they act as cathodic, anodic or together, as cathodic and anodic inhibitors, nevertheless, as a general rule, act through a process of surface adsorption, designated as a film-forming. Naturally the occurrence of molecules exhibiting a strong affinity for metal surfaces compounds showing good inhibition efficiency and low environmental risk. [47] These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal. [42]

In the (Figure I-16) , that shows a theoretic potentiostatic polarization curve, it can be seen that the effect of the solution containing organic inhibitor on the metal presents an anodic and cathodic behavior. After the addition of the inhibitor, the corrosion potential remains the same, but the current decreases from I_{cor} to I'_{cor} .

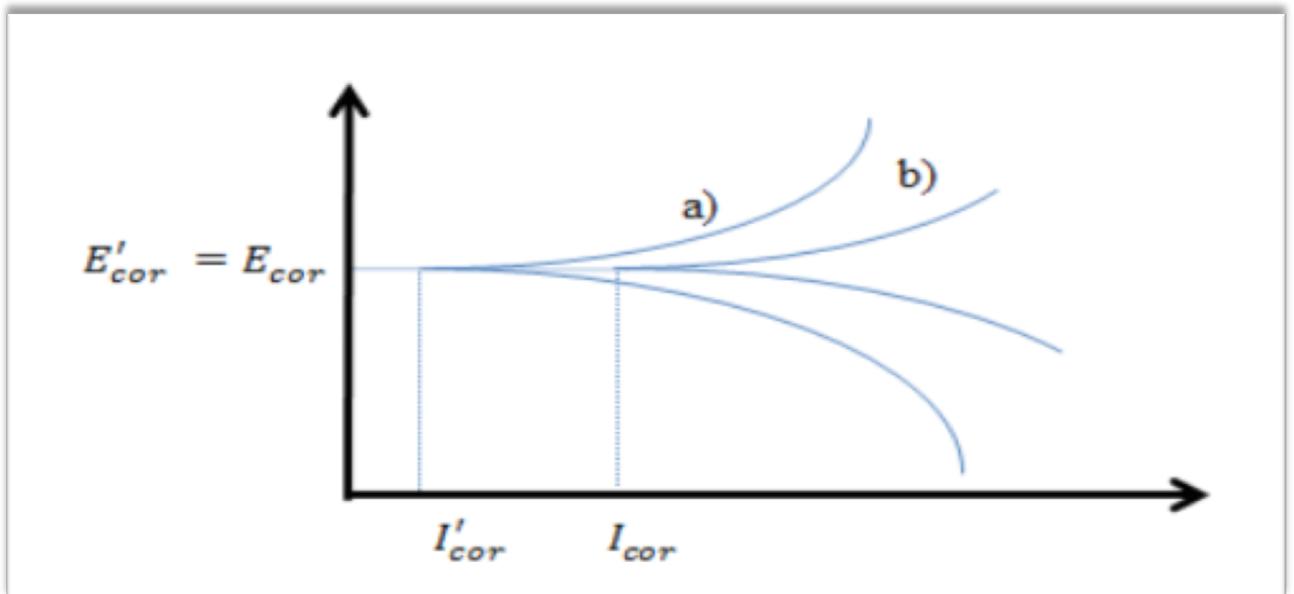


Figure I-16 : Theoretical potentiostatic polarization diagram: electrochemical behavior a metal on a solution containing a cathodic and anodic inhibitor (a) compared to the same solution without the inhibitor (b).

Is showed in (Figure I-17) the mechanism of actuation of organic inhibitors, when it is adsorbed to the metal surface and forms a protector film on it.

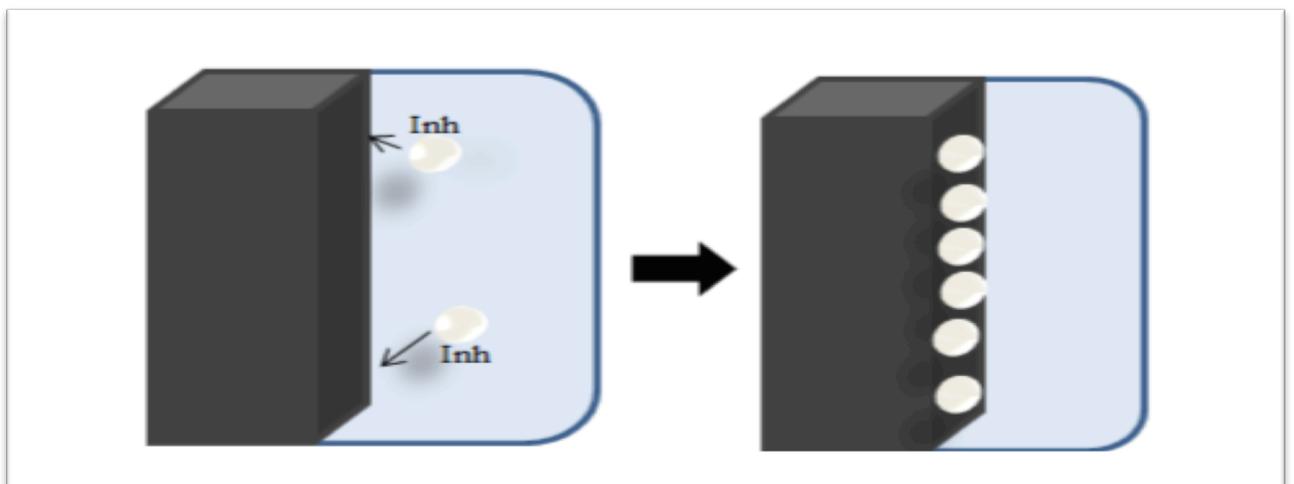


Figure I-17 : Illustration of the mechanism of actuation of the organic inhibitor: acting through adsorption of the inhibitor on the metal surface. Where the Inh represents the inhibitor molecules.

There are essentially two types of interactions between the adsorbed organic species and the metal surface:

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- a) Physical adsorption (physisorption) [66,67]
- b) Chemical adsorption (chemisorption) [65,68]

We can find both types simultaneously [64,69].

Table I.2: Difference between physical adsorption and chemisorption are as following:

PHYSISORPTION	CHEMISORPTION
The forces operating in these are weak vander Waal's forces.	The forces operating in these cases are similar to those of a chemical bond.
The heat of adsorption are low i.e. about 20 – 40 kJ mol ⁻¹	The heat of adsorption are high i.e. about 40 – 400 kJ mol ⁻¹
No compound formation takes place in these cases.	Surface compounds are formed.
The process is reversible i.e. desorption of the gas occurs by increasing the temperature or decreasing the pressure.	The process is irreversible. Efforts to free the adsorbed gas give some definite compound.
It does not require any activation energy.	It requires any activation energy.
This type of adsorption decreases with increase of temperature.	This type of adsorption first increases with increase of temperature. The effect is called activated adsorption.
It is not specific in nature i.e. all gases are adsorbed on all solids to some extent.	It is specific in nature and occurs only when there is some possibility of compound formation between the gas being adsorbed and the solid adsorbent.
The amount of the gas adsorbed is related to the ease of liquefaction of the gas.	There is no such correlation exists.
It forms multimolecular layer.	It forms unimolecular layer.

I.8.Green Inhibitors

Corrosion problems in the oil and petrochemical industry usually have been solved by the selection of suitable materials and/or by changing the environment to make it less aggressive [48]. Acid solutions are widely used in the industry. The most important areas of application are acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [49]. Corrosion inhibitors are needed to reduce the corrosion rates of metallic materials in these acid media [50-55]. An inhibitor is usually added in small amount in order to slow down the rate of corrosion through the mechanism of adsorption [56-57]. Over the years, several inhibitors have been synthesised or chosen from existing compounds and it has been found that the best inhibitors are those that have centre for π electron donation (usually enhanced by the presence of hetero atoms in aromatic compound) while others may be gotten from extracts of naturally occurring compounds [58-60]. This class of inhibitors (green inhibitors) are significant because they are non toxic and do not contain heavy metals hence they are environmentally friendly [61-62]. The present study is aimed at investigating the inhibitive and adsorption properties of GA extract for the corrosion of carbon steel in HCl.

Table I.3: Green corrosion inhibitors used for corrosion inhibition for different metals [80]

S. no.	Metal	Inhibitor source	Active ingredient
1.	Steel	<i>Emblica officinalis</i>	–
2.	Steel	<i>Terminalia bellerica</i>	–
3.	Steel	Eucalyptus oil	Monomtrene 1,8-cineole
4.	Aluminium	<i>Azadirachta indica</i> and <i>carica papaya</i>	–
5.	C-steel, Ni, Zn	Lawsonia extract (Henna)	Lawson (2-hydroxy-1,4-naphthoquinone resin and tannin, coumarine, gallic, acid and sterols)
6.	Mild steel	<i>Musa sapientum</i> peels (Banana peels)	–
7.	Mild steel	Garcinia kola seed	Primary and secondary amines Unsaturated fatty acids and Biflavnone
8.	Steel	<i>Hibiscus sabdariffa</i> (Calyx extract) in 1M H_2SO_4 and 2 M HCl solutions, Stock 10–50 %	Molecular protonated organic species in the extract. Ascorbic acid, amino acids, flavonoids, pigments and carotene
9.	Al, steel	Aqueous extract of tobacco plant and its parts	Nicotine
10.	Al	<i>Prosopis cineraria</i> (khejari)	–
11.	Al	Tannin beetroot	–
12.	Al	Saponin	–

I.8.1.Mechanism of Action of Green Inhibitors

Many theories to substantiate the mode of action of these green inhibitors have been put forth by several workers. Mann has suggested that organic substances, which form onium ions in acidic solutions, are adsorbed on the cathodic sites of the metal surface and interfere with the cathodic reaction. Various mechanisms of action have been postulated for the corrosion inhibition property of the natural products.

I.8.2.Gum Arabic

Gum arabic, or gum acacia, is the oldest and best known of all the tree gum exudates and has been used as an article of commerce for >5000 years [63]. Ancient Egyptian inscriptions make frequent mention of gum arabic, called 'kami' which was used largely as an adhesive for mineral pigments in paints and for the flaxen wrappings used to embalm mummies [64] . Eventually, the gum found its way into Europe through various Arabian ports and acquired the name 'gum arabic' after its place of origin or port of export.

The gum is the exudation from certain acacia trees which occur in a wide belt of semi-arid land stretching across sub-Saharan Africa. The gum belt occurs as a broad band from Mauritania, Senegal and Mali, in the west, through Burkina Faso, northern Benin, Niger, northern parts of Nigeria, Cameroon and Chad, northern central Africa, Sudan, Eritrea, Ethiopia and Somalia in the 'Horn of Africa'. From here, it extends through east Africa to southern Africa covering southern Angola, Namibia, Zimbabwe, Botswana, South Africa and parts of Mozambique.

Sudan is the world's largest producer, with production reaching 40 000 tons in 1996. Nigeria is the second largest producer, followed by Chad, Mali and Senegal. It is a reality, however, that much of the gum exported from Chad and Ethiopia, for example, originates in the Sudan, but enters through illegal cross-border trade. The best quality gum is traditionally associated with Sudan, but recently indigenous gum from Chad is being produced at comparable quality.



Figure I-18 : Gum Arabic on tree branch, waiting to be collected.

The gum of commerce is not collected from a single botanical species. *Acacia senegal*, *Acacia seyal* and *Acacia polyacantha* have the widest distribution in the gum belt. Even these species are found in more than one variety.

- *Acacia senegal* has three positively identified varieties and taxonomists are still undecided about a fourth. These are (8):
 - *A.senegal* (L) Willd var. *senegal* (syn. *A.verek* Guill and Perry);
 - *A.senegal* (L) Willd var. *Kerensis* Schweinf;
 - *A.senegal* (L) Willd var. *rostrata* Brenan;
 - *A.senegal* (L) Willd var. *leiorhachis* Brenan.
- *Acacia seyal* occurs as two varieties:
 - *A.seyal* Del. var. *seyal*;
 - *A.seyal* Del var. *fistula* (Schweinf) Olivo



Figure I-19 : Acacia Seyal Tree, a Tree of the African Savanna.

Gum arabic (GA, E-Number 414) is an edible, dried, gummy exudate from the stems and branches of *Acacia senegal* and *A. seyal* that is rich in non-viscous soluble fiber (Williams and Phillips, 2000). It is defined by the FAO/WHO Joint Expert Committee for Food Additives (JECFA) as ‘a dried exudation obtained from the stems of *A. senegal* (L).



Figure I-20 : Gum Arabic. Popular Candies Using Gum Arabic as an Ingredient.

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GA has wide industrial uses as a stabilizer, thickening agent and emulsifier, mainly in the food industry (e.g. in soft drinks syrup, gummy candies and marshmallows), but also in the textile, pottery, lithography, cosmetics and pharmaceutical industries (Verbeken et al., 2003). It has a complex chemical composition (see below).



Figure I-21 : Gum Arabic shown as Ingredient in Popular American Diet Drink.



Figure I-22 : Gum Arabic as Ingredient in a Popular Mint.

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In folk medicine, GA has been reported to be used internally for the treatment of inflammation of the intestinal mucosa, and externally to cover inflamed surfaces (Gamal el-din et al., 2003). Despite the fact that GA is widely used as a vehicle for drugs in experimental physiological and pharmacological experiments, and is assumed to be an “inert” substance, some recent reports have claimed that GA possesses anti-oxidant, nephroprotectant and other effects (Rehman et al., 2001; Gamal el-din et al., 2003; Ali et al., 2008). Clinically, it has been tried in patients with chronic renal failure, and it was claimed that it helps reduce urea and creatinine plasma concentrations and reduces the need for dialysis from 3 to 2 times per week (Suliman et al., 2000). These findings are not universally accepted and their confirmation, validity, reliability and mode of action await further studies.



Figure I-23 : Gum Arabic. Ladies Removing Straw and Dirt by Hand. Niamey, Niger,

GA is a branched-chain, complex polysaccharide, either neutral or slightly acidic, found as a mixed calcium, magnesium and potassium salt of a polysaccharidic acid (arabic acid). The backbone is composed of 1,3-linked b-D-galactopyranosyl units. The side chains are composed of two to five 1,3-linked b-D-galactopyranosyl units, joined to the main chain by 1,6-linkages. Both the main and the side chains contain units of a-L-arabinofuranosyl, a-L-rhamnopyranosyl, b-D-glucuronopyranosyl and 4-O-methyl-b-D-glucurono- pyranosyl, the last two mostly as end

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units (Anderson and Stoddart, 1996; Islam et al., 1997; Verbeken et al., 2003). Idris et al. (1998) reported GA to be comprised of 39–42% galactose, 24–27% arabinose, 12–16% rhamnose, 15–16% glucuronic acid, 1.5–2.6% protein, 0.22–0.39% nitrogen, and 12.5–16.0% moisture.

The chemical composition of GA can vary with its source, the age of the trees from which it was obtained, climatic conditions and soil environment (Al-Assaf et al., 2005; Anderson et al., 1968; Idris et al., 1998; Islam et al., 1997; Karamalla et al., 1998; Verbeken et al., 2003). GA is a highly heterogeneous material, but was separated into three major fractions by hydrophobic affinity chromatography (Randall et al., 1989). Most of the gum (88.4% of total), an arabinogalactan (AG), had a very low protein content (0.35%) and a molecular mass of 3.8×10^5 Da [from gel permeation chromatography (GPC) data; 2.79% 10^5 Da from light scattering]. The second fraction (10.4% of total), an arabinogalactan-protein complex (AGP), contained 11.8% protein and had a molecular mass of 1.45×10^6 Daltons (both methods). The third fraction (1.2% of total gum), referred to as a low molecular weight glycoprotein (GP), had a protein content of 47.3%, and a molecular mass of 2.5×10^5 Da (GPC data). Ray et al. (1995) fractionated GA by both hydrophobic affinity chromatography and GPC; their results were in broad agreement with those of Randall et al. (1989). The major amino acids present in the protein of AG and AGP were hydroxyproline, serine and proline, whereas in GP, aspartic acid was the most abundant (Islam et al., 1997).

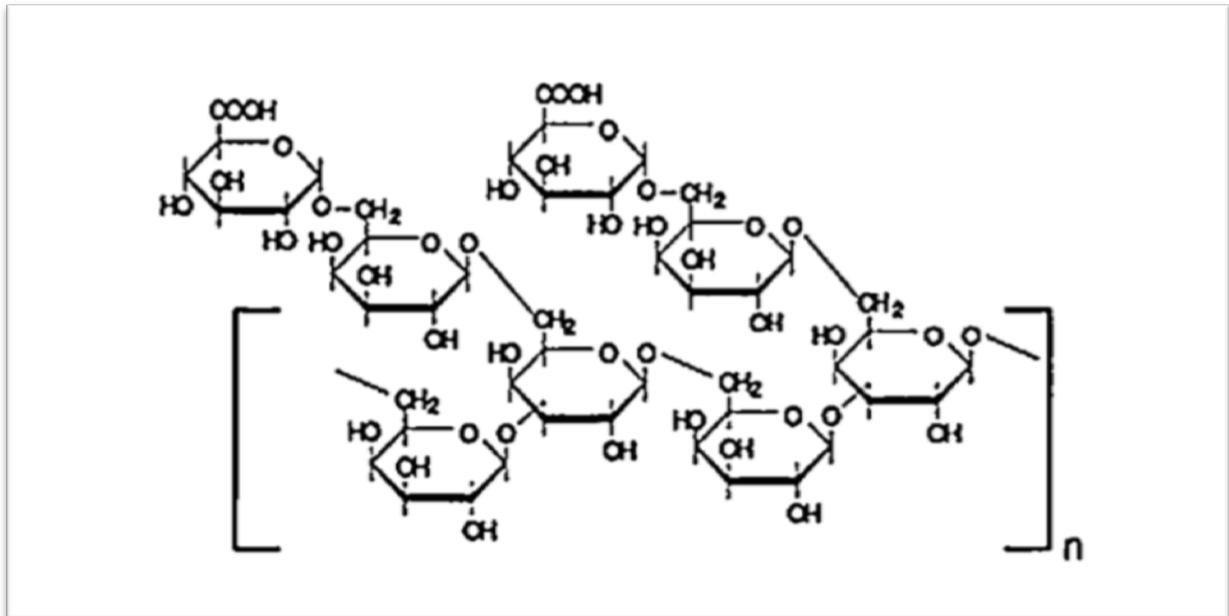


Figure I-24 : Structure of Gum Arabic.

It is clear here that the functional groups of the gum arabic are the carboxyl radical (-COOH) and the hydroxyl radical (-OH).

A wattle blossom model was proposed for describing the structure of the AGP complex. It was postulated that the high molecular weight fraction of the gum is composed of large carbohydrate blocks with a molecular mass of approximately $2.5 \cdot 10^5$ Da; these are attached covalently to a polypeptide chain (Fincher et al., 1983; Connolly et al., 1987, 1988). An alternative model was suggested by Qi et al. (1991), but more recent studies have indicated that the molecules of the AGP complex have a globular structure, which supports the wattle blossom model (Verbeken et al., 2003, and references quoted therein).

Osman et al. (1993) fractionated GA by hydrophobic interaction chromatography to yield four fractions, all of which had a similar carbohydrate composition, but differed in their content of protein, amino acid composition and molecular mass distribution. All four fractions reacted with an array of anti-arabinogalactan-protein monoclonal antibodies via anti-carbohydrate epitopes and were precipitated by Yariv's reagent, which indicated that all four fractions were AGPs. It was shown that at least one protein was unique to each fraction.

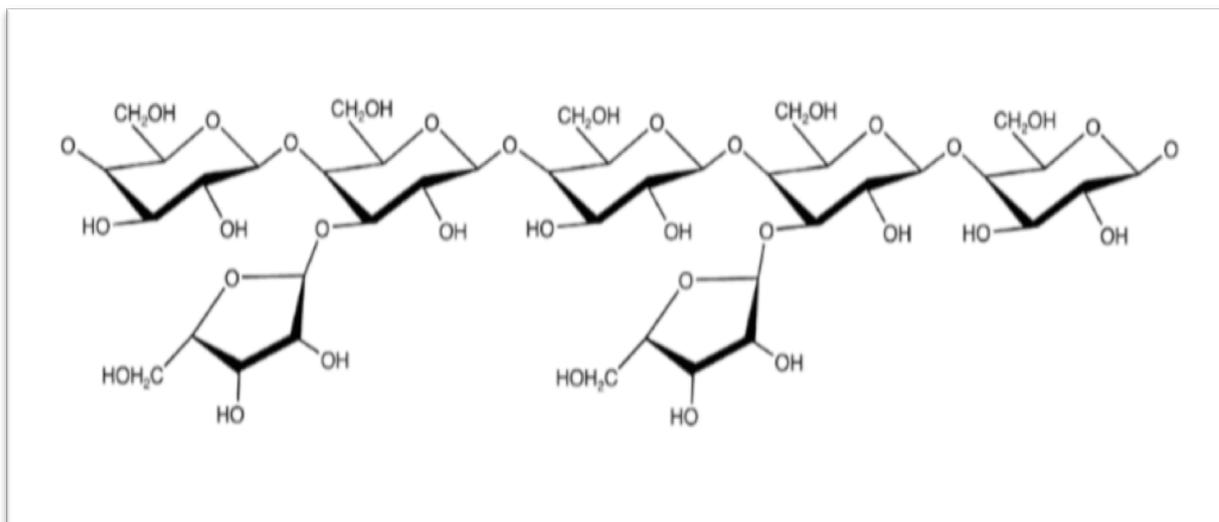


Figure I-25 : The molecular structure of Arabinogalactan.

❖ Exudate Gum from *Acacia Trees* as Green Corrosion Inhibitor for carbon Steel in Acidic Media :

The inhibition effect of exudate gum from *Acacia trees* (*Gum Arabic*, GA) on the corrosion of carbon steel in acidic media was studied by weight loss and electrochemical polarization methods; also, surface morphology was analyzed by optical microscopy, and X-ray diffraction (XRD) techniques.

The results of weight loss and electrochemical polarization methods indicated that inhibitor efficiency (I%) increased with increasing inhibitor concentration.

Electrochemical polarization studies showed that GA *Gum Arabic* acts as mixed type inhibitors. The results reveal that *Gum Arabic* provided a very good protection to carbon steel against corrosion in acidic media.

The inhibitory effect of gum arabic (0.5 g/L maximum concentration) for carbon steel in sulfuric acid medium at 30-60C ° was studied by *Umoren* [70] et *Umoren et al* [65].

Chapter II :

Experimental Setup

And

Equipment Used

Chapter II : Experimental setup and Equipment used

This chapter gives all the experimental techniques used in this study. Thus, a minimum of essential information for understanding the experimental methods and knowing all used materials .

II.1. Our study skills

To study corrosion in various corrosive media and inhibitor properties (Gum Arabic), three types of methods were used:

- ❖ Weight loss measurements.
- ❖ Electrochemical methods allow us first of all to have a well knowledge of the corrosion mechanism in different corrosive mediums and to assess and estimate the efficacy of our inhibitor and its mechanism of action .
- ❖ Surface analyzes were used to determine the state of the working electrode and the nature of the layer that forms on its surface. So, confirm the effectiveness of the studied inhibitor.

II.1.1. Weight loss measurements

The simplest, and longest-established, method of estimating corrosion losses in plant and equipment is weight loss analysis. A weighed sample of the metal or alloy under consideration is introduced into the process, and later removed after a reasonable time interval. The sample is then cleaned of all corrosion product and is reweighed. The weight loss is converted to a corrosion rate (CR) or metal loss (ML), Weight loss determination has a number of attractive features that account for its sustained popularity:

- Simple : No sophisticated instrumentation is required to obtain a result.
- Direct : A direct measurement is obtained, with no theoretical assumptions or approximations.
- Versatile : It is applicable to all corrosive environments, and gives information on all forms of corrosion.

II.1.2. Electrochemical techniques

Electrochemical techniques are based on the characterization of the oxidation-reduction reactions which are the area of an exchange of electrons between the oxidant and the

Chapter II : Experimental setup and Equipment used

reductant. Obtained by this measurement the characterization of the modification of the metal/medium interface.

The quantitative aspect (polarization curves plot) allows to access the physical parameter describing the state of the system (corrosion current, inhibition rate, capacity of double layer, charge transfer resistance).

II.1.2.1. Polarization curves

An electrochemical reaction on an electrode is governed by the overvoltage η , which is the difference between the potential E electrode/solution and the equilibrium potential of the reaction E_{EQ} . The intensity of the current through the material is a function of potential E , represented by the curve $\hat{i} = f(E)$, or $\log \hat{i} = f(E)$, which is the sum of the currents of the electrochemical reactions occurring at the electrode surface. Its determination in a corrosive environment allows others the studies of corrosion. The polarization curves are determined by applying a potential between the working electrode and the reference electrode. A stationary current is established after some time (minutes to hours). It is measured between the working electrode and the auxiliary electrode. In kinetic side, two control modes are distinguished [81].

- The transportation of charges at the interface metal /electrolyte (activation).
- Mass transportation of electroactive species or reaction products.

The polarization curves of controlled reactions following by the law of *Butler-Volmer* [10].

$$i = i_0 \exp\left(\frac{\eta}{b_a}\right) - i_0 \exp\left(-\frac{\eta}{b_c}\right) \quad \text{Eq II -1}$$

- i : the electrode current density,
- i_0 : the exchange current density,
- η : activation overpotential ($E - E_{corr}$),
- E : electrode potential.

Their plot in logarithmic scale reveals, far from equilibrium, the existence of two linear branches, said Tafel straight lines, which means that the reaction related to the applied polarization is predominant. The slopes of the lines, or Tafel coefficients b_a and b_c , and the

Chapter II : Experimental setup and Equipment used

exchange current density i_0 , related to velocities of the anodic and cathodic partial reactions at equilibrium, are representative of the reaction mechanism and the metal dissolution rate.

II.1.2.2. Polarization resistance R_p

R_p is determined by the inverse of the slope corresponding to the linear portion of the curve $i = f(E)$ at the neighbourhood of E_{corr} .

On note here that the determination of R_p is based on a potential sweep with velocity $dE/dt = 0,2 \text{ mV/s}$ de $E_{\text{initial}} = -10 \text{ mV}$ in comparison to E_{corr} to $E_{\text{final}} = +20 \text{ mV}$ compared with E_{initial} . R_p is calculated by finding the best linear regression.

La figure II-1 shows the polarization in the vicinity of E_{corr} to determine R_p .

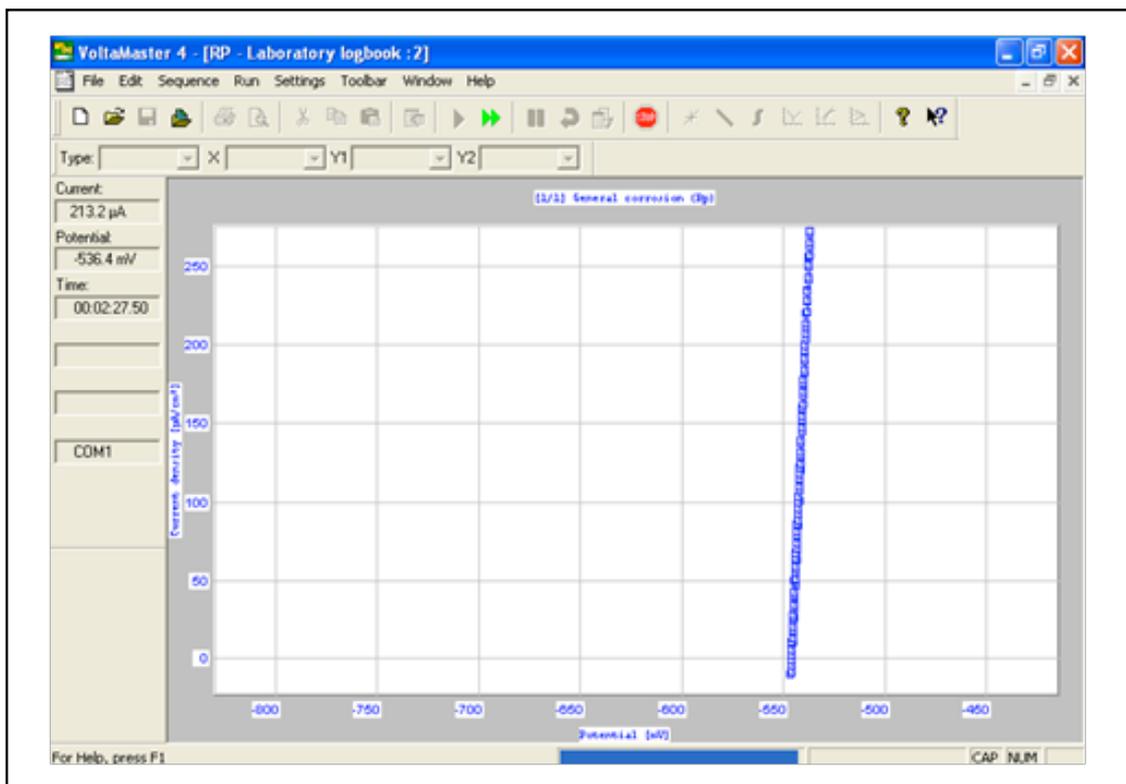


Figure II-1 : Polarization of API 5L (X60 ; X42) in 1M hydrochloric acid medium, in the vicinity of corrosion potential .

Chapter II : Experimental setup and Equipment used

II.1.2.3. Cyclic voltammetry

Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as desired. The current at the working electrode is plotted versus the applied voltage (i.e., the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution. [82 -84]

This method is very similar to the previous one. The potential sweep is initially effected in the same manner, but arrived at the final potential, it is reversed and a half cycle it is performed at a rate v' which may be equal or different from v , of the half cycle proceed .

CV uses to study only the passivation region of API 5L (X60 ; X42).

II.2. Experimental conditions

II.2.1. Working electrodes

II.2.1.1. Nomenclature

They are elaborated by organizations or entities, for example : *The European Committee for Standardization (CEN, French: Comité Européen de Normalisation)*, *International Organization for Standardization (ISO)* , or by professional organizations or certification organizations, for example : *American Iron and Steel Institute (AISI)* or *American Petroleum Institute (API)*.

Carbon steel is a steel alloy whose main component is carbon, between 0,12 and 2,0%, other alloy elements are in very small quantities. The *American Iron and Steel Institute (AISI)* defines carbon steel as follows:

“Steel is considered to be carbon steel when no minimum content is specified or required for chromium, cobalt, columbium [niobium], molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect; when the specified minimum for copper does not exceed 0.40 per cent; or when the maximum content specified for any of the following elements does not exceed the percentages noted: manganese 1.65, silicon 0.60, copper 0.60”.

Carbon steel can be classified, according to various deoxidation practices, as rimmed, capped,

Chapter II : Experimental setup and Equipment used

semi-killed, or killed steel. Deoxidation practice and the steelmaking process will have an effect on the properties of the steel. However, variations in carbon have the greatest effect on mechanical properties, with increasing carbon content leading to increased hardness and strength. As such, carbon steels are generally categorized according to their carbon content. Generally speaking, carbon steels can be subdivided into **low-carbon steels, medium-carbon steels, high-carbon steels, and ultrahigh-carbon steels**; each of these designations is discussed below.

As a group, carbon steels are by far the most frequently used steels. More than 85% of the steel produced and shipped in the United States is carbon steel.

- **Low-carbon** steels contain up to 0.30% C. The largest category of this class of steel is flat-rolled products (sheet or strip), usually in the cold-rolled and annealed condition. The carbon content for these high-formability steels is very low, less than 0.10% C, with up to 0.4% Mn. Typical uses are in automobile body panels, tin plate, and wire products.

For rolled steel structural plates and sections, the carbon content may be increased to approximately 0.30%, with higher manganese content up to 1.5%. These materials may be used for stampings, forgings, seamless tubes, and boiler plate.

- **Medium-carbon** steels are similar to low-carbon steels except that the carbon ranges from 0.30 to 0.60% and the manganese from 0.60 to 1.65%. Increasing the carbon content to approximately 0.5% with an accompanying increase in manganese allows medium carbon steels to be used in the quenched and tempered condition. The uses of medium carbon-manganese steels include shafts, axles, gears, crankshafts, couplings and forgings. Steels in the 0.40 to 0.60% C range are also used for rails, railway wheels and rail axles.
- **High-carbon** steels contain from 0.60 to 1.00% C with manganese contents ranging from 0.30 to 0.90%. High-carbon steels are used for spring materials and high-strength wires.
- **Ultrahigh-carbon** steels are experimental alloys containing 1.25 to 2.0% C. These steels are thermomechanically processed to produce microstructures that consist of ultrafine, equiaxed grains of spherical, discontinuous proeutectoid carbide particles.

Chapter II : Experimental setup and Equipment used

The API 5L X60 steel is a carbon steel designated by its elastic limit .

The chemical composition is given in Table II-1.

- API 5L means: pipeline.
- X60 ; X42 means: the steel grade. Other grades are, for example, X46, X52, X56 X70...
- The number 60 indicates: 60000 psi is the minimum yield strength of steel in psi "*pound per square inch*" (psi).
- The number 42 indicates: 42000 psi is the minimum yield strength of steel in psi "*pound per square inch*" (psi).
-

Each grade of API 5L having unique properties, execution, tolerances, lengths, and mechanical & chemical properties. Different grades used in different atmosphere depends upon temperature, pressure & climatically conditions.

Table II-1: Chemical composition of the (X60) pipeline steel (wt%). [85]

C	Mn	Si	P	S	N	Cr	Ni	Nb	Ti	Mo	Cu	Fe
0,052	1,5	0,15	0,007	0,0027	0.009	0,07	0,19	0,067	0,022	0.096	0.18	Bal

Table II-2: Chemical composition of the (X42) pipeline steel (wt%). [86]

C	Mn	Si	P	S	Cr	Ni	Nb	Ti	Fe
0,2	1,18	0,1	0,025	0,01	0,4	0,4	0,035	0,02	Bal

Chapter II : Experimental setup and Equipment used

Table II-3: Major effects of alloying elements in High Strength Line Pipe Steels [87]

Element	Effects
C	<ul style="list-style-type: none"> •Matrix strengthening (by precipitation). •Formation of ferrite, bainite and martensite largely depend on C%. •Improves hydrogen induced cracking [HIC] resistance •Excess C in alloy decrease toughness, weld ability and ductility.
Si	<ul style="list-style-type: none"> •Improvement in strength (solid solution), Matrix strengtheners. •detrimental effect on both base steel and HAZ toughness, improves ferrite ductility by increasing driving force for carbon migration in austenite, suppresses carbide formation
Mn	<ul style="list-style-type: none"> •Matrix strengtheners. •Delays austenite transformation during cooling •increases harden ability •Decreases ductile to brittle transition temperature •Indispensable to obtain a fine-grained lower bainite microstructure
S	<ul style="list-style-type: none"> •Reduces low temperature toughness, hot shortness •Forms elongated MnS after rolling thus forms starting points for HIC
P	<ul style="list-style-type: none"> •Detrimental effect on pipe making and field weldability. •Segregate at centre in casting steel slab and cause grain boundary fracture
Al	<ul style="list-style-type: none"> •Fixes free nitrogen in HAZ • decreases toughness and formability • Fine oxide dispersant during deoxidation.
Ti	<ul style="list-style-type: none"> •Grain refinement by suppressing the coarsening of austenite grains (TiN formation) •Strong ferrite strengtheners. •Fixes the free Ni (prevent detrimental effect of Ni on harden ability)
V	<ul style="list-style-type: none"> •Leads to precipitation strengthening during the tempering treatment •strong affinity to carbon and nitrogen

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	<ul style="list-style-type: none"> •With Nb, reduces HAZ softening •VN precipitate predominant ferrite strengtheners.
Cu	<ul style="list-style-type: none"> •Improves corrosion resistance (with Cr and Ni) and HIC • restricts hydrogen formation by forming a protective layer •lowers austenite to ferrite transformation temperature •high copper content can cause embrittlement crack at time of hot rolling •higher amount of copper induces excessive precipitation hardening
Ni	<ul style="list-style-type: none"> •Improves the properties of low-carbon steels without impairing field weld ability and low temperature toughness • In contrast to Mg and Mo, Ni tends to form less hardened micro structural constituents detrimental to low temperature toughness in the plate (increases fracture toughness) •increases bainitic fraction
Cr	<ul style="list-style-type: none"> •Improves strength and quench hardenability • improves corrosion and HIC resistance • lowers carbon activity in ferrite, high strength, low YS/UTS
N	<ul style="list-style-type: none"> •TiN restricts austenite grain growth and improves low temperature toughness
B	<ul style="list-style-type: none"> •Improves quench hardenability with Nb and Mo, helps forming lower bainite and lath martensite
Mo	<ul style="list-style-type: none"> • Suppresses austenite recrystallisation and grain growth •Improves hardenability and strength, thereby promotes the formation of the desired lower bainite microstructure

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Nb	<ul style="list-style-type: none">•Reduces temperature range in which recrystallization is possible between rolling passes•Retard recrystallization and inhibit austenite grain growth (improves strength and toughness by grain refinement)•NbC effective strengtheners than VN•higher solubility in austenite at low carbon level•Promotes refined ferrite and large volume fraction of acicular ferrite
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II.2.1.2. Metallurgical review

To determine the metallurgical structure of API 5L X60/ API 5L X42, a sample was polished on SiC abrasive discs of different sizes (P120, P180, P400, P600, P800, P1000, P1200), then we rinsed it with distilled water and dried it well with a tissue. After this metallographic etching deeply in the surface of API 5L X60/ API 5L X42, the various constituent phases of the sample have been highlighted.



Chapter II : Experimental setup and Equipment used

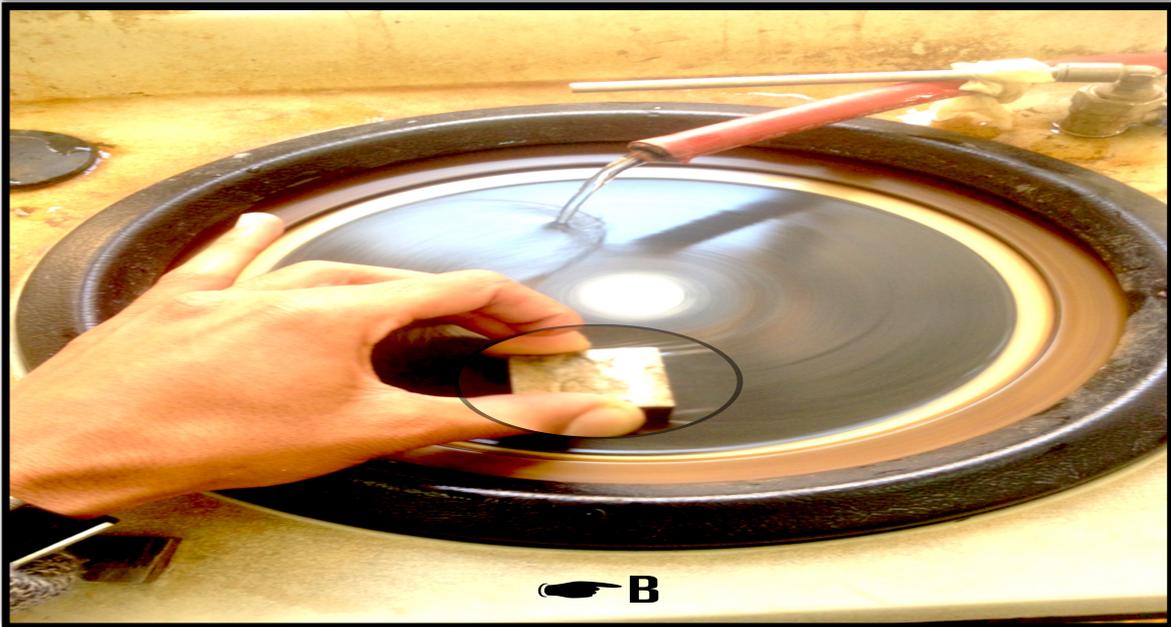


Figure II-2 : Photographs of the apparatus used. A: Polisher ; B :Sample polished on abrasive disc



Figure II-3 : Appearance of API 5L X60 samples with resin coating before the immersion test.

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The action of attacking has been carried by a quick dip (30 seconds) the previously polished steel or our samples in a solution of " Nital 4%" (mixture of nitric acid 96% and alcohol (ethanol) 4%).

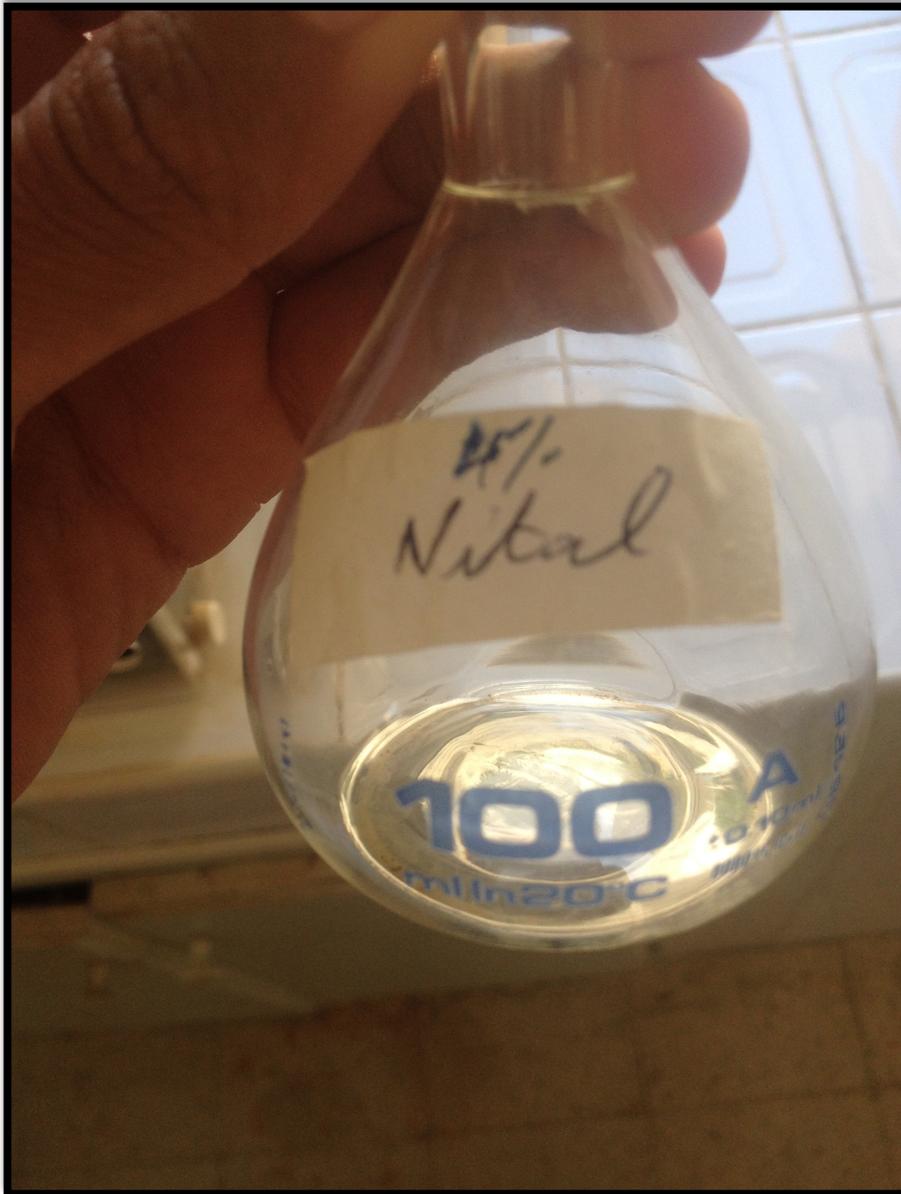


Figure II-4 : Solution of " Nital 4%" used for the attacking process .

Analysis under an optical microscope reveals that the steel (API 5L X60/ API 5L X42) has a microstructure characteristic of a ferrito-perlitique steel (Figure II-5/ Figure II-6).

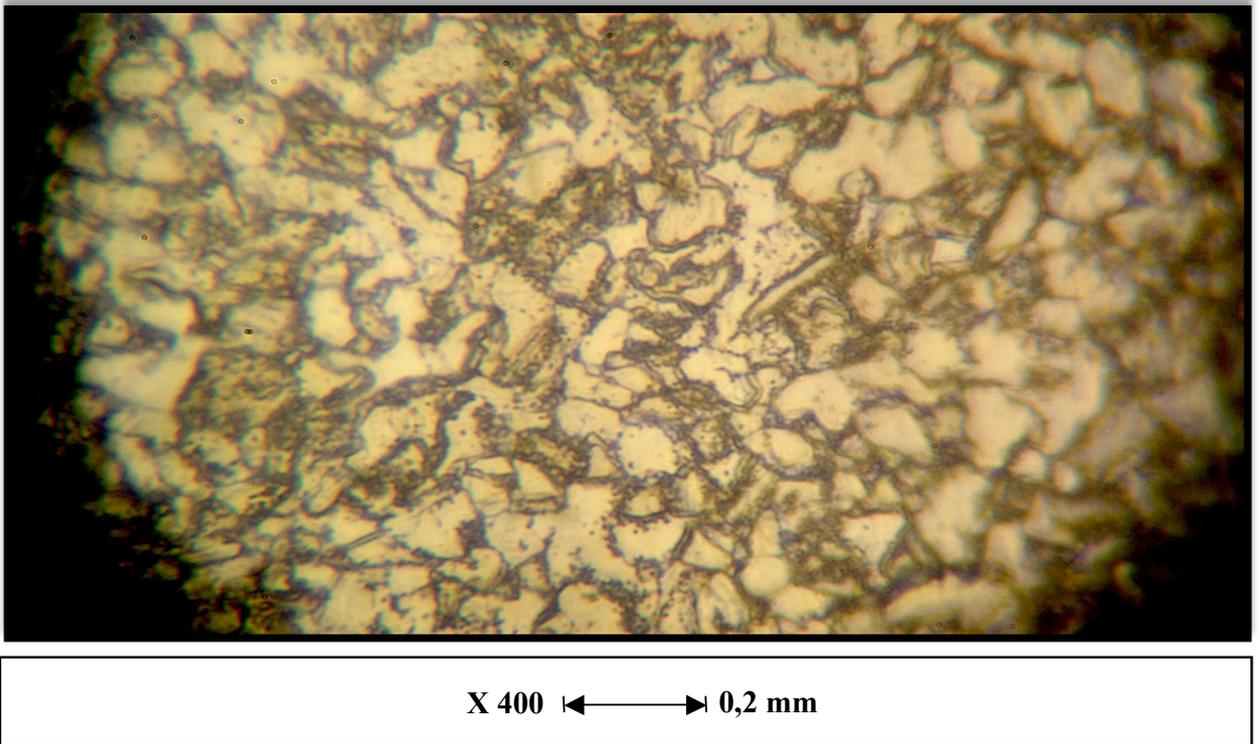


Figure II-5 : Metallographic structure of carbon steel API 5L X60 performed after an attack by nital 4%.

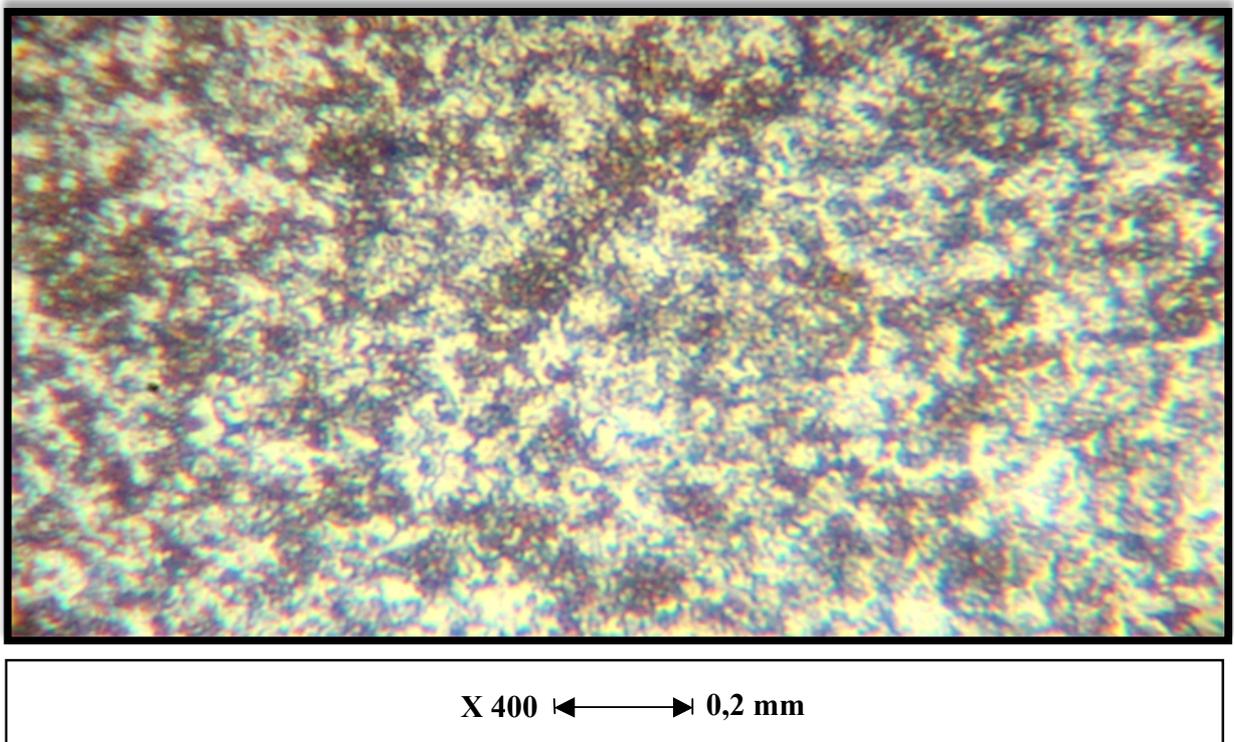


Figure II-6 : Metallographic structure of carbon steel API 5L X42 performed after an attack by nital 4%.

Chapter II : Experimental setup and Equipment used

II.2.2. Our electrolytic medium

Industrial purpose of this study guide us to the selection of the electrolyte to aqueous solution:

- ✓ Hydrochloric acid : HCl aggressive solutions were prepared by dilution of 37% HCl acid with distilled water.

II.2.3. Electrochemical measurements

Electrochemical tests were performed using a Potentiostat with a Radiometer PGZ301 Volta Master 4 software, in a conventional cell (Pyrex glass of 300 ml) with three electrodes,

- The working electrode (API 5L X60/ API 5L X42 steel)
- The Saturated calomel electrode (SCE) is a reference electrode
- An inert electrode (platinum).

Before each experience , the cell was cleaned with ethanol, rinsed with distilled water and dried with absorbent paper. . The system was connected to a computer.

Before measurement, the working electrode is immersed in the test solution at an open circuit potential for 1 hour to arrive to the stable state. Note that a thermostatic bath was used to maintain and save the temperature of the solution to the desired value (Figure II-7).

To draw curves, treat and analyze the electrochemical measurements, all results are transferred from Volta Master 4 to ORIGIN 6.0 software (processing software and scientific data analysis).



Figure II-7 : Electrochemical measurement device

Chapter II : Experimental setup and Equipment used

II.2.3.1. Polarization curves

The anodic and cathodic branches were obtained consecutively -700 mV/ ECS to -300 mV/ECS with speed (sweeping) 0.3 mV/sec. The density of the corrosion current I_{corr} ($\mu\text{A}/\text{cm}^2$) was calculated from the *Stern-Geary* equation [88]:

$$I_{\text{corr}} = \frac{|b_a| \times |b_c|}{2,3 \times (|b_a| + |b_c|) \times R_p} \quad \text{Eq II -2}$$

where b_a et b_c are the coefficients of the anodic and cathodic Tafel respectively (Tafel slopes) and R_p is the polarization resistance ($\Omega \text{ cm}^2$). we have the case of presence of a degree of non-linearity of Tafel slopes, Tafel coefficients were calculated from the slope of the points after 50 mV/ECS of corrosion potential E_{corr} . The values of the inhibitory efficiency, by the polarization method η_{POL} , were calculated using the following equation:

$$\eta_{\text{POL}} \% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100 \quad \text{Eq II -3}$$

Where I_{corr} et $I_{\text{corr(inh)}}$ represent the values of corrosion current density with and without inhibitor (GA) respectively. (Figure II-8) shows a polarization curve, during our tests, the API 5L X60/API 5L X42 steel in hydrochloric acid medium.

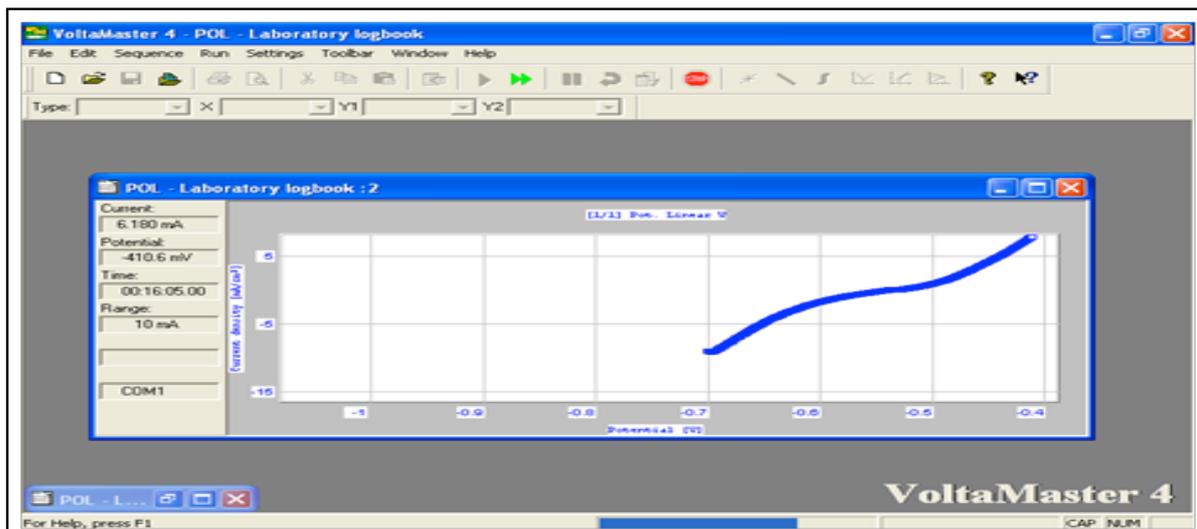


Figure II-8 : Polarization curve of API 5L X42 in hydrochloric acid medium 0.1 M (during the test).

Chapter II : Experimental setup and Equipment used

II.2.4. The X-ray diffraction (XRD)

To determine the nature of compounds formed after the immersion test, X-ray diffraction analysis were carried out with a diffractometer Panalytical X'Pert (Figure II-9).

The monochromatic X-ray produced by a copper anticathode. The filter is made of nickel and allows only the ray $K\alpha$ ($\lambda\alpha = 1.5406 \text{ \AA}$). The feeding tube is provided by a generator delivering a d.d.p de 45 KV and a current 40 mA.



Figure II-9 : X'Pert diffractometer Panalytical (D8 ADVANCE) BRUKER.

The results were compared using XRD reference diagrams. As an example (Figure II-10) shows the reference XRD hematite (Fe_2O_3) with the diagram formed in the reference [89].

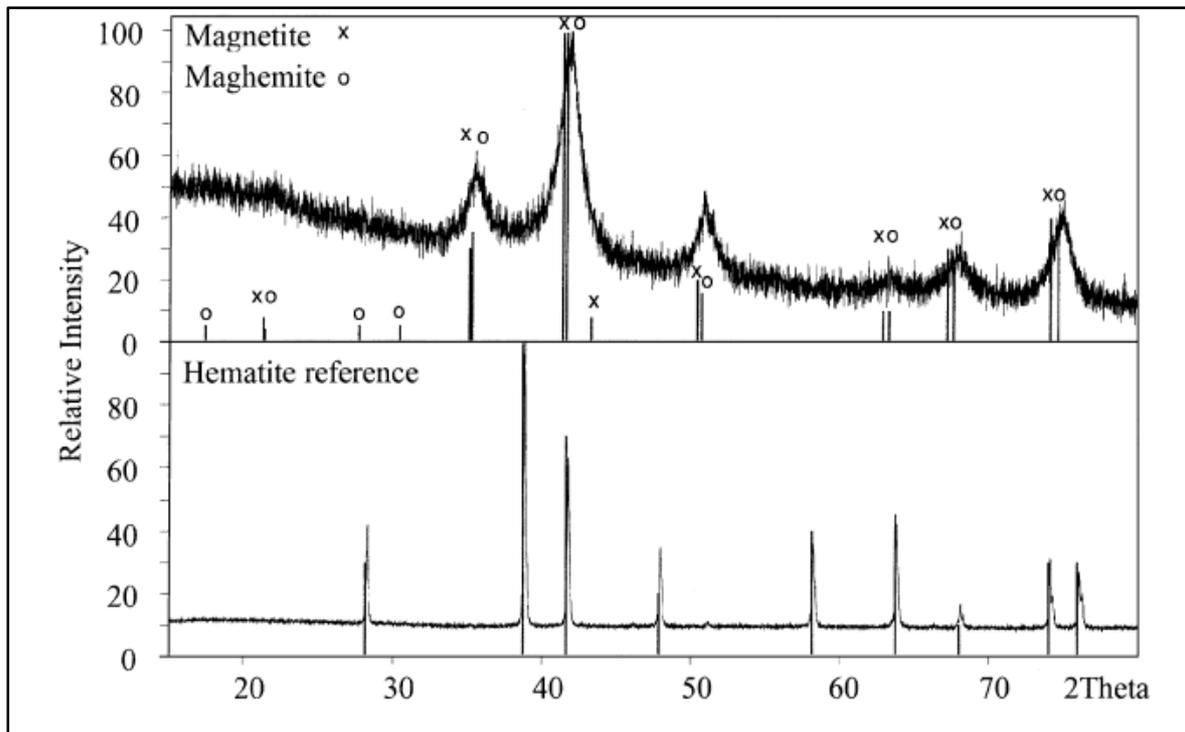


Figure II-10 : XRD of a powder (top) and hematite reference (bottom)

II.2.5. Optical microscopy

The observations of the metallurgical structure to receive state and bites that occur after the immersion tests were performed with an optical microscope type HUND-T100 WETZLAR (Figure II.11).



Figure II-11 : Optical microscope HUND T100-WETZLAR

Chapter III :

Results and Discussion

III.1. Part 1: Study of API 5L-X60/API 5L X42 in HCl medium according to operational variables.

This part is focussed to the evaluation of operational variables that have a fairly marked and noticeable influence on the kinetic of corrosion process of steel API 5L X60 in HCl medium .

Among these,

- ❖ The effect of immersion time,
- ❖ The concentration of the electrolyte,
- ❖ The passive layer ,

For this, a serie of electrochemical tests and surface analyzes were performed.

From electrochemical tests the corrosion rate for the different experimental conditions was determined order to better understand the influence of each parameter on the corrosion.

III.1.1. Corrosion Characterization of API 5L X60/API 5L X42

III.1.1.1. Immersion tests

Before starting anything, it became necessary to determine the immersion time before any electrochemical measurement.

We note that all experiments were carried out in 1 M HCl. The aggressive solution of 1M HCl was prepared by dilution of 36% HCl with distilled water.

▪ Weight loss measurements

In the weight loss experiments, the pre-cleaned carbon steel coupons were immersed in test bath containing test solution (HCL 1M ; HCL 1M + GA 2 g/L). The weight loss was determined by retrieving the coupons for several days, washed with distilled water cleaned with bristle brush, rinsed with acetone, dried and reweighed. The weight loss was taken to be the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out for both the inhibited and uninhibited solutions (blank).

The corrosion rate was computed using the expression:

$$\text{Corrosionrate (CR)} = \frac{m_1 - m_2}{At} \quad \text{Eq III -1}$$

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Where, m_1 and m_2 are the weight (mg) before and after immersion in the test solutions, respectively, A is the surface area of the specimens (cm^2) and t is the exposure time (Day).

The inhibition efficiency (I%) of GA was evaluated using the following equation:

$$I\% = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) \times 100\% \quad \text{Eq III -2}$$

Table III-1: Comparison of the weights of the samples of API 5L X60 before and after immersion in HCL (1M).

Immersion conditions	A (mm^2)	Weight, g			CR($\text{g}/\text{mm}^2.\text{Day}$)
		Before(m_1)	After(m_2)	Difference	
Specimen.1 ($t=11$ Day)	240.40	18.4777	18.1145	0.3632	0.00013735
Specimen.2 ($t=18$ Day)	193.92	22.4543	20.9887	1.4656	0.00041988
Specimen.3 ($t=26$ Day)	230.00	19.1438	16.3024	2.8413	0.00047513
Specimen.4 ($t=34$ Day)	187.28	17.6391	14.5876	3.0515	0.00047923
Specimen.5 ($t=41$ Day)	161.50	17.0448	13.2650	3.7798	0.00057084

- ✓ The weight loss of carbon steel samples increases with increasing immersion time (Day) from 0.3632 to 3.7798 ((Table III-1).
- ✓ The corrosion rate (CR) ($\text{g}/\text{mm}^2.\text{Day}$) of carbon steel samples increases with increasing immersion time (Day) from 0.00013735 to 0.00057084 $\text{g}/\text{mm}^2.\text{Day}$ (Table III-1).

Chapitre III : Results and Discussion

Table III-2: Comparison of the weights of the samples of API 5L X60 before and after immersion in HCL (1M) + Inhibitor ((GA) 2 g/l)

Immersion conditions	A (mm ²)	Weight, g		Difference	CR(g/mm ² .Day)
		Before(m ₁)	After(m ₂)		
Specimen.1 (t=8 Day)	208.65	18.4193	18.2095	0.2098	0.00012569
Specimen.2 (t=16 Day)	193.92	17.1592	16.4560	0.7032	0.00022664
Specimen.3 (t=29 Day)	412.00	18.0485	16.9749	1.0736	0.00023781
Specimen.4 (t=32 Day)	399.05	28.5306	26.6061	1.9291	0.00023897
Specimen.5 (t=39 Day)	411.00	35.0603	32.7020	2.3587	0.00023581

- ✓ The corrosion inhibitor significantly reduces the weight loss.
- ✓ The corrosion inhibitor significantly reduces the corrosion rate (**CR**).

We compared between (the Samples of API 5L X60 weight loss in HCL (1M) and the Samples of API 5L X60 weight loss in in HCL (1M) + Inhibitor (GA, 2 g/l) , the comparison showed in the chart below (figure III-1). :

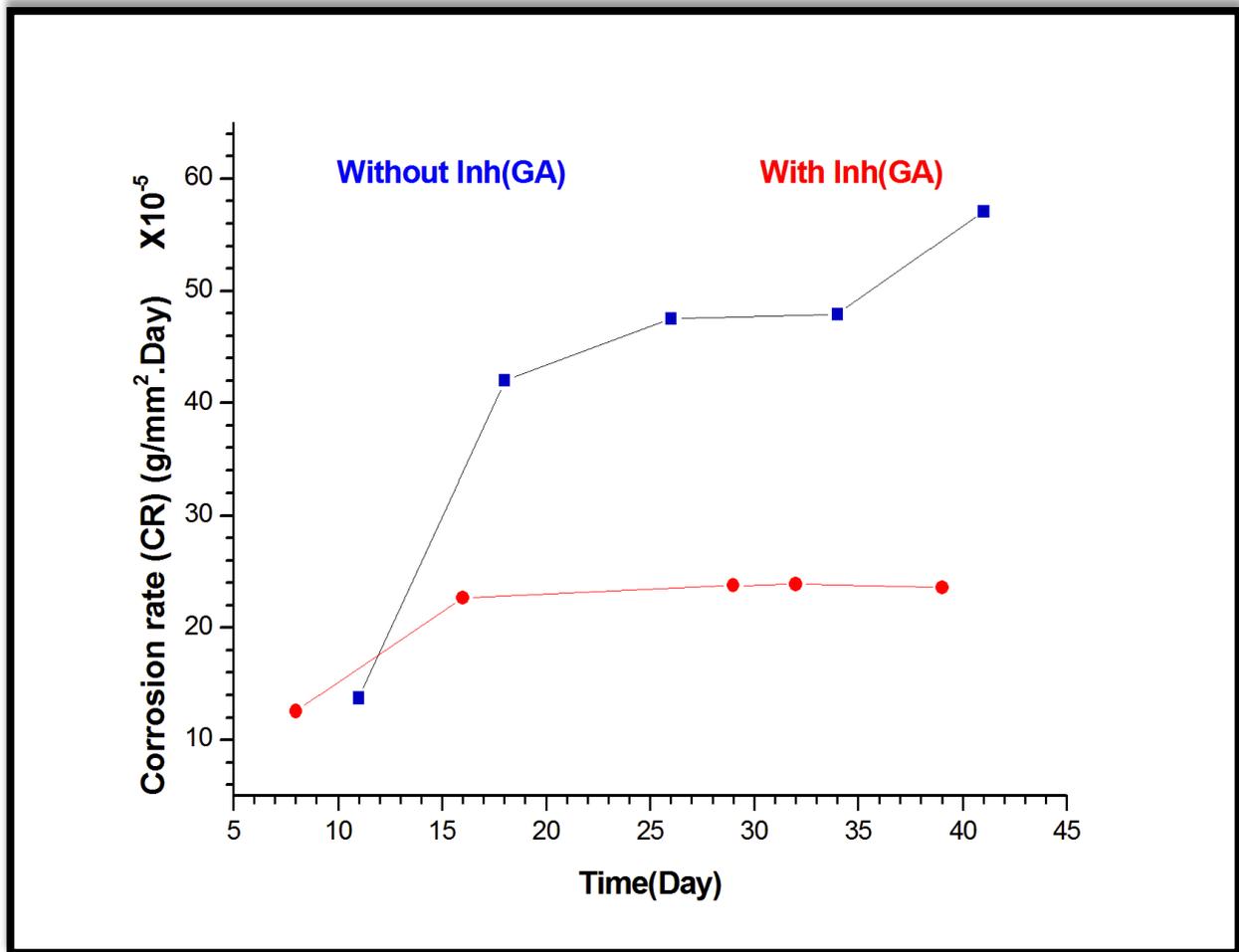


Figure III-1: Relationship between the corrosion rate (CR) and immersion time (Day) with and without GA (2g/l) in 1 M HCl.

To determine the nature of the corrosion products which form on the carbon steel surface, samples were immersed in a hydrochloric acid bath for a duration. The immersion test was exposed to air. After that all samples are examined by X-ray .

The results show that the corrosion products consist essentially of hematite (Fe_2O_3), magnetite (Fe_3O_4) (figure III-2).

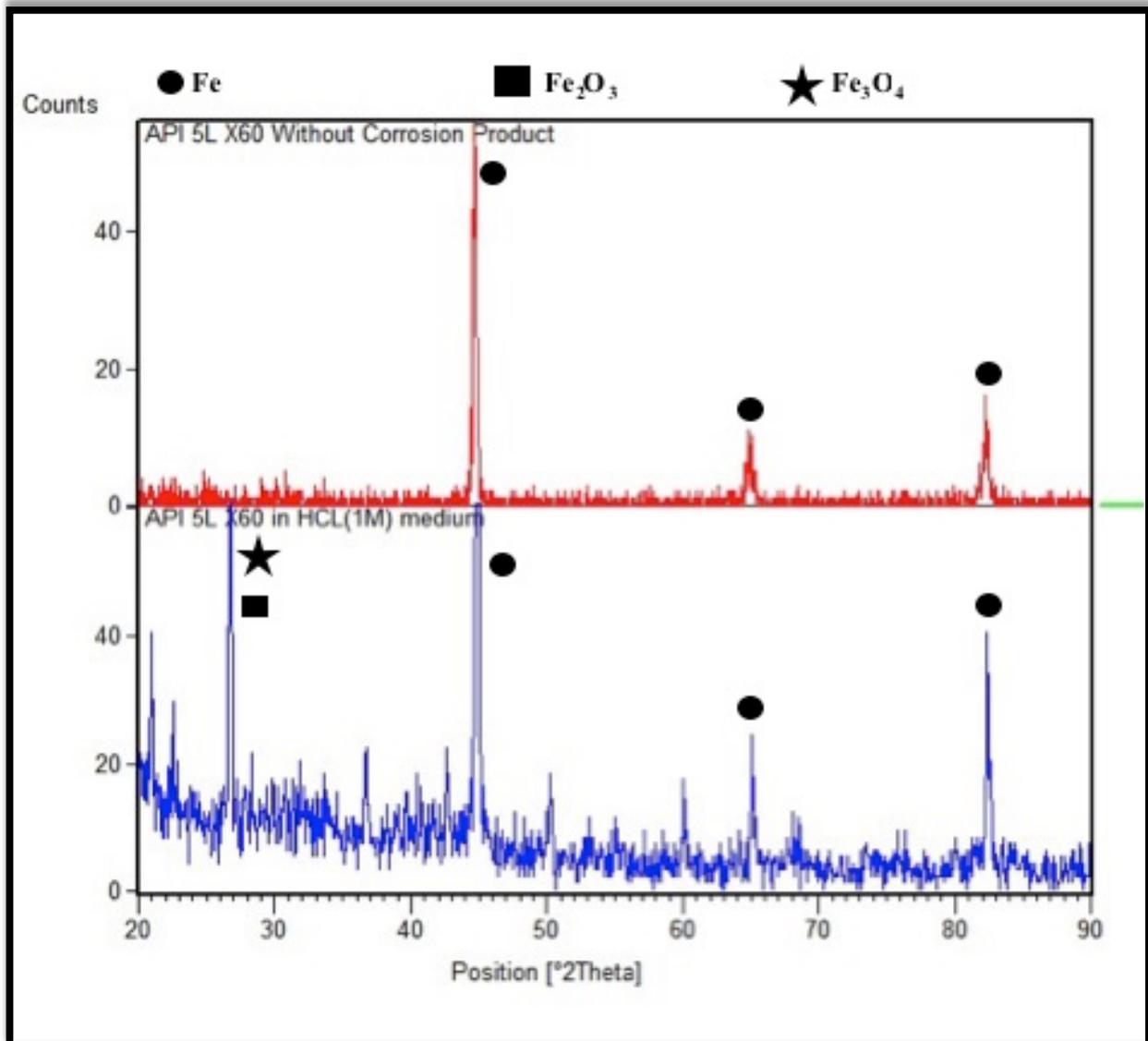


Figure III-2 : XRD of API 5L X60 without corrosion product, with corrosion product in HCl medium (648 h) in 2D view.

- ✓ The results show (figure III-2) that the corrosion products consist essentially of hematite (Fe_2O_3), magnetite (Fe_3O_4).

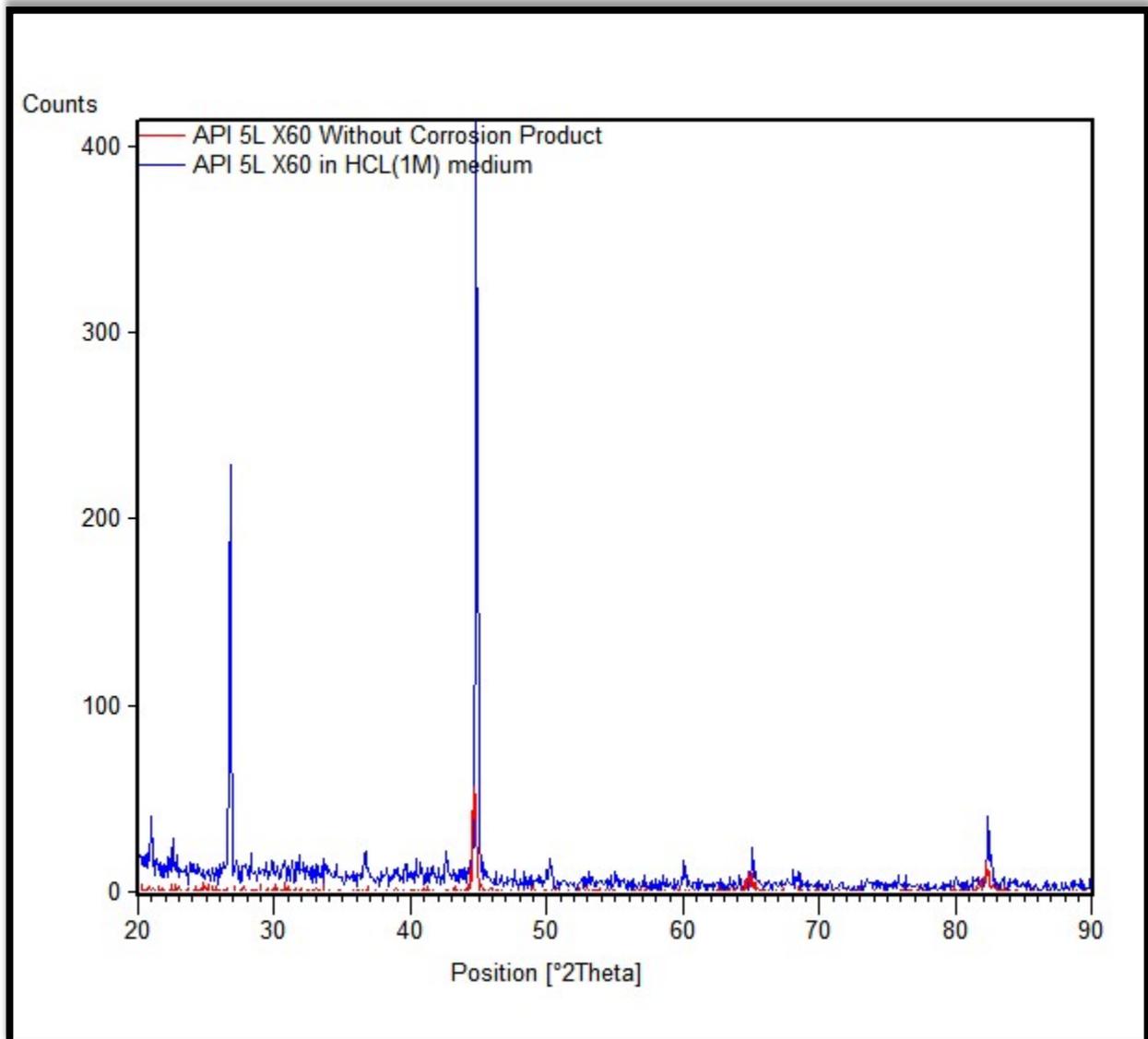


Figure III-3 : XRD of API 5L X60 without corrosion product, with corrosion product in HCl medium (648 h).

For carbon steel in relatively long duration (648 hours) in hydrochloric acid, the most intense peak is hematite and magnetite, which refers to a double layer of corrosion product where hematite is outer layer and the magnetite is the inner layer.

The surfaces of immersed samples were examined using an optical microscope which allowed to expose the light contrast. Figure III-4 shows the morphology of corrosion product in HCl.

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The red-brown color of the steel surface, Figure III-3 (b), it is the color of hematite.

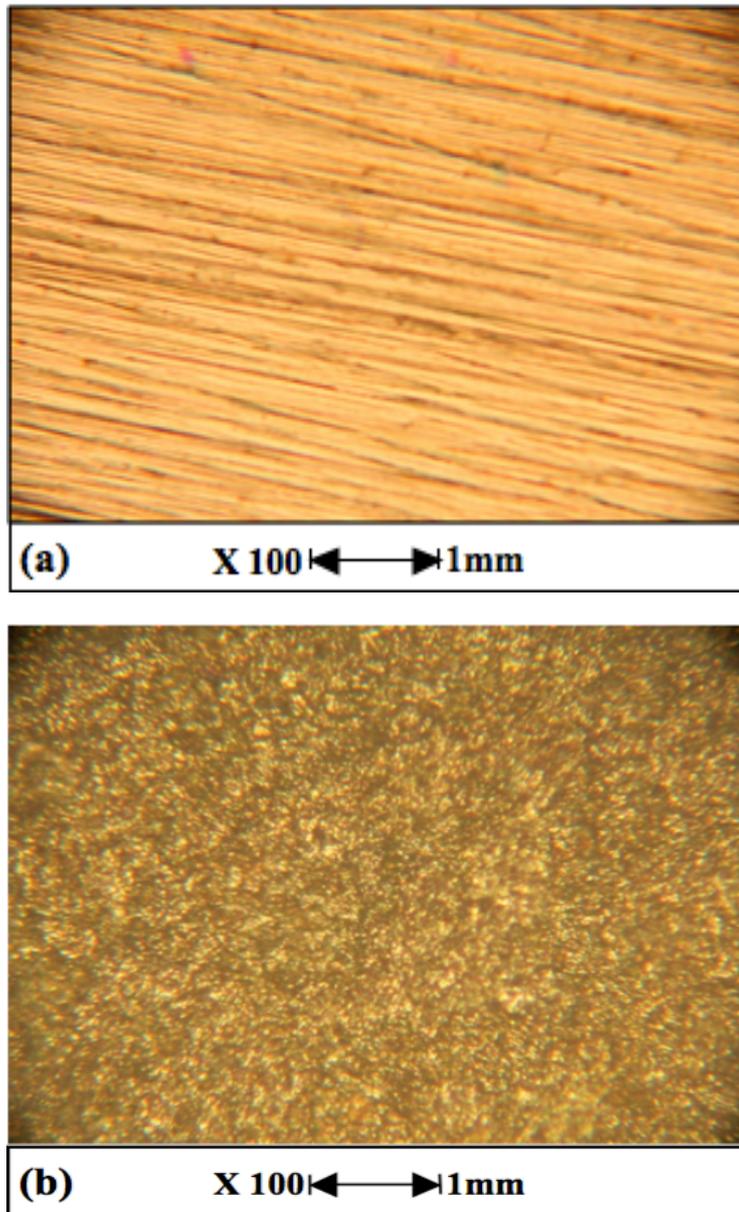


Figure III-4 : The steel corrosion product morphology API 5L X42 by the optical microscope (x100),
(a) the steel without corrosion product, (b) immersing the steel in HCl (116 hours).

We can see that in Figure III-4 (b) reflects the general corrosion of API 5L X42 steel in HCl.

Chapitre III : Results and Discussion

Bright areas, but remain less bright as Figure III-4 (a) represent the general corrosion, on the other side the dark areas are probably pitting.

To evaluate pitting corrosion of carbon steel after immersion tests, it was necessary to remove or reduce the corrosion product layer to reach the naked steel (Figure III-4 (a)). The corrosion products were removed by polishing the surface by a pipe maker 5000 degree for 60 seconds.

III.1.1.2. Electrochemical testing

III.1.1.2.1. Cyclic voltammetry

To determine potential field of general corrosion and pitting, a test of cyclic voltammetry has been realized (API 5L X42 /API 5L X60) in HCl.

Figure III-5 shows the cyclic voltammetry curve of our steel on HCl medium.

There are three areas:

- Zone I (cathodic area),
- Zone II (active dissolution area)
- Zone III (transpassive area).

It has been observed that there is no passivation area in HCl.

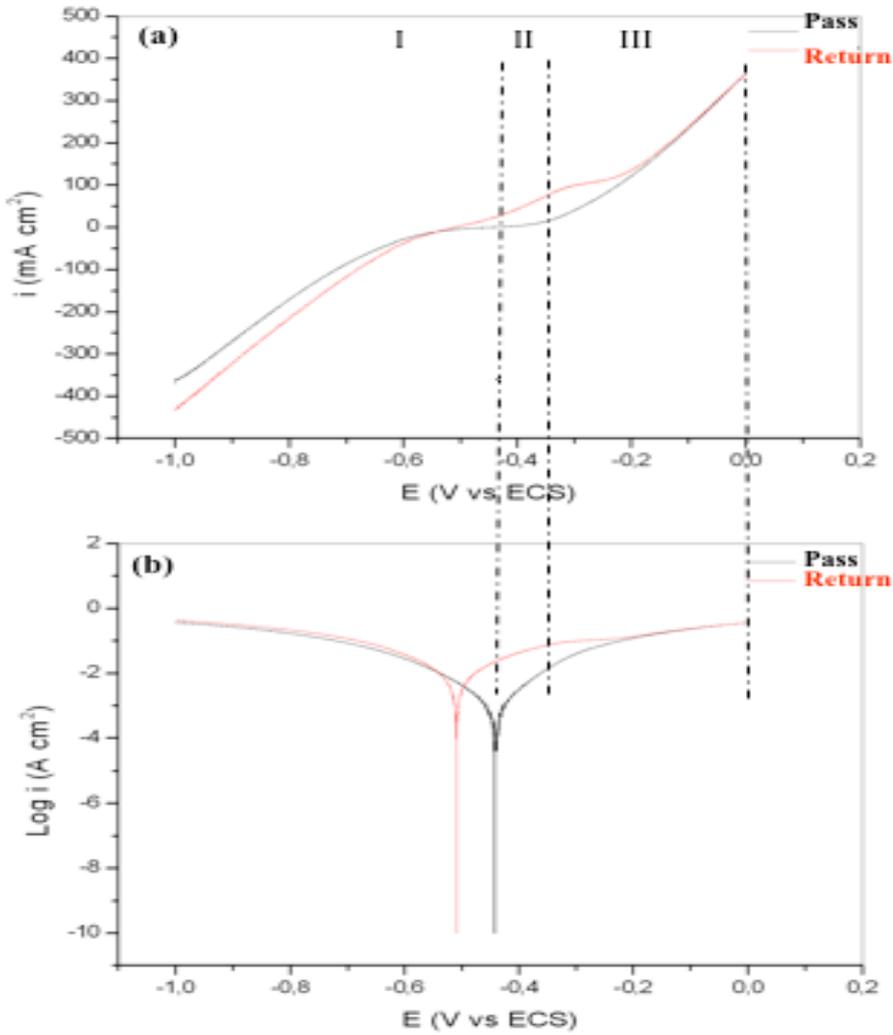


Figure III-5: Cyclic voltammetry of API 5L X42 in HCl medium, (a) Linear curve, (b) Logarithmic curve.

III.1.1.2.2. Polarization curves

The scanning speed used for the cyclic voltammetry method is almost fast (5 mv/s). To identify potential areas must carefully apply a slow scanning speed. A scan rate 0.3 mV/s is so suitable.

Figure III-6 is the linear and logarithmic polarization curve of API 5L X42 steel in HCl medium.

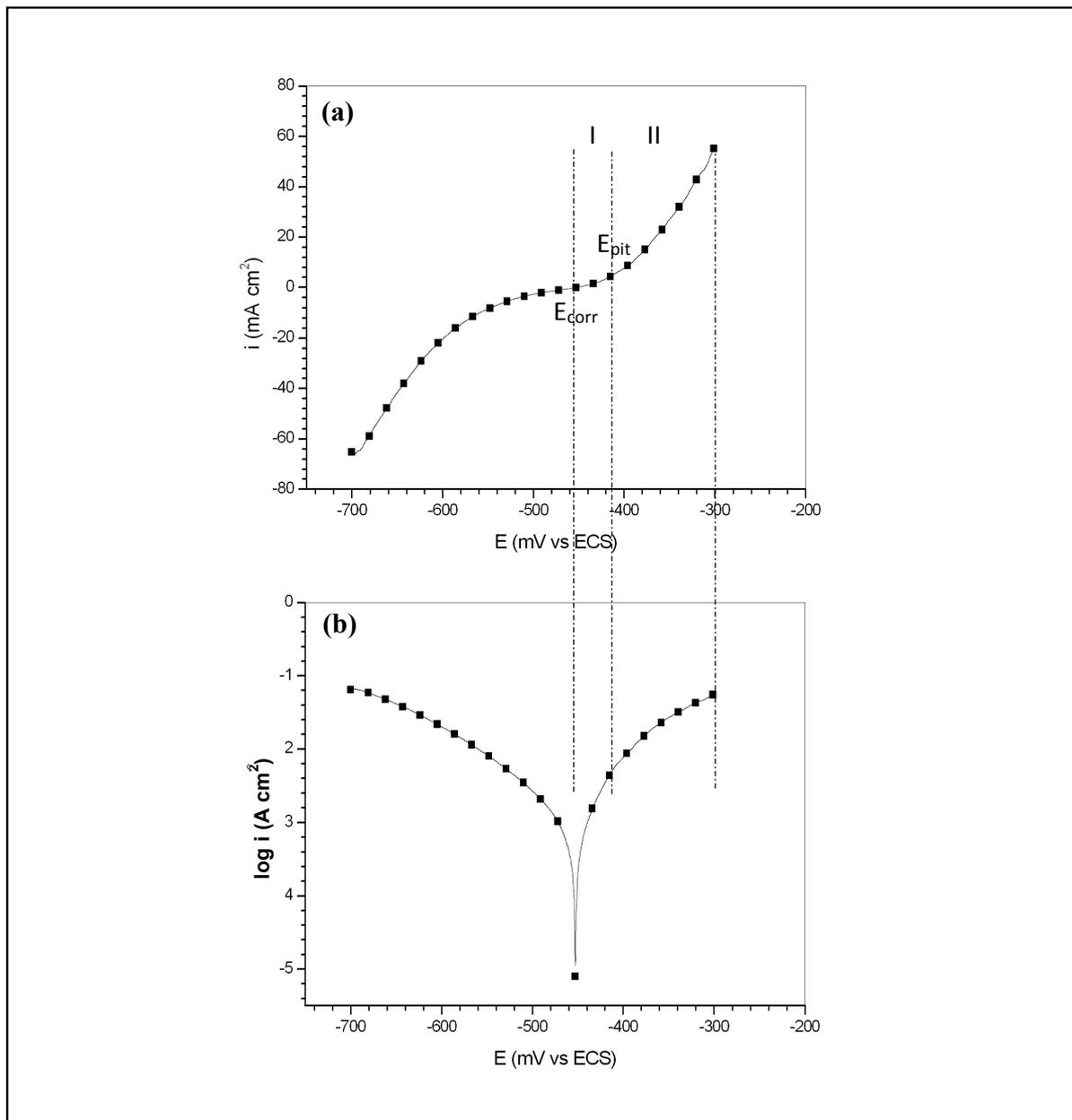


Figure III-6: Polarization curves of API 5L X42 in HCl medium at 35 °C, (a) linear curve, (b) logarithmic curve.

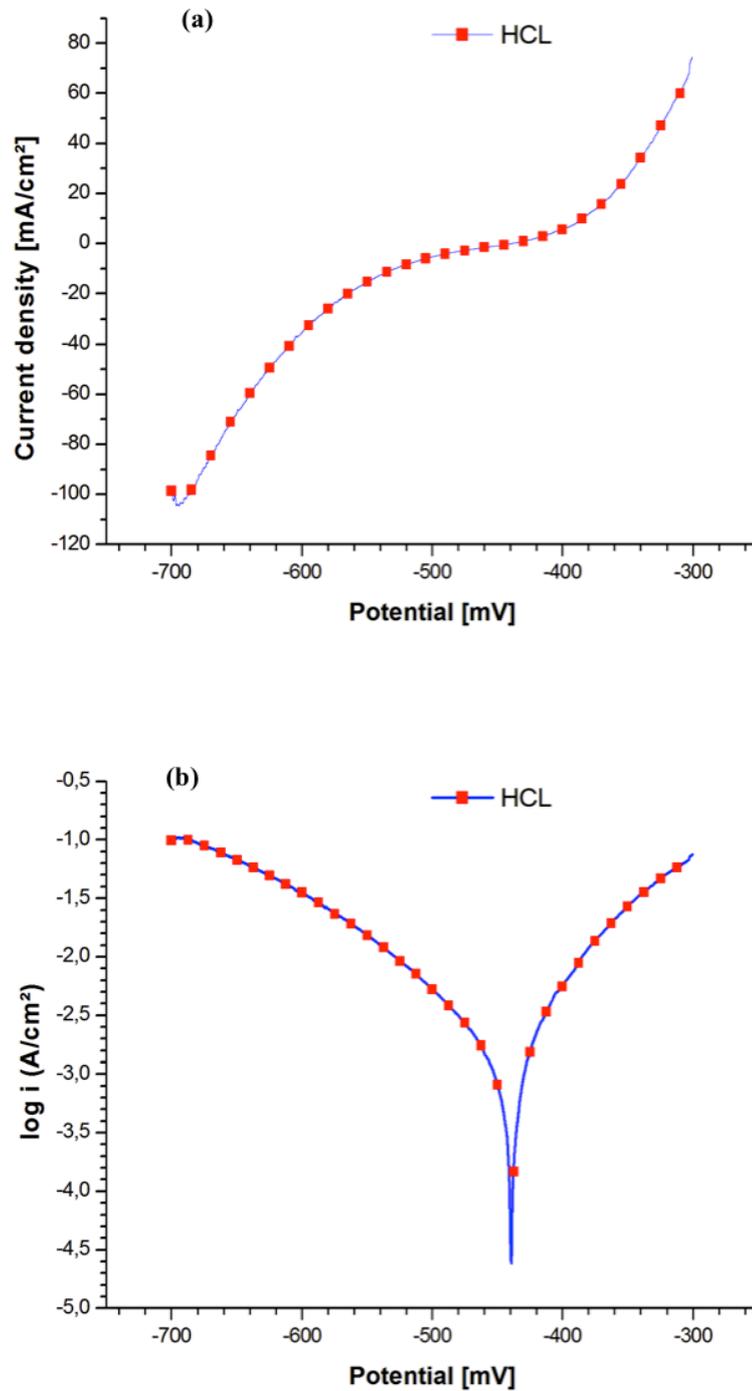


Figure III-7: Cyclic voltammetry of API 5L X60 in HCl medium at 45 °C, (a) Linear curve, (b) Logarithmic curve.

Chapitre III : Results and Discussion

Table III-3 the values of electrochemical parameters determined from the polarization curves previously obtained

Table III -3: The values of the electrochemical parameters of the API 5L X42 steel in HCl at 35 ° C.

Milieu	E_{corr} (mV)	E_{pit} (mV)	I_{corr} ($\mu\text{A cm}^{-2}$)	-bc (mV/dec)	ba (mV/dec)	R_p (Ω)
HCl	-453	-421	1293	98	79	14,7

- API 5L X42 steel in HCl

The anodic polarization curve of API 5L X42 steel therefore comprises two areas of potential:

- ✓ Active area (zone I): situated between E_{corr} et E_{pit} , in this area there is an active dissolution of the steel according to the equation Eq I-1. The electrons released by active dissolution are taken by the protons of medium to form hydrogen gas molecules according to the reaction Eq I-2. The corrosion kinetic is fully determined by the charge-transfer reactions.
- ✓ Zone II : this is the pitting corrosion zone, afterwards E_{pit} the current density increases rapidly. It was observed the absence of the passive layer because of the presence of anions Cl^- .

III.1.2. Influence of adding an oxidizing agent on the corrosion of API 5L X42

The ferric ion (Fe^{3+}) is one of the best known oxidizing agents in the petroleum industry. Even though an inhibitor is added, the total concentration of iron ions ($\text{Fe}^{3+} + \text{Fe}^{2+}$) should be monitored periodically (at least every 30 minutes) during acid cleaning. When the total concentration of iron ions reached or arrived to 2 -3%, the cleaning solution needs to be replaced [75]. We studied the influence of a concentration 2,54% Fe^{3+} in HCl on the corrosion of API 5L X42.

Chapitre III : Results and Discussion

Figure III-8 shows the influence of the oxidizing agent Fe^{3+} on the corrosion of API 5L X42 in 1M HCl medium at 35 °C.

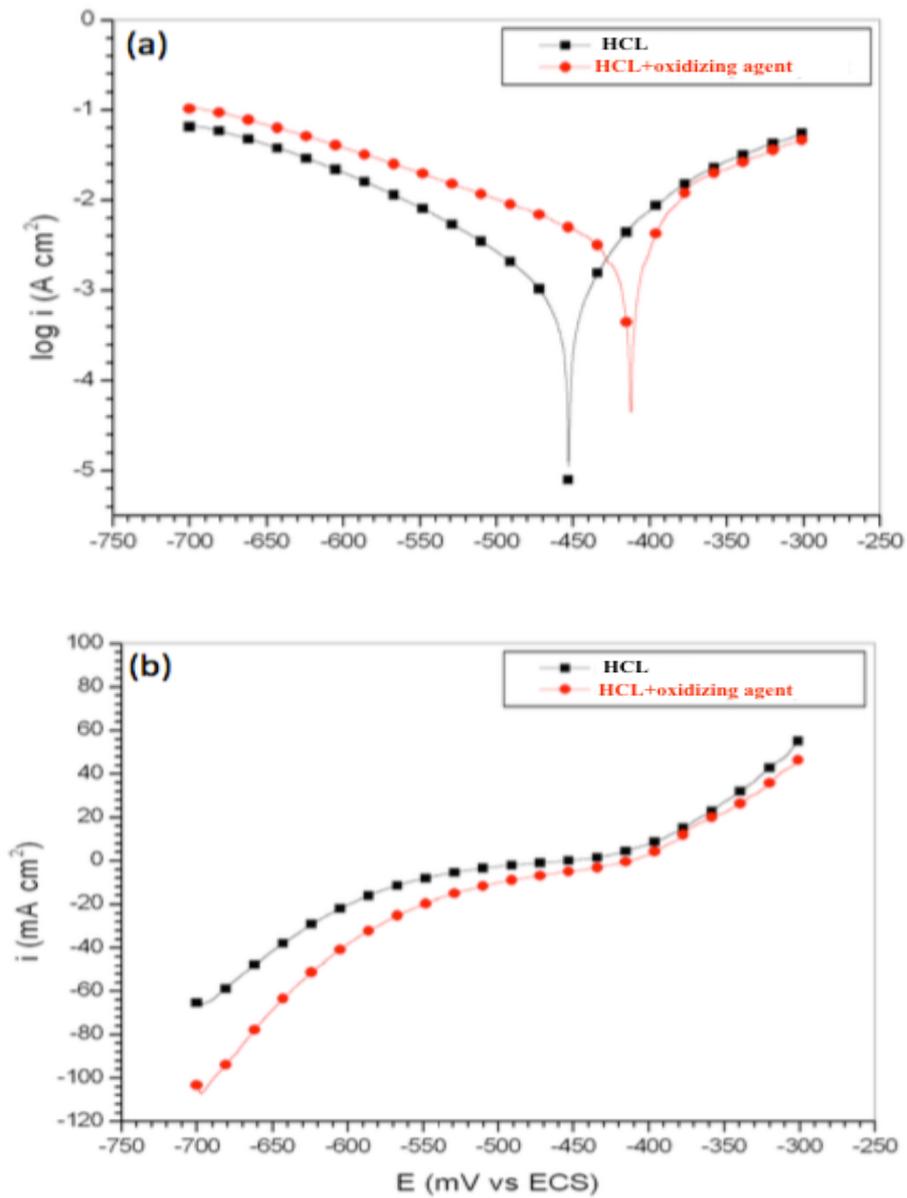


Figure III-8 : logarithmic polarization curves (a) ; linear (b) of API 5L X42 steel in 1M HCl medium without and with Fe^{3+} at 35 °C.

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The values of the electrochemical parameters are shown in Table III-4.

Table III-4 : electrochemical parameters of the polarization curves of API 5L X42 in 1M HCl medium with and without oxidizing agent Fe³⁺ at 35 ° C.

Medium	E _{corr} (mV)	I _{corr} (μAcm ⁻²)	-bc (mV/dec)	ba (mV/dec)	Rp (Ω m ²)
HCl	-453	1293	98	79	14,7
HCl+ 2,54% Fe ³⁺	-413	1924	152	59	09,6

The API 5L X42 corrosion potential in the absence of Fe³⁺ is about -453 mV/ECS. The corrosion potential increases slightly in the presence of the oxidizing agent from -453 to -413 mV/ECS. on the other side the corrosion rate increases greatly from 1293 to 1924 μA cm².

The anodic reaction with and without the oxidant Fe³⁺ is the same, in general active dissolution according to the reaction:



Against that, the cathodic reaction is not the same. In the absence of the oxidizing agent Fe³⁺, there is just a single reaction: the reduction of H⁺ according to the equation :



But in the presence of the oxidizing agent Fe³⁺, in addition to the above reaction, there is another cathodic reaction, it is the reduction of ferric ions Fe³⁺ ferrous ions Fe²⁺ according to the following equation:



Then, in the presence of ferric ion Fe³⁺, the kinetic of the cathodic reaction accelerates and there is a changing of the value of the cathodic Tafel coefficient | bc | of 98 -152 mV shows that acceleration. This increase in the kinetics of the cathodic reaction leads to an increase in the kinetics of the anode reaction and finally increasing the corrosion rate.

III.2. Part 2: Evaluation of Gum Arabic against corrosion

This part is devoted to the evaluation of a treatment against corrosion of API 5L X42 steel in HCl.

Concentrations of gum arabic were optimized to obtain an inhibitor that can ensure a low cost and a high quality of protection. Also, the mode of action has been studied. All the electrochemical experiments were carried out in aerated solutions.

III.2.1. Characterization of the inhibitory action of Gum Arabic

III.2.1.1. Explanation of GA inhibition

The interfacial activity of gum arabic is attributed to its amphiphilic character it means having both hydrophilic and hydrophobic parts. The polysaccharide fractions are very soluble in water, containing a hydroxyl functional group (-OH), and a carboxyl functional group (-COOH) [90] (figure I-24). The fraction rich on protein responsible for its hydrophobic behavior [93].

In acid solution, the carbonyl compound ($C = O$) can be protonated and the molecule exists in the form of polycation. However, in HCl solution, the load of the metal surface can be determined from the value of $E_{corr} - E_{q=0}$. $E_{q=0}$ it is the potential of zero charge [94].

$E_{q=0}$ of iron is equal to -530 mV/ECS in HCl [95]. In this study, the E_{corr} obtained in HCl medium equals -453 mV/ECS. So, the surface of API 5L X42 steel in HCl medium positively charged because $E_{corr} - E_{q=0} > 0$. Cl^- anion is specifically adsorbed to the surface of the carbon steel [96] which leads to charge the surface of the steel negatively. The formation of positively charged species facilitates the adsorption of the compound to the metal surface by the electrostatic interaction between the molecule of GA and the carbon steel surface (physisorption).

So it has a hydrophobic part (more voluminous) and a hydrophilic part, While the hydrophilic part may be drawn to the surface of the metal because it has a high proportion of hydroxyl and carboxyl functional groups, the hydrophobic part tends to soften and swell the coating to assist in the isolation of the metal surface.

To confirm that GA is an effective inhibitor, a test of immersion of (API 5L X42/ API 5L X60) steel samples in HCl medium, with and without inhibitor GA, have been realised (figure III-9), before the X-ray examination (figure III-10 and figure III-11).

It is clear that the percentage of brown red colour (hematite) in Figure III-9 (b), representing an immersion test in HCl medium with 4g/l of GA, is less than in Figure III-9 (a), representing an

Chapitre III : Results and Discussion

immersion test in HCl medium without GA. Therefore in the presence of GA, the corrosion products are not formed through the inhibition of carbon steel.

In HCl medium without GA, the most intense peak represents double layer of hematite and magnetite. In the presence of GA this peak disappeared completely which indicates that the corrosion product layer was not formed (Figure III-10). Figure III-12 shows the influence of GA on pitting corrosion of carbon steel API 5L X42 in HCl medium . It is clear that in the presence of GA, the bites disappeared. In HCl medium, after 264 hours, the surface of carbon steel in inhibited medium (4 g/L GA) remains almost intact.

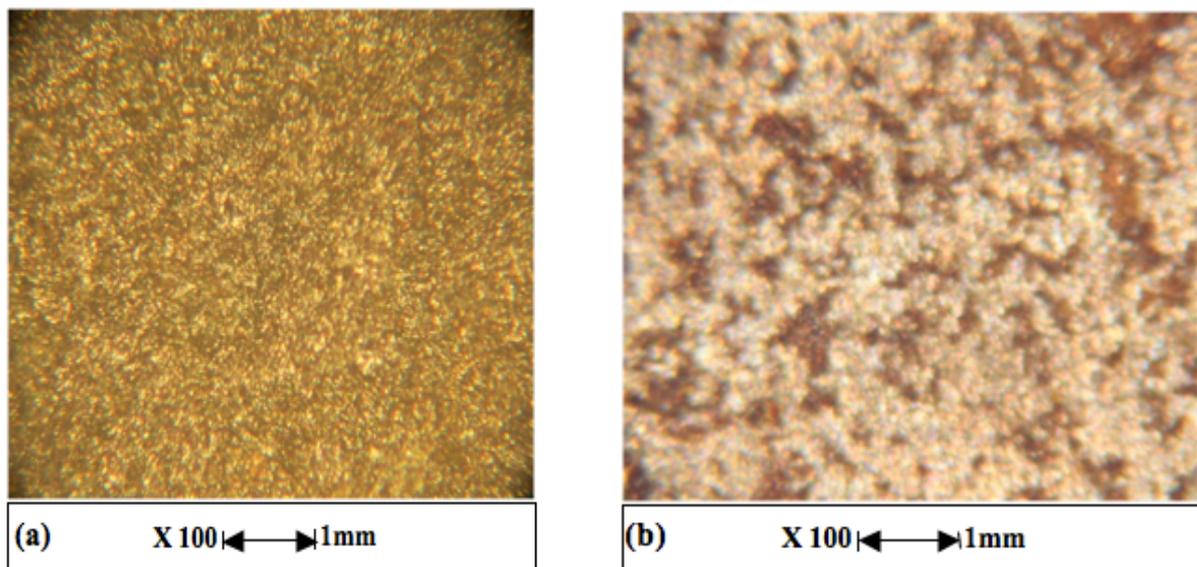


Figure III-9 : The morphology of API 5L X42 corrosion products by the optical microscope (x100), (a) immersing the carbon steel in HCl (116 hours) without GA, (B) immersing the carbon steel in HCl (116 hours) with 4g /L GA.

- ✓ The percentage of brown red colour (hematite) in Figure III-9 (b), representing an immersion test in HCl medium with 4g/l of GA, is less than in Figure III-9 (a), representing an immersion test in HCl medium without GA.

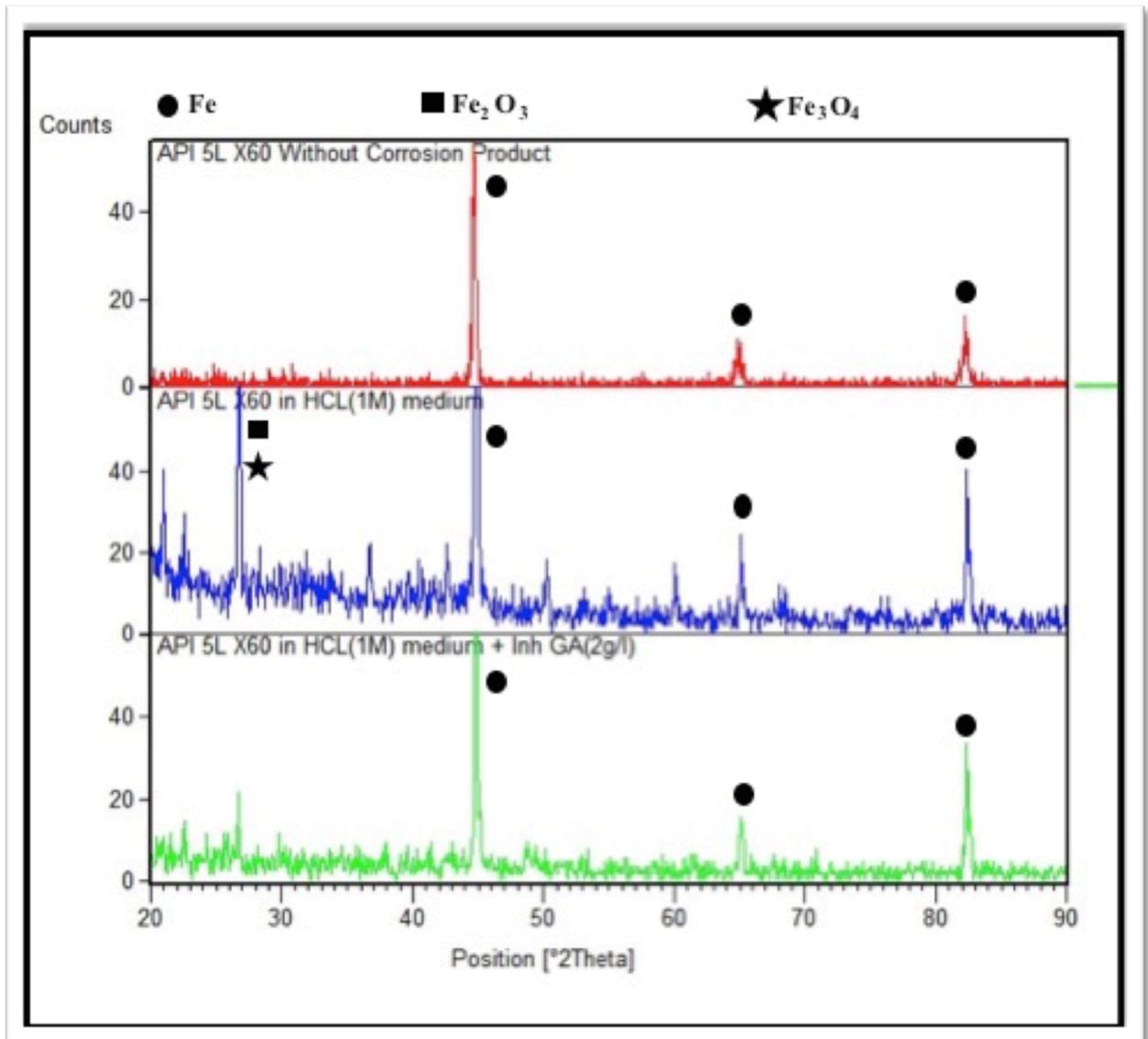


Figure III-10: XRD of API 5L X60 in HCl (648 h) without and with GA (2g/L).

- ✓ In HCl medium without GA, the most intense peak represents double layer of hematite and magnetite.
- ✓ In the presence of GA this peak disappeared completely which indicates that the corrosion product layer was not formed (Figure III-10).

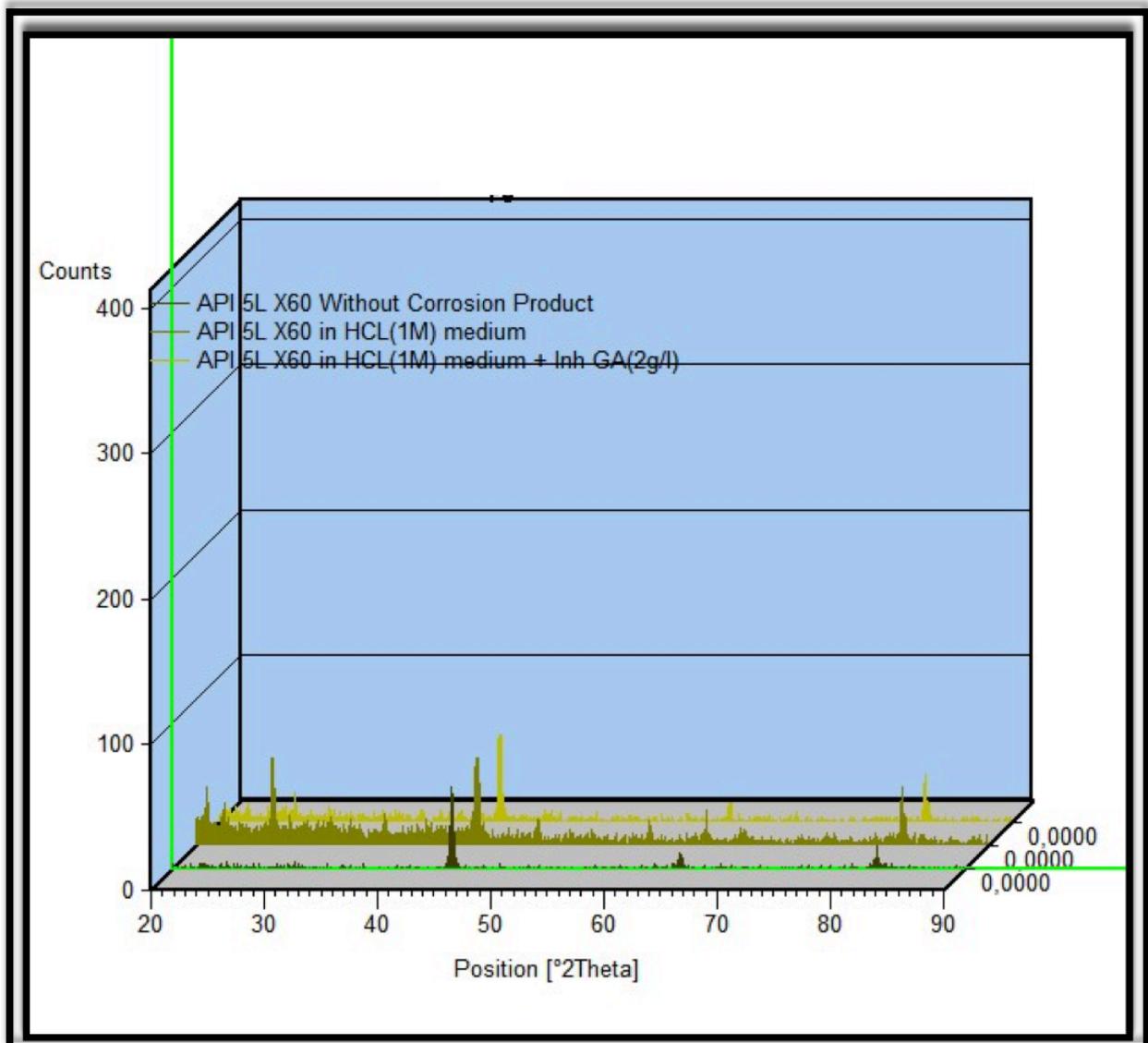


Figure III -11: XRD of API 5L X60 in HCL(648 h) without and with GA(2g/L) in 3D view.

- ✓ In HCL medium without GA, the most intense peak represents double layer of hematite and magnetite.
- ✓ In the presence of GA this peak disappeared completely which indicates that the corrosion product layer was not formed (Figure III-11).

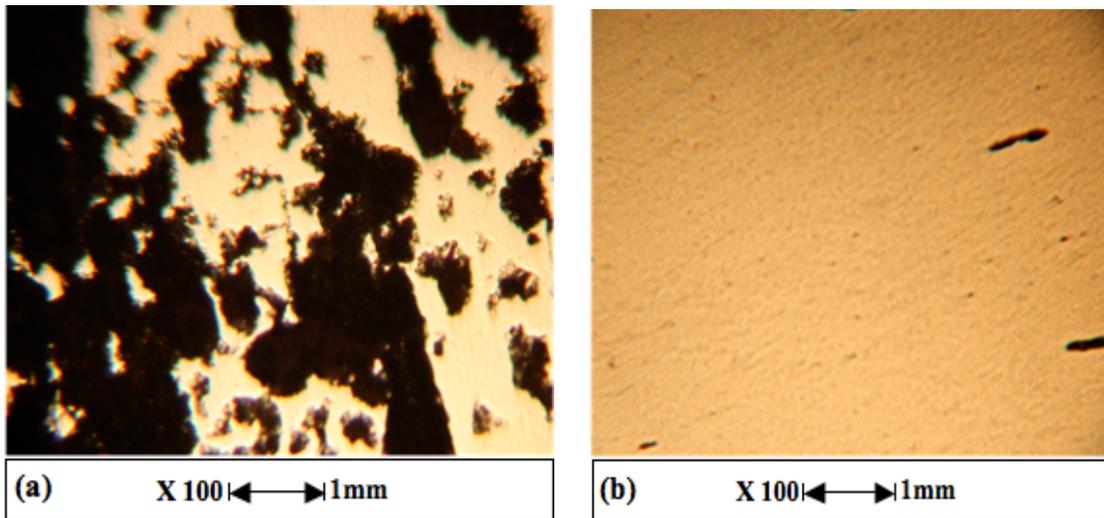


Figure III-12 : Photography by the optical microscope shows the effectiveness of GA after the immersion test. (a) HCl medium without GA (264 hours), (b) HCl medium with GA (264 hours).

- ✓ (Figure III-12) shows the influence of GA on pitting corrosion of carbon steel API 5L X42 in HCl medium . It is clear here that in the presence of GA, the bites fade.

Chapitre III : Results and Discussion

The efficacy of GA was evaluated by macroscopic photograph, for a long immersion test, 264 and 437 hours in the absence and in the presence of 4 g/L GA (Figure III-13)

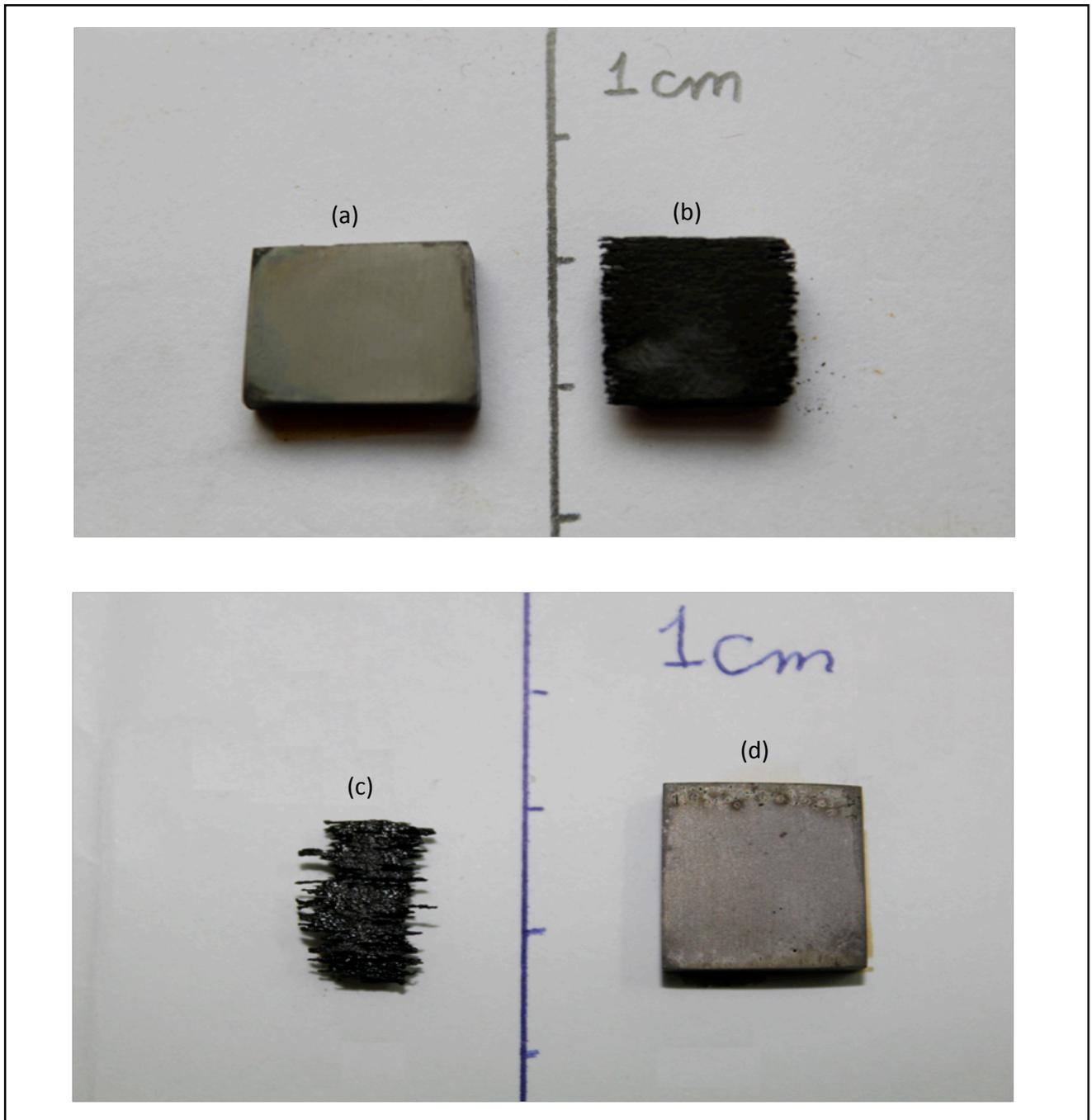


Figure III-13 : Microscopic morphology of API 5L X42 carbon steel after immersion test (264 hours) in HCl medium with 4g/L GA (a), without GA (b). After Immersion test (437 hours) in HCl medium without GA (c), with 4g/L GA (d).

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✓ The values of the electrochemical parameters of API 5L X60 are shown in Table III-5.

Table III-5: Electrochemical parameters of the polarization curves of API 5L X60 in 1M HCl medium in the absence and presence of various concentrations of GA at 45 ° C.

Inhibitor (GA) (mg.L⁻¹)	I_{corr} (μAcm⁻²)	-bc (mV/decade)	ba (mV/decade)	Rp (Ω m²)	(η_{pol}) (%)	(ηRp) (%)
Blank	2226,37721	108	81	9,039	None	None
0,1	1370,352152	101	63	12,31	31,2974107	26,571893
0,5	604,76614	94	57	25,51	69,6800566	64,566837
1	294,577859	95	52	49,6	85,2313424	81,068548
2	215,281956	98	71	83,15	89,2068416	89,129284
3	194,744248	100	63	86,29	90,2364994	89,524858
4	143,471363	104	51	103,7	92,8070649	91,283510
5	158,872852	109	68	114,6	92,0349114	92,112565

✓ These is here (Table III-5) a noticeable increase in Polarization resistance (Rp) from 9,039 to 114,6 (Ω m²) with the increase in GA concentration.

✓ These is here (Table III-5) a noticeable increase in inhibition efficiency (η_{Rp}) from 26,571893 to 92,112565 (%) with the increase in GA concentration.

✓ These is here (Table III-5) a noticeable increase in inhibition efficiency (η_{pol}) from 31,2974107 to 92,0349114(%) with the increase in GA concentration.

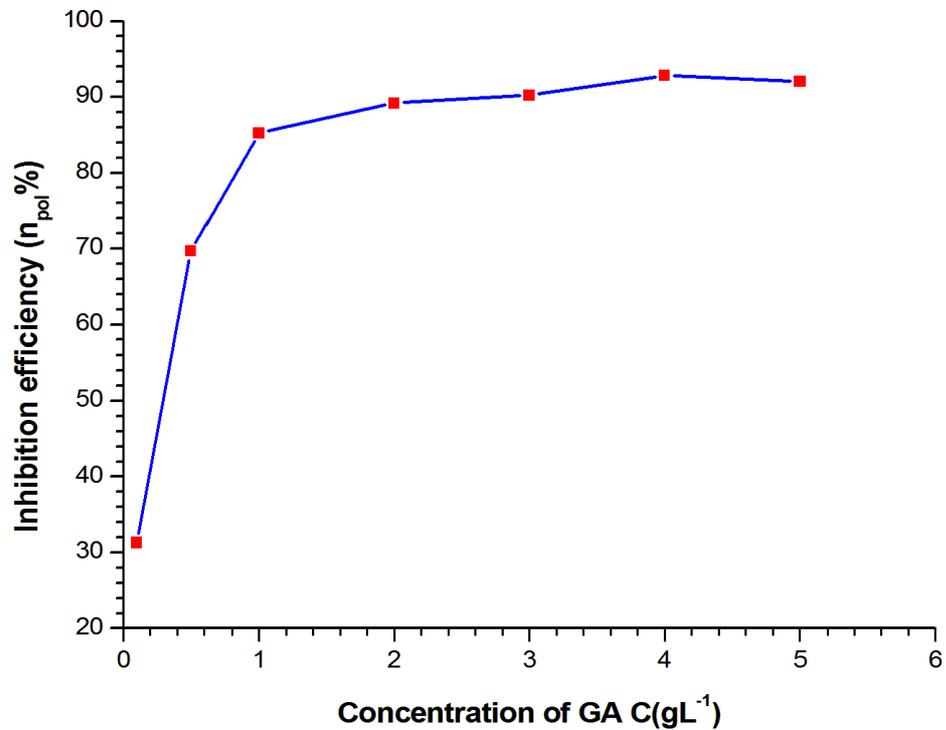


Figure III-14 : Relationship between inhibition efficiency (η_{pol}) and concentration of GA (g L^{-1}) in 1 M HCl at 45 °C (API 5L X60 pipeline).

Generally, an increase in inhibition efficiency with the increase in GA concentration due to the adsorption of the GA on the steel metal surface has been observed, the adsorption of GA on the carbon steel surface makes a barrier for mass and charge transfer. Consequently, the metal is protected from the aggressive anions of the acid. However, the presence of chloride ions from the hydrochloric acid in solution containing GA play a significant role in the adsorption process that results from increased surface coverage as a result of ion-pair interactions between the organic cations and the chloride ions.

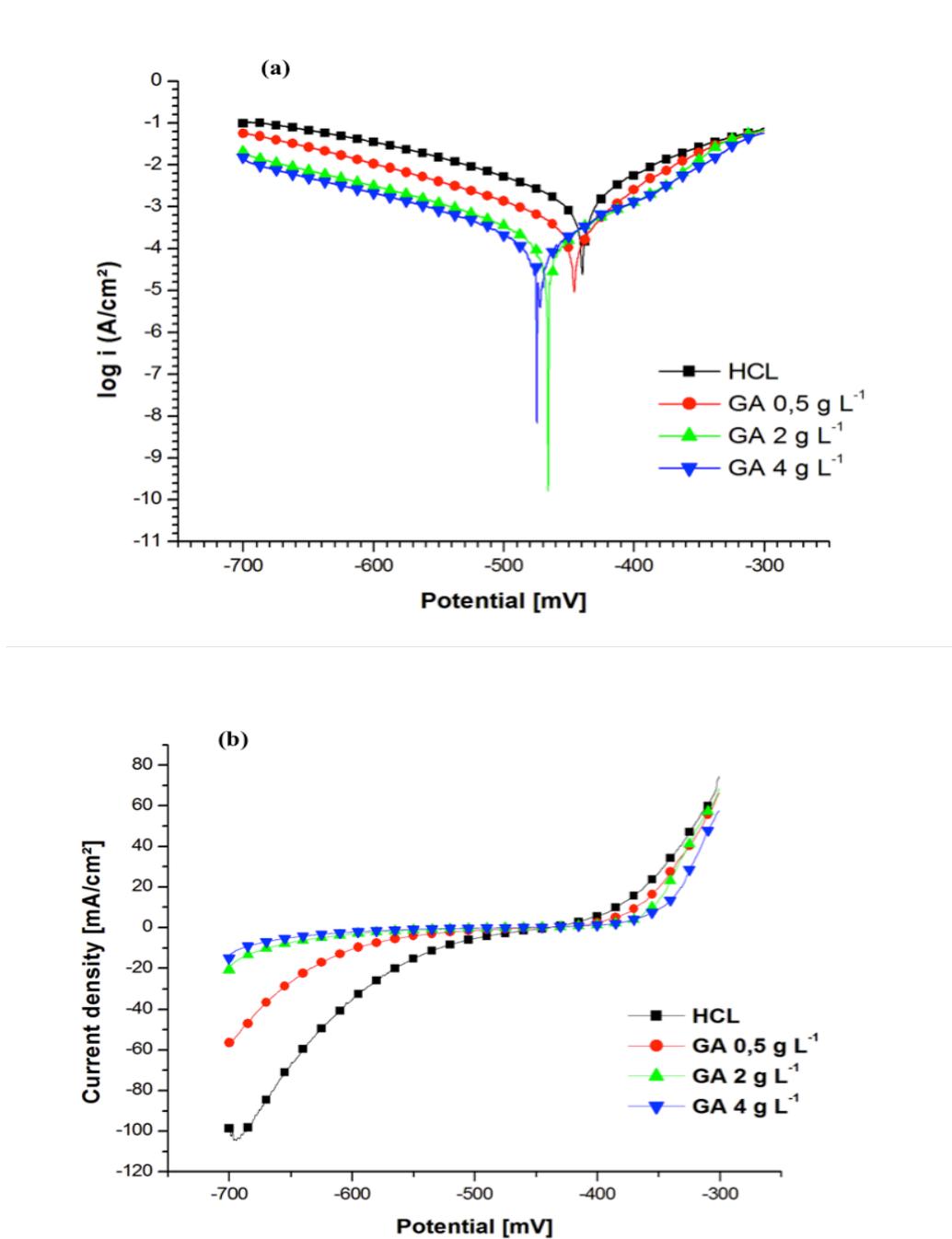


Figure III-15 : Potentiodynamic polarization curves for API 5L X60 pipeline steel in 1 M HCl without and with various concentrations of GA at 45 °C, (a) Logarithmic,(b) Linear curve curve. .

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This confirms the mixed mode (anodic and cathodic) inhibition action of the Gum Acacia. As shown in Table III-5 and Table III-6, it is obvious that the anodic Tafel constant (**ba**) is greater than the cathodic (**bc**) Tafel constant at all inhibitors' concentrations suggesting that the inhibitors' effect on the anodic polarization is more pronounced than that on cathodic polarization. Furthermore, inspection of Table III-5 and Table III-6 reveal that the inhibition efficiency (I%) increases with increasing the concentration of inhibitor. The obtained values of inhibition efficiency (I%) from polarization study were in good agreement with those obtained from the weight loss study with small variation.

✓ The values of the electrochemical parameters of API 5L X42 are shown in Table III-6.

Table III-6: Electrochemical parameters of the polarization curves of API 5L X42 in 1M HCl medium in the absence and presence of various concentrations of GA at 45 ° C.

Inhibitor (GA) (mg.L⁻¹)	E_{corr} (mV)	I_{corr} (μAcm⁻²)	-bc (mV/decade)	ba (mV/decade)	(η_{pol})
Blank	-503	501	116	89	None
0,4	-487	161	105	81	68
0,5	-491	89	113	69	82
1	-495	65	119	81	87
1,5	-487	43	115	78	91
2	-480	34	129	77	93

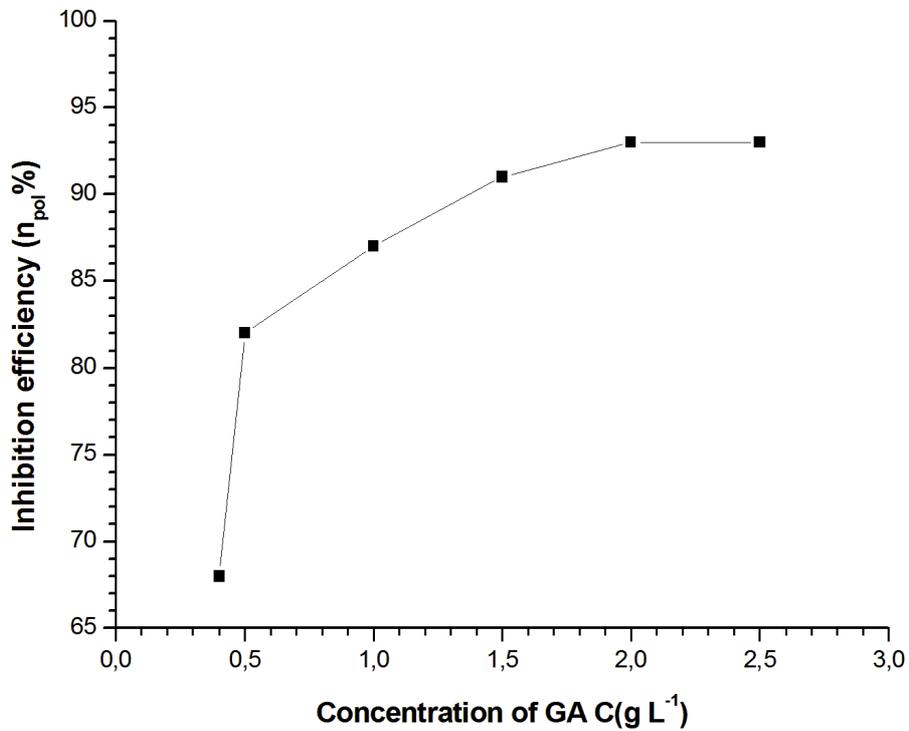


Figure III-16 : Relationship between inhibition efficiency (η_{pol}) and concentration of GA (g L^{-1}) in 1 M HCl at 25 °C(API 5L X42 pipeline) .

- ✓ The increase in inhibition efficiency (η_{pol}) is noticeably from 68 to 93 (%) with the increase in GA concentration.

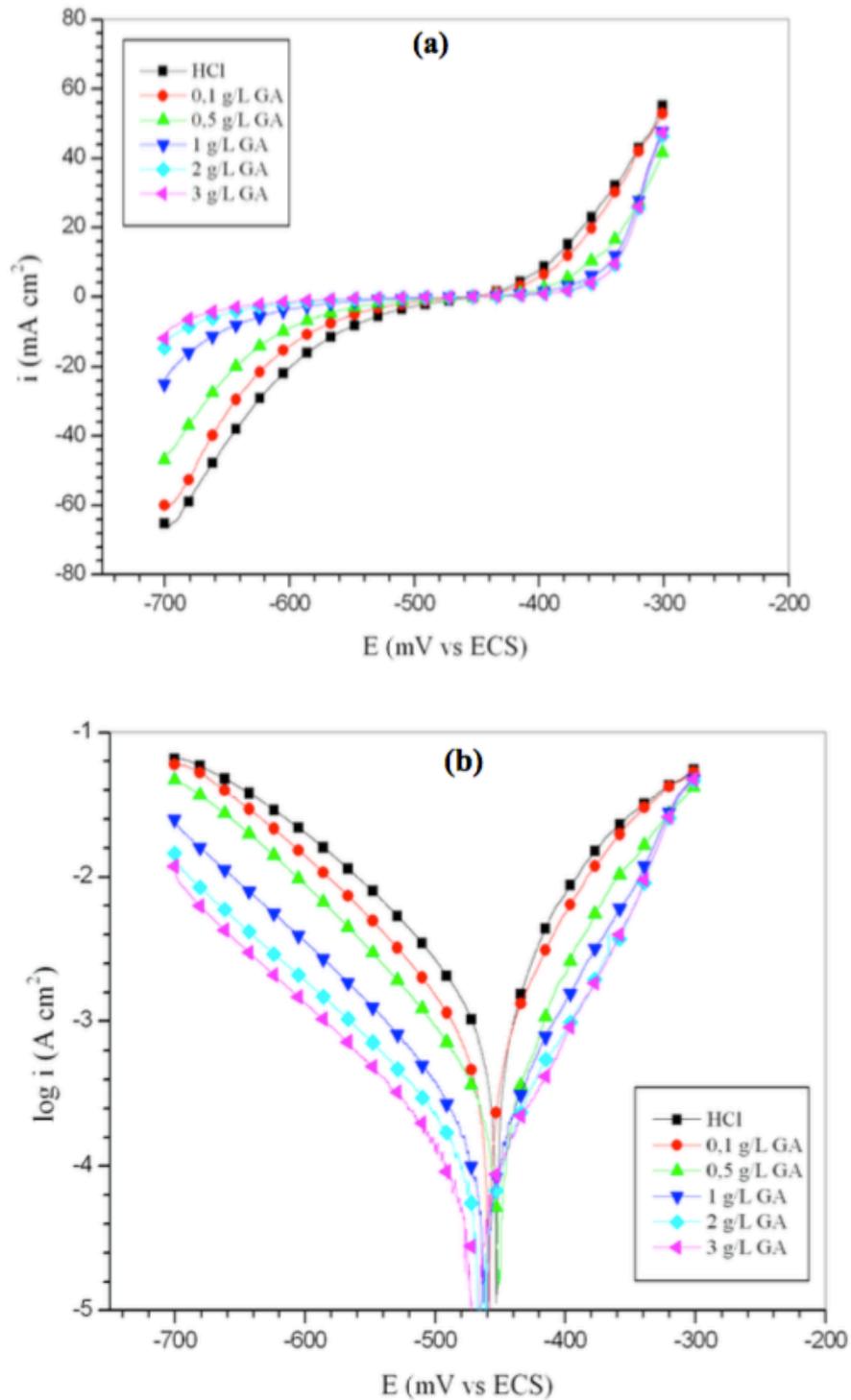


Figure III-17 : Potentiodynamic polarization curves for API 5L X42 pipeline steel in 1 M HCl without and with various concentrations of GA at 35 °C, (a) Linear curve,(b) Logarithmic .

Chapitre III : Results and Discussion

Tables III-5 and III-6 reveal that the inhibition efficiency (η_{pol}) increases with increasing the concentration of inhibitor (GA) (Figure III-14 and Figure III-16). The obtained values of inhibition efficiency (η_{pol}) from polarization study were in good agreement with those obtained from the weight loss study with small variation.

The results of both weight loss and polarization methods revealed that the Gum Arabic (GA) provide a very good protection to carbon steel against corrosion in hydrochloric acid. This can be attributed to the relative stability of the Gum Arabic (GA) film that formed on the surface of carbon steel due the synergistic effect as a result of ion pair interactions between the Gum Acacia and the chloride ions.

Conclusion and perspectives

The main purpose of this study was to evaluate the inhibitory properties of a natural compound proposed as a corrosion inhibitor which has no negative impact on the environment and human health. For this purpose the inhibitory efficacy of Gum Arabic was mainly determined by electrochemical measurements. This product was chosen because it is characterized by non-toxicity, biodegradability, cheap, readily available from renewable sources.

The first objective of this study was to understand the corrosion of carbon steel in hydrochloric acid medium then to evaluate the inhibitory properties of Gum Arabic. To do this, the effect of immersion time, the results of weight loss and oxidizing agent Fe^{3+} on the corrosion process in the absence of inhibitor were investigated by weight loss, measurements electrochemical measurements (polarization curves) and surface analysis.

The characterization of the carbon steel surface without inhibitor by the X-ray diffraction showed that there is a formation of corrosion products mainly consisting of hematite, magnetite. Examination by the optical microscope confirms the results obtained by the XRD, where the red brown color of the steel surface, in HCl, after a while or space of time, that is the color of the hematite.

Then, the inhibitory properties of Gum Arabic were studied using weight loss measurements, electrochemical measurements and surface analysis.

The characterization of the steel surface in media containing 2 g/L GA, by X-ray diffraction showed that no corrosion product has been trained on the (API 5L X60/API 5L X42) steel surface. The review by the optical microscope confirmed the results obtained by XRD and has mounted that the resistance to pitting corrosion of steel in the presence of 2 g/L GA, increased.

The results from weight loss and polarization methods proposed the potential applicability of Gum Arabic as a green corrosion inhibitor for carbon steel in acidic media.

The inhibition effect of Gum Arabic (GA) on the corrosion of (API 5L X60/API 5L X42) pipeline steel in 1M HCl solution was investigated for the first time by weight loss

Conclusion and Perspectives

measurements, potentiodynamic polarization curves, the results show that GA is a good inhibitor in 1M HCl. The maximum percentage inhibition efficiency was found to be 92% at 2 g/L . Polarization curves reveal that GA acts as a mixed-type inhibitor in hydrochloride acid.

- ✓ The following points can be concluded from this research:
1. The results from weight loss and polarization methods proposed the potential applicability of Gum Arabic as a green corrosion inhibitor for carbon steel in acidic media.
 2. Polarization measurements showed that the inhibitor (GA) is a mixed type inhibitor (anodic and cathodic).
 3. GA acts as a good inhibitor for the corrosion of carbon steel pipeline in 1 M HCl. Inhibition efficiency increases with the inhibitor concentration, and the maximum value is 92% at 2 g L⁻¹.
 4. Langmuir adsorption isotherm was found to give the best description of the adsorption behavior of the studied inhibitor.

In perspective, it would be better to study the influence of hydrodynamic conditions in the same operating conditions, It would also be desirable to achieve this study with other techniques such as photoelectron spectroscopy XPS (X-Ray Photoelectron Spectroscopy) and Raman spectroscopy to determine more accurately the formation of corrosion products and their interaction with Gum Arabic in order to improve its ability to protect against corrosion.

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Appendix