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Presented by:

- OMRANI Soufiane
- NESRAT Yasine
- REGHIOUA Ramadana

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Board of Examiners:

Dr. Boudooh Issam	**Chairman**
Dr. Chaibiya Al-Nasser	**Supervisor**
Dr. Ben Omar Mohamed Al-Arabi	**Examiner**

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شكـــر وامتنـــان

{ يرْفَعُ اللَّهِ الَّذِينَ آمَنُوا مِنْكُم وَالَّذِينَ أُوتُوا العِلْمَ دَرَجات }

الحمد لله الذي بعزته وجلاله تتم الصالحات يا رب لك الحمد كما ينبغي لجلال وجهك وعظيم سلطانك وصل اللهم وسلم وبارك على سيدنا وحبيبنا ومولانا محمد صلى الله عليه وسلم

بعد شكر لله تعالى على توفيقه لنا لإتمام هذا البحث المتواضع نتقدم بجزيل الشكر إلى من شرفنا بإشرافه على مذكرة بحثنا الأستاذ والدكتور**محمد العربي بن عمر** الذي نسأل المولى عزوجل أن يتقبل منه حجه ويعيده بصحة و عافية ولا ننسى من كان له الفضل علينا بعد المولى عزوجل في هذا العمل الدكتور **العانز الحفناوي** الذي لن تكفي الكلمات و العبارات لشكره و إيفائه حقه بصبره الكبير ولتوجيهاته العلمية التي لا تقدر بثمن والذي لم يبخل علينا بتقديم نصائحه وتوجيهاته و مد لنا يد العون في كل خطوة من خطوات هذا البحث.

كما أخص بالشكر المهندس **علي طليبية** مهندس مخبر VTRS على مجهوداته المبذولة في سبيل إتمام هذا العمل و على رقي أخلاقهم و حسن تعاملهم ولكل الفريق القائم على المخبر

كما نشكر كل الأساتذة الأفاضل الذين كانو معنا خلال مشوارنا الجامعي بقسم الهندسة طرائق.

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رمضان

Abstract:

Our experimental study aims to investigate the extent to which the studied extracts inhibit steel corrosion. We observed that at hour 0, the inhibition rates at various concentrations range from 20.79% to 99.39%. After 5 hours, the inhibition rates range from 98.76% to 99.53%, considering the values increase over time, specifically for the plant *Origanum majorana.*

For the plant *Cotula cinerea*, we noted that at hour 0, the inhibition rates vary from 95.3% to 98.34% at different extract concentrations. After 5 hours, the inhibition rates increase to a range of 99.15% to 99.66%. This is due to the natural composition and characteristics of each plant.

In conclusion, we found that some plants exhibit low inhibition rates while others show high rates. In our experiments, *Cotula cinerea* performed significantly better than *Origanum majorana* at hour 0. However, by hour 5, the inhibition rates of both plants become comparable.

Keywords: Impedance spectroscopy, Tafel, Corrosion, Electrochemical.

Résumé:

Notre étude expérimentale visait à explorer l'efficacité des extraits étudiés dans l'inhibition de la corrosion de l'acier. Nous avons observé que les taux d'inhibition au temps 0 heure variaient entre 20,79% et 99,39% à différentes concentrations d'extraits. Après 5 heures, ces taux ont augmenté pour varier entre 98,76% et 99,53%. Il semble y avoir une augmentation progressive des taux avec le temps, en particulier pour la plante Origanum majorana. Pour la plante Cotula cinerea, nous avons remarqué une variation des taux d'inhibition entre 95,3% et 98,34% au temps 0 heure à différentes concentrations, et après 5 heures, ces taux ont augmenté pour varier entre 99,15% et 99,66%. Cela est attribué à la composition naturelle et aux propriétés chimiques de chaque plante. En résumé, certaines plantes ont montré des taux d'inhibition bas tandis que d'autres ont montré des taux plus élevés. Initialement, la performance de la plante Cotula cinerea était nettement meilleure que celle de l'Origanum majorana, mais après 5 heures, les taux d'inhibition des deux plantes sont devenus similaires.

Mots-clés: Analyse spectroscopique, Tafel, Corrosion, Électrochimie

الملخص :

هدفت دراستنا التجريبية إلى استكشاف فعالية المستخلصات المدروسة في تثبيط تآكل الصلب. لوحظ أن نسب التثبيط في الزمن 0 ساعة تتراوح بين 20.79% و 99.39% عند مختلف تراكيز المستخلصات. وفي الزمن الفاصل بعد 5 ساعات، ازدادت هذه النسب لتتراوح بين 98.76% و 99.53%. يبدو أن هناك زيادة تدريجية في النسب مع مرور الوقت، وهذا ينطبق بشكل خاص على نبات *Origanum majorana*.

بالنسبة لنبات *Cotula cinerea* ، لاحظنا في الزمن 0 ساعة تبايناً في نسب التثبيط بين 95.3% و 98.34% عند مستويات التركيز المختلفة، وبعد 5 ساعات، ارتفعت هذه النسب لتتراوح بين 99.15% و 99.66%. يعزى ذلك إلى التركيب الطبيعي والخصائص الكيميائية لكل نبات.

باختصار، أظهرت بعض النباتات نسب تثبيط منخفضة في حين أظهرت أخرى نسبًا أعلى. في البداية، كان أداء نبات *Cotula cinerea* أفضل بشكل ملحوظ من *Origanum majorana*، إلا أنه في الزمن الفاصل بعد 5 ساعات، أصبحت نسب التثبيط لكلا النباتين متقاربة.

الكلمات المفتاحية : التحليل الطيفي ,Tafel ,التآكل, الكهروكيمياء.

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List of symbols

Symbols	Meaning	Units
Rtc	charge transfer resistance	Ωcm^2
Rs	solution resistance	Ωcm^2
Icorr	Corrosion current	mA/cm^2
βa	anodic Tafel slopes	mV/dec
βc	cathodic Tafel slopes	mV/dec
EI	inhibition efficiency	%
E_{corr}	corrosion potential	mV

General Introduction

General Introduction

The development and utilization of minerals in all fields contribute to the advancement and prosperity of the economy. In the present age, this is because we need them in transportation, construction, and even food production, among other areas [1].

Among these metals, iron is considered one of the most important and fundamental metals, especially when it is converted into steel. Steel, also known as iron alloy, is a metallic alloy primarily composed of iron and usually containing varying proportions of other elements (such as carbon, chromium, nickel, manganese, etc.). Industries and applications heavily rely on it due to its widespread availability, low cost, and strong durability [2,3].

However, this does not negate its being the most susceptible material to the phenomenon of corrosion, which is considered a natural, relentless phenomenon in which no material is exempt from damage or deterioration [1].

Due to corrosion, significant financial losses estimated in millions of dollars annually occur, as seen in the deterioration of industrial infrastructure such as petroleum and gas pipelines, tanks, and the wear and tear in sectors like transportation, military equipment, and household appliances. All of these contribute to the degradation of advanced industries, rendering them inoperable and unfit for use, in addition to the costs of maintenance, protection, and declining productivity. Approximately 20% of the steel produced by Americans is utilized to compensate for previously produced and damaged steel. Moreover, there are considerable human losses resulting from daily accidents and industrial incidents, as well as diseases and epidemics caused by the leakage of toxic substances from buried industrial waste into the ground, affecting plants, water bodies, and consequently humans, or the presence of rust in water sources derived from corroded pipelines and tanks, and the contamination of food sources, among other factors. All of these contribute to the destruction of living organisms and significant environmental damage if not prevented or mitigated in any way [4,5].

Understanding the cause of this problem and how to resolve it is crucial for us to effectively address and prevent it. Among the scientific solutions for protection against corrosion, we find: [4]

Inhibitors are one of the ways we contribute to protecting against the risk of corrosion and its damages. They vary in types, mechanisms of action, classification,

and degree of hazard. Some of them harm the environment over time due to their persistence and non-degradation, while others are environmentally friendly, such as plant extract inhibitors, which have proven their effectiveness in inhibition in many cases and are distinguished by their abundance in nature. [6]

At the end of our study, we conducted an experimental trial to determine the effect of plant extracts on inhibiting steel corrosion in acidic environments. This trial was divided into two parts:

Part One: Consists of two sections. The first section provides general information about corrosion, its types, and protection methods, while the second section introduces the studied plants and extraction methods.

Part Two: The experimental part, divided into two sections. The first section presents the experimental protocol for electrochemical experiments, the equipment used, and experimental conditions. The second section contains the essence of the obtained results along with their discussion.

Finally, the research findings obtained during the preparation of this memorandum are summarized.

PART I: Literature Review

CHAPTER 1: Generalities about corrosion and methods of protection against it

I.1.1. Introduction:

Corrosion can be defined as a physicochemical reaction between metal and its surrounding environment, resulting in changes in the properties of the metal and potentially leading to significant deterioration in the function of the metal, the surrounding environment, or the technical system to which they belong. In fact, in most industrialized countries, the total cost of corrosion is estimated to be between 2 and 4% of the gross domestic product (GDP). However, 20 to 25% of these losses from the total cost can be saved through a better understanding of the causes of corrosion and the application of improved protection techniques [7].

Steel is widely used in industrial structures, often in pump stations and water pipes that are prone to corrosion when in contact with natural water, especially in southern regions. Natural water contains sodium chloride and sodium sulphate, which unfortunately often create aggressive environments for steel. Its corrosion resistance depends significantly on numerous factors that interact not individually, but rather interdependently, to varying degrees of complexity, such as the environment and its chemical characteristics, temperature, applied pressures, and others [8].

I.1.2Definition of corrosion:

Corrosion is defined as the deterioration of a material (metal, non-metal, plastic, wood, etc.) due to a chemical or electrochemical reaction with the surrounding environment. It is also known as a natural automatic process in which metal is returned to its stable natural state (raw state) that it had in nature before extraction, and it is a non-reversible reaction. Some people mistakenly use the term "rust" instead of corrosion, as rust refers specifically to the material resulting from the corrosion of iron (iron oxide) only[9,1,3].

I.1.3The mechanism of corrosion:

Why does corrosion occur?

The reason behind corrosion is the lack of stability or steadfastness of the metal, and due to the influence of free energy, metals tend to revert to their original raw states prior to extraction. Corrosion occurs as a result of the reaction between the metal and the

surrounding environment, whether liquid or gaseous, leading to metal oxidation as follows:[2]

$$M \rightarrow M^{+n} + ne^{-}$$

M=Represents any metal

While the oxidant is returned according to its type and medium.


Figure .I.1: Pictures of materials subjected to corrosion phenomena

I.1.4.The Factors Affecting Corrosion:

The Table.I.1. of factors affecting corrosion.

The external factors	Internal Factors
Increasing the hydrogen ion concentration (pH) in the medium leads to an increase in the concentration of hydrogen ions, thus increasing the acidity of the medium, which affects the rate of corrosion. **Temperature**: An increase in temperature by 30°C causes a proportional increase in corrosion rate. **Soluble salts:** Increasing soluble salts in the medium increases the speed of electrical current transmission and thus increases the speed of corrosion [2].	**The nature of the alloy:** An alloy that is heterogeneous or composed of different metals is more prone to corrosion. **Thermal Processing:** Thermal treatments lead to undesired changes in the structure of metals, contributing to their corrosion rate [2].

I.1.5.Types of corrosion:

a. Chemical corrosion(dry):

It is a chemical reaction that occurs between the surface of a metal and a non-electric gaseous medium. For example, the oxidation of plain steel at high temperatures by atmospheric oxygen is a type of chemical corrosion [1,10].

b. Electrochemical corrosion:

Metals are generally not monophasic. When immersed in a reactant, they are most often subject to electrochemical corrosion [11], which is primarily caused by the oxidation of a metal in the form of ions or oxides and the reduction of corrosive agents present in the electrolyte solution [12,13]. Additionally, it involves electronic transfers between a metal and an electrolytic solution in contact with it (flow of electric current)[14]. This type of corrosion can be caused by heterogeneity either in the metal or in the reactant. The presence of heterogeneity determines the formation of an electric cell [15],consequently, an electric current flows between anodes and cathodes in the reactant, and the areas constituting the anodes are attacked (corroded). It requires the presence of a reducing agent; H2O, H2, etc. Without it, the corrosion of the metal (anodic reaction) cannot occur [12,13]. Therefore, electrochemical corrosion must simultaneously meet four factors in order to occur [16] :

- **An anode**: it is the part of the metal where the oxidation reaction occurs, leading to dissolution of this part as positive cations in the aqueous medium.
- **A cathode:** it is the part of the metal where the reduction reaction of a species contained in the electrolyte occurs (release of hydrogen by reduction of H+ ions, formation of water by reduction of oxygen in acidic medium, formation of OH- ions by reduction of oxygen in basic medium, deposition of a metal by reduction of its cations, etc.).
- **An electrical conductor:** capable of carrying the electrons released from the anode to the cathode. This role is fulfilled by the metal itself.
- **An ionic conductor:** capable of allowing the migration of cations released from the anode to the anions released at the cathode to ensure electrical neutrality and close the electrical circuit. This role is played by the electrolytic medium itself.

c. Biochemical (bacterial) corrosion:

It results from the action of bacteria or products resulting from bacterial activity such as organic acids or gases like CO2 and SO2, on the metallic material [14]. Currently, combating this form of corrosion is achieved through the injection of bactericidal products into corrosive environments [16].

I.1.6.Form of corrosion:

The process of metal corrosion takes on many forms, which are primarily classified according to the appearance manifested on the corroded surface [17,18]:

- Uniform corrosion
- Localized corrosion.

a. Uniform (generalized) corrosion:

Uniform corrosion, also known as general corrosion, refers to the relatively uniform loss of material over the entire surface [19]. It is characterized by the uniform dissolution of the metal surface in contact with the aggressive agent [20]. The extent of this corrosion can be quantified relatively easily through measurements of mass loss or thickness, and its progression on the structure can be monitored through periodic inspections. Equipment designers can manage it by providing facilities for material consumption due to corrosion. Therefore, this type of corrosion is generally considered relatively mild, although it can be highly costly [21].

Figure I.2: General corrosion (rust) of a piece of steel [22,23]

b. Localized corrosion:

Localized corrosion occurs on a portion of the metal at a much higher rate than the rest of the surface , it can take several forms [24,25]. In general, if the corrosion progresses at a uniform rate across the entire surface, it is referred to as uniform corrosion. However, if the corrosion rates progress non-uniformly, it is termed localized corrosion [26].

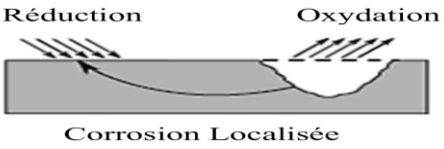


Figure I.3 Localization of one of the anodic or cathodic half-reactions generates localized corrosion [22].

The different forms of localized corrosion are:

- **Pitting corrosion:**

  Pitting corrosion is characterized by the formation, on the metal surface, of irregularly shaped cavities whose diameter and depth vary according to several parameters specific to the metal, the environment, and service conditions [27].

Figure I.3:Pitting corrosion [28].

Figure I.4:Types of punctures (a) deep cavity (b) cavernous cavity (c) hemispherical [29]

❖ **Selective corrosion:**

This form of corrosion is due to the oxidation of an alloy component, leading to the formation of a porous metallic structure [17] . This corrosion only occurs if the content of preferentially soluble elements (which oxidize) exceeds a certain threshold. The most well-known case of this form of corrosion is the phenomenon of dezincification in brass alloys [21].

Figure I.5: Selective corrosion of brass (Cu-Zn) [29]

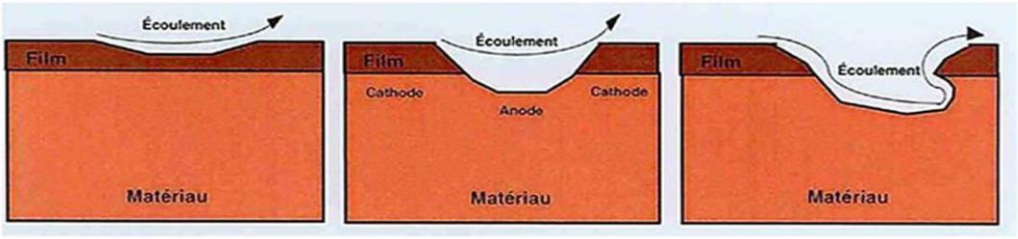
❖ **Cavernous corrosion:**

also known as crevice corrosion, is a form of differential aeration corrosion (difference in oxygen accessibility between two parts of a structure), thereby creating an electrochemical cell [30]. Selective attack of the metal occurs in the crevices and other areas with limited oxygen accessibility [31]. The primary recommendation to prevent cavernous corrosion is to optimize the design of the component to avoid any artificial crevices. An artificial crevice can be created by a poorly fixed joint, an unsmoothed or faulty weld, deposits, gaps between two plates, etc [32].

Figure I.6: Cavernous corrosion of an alloyed steel under a joint [30].

❖ **Erosion corrosion:**

Erosion corrosion affects many materials (aluminum, steel, etc.) [19]. It is due to the combined action of an electrochemical reaction and mechanical material removal [30].



1: Film erosion 2: Material corrosion 3: Progression of the attack

Figure I.7: Corrosion erosion of a copper tube conveying water [33].

❖ **Galvanic corrosion:**

also known as bimetallic corrosion, is one of the most common forms of corrosion in aqueous environments. It occurs due to the formation of an electrochemical cell between two materials, where one electrode (the anode) corrodes in favor of the other (the cathode), which remains intact. This selectivity of reactions arises from heterogeneity originating from either the material itself, the environment, or the physicochemical conditions at the interface [20,23,30].

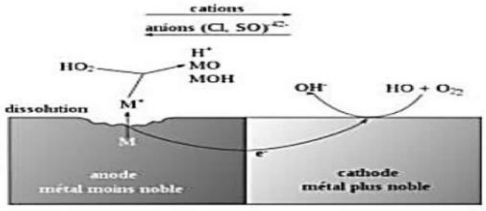


Figure I.8: Galvanic Corrosion [31]

❖ Stress Corrosion Cracking:

Stress corrosion cracking is a metal cracking phenomenon resulting from the combined action of mechanical stress and electrochemical reaction [19].This particularly dangerous phenomenon occurs due to the combined effects of three parameters:

- Temperature: Stress corrosion cracking rarely develops below 50°C.
- Applied or residual stresses experienced locally by the component;
- Corrosiveness of the environment: presence of Cl-, H2S, or caustic environments like NaOH, chlorinated environments, and even more pronounced in H2S environments [32].

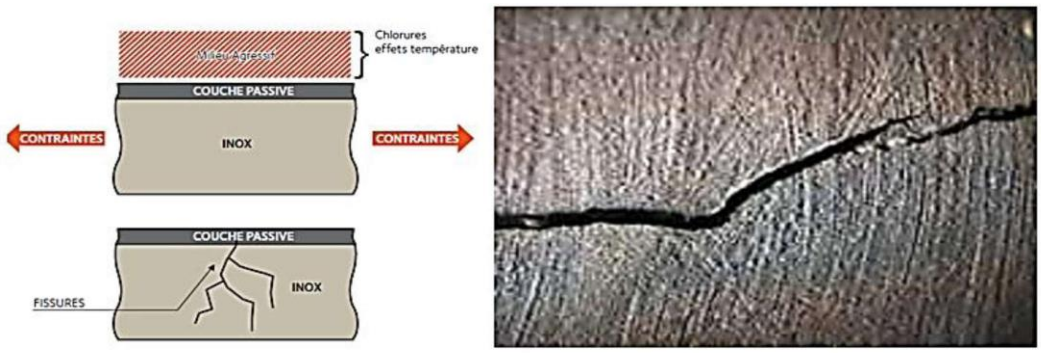


Figure I.9: Stress corrosion.

❖ Intergranular Corrosion:

This is a form of corrosion that spreads within the metal by consuming only the areas associated with grain boundaries. It can be related to the atomic structure and composition of grain boundaries in the absence of precipitation (precipitation-free intergranular corrosion) or to the decoration of grain boundaries by precipitation of a second phase (precipitation-related intergranular corrosion) [34].

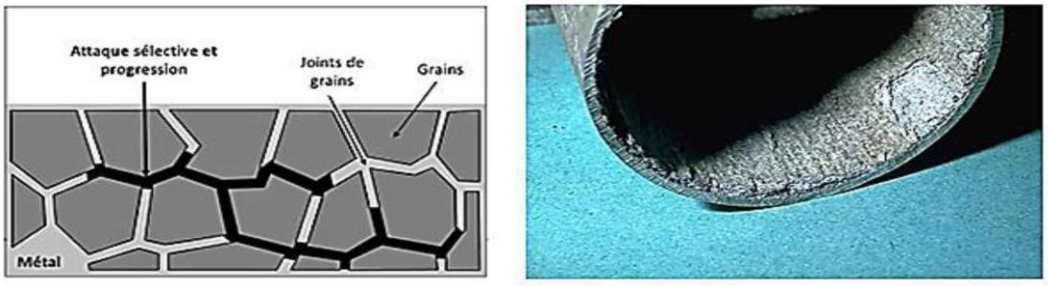


Figure I.10: Intergranular corrosion.

❖ **Filiform corrosion:**

It is the form of corrosion that occurs within certain coatings in the form of randomly distributed filiform filaments, as seen in paint, for example [35].

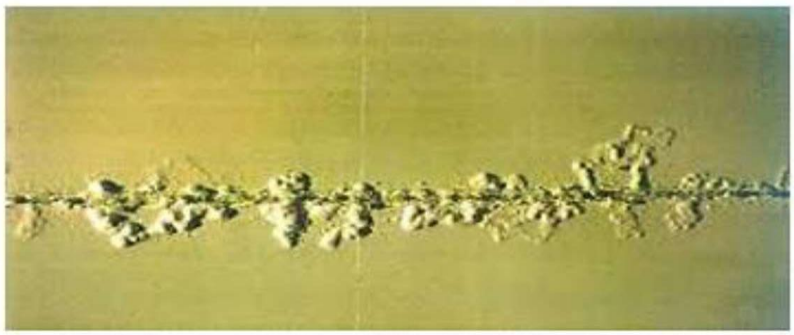


Figure I.11: Filiform corrosion

I.1.7.Corrosion Protection:

Scientifically, corrosion cannot be completely prevented, but the resistance of metals and alloys can be improved, extending their lifespan, through various methods and techniques, including [9]:

a. **Protection through appropriate design from stress**: Appropriate design must take into account all the stresses that occur throughout the machine's lifespan, including forming stresses, thermal stresses during manufacturing, vibration, as well as testing and operational stresses.

b. Protection through proper design in terms of shape and appearance.

c. Protection using coating: Coating is one type of corrosion protection and varies according to its types [4,36].

d. Cathodic protection: It is a continuous process of injecting the metal to be protected with negative electrons, so that it becomes cathodic, while its counterpart pole is simultaneously anodic [4].

e. Elevator Protection: It involves applying an external elevator current to the surface of the submerged metal in the conductive solution, to divert the corrosion current to the negative area [4,37].

f. Protection using corrosion inhibitors: Inhibitors are another type of corrosion protection, varying in classification and mechanism of action [9,4,38].

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CHAPTER 2:The studied plants and extraction methods.

I.2. Studied plants

I.2.1. *Cotula cinerea* plant:

I.2.1.1.Definition of the *Cotula cinerea* plant:

The plant *Cotula cinerea*, known as "Shihiya," emits a strong, pleasant odor reminiscent of a certain type of thyme scent. Shihiya is a herbaceous plant with light green coloration and an average height of up to 30 cm. Its entire structure is covered with dense, whitish hairs. The leaves are thick and divided at the upper part into two or three lobes. The branches terminate in compound flowers that resemble yellow disks. This plant grows in spring and blooms towards the end of the season.

The plant "Shihia" is found scattered in the wilderness and plateaus, but it thrives in highlands and semi-arid areas near agricultural regions, where it may form dense communities and proliferate abundantly. It is particularly widespread in the southern part of the globe in general and in the Arabian desert regions specifically. In Algeria, it grows in desert areas and semi-arid regions, especially in the southeastern part of the country,This plant contains many active compounds, including flavonoids, terpenes, and volatile oils, the latter of which give it its strong scent [39,40].

I.2.1.2.The botanical classification of *Cotula cinerea* :

The scientific name :*Cotula cinerea Del*

Common Name: Al-Sheehyah, Al-Rubeetah, Sheehat Al-Bal.

Classification Table.I.2. for *Cotula cinerea*

Species	***Cinerea***
Genus	***Cotula***
Family	**Asteraceae (Composites)**
Order	**Tubiflorales**
Class	**Dicotyledons**
Phylum	**Angiosperms**
Kingdom	**Plants**

I.2.1.3.The botanical description of *Cotula cinerea*:

Size and Shape: An herbaceous plant ranging from 10 to 40 cm in height, characterized by a strong distinctive odor. It is covered with fine, whitish hairs. The stems are erect or slightly creeping, cylindrical, yellowish-green, and the leaves are greenish-white, bearing dense woolly hairs. The appearance is thick and stout.

Tissues and Structure: *Cotula cinerea* plants consist of herbaceous tissues that depend on soil type and surrounding conditions.

Primary Root: *Cotula cinerea* is characterized by its superficial roots that assist in absorbing water and nutrients from sandy soil.

Flowers: *Cotula cinerea* flowers grow on long stems and typically consist of several small blooms. These flowers are characterized by their yellow color.

These characteristics may vary slightly depending on the surrounding conditions and the geographical location of plant growth .[41,42]

Figure I.12:A photographic image of *Cotula cinerea*.

I.2.1.4.The economic and medical uses of *Cotula cinerea*:

Cotula cinerea plant is used as a spice and added as a flavoring agent to tea and coffee in some countries. It is also used in folk medicine to treat abdominal pain, especially as an aid to digestion. Additionally, it is used against respiratory tract infections due to its pain-relieving properties for coughs. It has been observed that leaf extracts of *Cotula cinerea* exhibit antifungal activity. Flavonoid compounds extracted from this plant have analgesic, anti-inflammatory, and antiseptic effects. [43,44,45,46]

I.2.2Plant *Origanum Majorana*:

I.2.2.1.Definition of the *Origanum Majorana* plant:

The name *Origanum* originates from two Greek words, "oros" meaning mountains, and "gonos" meaning brightness or delight. Hence, it became known as the "delight of the mountains" for its beauty and abundance in mountainous regions around the Mediterranean basin [47].

Formerly known as Majorana hortensis Moench, it is characterized by significant morphological and chemical diversity and has forty-nine recognized subspecies[48]. Commonly known as oregano, its native habitat is Anatolia (Turkey) and Cyprus, and it is spread across parts of the Mediterranean region, especially Egypt [49].

Oregano was initially used as a disinfectant and a good home remedy for chest infections, coughs, and sore throats [50].

I.2.2.2.The botanical classification for *Origanum Majorana*:

The scientific name： *Origanum majorana*.

Common name: *Marjoram.*

Classification Table.I.3 for *Origanum Majorana*

Species	***Majorana***
Genus	***Origanum***
Family	**Lamiaceae**
Order	**Lamiales**
Class	**Magnoliopsida**
Phylum	**Magnoliophyta**
Kingdom	**Plants**

I.2.2.3.The botanical description of *Origanum Majorana*:

General Appearance: *Origanum Majorana* is a perennial herb with small green leaves and small white or pink flowers.

Smell and Taste: *Origanum Majorana* leaves have a strong aromatic scent and a distinctive floral flavor. This aroma and taste are the main features that distinguish it from other herbs.

Height: The plant can reach a height of about 30-60 centimeters.

Climate: *Origanum Majorana* prefers warm and moderate climates.

Soil: *Origanum Majorana* grows well in well-drained soil that is alkaline to neutral.

Cultivation: *Origanum Majorana* can be cultivated from seeds or cuttings, and it is preferable to grow it in sunny locations away from extreme cold.[51,52]

Figure I.13: Photograph of *Origanum majorana*

I.2.2.4.The economic and medical uses of *Origanum Majorana*:

Origanum Majorana is used in the production of essential oils and cosmetics due to its attractive aromatic scent. It's a good home remedy for chest infections, coughs, sore throats, and rheumatic pain. The leaves of Origanum Majorana contain a variety of nutrients including vitamins like vitamin K and vitamin A, minerals (such as iron and calcium), and compounds with antioxidant properties. Origanum Majorana is used in folk medicine to treat some diseases such as digestive disorders, muscle spasms, and insomnia.[53,54]

I.2.3.The methods of extraction:

It's possible to prepare extracts from various substances using several methods. The method varies depending on the type of substance you want to extract. Some of these methods include:

a. Organic Solvent Extraction: This method involves using an organic solvent such as ethanol or ether to extract active compounds from the original substance. The plant or organic material is ground and then submerged in the solvent for a period of time. Subsequently, the solvent saturated with the active compounds is separated, and then concentrated to obtain the extract.

b. Water extraction: This type of extraction is used in the preparation of herbal extracts. The plant materials are boiled in water for a specific period of time. Afterward, the mixture is filtered to separate the solid and liquid materials, and the water extract is concentrated to obtain the final extract.

c. Compression extraction: This method is used to extract oil-based materials such as plant oils. The plant material is subjected to high pressure and high temperature. The oil-based materials that evaporate under those conditions are collected and concentrated.

d. Distillation Extraction: Distillation is considered one of the oldest methods of extraction. This method is used to extract organic substances that vaporize easily. The original materials are heated to vaporize the active substances, which are then condensed to obtain the extract.

I.2.3.1. Preparation of Extract:

Extraction method	Collecting samples
A extract was prepared as follows: 10 grams of the plant were soaked in 150 milliliters of distilled water for 24 hours, then filtered and the solution retained. Afterwards, an equal amount of distilled water was added to the previously used plant, and this process was repeated for 3 days to obtain the resulting solution (extract + water). Following that, a drying process was conducted using a rotary evaporator to obtain the final extract.	We first collected the plants to be studied, which are: •*Cotula cinerea*, commonly known as "Shiheya" in Arabic. •*Origanum majorana*, commonly known as "Marqa'oush" in Arabic. These plants were collected from a semi-desert forest area in southeastern Algeria, specifically from the El Oued province.

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PART II: Results and Discussions

CHAPTER 1: Experimental

II.1.1. Introduction:

All experiments in this work were carried out at the laboratory level of valorization and technology of Saharan resources at the Faculty of Science and Technology of the University of Echahhid Hamma Lakhdar-El-Oued. Electrochemical impedance spectra were obtained using a three-electrode setup at 25

II.1.2. Electrochemical installation and equipment :

Figure II.1 shows the setup used for measuring electrochemical impedance spectra. In this setup, a potentiostat is connected on one side to an electrochemical cell with a capacity of 15 ml. The cell consists of three electrodes: a working electrode, a reference electrode, and an auxiliary electrode, as well as two ports for introducing certain parameters. The entire setup is connected to a microcomputer equipped with voltamaster4 software

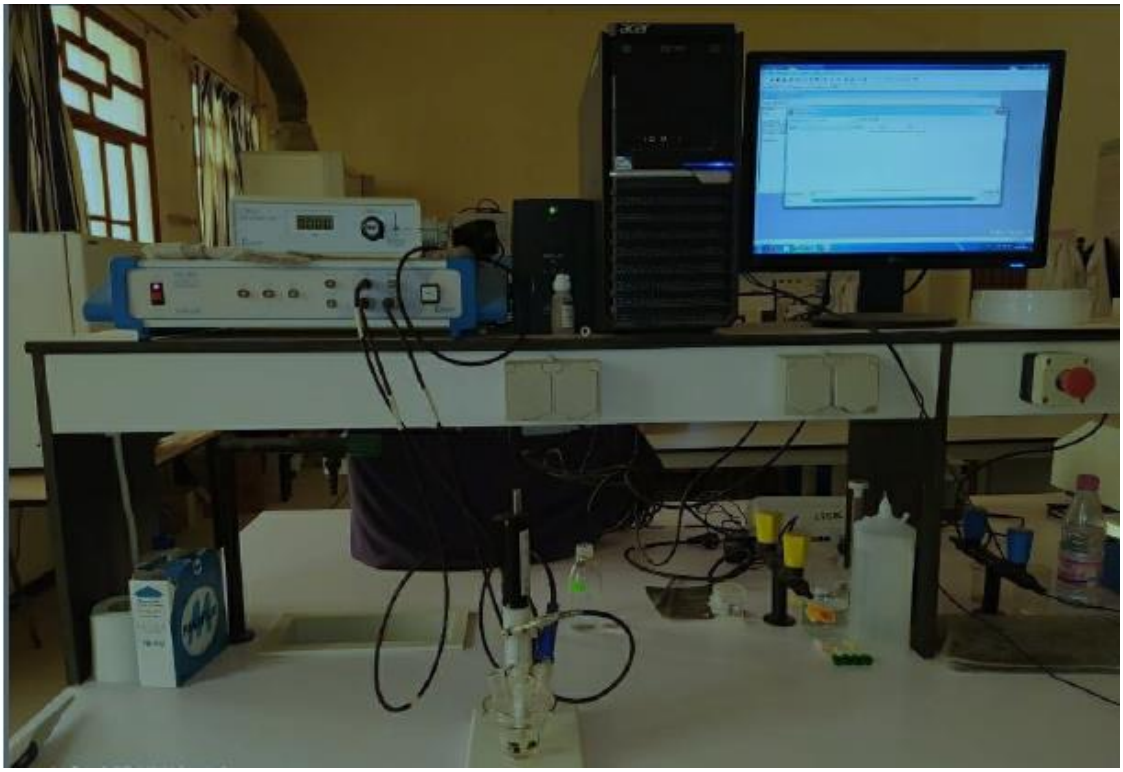


Figure.II.1 Experimental setup used for measuring electrochemical impedance spectra

II.1.3. The electrochemical cell:

It is a 15ml glass cell for electrolysis containing a lid with five holes for inserting the working electrode, a reference electrode, and an auxiliary electrode, and two holes for inserting suffixes such as thermometers (Figure II.2).

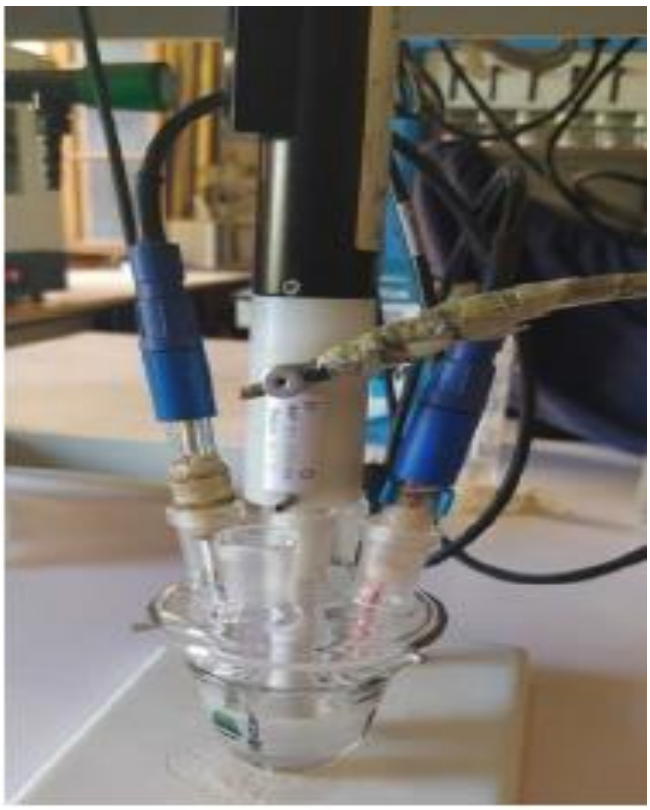


Figure II.2: The electrochemical cell

II.1.3.1.Reference electrode:

It is a saturated calomel reference electrode in potassium chloride solution, consisting of the Hg2/HgCl2 KCl system. This reference electrode, noted ECS, is non-polarizable, its potential is rigorously constant, and it is located at 0.241 V compared to the normal hydrogen electrode, which is assigned a potential of 0 V.

Figure II.3: Reference electrode

II.1.3.2.Auxiliary electrode:

The auxiliary electrode is used to allow current to flow in the electrochemical cell without damaging the reference electrode and to minimize the effects of ohmic drop. This third electrode, usually made of platinum, is introduced for this purpose.

This results in reducing the distortion of voltammperograms and closing the electrolysis circuit. However, it is necessary to limit the ohmic drop to a reasonable value. Hence, it is necessary to add, in addition to the counter electrode, a supporting electrolyte to the solution to be analyzed.

Figure II.4: Auxiliary electrode

II.1.3.3. Working electrode:

The working electrode used consists of a cylindrical part with a length of 1 cm and a diameter of 0.3 cm, with an active surface area of 0.07065 cm^2. The material studied is carbon steel XC52. Its chemical composition according to the laboratory of the Ghardaïa conduit, where it was analyzed, is given in the table:

Figure II.4: Auxiliary electrode

Table II.1: Chemical composition of carbon steel XC52

The chemical composition	Percentage (%)
C	0.1038
Si	0.1261
Mn	0.971
P	<0.0021
S	0.0021
Cr	<0.0010
Mo	<0.005
Ni	<0.005
Ai	0.0320
Co	0.05
Cu	<0.010
Nb	0.0419
Ti	0.0025
V	<0.005
W	<0. 05
Sn	<0.005
Fe	<98. 7

II.1.4.Experimental conditions:

II.1.4.1.Preparation of sulfuric acid solution:

For the study and characterization of the effectiveness of the inhibitor selected in our study on protecting steel from corrosion in a solution containing hyaluronic acid.

We added 1 ml of hyaluronic acid at a concentration of 11 ml and then added 11 ml of distilled water.Thus, we obtained a 12 ml solution of hyaluronic acid with a concentration of 1 M

II.1.4.2.Inhibitor preparation:

a. *Origanum majorana*

To prepare *Origanum majorana* extract, we measured 10 grams of the plant and added 150 ml of distilled water to cover the quantity. We then left it for 24 hours.

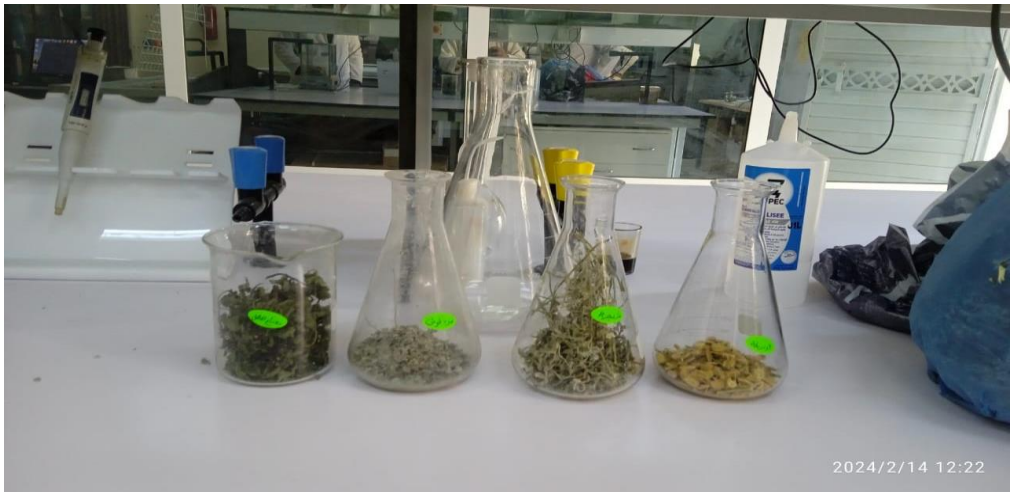


Figure II.5 Images for preparing the extract

After 24 hours, we filter the sample to obtain the extract, which contains a certain amount of water.

We repeat the process for three consecutive days to obtain the total extract in the end.

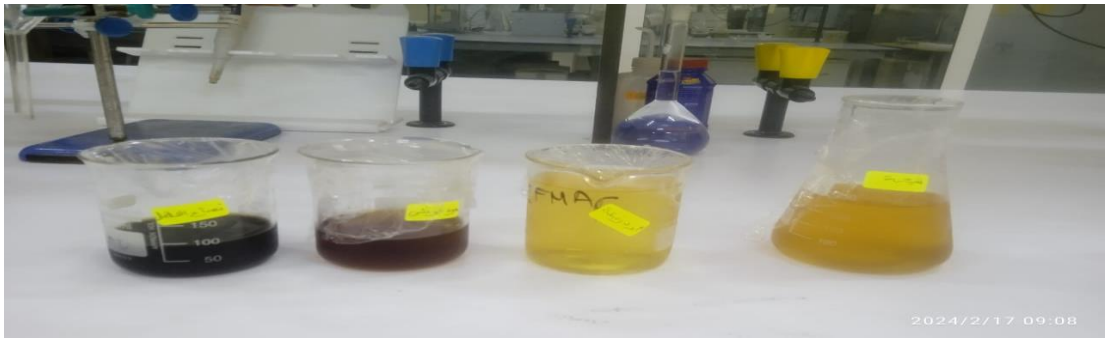


Figure II.6 The extract containing a certain amount of water

In this process, we need a rotary evaporator as shown in the image below. We place the extract *Origanum majorana* in the round-bottomed flask and fill the evaporator flask

with distilled water. Then, we start the device and lower the flask into a water bath until half of it is submerged.

Figure II.7: VTRS: Vapor Thermal Recompression System

Then, water vapor begins to exit through the condenser with the water bath temperature maintained between 45 to 50 degrees Celsius. At the end of the process, we notice that only a small amount of the extract remains completely free of water.

b.Surface preparation:

The steel samples underwent, before each experiment, polishing with silicon carbide (SiC) abrasive paper, with decreasing granulometry (from 120 to 2500 µm). Then, the surface of the samples was rinsed with distilled water to remove any remaining suspension grains that might be on the surface.

II.1.4.3.Work on the device:

The electrochemical impedance spectra were plotted at equilibrium potentials between 100 kHz and 100 mHz, with5 points per decade and a sinusoidal excitation of 10mV amplitude, to ensure being in the electrochemical linearity domain.

a.Potential curve:

For each impedance measurement at different times and inhibitor concentrations, it is necessary to find the equivalent potential values by measuring the Open Circuit Potential (OCP), which involves measuring the potential of XC52 steel immersed in an electrolyte over time. Measuring this OCP potential also provides, firstly, an initial idea about the behavior of the surface in contact with the solution. Secondly, it allows determining the time needed to reach a steady state, which is essential for potentiodynamic plots and impedance measurements

Figure II.8 Graph when measuring Open Circuit Voltage (OCV)

We repeat the experiment steps, but this time with the plant ***Cotula cinerea.***

Chapter 2: Interpretation of Results

II.2.1. Introduction:

The experimental investigation was carried out at the VTRS laboratory utilizing an electrochemical deposition technique apparatus. Oxidation curves were generated over various durations spanning from 1 to 6 hours, both in the absence and presence of distinct inhibitor concentrations. The primary objective was to ascertain the thickness of the deposition layer on a specimen of XC52 carbon steel. Prior to immersion in the electrolytic solution, the steel sample underwent meticulous preparation. This involved abrasive polishing until achieving a mirror-like surface finish. Subsequently, it was rinsed with distilled water to eliminate any residual heat from the metal. Following this, the specimen was meticulously dried using acetone to ensure complete cleanliness and removal of any oily residues, whether from handling or the laboratory environment. These measures were undertaken to mitigate any potential influence of electrolytes on the experimental outcomes.

II.2.2.Tafel curves:

Tafel curves, indicative of oxidation kinetics, were executed under varying inhibitor concentrations sourced from *Origanum majorana L* and *Cotula cinerea* plants. The experiments were conducted within an HCl medium of 1M concentration at a standardized temperature of 25 degrees Celsius. Following designated time intervals of open circuit potential (OCP) measurements, a voltage scan was initiated at a controlled scan rate of 0.1 volts per second.

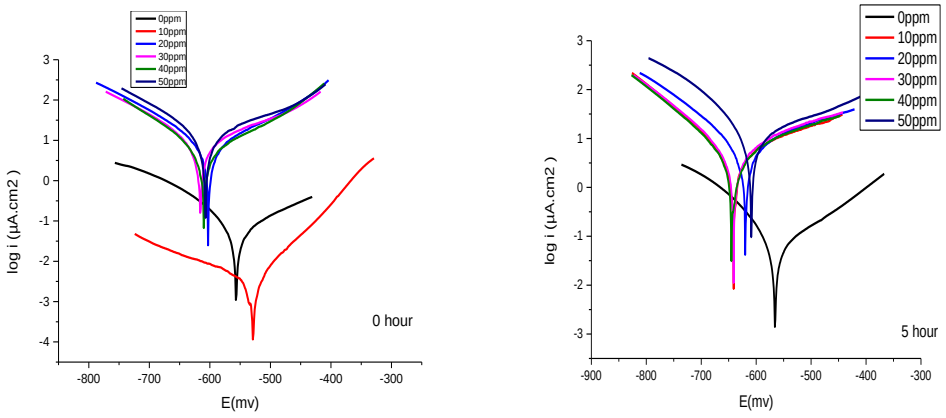


Figure II.9: The effect of changing the concentration on the Tafel polarization curve of carbon steel XC52 in acidic medium HCl with a concentration of 1M for various concentrations of *Origanum majorana L* extract. {**Appendix A**}

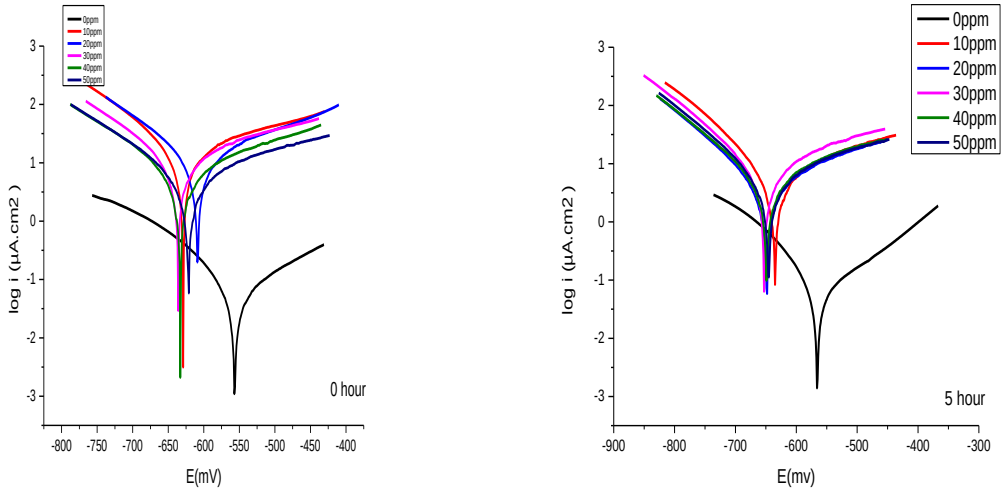


Figure II.10: The effect of changing the concentration on the Tafel polarization curve of carbon steel XC52 in acidic medium HCl with a concentration of 1M for various concentrations of *Cotula cinerea* extract. { **Appendix B**}

Corrosion behavior of carbon steel was assessed within a 1M HCl medium, with and without the incorporation of varied inhibitor concentrations at different immersion durations.

It is noteworthy that the profiles of the corrosion curves exhibit remarkable similarity across diverse immersion periods. Additionally, the supplementation of inhibitors derived from *Origanum majorana* and Cotula cinerea consistently yields a discernible decrease in both cathodic and anodic current densities.

Within the realm of cathodic protection, the introduction of inhibitors into the acidic corrosive milieu induces a parallel displacement of the cathodic Tafel slope (Fletcher, 2009). This observation suggests that the inclusion of inhibitors within a 1M HCl solution does not disrupt the fundamental mechanism governing hydrogen evolution or the reduction of H^+ ions on the surface of carbon steel (Nesic, 2012). These processes predominantly proceed via a charge transfer mechanism, as delineated by the subsequent equations (Gileadi *et al.*, 2005):

$$Fe + H^+ \rightarrow (FeH^+)ads$$

$$(FeH^+)ads + e^- \rightarrow (FeH)ads$$

$$(FeH)ads + H^+ + e^- \rightarrow Fe + H_2$$

In the domain of anodization, alterations in the tilt angles of the anode are observed upon the introduction of the plant extract. Evidently, the extract exhibits an initial affinity for the metal surface, followed by a mode of action primarily characterized by the obstruction of active sites on the metal surface. Importantly, this process does not appear to influence the mechanism underlying the anodic reaction.

$$Fe + Cl^- \rightarrow (FeCl^-)ads$$

$$(FeCl^-)ads \rightarrow (FeCl)ads + e^-$$

$$(FeCl)ads \rightarrow (FeCl^+)ads + e^-$$

$$(FeCl^+)ads \rightarrow Fe^{2+} + Cl^-$$

Additionally, two distinct linear segments are discerned: the first, denoted as βa1, corresponds to the low anodic voltage range, while the second, labeled as βa2, emerges subsequent to the absorption potential (Xu *et al.*, 2017), precipitating a notable escalation in the anodic current density within the high voltage disparity region. This augmentation is consistently observed within the voltage range spanning from -600 to -650 millivolts across all concentrations. This voltage range is construed as the absorption potential for inhibited molecules adsorbed onto the metal surface (Gopiraman *et al.*, 2012).

The Table provided enumerates the values for the corrosion current density (i_{corr}) in milliamperes per square centimeter (mA cm-2), corrosion potential (Ecorr) in millivolts (mV), as well as the cathodic and anodic Tafel slopes (βa and βc) in millivolts per decade (mV/dec), alongside the inhibition efficiency (EI %).

The inhibitory efficiency obtained from Tafel curve measurements was calculated using the following equation (Sığırcık *et al.*, 2016):

$$EI\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$

These data pertain to various concentrations of extracts derived from *Origanum Majorana* and *Cotula cinerea*, evaluated within a 1M HCl medium at a temperature of 25 degrees Celsius.

Table II.2. Inhibition Efficiency of *Origanum Majorana L* Extract on Carbon Steel Corrosion in 1M HCl Medium { **Appendix C**}

Time (h)	C (ppm)	i_{corr} (mA/cm^2)	E_{corr} (mV)	βa (mV/dec)	βc(mV/dec)	EI%
h0	0ppm	0.2467	-556.5	311.5	-182.6	/
	10ppm	0.0015	-524.5	55.7	-133.5	20.79
	20ppm	11.166	-602.2	153.8	-133.9	41.57
	30ppm	10.503	-615.8	220.1	-131.7	44.26
	40ppm	5.378	-609.7	153.2	-102.8	50.07
	50ppm	14.574	-607.3	218.4	-123.2	99.39
h5	0ppm	0.036	-565.6	116.1	-53.3	/
	10ppm	5.107	-640.7	255.7	-113.2	98.76
	20ppm	7.867	-619	282.9	-130.9	99.27
	30ppm	6.051	-640.6	246.5	-120.2	99.28
	40ppm	5.166	-643	251.4	-116.1	99.39
	50ppm	2.977	-608.6	486.2	-157.6	99.53

The provided data exclusively pertains to the inhibition efficiency of *Origanum Majorana L* extract on the corrosion behavior of carbon steel immersed in a 1M HCl medium over varying time intervals. The investigation involved monitoring the corrosion current density (i_corr), corrosion potential (E_corr), cathodic Tafel slope (βc), anodic Tafel slope (βa), and inhibition efficiency (EI %) at different concentrations of the *Origanum Majorana L* extract (0ppm, 10ppm, 20ppm, 30ppm, 40ppm, and 50ppm) at two distinct time points (h0 and h5).

At the initial time point (h0), it was observed that the absence of *Origanum Majorana L* extract (0ppm) resulted in a corrosion current density of 0.2467 mA.cm^{-2}, with a corrosion potential (E_corr) of -556.5 mV. Upon the introduction of increasing concentrations of the *Origanum Majorana L* extract, a noticeable reduction in the corrosion current density was evident, coupled with shifts in the corrosion potential towards more positive values. This trend is further supported by the progressive decrease in both cathodic and anodic Tafel slopes with increasing concentrations of the *Origanum Majorana L* extract, indicative of a mitigation of corrosion processes.

Similarly, at the subsequent time point (h5), the inhibition efficiency of the *Origanum Majorana L* extract remained significant, with a notable reduction in corrosion current density observed across all concentrations of the extract compared to the control (0ppm). Notably, the highest inhibition efficiencies were observed at the highest concentrations of the *Origanum Majorana L* extract (40ppm and 50ppm), with corrosion current densities markedly lower than those at h0.

Table II.3. Inhibition Efficiency of *Cotula cinerea* Extract on Carbon Steel Corrosion in 1M HCl Medium { **Appendix D**}

Time (h)	C (ppm)	i_{corr} (mA/cm^2)	E_{corr} (mV)	βa (mV/dec)	βc(mV/dec)	EI%
h0	0ppm	0.2467	-556.5	311.5	-182.6	/
	10ppm	14.886	-9629	287.8	-114.4	95.3
	20ppm	10.154	-608.8	206.7	-113.2	96.13
	30ppm	10.009	-636.5	261.7	-122.1	97.54
	40ppm	6.359	-633.1	236.7	-129.7	97.57
	50ppm	5.291	-621.5	234.4	-129.7	98.34
h5	0ppm	0.036	-565.6	116.1	-53.3	/
	10ppm	11.043	-635.1	463.5	-133.8	99.15
	20ppm	4.343	-648.7	237.6	-118.1	99.28
	30ppm	6.289	-652.8	222.2	-110.6	99.29
	40ppm	5.229	-648.6	245.9	-124.6	99.41
	50ppm	5.141	-645.8	255	-119.2	99.66

The provided dataset exclusively focuses on the inhibition efficiency of *Cotula cinerea* extract on the corrosion kinetics of carbon steel immersed in a 1M HCl medium over varying time intervals. The investigation encompasses an examination of corrosion current density (i_corr), corrosion potential (E_corr), cathodic Tafel slope (βc), anodic Tafel slope (βa), and inhibition efficiency (EI %) across different concentrations of *Cotula cinerea* extract (0ppm, 10ppm, 20ppm, 30ppm, 40ppm, and 50ppm) at two distinct time points (h0 and h5).

At the initial time point (h0), it is evident that in the absence of *Cotula cinerea* extract (0ppm), the corrosion current density is recorded at 0.2467 mA.cm^{-2}, with a corresponding corrosion potential (E_corr) of -556.5 mV. With the introduction of increasing concentrations of *Cotula cinerea* extract, a noticeable reduction in the

corrosion current density is observed, coupled with a shift in the corrosion potential towards more positive values. This reduction is further corroborated by a progressive decrease in both cathodic and anodic Tafel slopes with increasing concentrations of the *Cotula cinerea* extract, indicative of a suppression in corrosion activity.

Subsequently, at the subsequent time point (h5), the inhibition efficiency of the *Cotula cinerea* extract remains pronounced, with a significant reduction in corrosion current density observed across all concentrations of the extract compared to the control (0ppm). Particularly noteworthy is the substantial inhibition efficiency observed at the highest concentrations of the *Cotula cinerea* extract (40ppm and 50ppm), where corrosion current densities are markedly lower compared to those at h0.

In literature (Anejjar *et al.*, 2017), it is established that if the difference in corrosion potential (E_corr) between the inhibited and uninhibited solutions exceeds ±85 mV/ECS, the inhibitor is categorized as either anodic or cathodic in nature. Notably, a distinct shift of -250 mV towards cathodic values is discerned at the highest concentration of extracts (*Origanum Majorana L* and *Cotula cinerea*), affirming their cathodic character and unequivocally evidencing their capability to diminish the anodic dissolution rate of iron and the reduction rate of protons (H^+) (Googan, 2021).

II.2.2.Electrochemical Impedance Spectroscopy (EIS):

To validate the findings derived from Tafel curves and to glean further insights into corrosion mechanisms, we embarked on a study to explore the impact of our plant extracts (*Origanum Majorana L* and *Cotula cinerea*) on carbon steel in a 1M HCl environment utilizing electrochemical impedance spectroscopy (EIS).

Electrochemical impedance spectra were acquired for Naiquoist electrodes both with and without the incorporation of various concentrations of inhibitor extracts (*Origanum Majorana L* and *Cotula cinerea*) in 1M HCl. Measurements were conducted hourly (h6-h5-h4-h3-h2-h1-h0) by monitoring the open circuit potential (OCP) voltage. The frequency range spanned from 100 kHz to 100 mHz, with a signal amplitude perturbation of 10 mV using an alternating current (AC) signal.

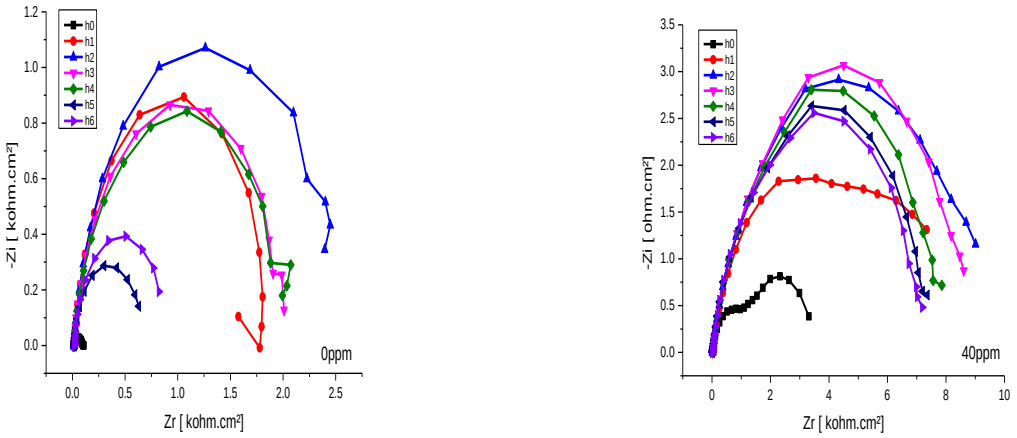
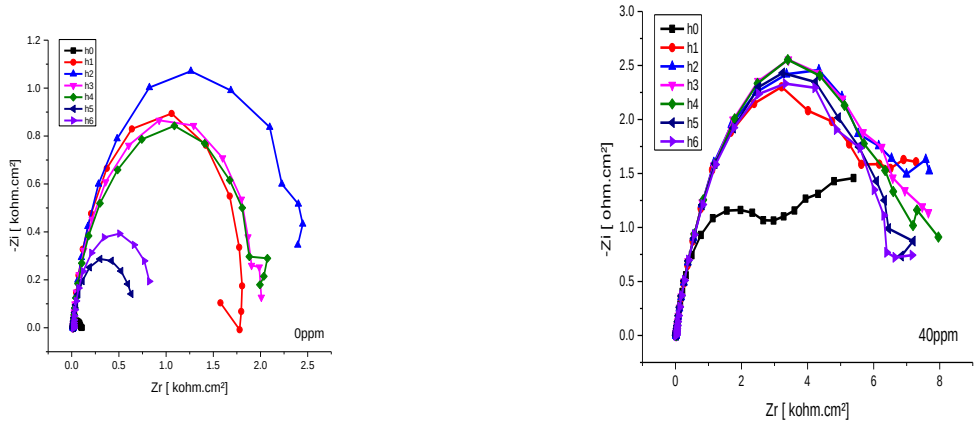


Figure II.11: The Nyquist plot of carbon steel XC52 in acidic medium (HCl. 1 M) in the presence of *Origanum majorana* extract (inhibitor) at different time intervals. {**Appendix E**}



FigureII.12: The Nyquist plot of carbon steel XC52 in acidic medium (HCl. 1 M) in the presence of *Cotula cinerea Del* extract (inhibitor) at different time intervals. {**Appendix F**}

At high frequencies, Nyquist diagrams exhibit prominent capacitive loops, indicative of the predominance of a charge transfer process in controlling the corrosion of carbon steel in 1M HCl solution, with and without the presence of inhibitors. Conversely, the presence of small inductive loops at lower frequencies may be ascribed to relaxation processes induced by adsorbed species, such as H+ ions or inhibitory species, on the electrode surface (Meraghni *et al.*, 2023). This phenomenon could also be linked to the redissolution of passivated surfaces at low frequencies. The imperfect semi-circles observed in Nyquist plots are often attributed to frequency dispersion stemming from surface heterogeneity, which can arise from various factors including

surface roughness, impurities, dislocations, fractal structures, distribution of activity centers, adsorption and desorption phenomena of the inhibitor, and the formation of porous layers (Dhillon *et al.*, 2017).

The electrochemical parameters, including solution resistance (Rs) in ohm centimeters squared (Ω cm2), charge transfer resistance (Rtc) in ohm centimeters squared (Ω cm2), double-layer capacitance, and inhibitory efficiency (%), are summarized in the **Table II.4.** { **Appendix G**}

The inhibitory efficacy was calculated using the following equation:

$$EI\% = \left(\frac{R_{tc} - R_{tc}^{0}}{R_{tc}}\right) \times 100$$

C=40ppm			C=0ppm			concentration
EI%	**Rtc**(Ωcm^2)	**RS**(Ωcm^2)	**EI%**	**Rtc**(Ωcm^2)	**Rs**(Ωcm^2)	**t(hour)**
	3.294	0.0162		0.095	0.01407	**h0**
54.99	7.320	0.0194	93.94	1.57	0.012	**h1**
63.38	8.996	0.0183	96	2.375	0.020	**h2**
61.70	8.602	0.0183	95.24	1.996	0.012	**h3**
58.04	7.852	0.0174	95.18	1.974	0.016	**h4**
55.17	7.348	0.01365	84.53	0.6142	0.01572	**h5**
54.11	7.179	0.01941	88.16	0.8031	0.01646	**h6**

The presented data offers a comparative analysis of electrochemical parameters and inhibition efficiency (EI%) at varying concentrations of plant extract (0ppm and 40ppm) over different time intervals (h0-h6). The electrochemical parameters assessed include solution resistance (Rs) and charge transfer resistance (Rtc), both critical indicators of corrosion behavior and inhibition effectiveness.

At the initial time point (h0), negligible differences are observed between the Rs and Rtc values for both concentrations of plant extract. However, as the immersion time progresses, notable variations emerge. For instance, at h1, there is a significant increase in Rtc for both concentrations, indicating a substantial rise in charge transfer resistance. This enhancement in Rtc is accompanied by a considerable improvement in inhibition efficiency, particularly evident at 40ppm concentration, where the inhibition efficiency reaches 93.94%.

Throughout the subsequent time intervals (h2-h6), similar trends persist, with fluctuations in Rs and Rtc values reflective of changing corrosion kinetics and inhibition effectiveness. Notably, at higher concentrations of plant extract (40ppm), consistently higher inhibition efficiencies are observed compared to the control (0ppm),

underscoring the potency of the plant extract in mitigating carbon steel corrosion.

TableII.5. {**Appendix H**}

C=40ppm			C=0ppm			concentration
EI%	**Rtc**(Ωcm^2)	**Rs**(Ωcm^2)	**EI%**	**Rtc**(Ωcm^2)	**Rs**(Ωcm^2)	**t(hour)**
	5.357	0.0254		0.095	0.01407	**h0**
26.56	7.295	0.0136	93.94	1.57	0.012	**h1**
30.20	7.676	0.0091	96	2.375	0.020	**h2**
30.99	7.764	0.0213	95.24	1.996	0.012	**h3**
32.70	7.960	0.0110	95.18	1.974	0.016	**h4**
33.23	6.828	0.0194	84.53	0.6142	0.01572	**h5**
21.54	7.137	0.0194	88.16	0.8031	0.01646	**h6**

This study investigates the influence of plant extract concentration on electrochemical parameters and inhibition efficiency (EI%) in carbon steel corrosion, comparing two concentrations (0ppm and 40ppm) over varying time intervals (h0-h6). The electrochemical parameters assessed include solution resistance (Rs) and charge transfer resistance (Rtc), crucial indicators of corrosion kinetics and inhibition effectiveness.

At the onset (h0), both concentrations exhibit comparable Rs and Rtc values. However, as immersion time progresses, notable differences emerge. Notably, at h1, a significant increase in Rtc is observed for both concentrations, indicative of enhanced charge transfer resistance. Correspondingly, inhibition efficiency substantially improves, particularly evident at 40ppm concentration, reaching 93.94%.

Throughout subsequent intervals (h2-h6), fluctuating trends in Rs and Rtc reflect dynamic corrosion processes and inhibition effectiveness. Interestingly, at 40ppm concentration, consistently higher inhibition efficiencies are observed compared to the control (0ppm), highlighting the efficacy of the plant extract as a corrosion inhibitor.

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General Conclusion

Through our experimental study on the effect of inhibiting metal corrosion (XC52) in a medium of hydrochloric acid (HCl) using plant extracts of Origanum majorana and Cotula cinerea employing electrochemical techniques, specifically Impedance Spectroscopy and Tafel curves, along with measuring the inhibition efficiency at various times and concentrations, the following results were obtained:

- The inhibitory effectiveness increases with the increase in inhibitor concentration, reaching a high inhibitory efficacy of approximately 99.53% for Origanum Majorana extract and 99.66% for Cotula cinerea extract at a concentration of 50 ppm.
- The extracts of Cotula cinerea and Origanum majorana exhibit somewhat comparable inhibitory efficacy.
- The Tafel curves illustrate that increasing the concentration of the inhibitors studied leads to a decrease in current densities, demonstrating their cathodic behavior pattern.
- From the information provided by the summarized Nyquist plots in the table, we deduce that an increase in the concentration of inhibitors increases the values of charge transfer resistance (Rtc), leading to an increase in the inhibitory efficiency ratio.
- Therefore, plant extracts are considered excellent inhibitors of corrosion and should be exploited in the future and enhanced as additives with nano- or ion compounds to achieve better results, especially since they are natural, environmentally friendly, non-toxic, readily available, and cost-effective.

Appendices

Appendix A: The Tafel curves indicating the kinetics of oxidation under different concentrations of inhibitors from *Origanum majorana* extract.

Appendix B: The Tafel curves indicating the kinetics of oxidation under different concentrations of inhibitors from *Cotula cinerea* extract.

Appendix C: Efficiency tables of the inhibitory extract of *Origanum majorana* on the corrosion of carbon steel XC52.

Appendix D: Efficiency tables of the inhibitory extract of *Cotula cinerea* on the corrosion of carbon steel XC52.

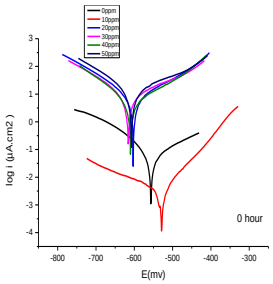
Appendix E: Representing the Nyquist plot of carbon steel XC52 with the presence of *Origanum majorana* plant extract at different time intervals.

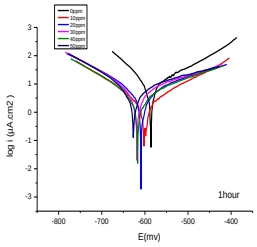
Appendix F: Representing the Nyquist plot of carbon steel XC52 with the presence of *Cotula cinerea* plant extract at different time intervals.

Appendix G: Electrochemical parameters table of XC52 carbon steel obtained by electrochemical spectroscopy before and after adding different concentrations of *Origanum majorana* extract at different times.

Appendix H: Electrochemical parameters table of XC52 carbon steel obtained by electrochemical spectroscopy before and after adding different concentrations of *Cotula cinerea* extract at different times.

Appendix A


0ppm
10ppm
20ppm
30ppm
40ppm
50ppm
log i (µA.cm2)
E(mv)
0 hour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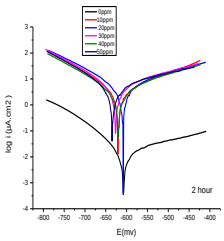
E(mv)
1hour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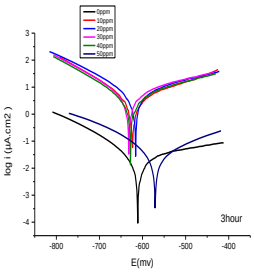
E(mv)
2 hour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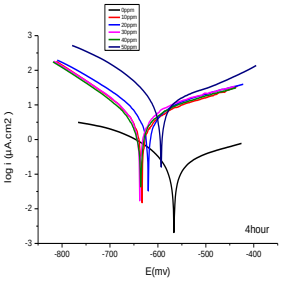
E(mv)
3hour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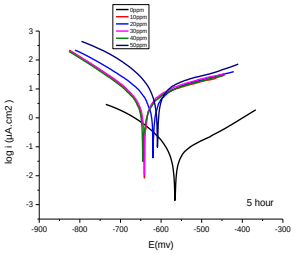
E(mv)
4hour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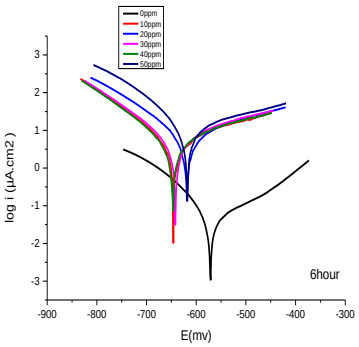
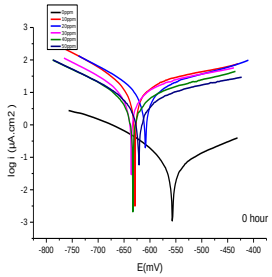
E(mv)
5 hour


0ppm
10ppm
20ppm
30ppm
40ppm
50ppm
log i (µA.cm2)
E(mv)
6hour

Appendix B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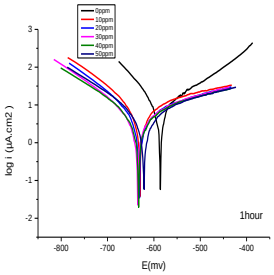
E(mV)
0 hour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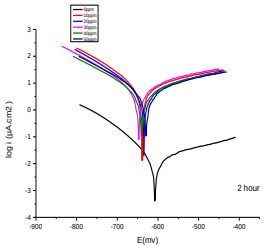
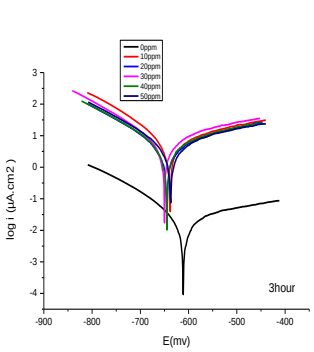
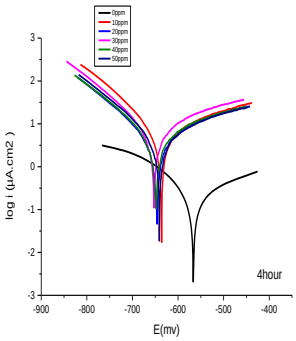
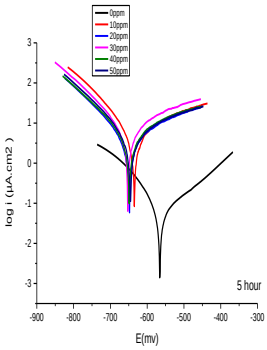
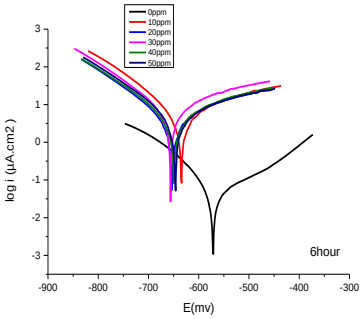
E(mv)
1hour


log i (μA.cm2)
E(mv)
2 hour


0ppm
10ppm
20ppm
30ppm
40ppm
50ppm
log i (μA.cm2)
E(mv)
3hour


0ppm
10ppm
20ppm
30ppm
40ppm
50ppm
log i (μA.cm2)
E(mv)
4hour


0ppm
10ppm
20ppm
30ppm
40ppm
50ppm
log i (μA.cm2)
E(mv)
5 hour


0ppm
10ppm
20ppm
30ppm
40ppm
50ppm
log i (μA.cm2)
E(mv)
6hour

Appendix C

Time (h)	C (ppm)	i_{corr} (mA cm^{-2})	E_{corr} (mV)	Ba(mV/dec)	Bc(mV/dec)	EI%
h0	0ppm	0.2467	-556.5	311.5	-182.6	/
	10ppm	0.0015	-524.5	55.7	-133.5	20.79
	20ppm	11.166	-602.2	153.8	-133.9	41.57
	30ppm	10.503	-615.8	220.1	-131.7	44.26
	40ppm	5.378	-609.7	153.2	-102.8	50.07
	50ppm	14.574	-607.3	218.4	-123.2	99.39
h1	0ppm	6.439	-586	114.5	-61.7	/
	10ppm	2.079	-598.7	126.7	-108	1.12
	20ppm	5.795	-608.2	214.2	-131.6	7.21
	30ppm	5.198	-618.4	207.5	-114.8	19.27
	40ppm	3.899	-616.8	189.3	-119.4	39.43
	50ppm	6.512	-626.1	246.9	-120	67.71
h2	0ppm	0.0233	-607.5	358.9	-93.3	/
	10ppm	3.531	-619.8	174.5	-111	99.28
	20ppm	6.128	608.9	233.6	-136.4	99.52
	30ppm	5.401	-626.4	233.3	-119.6	99.56
	40ppm	3.264	-619.9	190	-116.3	99.61
	50ppm	4.927	-634	247.5	-115	99.85
h3	0ppm	0.058	-610.7	105.9	-151.2	/
	10ppm	3.792	-623.4	204.7	-110.2	16.96
	20ppm	6.646	-616.2	259	-131.8	98.41
	30ppm	5.11	-631.9	231.6	-116.9	98.45
	40ppm	3.701	-628.7	195	-113.3	98.85
	50ppm	0.050	-570.6	224.5	-138.9	99.11
h4	0ppm	1.069	-566.4	110.7	-428.5	/
	10ppm	4.958	-633.9	262.6	-114.1	54.45
	20ppm	7.192	-620.2	268.1	-129.8	77.88
	30ppm	6.336	-637.5	269.4	-122.9	78.42
	40ppm	4.837	-635.9	245.2	-117.4	83.11
	50ppm	1.652	-593.2	223.7	-109.5	85.99
h5	0ppm	0.036	-565.6	116.1	-53.3	/
	10ppm	5.107	-640.7	255.7	-113.2	98.76
	20ppm	7.867	-619	282.9	-130.9	99.27
	30ppm	6.051	-640.6	246.5	-120.2	99.28
	40ppm	5.166	-643	251.4	-116.1	99.39
	50ppm	2.977	-608.6	486.2	-157.6	99.53
h6	0ppm	0.128	-571.6	180.5	-117.6	/
	10ppm	5.201	-645.2	253.7	-113.5	94.67

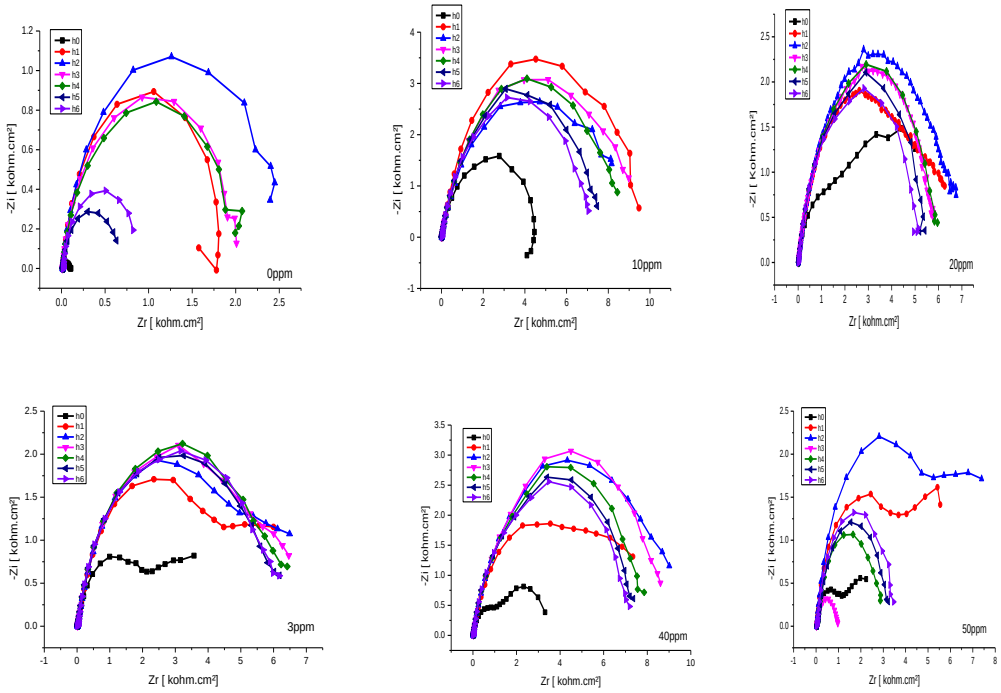
	20ppm	8.792	-618.9	299.7	-130.4	97.51
	30ppm	6.117	-641.7	244	-119.6	97.52
	40ppm	5.175	-647.3	245.4	-114	97.89
	50ppm	2.415	-618	589.1	-136.1	98.53

Appendix D

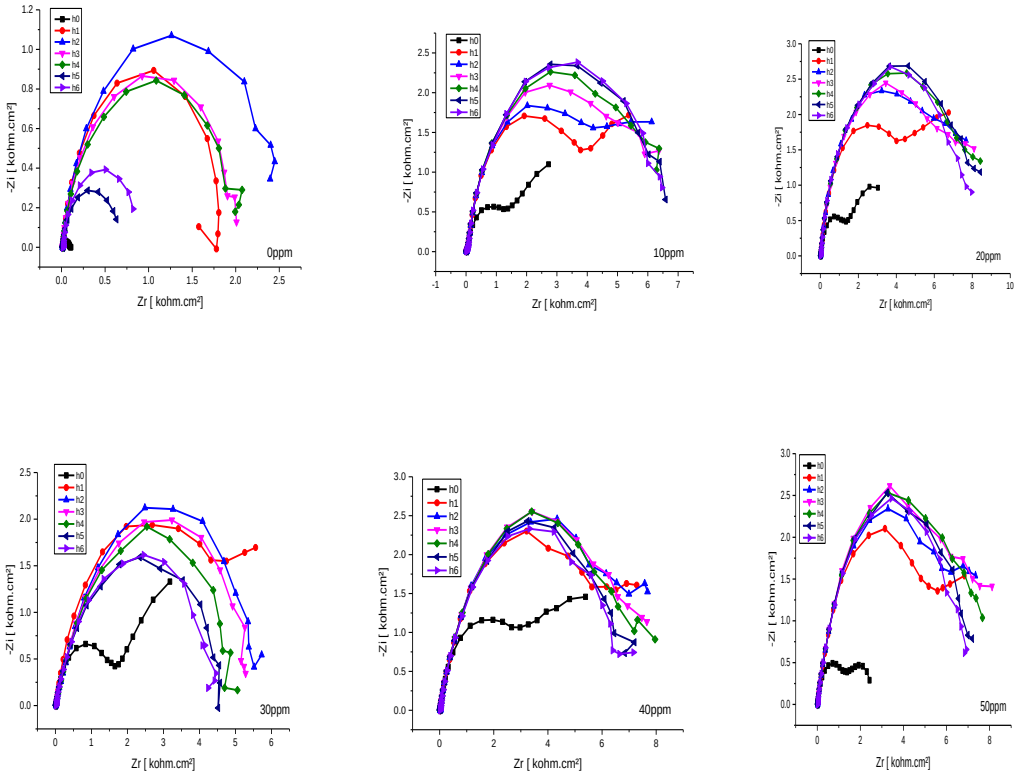
Time (h)	C (ppm)	i_{corr} (mA cm^{-2})	E_{corr} (mV)	Ba(mV/dec)	Bc (mV/dec)	EI%
h0	0ppm	0.2467	-556.5	311.5	-182.6	/
	10ppm	14.886	-9629	287.8	-114.4	95.3
	20ppm	10.154	-608.8	206.7	-113.2	96.13
	30ppm	10.009	-636.5	261.7	-122.1	97.54
	40ppm	6.359	-633.1	236.7	-129.7	97.57
	50ppm	5.291	-621.5	234.4	-129.7	98.34
h1	0ppm	6.439	-586	114.5	-61.7	/
	10ppm	10.875	-630	407.4	-127.8	1.13
	20ppm	6.525	-631.4	289.3	-117.3	6.81
	30ppm	6.004	-635.4	274.7	-126.6	17.82
	40ppm	5.027	-633.2	245.1	-131	21.92
	50ppm	5.291	-621.5	234.4	-129.7	68.89
h2	0ppm	0.023	-607.5	358.9	-93.3	/
	10ppm	9.275	-638.6	375.5	-119.5	99.44
	20ppm	5.888	-634.3	283.6	-113.8	99.49
	30ppm	7.464	-647.8	290.7	-125.6	99.6
	40ppm	4.654	-640	235.7	-126.3	99.68
	50ppm	4.631	-629.3	229.4	-123.8	99.74
h3	0ppm	0.058	-610.7	1059.3	-151.2	/
	10ppm	8.417	-638.7	348.8	-116.6	98.61
	20ppm	4.373	-644.9	243.9	-120.1	98.67
	30ppm	7.198	-650.4	264.9	-120.6	98.65
	40ppm	4.234	-645.4	212.2	-116.7	99.15
	50ppm	4.432	-637.3	239.1	-119.1	99.3
h4	0ppm	1.069	-566.4	140.3	-428.5	/
	10ppm	7.733	-636.6	329.4	-116.3	77.05
	20ppm	4.662	-646.7	242.9	-122.7	78.88
	30ppm	9.087	-652.7	318.6	-128.1	79
	40ppm	5.096	-648.7	256.6	-124.6	86.17
	50ppm	5.066	-640.5	259.9	-123	88.23
h5	0ppm	0.036	-565.6	116.1	-53.3	/
	10ppm	11.043	-635.1	463.5	-133.8	99.15
	20ppm	4.343	-648.7	237.6	-118.1	99.28
	30ppm	6.289	-652.8	222.2	-110.6	99.29

	40ppm	5.229	-648.6	245.9	-124.6	99.41
	50ppm	5.141	-645.8	255	-119.2	99.66
h6	0ppm	0.128	-571.6	180.5	-117.6	/
	10ppm	10.636	-634.8	423.9	-132.7	96.72
	20ppm	3.933	-653.4	202	-110.3	97.43
	30ppm	7.921	-656.3	248.7	-119.5	97.72
	40ppm	5.022	-649.4	228.9	-121.3	97.74
	50ppm	5.706	-646.7	273.3	-122.0	98.78

Appendix E



Appendix F



Appendix G

	C=20ppm			C=10ppm			C=0ppm		concentration
El%	**Rtc(Ωcm^2)**	**RS(Ωcm^2)**	**El%**	**Rtc(Ωcm^2)**	**RS(Ωcm^2)**	**El%**	**Rtc(Ωcm^2)**	**Rs(Ωcm^2)**	**t(hour)**
	4.992	0,01066		4.077	0,0091		0,095	0,01407	h0
20,12	6.250	0,0151	56,77	9.439	0,0213	93,94	1,57	0,012	h1
17,06	6.019	0,01173	55,32	9.125	0,00255	96	2.375	0,020	h2
13,76	5.789	0,0166	54,34	8.930	0,0324	95,24	1.996	0,012	h3
10,42	5.573	0,00767	51,48	8.404	0,32423	95,18	1.974	0,016	h4
7,69	5.408	0,0116	45,09	7.426	0,023357	84,53	0,6142	0,01572	h5
1,33	4.926	0,0199	41,93	7.022	0,01557	88,16	0,8031	0,01646	h6
	C=50ppm			**C=40ppm**			**C=30ppm**		**concentration**
El%	**Rtc(Ωcm^2)**	**RS(Ωcm^2)**	**El%**	**Rtc(Ωcm^2)**	**RS(Ωcm^2)**	**El%**	**Rtc(Ωcm^2)**	**RS(Ωcm^2)**	**t(hour)**
	2.223	0,0116		3.294	0,0162		3.553	0,0193	h0
59,73	5.522	0,0213	54,99	7.320	0,0194	40,76	5.998	0,0106	h1
69,86	7.379	0,0136	63,38	8.996	0,0183	45,17	6.481	0,0189	h2
35,89	2.841	0,0284	61,70	8.602	0,0183	44,91	6.450	0,0183	h3
35,54	3.183	0,0387	58,04	7.852	0,0174	44,49	6.396	0,0183	h4
30,14	3.450	0,0203	55,17	7.348	0,01365	42,38	6.167	0,0183	h5
21,73	3.469	0,0193	54,11	7.179	0,01941	42,24	6.152	0,0183	h6

Appendix H

C=20ppm			C=10ppm			C=0ppm			concentration
EI%	Rtc(Ωcm^2)	Rs(Ωcm^2)	EI%	Rtc(Ωcm^2)	Rs(Ωcm^2)	EI%	Rtc(Ωcm^2)	Rs(Ωcm^2)	t(hour)
	3.030	0,0139		2.708	0,0148		0,095	0,01407	h0
55,37	6.790	0,0081	49,33	5.345	0,0130	93,94	1,57	0,012	h1
60,55	7.682	0,0091	55,70	6.114	0,0183	96	2.375	0,020	h2
62,47	8.073	0,0174	57,30	6.343	0,0183	95,24	1.996	0,012	h3
63,95	8.407	0,0113	56,77	6.264	0,0183	95,18	1.974	0,016	h4
63,84	8.381	0,0255	56,90	6.455	0,0189	84,53	0,6142	0,01572	h5
61,91	7.956	0,0174	58,61	6.544	0,0183	88,16	0,8031	0,01646	h6
C=50ppm			C=40ppm			C=30ppm			concentration
EI%	Rtc(Ωcm^2)	Rs(Ωcm^2)	EI%	Rtc(Ωcm^2)	Rs(Ωcm^2)	EI%	Rtc(Ωcm^2)	Rs(Ωcm^2)	t(hour)
	2.413	0,0142		5.357	0,0254		5.460	0,0130	h0
64,50	6.801	0,0189	26,56	7.295	0,0136	22,60	7.054	0,0021	h1
67,15	7.348	0,0078	30,20	7.676	0,0091	4,55	5.720	0,0106	h2
70,26	8.118	0,0174	30,99	7.764	0,0213	3,38	5.281	0,0046	h3
68,47	7.657	0,0274	32,70	7.960	0,0110	8,49	5.032	0,0196	h4
66,42	7.189	0,0194	33,23	6.828	0,0194	19,69	4.561	0,0091	h5
64,56	6.811	0,0189	21,54	7.137	0,0194	29,26	4.224	0,0197	h6