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Corrosion protection of copper alloys in acidic media by using environmentally friendly inhibitors

A thesis

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By

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ اللَّهُ نُورُ السَّمَاوَاتِ وَالْأَرْضِ مَثَلُ نُورِهِ كَمِشْكَاةٍ فِيهَا مِصْبَاحٌ الْمِصْبَاحُ

فِي زُجَاجَةٍ الزُّجَاجَةُ كَأَنَّهَا كَوْكَبٌ دُرِّيٌّ يُوقَدُ مِنْ شَجَرَةٍ

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Dedication

This thesis is dedicated to my paradise in life, my father and my mother.

To those who showed me the most beautiful thing in life, my brothers.

To everyone who helped complete this research from my dear doctors and all my friends.

Riam

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Riam

Summary:

The present thesis included electrochemical investigation of corrosion of copper in (0.5)M acidic solution of (HCl). The range of temperature were (298,303,308,313) K using potentiostatic polorization.

The experimental results revealed that:

1. The corrosion current density increased with increasing the acidity and temperature. It has a maximum value (44.8) $\mu A.cm^{-2}$ of (0.5) mol. dm^{-3} of hydrochloric acid at 313 K.
2. The characterization techniques for olive and eucalyptuse leaves extracts proved the presence of many organic compounds that responsible for inhibition activity for those extracts.
3. The inhibition efficiency and surface coverage increased with increasing the concentration of inhibitors (Olive and Eucalyptus leaves) and decreased by increasing the temperature. The results shows that inhibition efficiency of olive leaves extracts higher than that of eucalyptus
4. Kinetics of copper corrosion have been studied from the values of the corrosion current densities and their dependencies on temperature. It was found that values of (E_a) increased with inhibitor concentration increasing. That means the inhibitor raises the energy barrier for corrosion process. The values of (ΔH_a) were positive in presence and absence of inhibitors meaning that the corrosion process is endothermic. (ΔS_a) values were negative and this means decrease the overall degree of freedom throughout the formation of the activated complex for the reaction of copper with negative species leading to the formation of corrosion product.

5. The thermodynamic parameters for adsorption of inhibitors on copper surface showed that (ΔG_{ads}) were negative indicating spontaneous process and its values were between (33-35) $Kj.mol^{-1}$ which indicate that the adsorption process of plants extracts on copper surface operate mostly via both physical and chemical adsorption. He values of (ΔH_{ads}) were negative reveals that adsorption process is exothermic process, the values of (ΔS_{ads}) positive and this means randomness increased when the adsorption process occurred.
6. The surface examination studies by SEM showed that the inhibitors molecules gave a good protective film on to copper surface.

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List of Abbreviation

Meaning	***Abbreviation***
Corrosion current density	i_{corr}
Atomic weight	*a*
Adsorption	*ads*
Corrosion rate	*CR*
Part per million	*ppm*
Molary	*M*
Corrosion	*corr*
Inhibitor	*Inh*
Electron	e^-
Exchange current density	$i_\circ$
potential Corrosion potential	E_{corr}
Polarized potential	*E*
Arrhenius coefficient	*A*
Energy activation	*Ea*
gas constan	*R*
absolute temperature	*T*
Organic Inhibitors	*OI*
Open circuit potential	*OCP*
Weight loss	*WL*
Reference electrode	*R.E*
Working electrode potential	*W.E*

Avogadro's number	N
planks constant	h
entropy change	ΔS_a
Enthalpy change	ΔH_a
The Gibbs free energy change	ΔG
Anodic Tafel slope	b_a
Cathodic Tafel slope	b_c
The transfer coefficients of the anodic	α_a
The transfer coefficients of cathodic	α_c
Faraday constant	F
The Inhibition efficiency	*%IE*
The metal surface coverage	θ
Constant equilibrium for Langmuir Isotherm	K_L
concentration of inhibitor (ppm)	C_i
equilibrium constant of the adsorption / desorption	K_{ads}

Fourier Transform Infrared	*FTIR*
X-Ray diffraction	*XRD*
Gas Chromatography Mass Spectroscopy	*GC-MS*
Scanning Electron Microscope	*SEM*

1-1 General introduction on corrosion:

Corrosion is defined as a reaction that is interfacial and irreversible of a material (polymer, metal, and ceramic,) with its environment which leads to its dissolution and consumption or into a component material of the environment. In many instances, corrosion leads to effects tending to cause harm to the material usage concerned. Exclusively mechanical or physical processes such as mechanical fracture, melting, evaporation, and abrasion are not included in the word corrosion. (1)

Corrosion can be defined in different ways and the most common interpretation of the term is a destructive attack on the metallic materials (metals) within the surrounded environments. It is an electrochemical reaction and ordinarily begins at a metal surface which can be determined by either the change in weight of a given metal or by the change in the chemical or physical properties with time. (2)

Corrosion is an undesired phenomenon that naturally occur due to the fact that metals and their temporary unstable form of a pure metallic state have great tendency to convert to a high thermodynamically stable form which are represented as ores or natural minerals. The main reason metals are existed in many forms such as oxides or hydroxides, and other forms, according to their existing environment. (3)

The process of corrosion usually contains a set of oxidation/ reduction reaction that are in nature electrochemical. Hence, the metal is exposed to oxidization to the products of corrosion at sites that are anodic and some species are decreased at cathodic sites. In other words, corrosion is a naturally occurring process that leads to the degeneration of the materials properties through its:

a. Electrochemical corrosion: in this type the metal can be exposed to oxidization to yields the corrosion at anodic positions where lowering some species is made at cathodic locations. The regulation of the occurrence of reaction is done by the thermodynamic factor.

b. Chemical corrosion: which results from the effect of effective chemical, liquid and gaseous compounds, such as air and acid solutions. (4)

Alloys and metals are used widely in industrial applications such as architecture, petroleum refining, automobiles, and other applications. For example, copper occupies important position because of its work ability, good mechanical characteristics, low cost, and thermal conductivity, Nevertheless, this material includes resistance of low corrosion in acidic media, which can result in economic losses. Industrial processes as oil acidification, acid cleaning, and acid pickling use typically aggressive species that are aggressive, such as hydrochloric acid, which intensely attacks carbon steel, being vital for the use of inhibitors corrosion for protecting protect (5) (6).

However, the chemical inhibitors used such as nitrates, chromates, carbonates, phosphates, molybdates, silicates and other toxic compound as corrosion control inhibitors have proved to be effective inhibitors at relatively low cost on the other hand, these chemicals create more problems than the solution they offer. Hence, their use should be restricted and penalized due to environmental threat and regulation**.** (7)

For this reason, it is preferable to obtain from particular source for inhibitors that are environmentally safe. There has been an importance in plant extracts since they are readily available and acceptable environmentally. They are also a renewable source for a great range of inhibitors needed and they may be as effective inhibitors of corrosion.

The increasing interest in the development of green inhibitors for controlling metal corrosion in unfriendly environment is positive contributions toward safe guarding our challenging environment. (8)

1.2 *Types of Corrosion*:

1.2.1 General Attack Corrosion:

General attack corrosion is named as uniform attack corrosion. It represents a corrosion type that is extremely widespread and it is produced by chemical and electrochemical reacting that leads to the undermining of the all of the exposed metal surface. Ultimately, the metal becomes diminished to the degree of failure. General attack corrosion includes high destruction of metal by corrosion. However, it represents harmless corrosion form due to the fact that it is controllable, predictable, and often avoidable. Such as the dissolution of carbon steel in diluted HCl acid.

1.2.2 Localized Corrosion:

General attack corrosion attacks single area of the formation of the metal and it can be classified in to three categories:

1. Pitting: Pitting corrosion represents a highly-localized attack on the surface resulting holes (pits). That could expand to dig in within the inside of a metal and such a type can be observed on an alloy surface that is presented in certain environment, such as aluminium and stainless steel in halogen solutions.

2. Crevice corrosion: it is comparable to pitting; it appears at a specific position. It is often connected with a micro-environment that is stagnant as in ones which are under clamps, washers, and gaskets. Oxygen depletion in a crevice or acidic circumstances is the cause of crevice corrosion.

3. Filiform corrosion: occurs under painted or plated surfaces during the time the water cracks the coating; filiform corrosion begins with small imperfections in the coating and then it spreads to cause structural drawback.

1.2.3 Galvanic Corrosion:

Galvanic corrosion occurs when dissimilar dual metals are positioned simultaneously in an electrolyte that is corrosive. A galvanic couple can be produced in the middle of the dual metals, where single metal becomes the anode and the other metals the cathode. The sacrificial metal or anode, becomes progressively worse faster than it would be by itself, while the cathode becomes gradually corroded than it would be in different circumstances. Such as tin-coated steel sheets when scratching occurs.

1.2.4 Environmental Cracking:

Environmental corrosion is a process of corrosion that can occur from a set of ecological situations that influence the metal. Stress-related and chemical circumstances and temperature can be the cause of the subsequent types of environmental corrosion:

- Hydrogen-induced cracking
- Liquid metal embrittlement
- Fatigue Corrosion
- Stress Corrosion Cracking know as (SCC)

1.2.5 Flow-Assisted Corrosion (FAC):

Flow assisted corrosion occurs when an oxide protective layer is on a metal surface and it is liquefied or removed by water or wind, making the fundamental metal exposed with deteriorating and corroding:

- Cavitation
- Erosion-assisted corrosion
- Impingement

1.2.6 Intergranular corrosion:

Intergranular corrosion is a chemical or electrochemical attack on the metal grain boundaries. This often occurs because of the impurities that the metal includes and they have an inclination to be in greater contents that are near the boundaries of the grain. These boundaries are further liable to corrosion than the bulk of the metal. Such as corrosion of the thermal impact zone of welded stainless steel.

*1.2.7 De-Alloying (*selective leaching):

De-alloying is defined as the selective corrosion of a specific part in an alloy. Highly typical type of de-alloying is unstabilized brass de-zincification. The result of corrosion in these circumstances is a deteriorated and porous copper.

1.2.8 Fretting corrosion:

Fretting corrosion occurs due to the weight or vibration and wearing that occur frequently, on uneven rough surface. Corrosion, forming depths and grooves, occurs on the surface. Fretting corrosion is frequently found in impact and rotation machinery, bolted bearings and assemblies, in addition to surfaces that are exposed to vibration throughout the course of the transportation (9) (10).

1.3 parameters effect on Corrosion:

1.3.1 Temperature Effect:

The temperature effect on the corrosion rate has been studied over temperature range (298-313) K. The temperature rises the corrosion rate, but the inhibition efficiency decreases with increasing the temperature in most chemical reactions.(11) This effect can be expressed by the equation of Arrhenius in which the reaction rate of corrosion is correlated with the temperature (12).

$$\mathrm{i_{corr}} = \mathrm{Aexp} - \frac{\mathrm{Ea}}{\mathrm{RT}} \quad \text{........} \quad (1\text{-}1)$$

Where i_{corr} is "corrosion current” ($\mu A.cm^{-2}$), A represents "Arrhenius coefficient”, Ea refers to "Energy activation"(J/mole), R stands for "gas constan” (8.314 J/mole.K), and T is for "absolute temperature” (K).

1.3.2 Acid Concentration Effect:

Rising the acid center concentration increases corrosion rate because of the fact that hydrogen ions amounts increase by increasing the concentration of acid and the expression is usually expressed by increasing the activity of hydrogen by decreasing the values of (pH). (13)

1.3.3 Effect of inhibitor concentration:

There is a significant relationship between the concentration of the inhibitor and weight loss in the mineral sample. there was an increase in the inhibitor concentration; whenever the loss of weight decreases, it tends to become closer to a low fixed value which relies on the inhibitor properties used where the analysis of the plant powder for the purpose of knowledge of the active groups, and compounds is found in the inhibitor; it has the inhibitory effect and the cause is due to its many active groups; it is rich in aldehyde, ketone, amines, amides, alcohols, aromatics, or phenol. All these compounds possess known inhibitory properties. (14)

1.4 Transfer Coefficients

The anodic and cathodic transfer coefficients (α_a , α_c) are evaluated from cathodic and anodic Tafel slopes respectively using the equations (1.2) and (1.3). (15)

$$\alpha_a = \frac{2.3\,RT}{b_a\,nF} \;\ldots\ldots\; (1.2)$$

$$\alpha_c = \frac{2.3\,RT}{b_c\;nF} \;\ldots\ldots\; (1.3)$$

Where (b_a), refers to the anodic Tafel slope. And (b_c) represents the cathodic tafel slope, F is the Faraday constant (96500 C/equivalent), and n is the charge of ion in equivalent/mole.

1.5 adsorption

Adsorption capability of all solid substances to attract to their surfaces molecules of gases or solutions with which they are in contact. Solids that are used to adsorb gases or dissolved substances are called adsorbents; the adsorbed molecules are usually referred to collectively as the adsorbate. An example of an excellent adsorbent is the charcoal used in gas masks to remove poisons or impurities from a stream of air.

Adsorption refers to the collecting of molecules by the external surface or internal surface (walls of capillaries or crevices) of solids or by the surface of liquids. Absorption, is often confused, refers to processes in which a substance penetrates into the actual interior of crystals, of blocks of amorphous solids, or of liquids. Sometimes the word sorption is used to indicate the process of the taking up of a gas or liquid by solid without specifying whether the process is adsorption or absorption.

Adsorption can be either physical or chemical in nature. Physical adsorption resembles the condensation of gases to liquids and depends on the physical, or van der waals, force of attraction between the solid adsorbent and the adsorbate molecules. There is no chemical specificity in physical adsorption, any gas tending to be adsorbed on any solid if the temperature is sufficiently low or the pressure of the gas sufficiently high. In chemical adsorption, gases are held to a solid surface by chemical forces that are specific for each surface and each gas. Chemical adsorption occurs usually at higher temperatures than those at which physical adsorption occurs; furthermore, chemical adsorption is ordinarily a slower process than physical adsorption and, such as most chemical reactions, frequently involves an energy of activation. (16)

1.5.1 adsorption Isotherm:

The relationship between inhibitor and metal surface molecules can be interpreted by an adsorption isotherm model. It is known that in many corrosion systems, Langmuir model met the criterion of the inhibitors adsorption process since the surface of metal is monolayer (homogenous phase) and linear proportionality can be obtained between the c and c/θ values with best fitting correlation coefficient R^2.

The following equation gives Langmuir adsorption isotherm:

$$\theta = \frac{IE}{100} \ldots\ldots\ldots\ldots (1.4)$$

Where (θ) is″the degree of surface coverage″ and (IE) is″ inhibition efficiency″.

- **Langmuir adsorption Isotherm**

The amount of gas adsorbed by a quantity of know material or measuring the change in the weight of the surface of the gas at a known pressure. The relationship between the quantity of gas adsorbed in size or weight by a mass of know surface of the gas and pressure of equilibrium or concentration at the temperature is fixed by ″isothermic adsorption″; it can be calculated by the means of the following equation of Langmuir:

$$\theta = \frac{K_L \; C_i}{1+K_L C_i} \ldots\ldots\ldots (1.5)$$

Where K_L is "Constant equilibrium for Langmuir adsorption", which represents the adsorption degree (this means the higher its value (K_L) reflects that the inhibitor force fully sucked on the metal surface, and C_i is"concentration of inhibitor (ppm) ".

Reordering the equation (1.5) we get:

$$\frac{C_i}{\theta} = \frac{1}{K_L} + C_i \ldots\ldots\ldots (1.6)$$

Can draw $(\frac{C_i}{\theta})$ versus (C_i) we get values (k_L) "constant equilibrium".(17)

1.6 Copper and its alloys:

Copper and its alloys are materials that are widely used for their excellent thermal and electrical conductivities in many applications including electronics and in the integrated circuits manufacture. Copper is a relatively noble metal, needing strong oxidants for its dissolution or corrosion. The electrolytic plating or chemical dissolution are the main processes used in electronic devices fabrication. The corrosive solution that is most widely used include HCl, HNO_3 and H_2SO_4 (18) .

Copper can be used in industry applications as either in a pure metal state or alloying with other elements (e.g. Zn ,Ni ,Al, etc.) doping copper with such these elements can enhance its mechanical properties and higher corrosion resistance (19).

Alloyed copper with main elements for different industrial purposes can be mentioned as below:

- Coppers: alloys contain 99.3% of copper metal.
- Brasses: the main type of copper alloys (Cu+Zn) contains zinc as principle element with various percentages reaching up to 45%.
- Bronzes: alloys contain in as the only or principle element these alloys used for many outdoor applications.
- Copper-Nickel: these alloys contain nickel also known as nickel-slivers
- Copper-Leaded alloys: are alloys that contain lead with 20% or low as the principle element.
- Special alloys: other copper alloys that containing other elements that have not been mentioned above. (20).

1.7 Corrosion inhibitors:

Inhibitor is a substance that is put together to quite low concentration to protect the metal surface which is exposed to corrosion and eliminates or minimizes the metal corrosion. The use of inhibitors has been documented as an effective way to protect the metal materials from corroding (21). Due to the aggressive general acid solutions, inhibitors are used commonly to decrease the corrosive attack on metallic materials. Most of corrosion inhibitors are chemicals that synthetic and that are non-biodegradable, toxic, and expensive. For this reason, it is preferable to obtain from a particular source for inhibitors that are environmentally safe. Plant extracts became important since they are readily available, environmentally acceptable, and renewable source for inhibitors needed for a wide range. Plant extracts are seen as a rich source of naturally chemical synthesized compound which can be extracted by procedures that are simple and with low cost. Previously, natural products were used as inhibitors of corrosion for various metals in different environments and their concentrations that are optimum were reported. The obtained data reflected that plant extracts may serve an effective inhibitor of corrosion (22-24).

Nevertheless, the number of research dealing with this subject has recently increased in a continuous way. The major properties that enable them to be one of the classes of favourite new inhibitors of corrosion are their environmentally friendly behaviour, non-toxicity as well as their cheapness and renewability. However, the parameter that is the most important for the possibility evaluation to use such material as inhibitor of corrosion is the degree to which rate of corrosion is declined. The values of inhibition efficiency are over 90% in notable number of studies referring that some extracts of plant can be applied as corrosion inhibitors of efficient copper. (25).

An inhibitor of corrosion is a chemical compound that is used to decrease the rate of corrosion of a metal that is under exposure of an aggressive environment. Inhibitors of corrosion can be categorized based on their action mechanism of inhibitor as follows:

- Cathodic inhibitors
- Anodic inhibitors
- Mixed inhibitors. (26)

1.7.1 Cathodic Inhibitors

Cathodic inhibitors can reduce the rate of corrosion by either reducing the rate of reduction (cathodic poisons) or by a selective precipitating on active sties of cathodic. In most cases, the cathodic inhibitors decrease rate of cathodic reaction by limiting the diffusion of active (oxygen/hydrogen) reducible species on the surface of the metal thus reducing the rate of corrosion.

1.7.2 Anodic Inhibitors (Inorganic Inhibitors)

Anodic inhibitors operate by a significant shifting in corrosion potential towards anodic direction (noble direction). They block the anodic active sites by creating a protective layer; hence inhibit the dissolution of a metal. Inorganic anions such as molybdate, chromate and phosphate are usually used. The metal exhibits a special type of coating called "passive layer" which is formed because of the adsorption of these anions on the surface of the metal. The passivation phenomenon that occurred for some metals in certain environments is not quite understood; However, the formation of passive layer depends on the amount of oxygen, the environment nature and the concentration of ions that are aggressive.

1.7.3 Mixed-type Inhibitors (Organic Inhibitors)

Mixed-type inhibitors are also called Adsorption inhibitors are inhibitors that can be adsorbed on both anodic and cathodic active sites. As a result, they can retard both cathodic and anodic reactions and subsequently reduce the rate of corrosion. About 80% of mixed-type inhibitors are organic inhibitors. The most significant key property of organic inhibitors effectiveness comes from its adsorption characteristics which rely on the inhibitors chemical structure, type of environment and the metal surface charge. The adsorption process of organic inhibitors occurred via two possible mechanisms: physisorption and chemisorption. The physical adsorption represents an electrostatic interaction between the metal surface and inhibitor's charged species despite occurring rapidly, physisorption breaks down with increasing temperature. Chemisorption involves sharing of charge transfer between the molecules of adsorbed inhibitor and the surface of metal. Since chemisorption involves formation of a coordinated bond between adsorbed inhibitor molecules and the metal surface is required longer time to formulate than physisorption. In contrast of physisorption, the chemisorption is increased with increasing temperature. Chemisorption greatly depends on the inhibitor molecular structure. Since chemisorption involves electron donation, the inhibitors must contain heteroatoms. Heterocyclic compounds containing double or triple bonds, hydrocarbon chain, sulfur containing compounds and nitrogen consisting of compounds are regarded to be effective inhibitors. The ability of a compound to adsorb chemically depends on amount of heteroatoms and their chemical characteristics such as electronegativity and basicity. The greater electronegativity of an atom the lower its tendency to coordinate as the follow order.

The recent emphasis has been on the properties of inhibition of the natural products of plant origin, which have demonstrated good inhibitory efficiency, inhibitors generally contain heterogeneous atoms such as (P, N, O, S). which have been found to have electronic densities suitable for acting as an antidote to corrosion an (P, N, O, S) are the active center of the adsorption process on the metal follows the inhibitory efficiency of P>S>N>O (27).

It is friendly to the environment:-

- Olive plant: the olive tree is an evergreen tree and has the ability to withstand harsh environmental (28).

Man has dealt with this tree since the beginning of the ages, relying on the oil of fruits because of its economic importance and food. The active compounds in olive tree leaves were extracted by many researchers as they were found to contain a group of active compounds through the use of a technical measure GC-MS (gas chromatography mas spectrometry).

The highest percentage of these compounds were compounds for turbines, essential oil, alkaloids, phenol compounds, alorubin and other compounds.

The phenolic compounds were extracted from olive leaves varieties consisting of gallic acid, caffeis acid, vanillic acid, P-hydroxy benzoic acid, and syringic acid (29) .

A lot of attention has been paid to the olive tree at the present time. The olive tree leaves are of high medical importance and olive trees have economic and environmental benefits and fruit of great benefits. In addition, its leaves have a lot of medical effects (30).

- Eucalyptus plant: it is a large long-standing tree that can grow up to several meters and grow in water reclaimed land. Its long roots, which are thirsty for water, can dry the earth, grow very fast and emit a strong odor that expels insects from its surroundings (31) .

It has been found that eucalyptus leaves extracts contain high percentage of turbines, essential oil, alkaloids, phenol compounds, alorubin and other compounds which can work as good effective corrosion inhibitors. (32)

1.8 mechanism of corrosion:

The main cause of the corrosion process is the lack of stability or stability of the metal (alloy) (33) .Corrosion occurs as a result of reactions oxidation and reduction where this corrosion type is known as electrochemical corrosion. The general interaction of electrochemical corrosion is:

$$\mathbf{M} \leftrightarrow \mathbf{M}^{n+} + \mathbf{n\,e}^{-} \ldots\ldots (1.7)$$

Where M refers to the metal and M^{n+} represents the ion of the metal and n stands for the number of electrons. The frontal interaction is a reaction of oxidation of an anodic reaction, the back interaction is the reaction of a cathode reaction. (34)

It can be proposed that $CuCl_2^-$ complex could be created either by direct formation from the metal: (35).

$$Cu + 2Cl \leftrightarrow CuCl_2 + e^{-} .... (1.8)$$

Or

$$Cu + Cl^{-} \leftrightarrow CuCl + e^{-} ..... (1.9)$$

$$CuCl + Cl^{-} \leftrightarrow CuCl_2 + e^{-} .... (1.10)$$

The dissolution could also have copper dissolution as the Cu^+ in the first example:

$$Cu \leftrightarrow Cu+ + e^{-} .... (1.11)$$

$$Cu+ + 2Cl^{-} \leftrightarrow CuCl_2 ...... (1.12)$$

At the current minimum, the surface CuCl coverage reached its maximum. However, CuCl species obtain sufficient protection, because of metal dissolution, reaction (1.10), film dissolution, and reaction (1.12), the current density increases progressively. The complex of cuprous chloride can further dissolve based on:

$$CuCl_{2,\ \mathbf{ads}} \leftrightarrow Cu^{2+} + 2Cl^{-} + e^{-} .... (1.13)$$

Hence, the whole reaction for copper corrosion can be illustrated by:

$$2Cu + 4H+ + 4Cl^{-} + O_2 \rightarrow 2Cu^{2+} + 4Cl^{-} + 2H_2O ..... (1.14)$$

1.9 Mechanism of copper corrosion inhibitor:

Copper and alloys corrode with formation of oxides layers (patina). However, these patinas have a tendency for degradation when exposed to polluted atmosphere (36).

The mechanism of the action of a corrosion inhibitor relies on its chemical nature. For instance, organic inhibitors (OI), when put together with the solution, it is adsorbed on the surface of the metallic by displacing the molecules of water and aggressive agents eventually such as chloride ions based on the reaction scheme illustrated below.

$$\mathbf{OI}_{\text{electrolyte}} + \mathbf{nH_2O}_{\text{ads. Surf,}} \Leftrightarrow \mathbf{OI}_{\text{ads. Surf,}} + \mathbf{nH_2O}_{\text{electrolyte}} \ldots\ldots. \quad (1.15)$$

In organic molecules, the heteroatoms presence such as O, N, and S, which have higher density of electron and operate as active centers for chemical or physical adsorption on the surface are the main reason for the molecule inhibition ability (7).

In contrast, in acidic solution the inhibitor could be expected to be adsorbed on a clean copper surface. (37)

1.10 Literature Survey:

Antonijevic. M. M and Petrovic M. B. **(2008)**, studied the copper electrochemical corrosion and likelihood of its prevention using the inhibitors that are examined. Inorganic compounds are examined as well. However, the organic compounds with their derivatives are in larger numbers. Research aims to influence the structure of compounds, method of application, concentration, as well as media that inhibitor is used in on efficiency of inhibition. Moreover, mechanisms of action are studied. The attempts to find models, which can help possibilities prediction of compounds that are newly synthesized to act as inhibitors of corrosion. Hence, combining practical investigations and theory and of substances with similar structure are quite important (38) .

Taleb H. Ibrahim, et al **(2011),** investigated mild steel corrosion inhibition in 2M in HCl solution employ potato peel extract(PPE) , using electrochemical techniques and weight loss. The results demonstrated increment in the efficiency of inhibition with increment (PPE) concentration. A sensible level of inhibition of corrosion was obtained at a 50 ppm concentration (>70% efficiency of inhibition). Nyquist plots from the data of resistance reflected that upon increment the concentration of PPE, the impedance increment of charge transfer and the double stratum capacitance fell. The film adsorption extract of the sample of mild steel was also identified to follow up isotherm of Langmuir adsorption. Pursuant to electrochemical tests conducted, (PPE) was identified to act as an inhibitor that is a mixed kind (39).

Ramananda S. Mayanglambam, **(2011),** investigated the effect of Musa paradisiaca extract on inhibition of corrosion of mild steel in aqueous 0.5 M sulphuric acid that was examined by the method of weight loss, electrochemical impedance spectroscopy (EIS), and the technique of potentiodynamics polarisation. The inhibition efficiency is identified to increase with rise in extract concentration. Polarization measurement shows that Musa paradisiaca acts as a mixed type inhibitor and the efficiency of inhibition declines with an increase in temperature. The inhibition is supposed to happen by the adsorption of molecules of inhibitor on the surface of metal, which follows the isotherm of Langmuir adsorption. Other thermodynamic parameters in addition to the activation energy (Ea) for the process of inhibition were calculated. These thermodynamic parameters shows a strong interaction between the mild steel surface and the inhibitor. SEM and AFM studies gave a confirmation in relation to the inhibitor molecules adsorption on mild surface of the steel.**(40)**

Rocha J.C. et al, **(2012)**, studied grapes pomace extracts as a friendly inhibitor of corrosion for carbon steel in 1 mol L^{-1} HCl solution. The action of inhibition of the extract was explored using impedance spectroscopy weight loss, surface analysis, and potentiodynamic polarization. The grape extract was found to be have effectiveness against steel corrosion .The inhibition efficiency was increased with rising extract concentration and decreased with rising temperature. The adsorption of the grape extract was followed isotherm of Langmuir adsorption (41).

Al-Rawashdeh N. et al, **(2012)**, studied the effect of secretion of gum from Acacia trees (Gum Acacia, GA), in acidic media on the mild steel corrosion which was examined by weight loss, methods of electrochemical polarization, and hydrogen evolution; also, morphology of surface was analyzed by scanning electron microscopy (SEM), and techniques of X-ray photoelectron spectroscopy (XPS). The hydrogen evolution results, methods of electrochemical polarization, and weight loss showed that the efficiency of the inhibitor was (I%) increment with concentration of increment inhibitor. The efficiency of inhibitor (I%) in hydrochloric acid indicated ton be more than ones in sulfuric acid because of the synergistic effect. The inhibition efficiency percentage (I%) of corrosion of steel with GA is highly increment in the availability of a field that is external and magnetic. Weight loss method results are quite consistent with ones gained by the method of hydrogen evolution, and both show that inhibitor efficiency rises with increasing concentration of inhibitor and the external magnetic field presence. Electrochemical polarization research reflected that Gum Acacia is seen as mixed type inhibitors. The results showed that Gum Acacia gave mild steel a high good protection against corrosion in media that is acidic (42) .

Pandian Bothi Raja, et al **(2013)**, explored the bark extract effect, 3b-isodihydrocadambine and N. cadamba leaves on the mild steel in 1 M HCL .Results proved that all these green inhibitors reflected excellent performance (which is more than 80% at 5 mg L^1) as inhibitors of corrosion. They inhibit corrosion through the process of adsorption and were identified to follow isotherm of Langmuir adsorption. Impedance studies showed that the inhibitors decreased the rate of corrosion by rising the system resistance, and the equivalent circuit was identified to match well with CPE. Potentiodynamic polarization research provided a confirmation that all the inhibitors were performed through mixed type of mechanism of corrosion inhibition **(43)**.

Hamdy and El-Gendy **(2013)**, studied the Different concentrations of henna leaves of steel of carbon in (1M) of hydrochloric acid, using polarization and weight loss. The test was conducted at two temperature levels (293-313)K. this study indicated that the inhibitory efficiency increasing with the rise of the concentration that is inhibitory but declining by reducing the temperature. The energy of the activation and the free energy were found to reach the metal surface where the process is random and the heat absorbent **(44)** .

Anbarasi and Vasudha, **(2014)**, studied the effect of Cucrubita maxima plant as inhibitory of steel of carbon in (1M) of (HCl) by weight loss; it has been found that Cucrubita maxima peel is a good inhibitor, where the of inhibition efficiency was reduced with risen inhibitor concentration and where it achieved the highest efficiency (93%) at the (2 v/v) concentration **(45)**.

Ajee and Zain alabdin, et al **(2014)** investigated the palm tail herb that was used as an inhibitor with different concentrations for corrosion of brass used in heat exchangers in industrial waters. The study was conducted in a way similar to those experienced for heat exchangers. Microscopy, electronic, and X-ray techniques were used. The results gained from the curves of polarization reflected an inhibition of 91.1% in (298) K **(46)**.

Eliane D'Eliaa **(2015)**, studied the toasted coffee extract conduct and its isolated high molecular weight fraction, carbon steel corrosion inhibitors which have been investigated in HCl solution through scanning electron microscopy analysis, measurements of weight lack, electrochemical impedance, and potentiodynamic polarization curves. All results indicated that the weight fraction that is high molecular and rich in melanoidins, presents a vital role in the action that is inhibitory of the toasted coffee extract in the carbon steel acid corrosion. **(47)**

Savita, et al, **(2015)**, studied The effect of Citrus aurantium (CAU), Capsicum annum (CAN), and Moringa oleifera (MOL), as a new environmentally friendly inhibitor in the copper corrosion in Nitric Acid solution. the techniques of Gravimetric and electrochemical spectroscopic and potentiodynamic polarization, which have been used for the inhibition efficiency evaluation and used in accordance with the electrochemical tests carried out these extracts that were identified to be shown as a mixed inhibitors which are cathodic predominantly. The film adsorption extract of copper sample was also recognized to follow up isotherm of Langmuir adsorption **(48)**.

Al-Fakih. A.M. et.al, (**2015**) examined the effect of turmeric and ginger extracts on mild steel corrosion in 1 M HCl. Their inhibition performance was examined using potentiodynamic polarization and the method of weight loss. Weight loss measurements were conducted at various temperatures for 1 h immersion time. The measurements of polarization reflected that both of inhibitors acted as mixed-type ones. The efficiency of inhibition rose with the rise of the inhibitors concentrations reaching up to 92 and 91% at 10 g/L of turmeric and ginger respectively. The adsorption of both inhibitors showed to be obeyed Langmuir adsorption isotherm **(49)**.

André de Mendonça Santos, et al **(2016)**, studied the castor bark powder effect for carbon steel as a inhibitor of corrosion in acidic media (HCl 0.5 mol.L^{-1}), weight loss measurements , polarization curves, electrochemical impedance spectroscopy (EIS), and scanning vibrating electrode technique (SVET). Which have been used to give the evaluation of the efficiency of inhibition. The gravimetric results and EIS showed increment the inhibitory efficiency with concentration of inhibitor by 83%.Fourier transform infrared spectroscopy (FTIR) analyses indicate a presence of heteroatoms of S, N and O. The Thermodynamic considerations showed that inhibitory molecules of low density on the surface of the metal (physisorption) according to the isotherm of Langmuir kind adsorption **(50)**.

Thiruvengadam Venugopal, et al, **(2016)** investigated the extract of prosopis juliflora which was examined as an inhibitor of corrosion for mild steel in 1M HCl using electrochemical impedance spectroscopy (EIS), weight loss measurements, and poten tiodynamic polarization. The efficiency of inhibition of Prosopis juliflora rises with an increase in temperature and concentration of inhibitor. Polarization research showed that prosopis juliflora acts as inhibitor that is a mixed type for mild steel in 1M HCl. AC impedance shows that the charge transfer resistance value rises with the rise in the concentration of the inhibitor. Thermodynamic parameters like enthalpy, activation energy, free energy, and entropy were calculated. The surface morphology of prosopis juliflora reflects a significant enhancement of the mild steel surface (51).

Roland T. Loto and Cleophas A. Loto, **(2016).** studied the allium sativum(garlic) extract effect which is considered as a ‘green’ inhibitor on α-brass in 0.5M HNO_3 and it was studied at temperature that is ambient. The rate of corrosion and weight loss and the techniques of potentiodynamic polarization measurement were employed for the experimental work. The results showed that the garlic extract effective corrosioninhibition on the test-specimens in the various concentrations of the test medium. There was rise of the performance of the inhibition with rising inhibitor concentration. The best performance of inhibition was accomplished with the 100% (as extracted) concentration of garlic. (52).

Abd El-Aziz S. Fouda, et al, (**2017).** Investigated the effect of calotropis procera (CP) extract on the inhibition of corrosion of 304 stainless steel (SS). Which was studied in 2M HCl. using electrochemical frequency modulation (EFM), methods of chemical weight loss electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PP) at 25ºC. The extract adsorption on 304 SS roof has a compatibility with isotherm of Langmuir adsorption. The plots of polarization reflected that the extract addition shifts the anodic and cathodic branches towards the currents that are lower. The shifts show that extract CP operates as a mixed-type inhibitor. The thermodynamic parameters of adsorption and activation processes were discussed and calculated. The morphology of surface of the 304 SS specimens was evaluated using various techniques and this is because of a physical adsorbed film formation on the surface of the metal. The SEM images of the 304 SS samples revealed that the metal was kept safe in the extract presence (53).

Sunday O. Ajeigbe, et al., **(2017)** examined the corrosion inhibition optimization of essential oils of alpinia galangal on mild steel by using methodology of response surface. The natural products of the plant were identified to be cheap, effective, and eco-friendly anticorrosion agents. Inhibitions of corrosion of essential oils of alpinia galanga were studied on mild steel in solution of hydrochloric acid by using the method of weight loss. The interactive effects of inhibitor concentration, time, and temperature were optimized for maximum response of efficiency of inhibition using methodology of response surface with central composite design. The optimum efficiency of inhibition of 88.5% at 775 ppm of inhibitor concentration, reaction time of 3.75 hours, and temperature of 320.4 K were achieved. The inhibitor effectiveness was also sustained by using scanning electron microscopy. The interaction mechanism of the inhibitor on mild steel surface was seen to have conformity to the isotherm of the Langmuir adsorption.(54)

Harshana Lakmal O. and Aashani Tillekaratne, **(2018**) studied the characterization and improvement of green inhibitors for corrosion using costus speciosus extract on the mild steel corrosion in 1M HCL. Inhibition of corrosion by natural compounds obtained attention to methods that are conventional because of the harmful effects associated with conventional synthetic inhibitors that are harmful to others and the environment. This study was investigated in the extraction of costus speciosus, which is widely found in Sri Lanka commonly known as Thebu; it has been investigated as a potential that is anti-corrosion. The methanol extract from thebu leaves showed a maximum 10% inhibition efficiency in HCl media, as evidenced by the results from electrochemical measurements and measurements of weight loss (both impedance spectroscopy and Tafel plot analysis). As indicated by isotherm adsorption, it investigates the mechanism of adsorption of the inhibitor molecules to the surface of the metal surface as determined by the chemisorption by creating a monolayer (55).

Bensouda Z. et al., **(2018)** explored thymus sahraouian essential oil (TSEO) as an environmentally friendly corrosion Inhibitor of Mild Steel in HCL media. TSEO operated as an efficient inhibitor of corrosion for mild steel in 1 M HCl, and its efficiency of inhibition rose with a concentration of 77.82 % at 2 g L^{-1}. The curves of polarization showed that TSEO operated as a mixed type inhibitor, with predominant anodic action. The EIS studies were fitted to a suitable equivalent circuit model, at 293 K, only reflecting a one-time constant characteristic of a charge transfer process. Besides, the higher is the temperature the lowest is the inhibiting efficiency. The kinetic parameters were in favour of an electrostatic character of TSEO components adsorption onto the mild surface of steel, and adsorption followed model of the Langmuir isotherm. Energy dispersive X-ray spectroscopy analyses and micrographic scanning electron microscopy provided a confirmation for the formation of a adsorbed protective film upon the mild surface of steel (56)

Khalifha and Al-Tikriti **(2018)**, studied the corrosion of carbon steel in H_2SO_4 solution using plant extracts which they are purslane and salsola. Their inhibition per formance was determined by using electrochemical and weght loss method. It was found that these inhibitors had a high efficiency against corrosion of carbon steel in (1M) H_2SO_4 the measurments revealed that extract of salsola plant is better inhibitor then purslane for the alloy with maximum efficiency 99.8%. The adsorption of these inhibitors on the alloy surface followed langmiur adsorption isotherm. SEM technique was used to study the surface of the metal befor and after corrosion with presence and absence of inhibitors.(57)

1.11 The aim of study:

The study objective is

1. Studying the copper behavior by using the static stress technique at different concentrations of hydrochloric acid (0.1-0.3-0.5) M and in four different degrees of temperature in the range of (298-313)k.

2. Characterization of olive and eucalyptus leaves extracts using GC-MS and techniques of FTIR.

3. The study of the inhibitors effect with different concentration of olive leaves and eucalyptus (50-100-200-400) ppm in copper corrosion at the concentration (0.5) M of acid and at four degrees of temperature in the range of (298-313)k .

4. Study copper surface morphology in presence and absence of 400 ppm of olive and eucalyptus leaves extracts using SEM technique.

2.1 Chemicals used

2.1.1 Copper Alloy

The copper alloy used consists of 99% copper and 1% impurities. Checked in Standardization and quality control device (Iraqi Ministry of science and technology).

2.1.2 Chemicals

The chemicals used in the study are shown in Table (2.1):

Table (2.1): The chemicals that are used in the study.

Material	Supplier	%purity
Hydrocloric Acid	CDH	98
Methanol	Sigma-aldrich	99
Acetone	ROMIL-SA	95
Diamond product spray	Struers	High quality diamond product

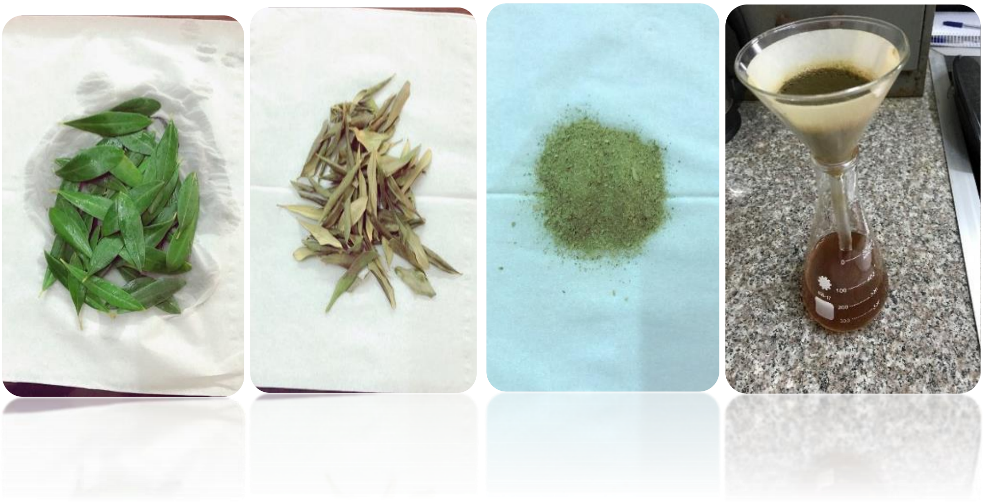
2.2 Extraction

In recent years, extracts of plant have been commonly used as environmentally friendly inhibitors of corrosion. There is no fixed way to extract them. In this study olive and eucalyptus leaves will be extracted by hydrochloric acid (0.5M).

2.2.1 Olive and eucalyptus leaves extraction

Olive and eucalyptus leaves were extracted in the following steps, as shown in Figures (2.1) (2.2).

1. Leaves of olive and eucalyptus were collected from the trees in Baghdad city and then they were washed and left for 3 days in the oven at a degree of 80 °C to dry.
2. The leaves that were dried are thoroughly grinded using an electric grinder for get a fine powder. The powder was sifted using a (90 µm × 17 cm) sieves.
3. 25 gm of olive and eucalyptus powder was taken and melt in 400 ml of 0.5M HCl and heated the mixture over the heat plate for 10 minutes and then cooled in room temperature and out of light.
4. Filter the mixture with filter paper. Then prepared different concentrations (50,100,200 and 400) ppm from stuck solution.



(1) (2) (3) (4)

Figure **(2.1):** Steps to extract Olive leaves

(1) (2) (3) (4)

Figure (**2.2)**: Steps to extract Eucalyptus leaves

2.3 Methods of preparation:

●Preparation of cell solution

According to the information on the winchester, the standard concentration of HCl is 11 M. The stock solution were prepared using the dilution law.

♦To obtain HCl at 1M concentration, 91 ml HCl was taken in 1000ml distilled water according to the mitigation law.

♦Prepare various concentrations HCl (0.1, 0.3, and 0.5) M through mitigation law by taking (100, 300 and 500) ml of HCl (1M) solution in to 1L distilled water.

● Specimen Preparation

The samples of copper were cut into circular pieces with thickness of 2 mm and a diameter of 2cm and they were refined using various emery paper grades of (180, 400, 800, 1200, 2000). Then, they were rinsed with the use of acetone and Diamond product spray. Finally, they were washed with the use of the distilled water and then they were left to dry and kept away from the air to prevent oxidation.

2.4 Devices and Technologies

The devices and techniques used in this research are shown in the Table (2.2).

Table (2.2): the instrument were use in this study.

Instrument	Origin	Model	Function	Work place
Potentiostat / Galvanostat	Germany	M Lab 200 with software	The Test of Corrosion	College of Education for Pure Sciences /Ibn Al-Haitham
Thermostated water bath	Germany	Julabo U3	Controlled the Temp of specimen	College of Education for Pure Sciences /Ibn Al-Haitham
Magnetic stirrer	England	Ms400	Mix the solution	College of Education for Pure Sciences /Ibn Al-Haitham
pH meter	England	Kent industrial measurement	Adjust the pH of the solution	College of Education for Pure Sciences / Ibn Al-Haitham
X- ray Diffractometer (XRD) powder	Bruker (Germany)	2D PHASER	Identify the corrosion products and crystline phases	Standardization and quality control device
Gas Chromatography Mass Spectrometer (GC-MS)	Japan	Shimadzu QP2010	Identify the major organic compounds present in a ample	The ministry of science and technology
FT-IR spectrophotometer	Japan	IRPrestige-21	Molecular composition	University of Baghdad –laboratories ibn Sina
Scanning Electron Microscopy (SEM)	FEI	Inspect-S50	Examine the morphoiogy of surface	Al-Nahrain University

2.4.1 Electrochemical test:

It is a system of measuring the corrosion on different alloys , which consists of several major parts and illustrated in Figure (2.3) .

Figure **(2.3)**: Electrochemical test

2.4.1.1 Potentiostat/ Galvanostat:

M lab is a significant major advance instrument for electrochemical measurements. It has a complete control station for electrochemical cell, the software of M lab cares for controlling the potentiostat, recording and processing data. It is provided with electrochemical calculation such as Tafel line evaluation.

Each M lab communicates with personal computer by a RS 232 serial cable. M lab is controlled by computer desktop. The M lab software cares for controlling the potentiostat, recording and processing data, as shown in figure (2.4).

Figure (**2.4**): Potentiostat Galvanostat device

2.4.1.2 Corrosion cell

The corrosion cell consists of 1L container made of pyrex, which contains a corrosion solution and is covered with a cover made of plastic containing openings for the rest of the cell parts. There is a connection between instrument M Lab and electrochemical cell and this can be done by an appropriate cable; the connector cable bears the two lines (potential sensing Line and current line) and the counter electrode line. The measurement of working electrode potential (W.E.) was conducted against reference electrode (R.E.), which is set in the electrochemical cell which is quite close to the working electrode surface.

2.4.1.3 The Corrosion Cell Electrodes:

a. Working Electrode:

Working electrode is the electrode that binds to the alloy and is placed inside the corrosion cell where the cover contains a hole with a diameter of 2 cm allows the contact alloy with the solution of corrosion The specimen is set between an electrically contacted brass plat and a mask with round opening, the specimen backside and the disk interior hole are sealed by washer to keep dryness in it, as shown in Figure(2.5).

Figure (**2.5**): Working pole

b. Reference Electrode:

Silver-silver chloride electrode was used owing to its simplicity and high reproducibility this electrode include silver chloride silver wire, and chloride ions (58). The electrode is usually brought in contact with electrolyte by a glass tube known as "Luggin capillary", as shown in Figure (2.6). The tip of the luggin capillary was put as closed as possible to the surface of the working electrode in the corrosion cell.

The reduction reaction which occurs in the silver-silver chloride electrode may be represented as:

$$AgCl + e \rightarrow Ag + Cl^{-} \qquad E^{\circ} = 0.2223\ V \ \ldots\ldots (2.1)$$

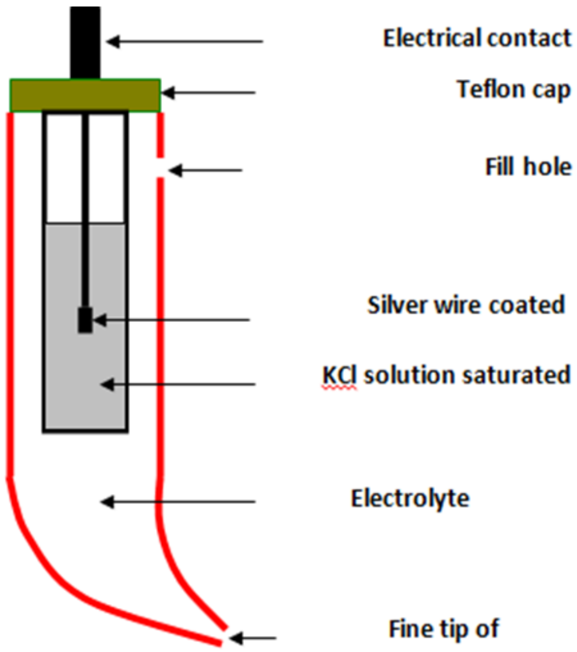


Figure **(2.6):** Reference electrode

c. *Auxiliary Electrode:*

Counter electrode or auxiliary electrode that is used in this study is electrode of platinum because of its high catalytic activity and large surface area. It give an access to the electrical current, which is essential to produce the potential difference which is required (59).

2.5 Magnetic stirrer:

A magnetic stirrer is defined as a laboratory instrument in which a rotating magnetic field is used to produce stirring bar.

2.6 Experimental procedure:

Polarization measurements were carried out according to the following points

1. One liter of solution (HCl) at a given concentration was transferred to the polarization cell.
2. The temperature of the solution was brought to the desired value within 0.01 C° by using thermostat water bath circulator.
3. The specimen of copper was mounted on the working electrode holder with mask opening size 1 cm^2 .
4. The reference electrode (silver-silver chloride) consists of two tubes, the inner tube contains Ag, AgCl; KCl. The outer tube was filled with the prepared salt solution. The reference electrode was placed as close as possible to the surface of the working electrode.(<2mm).
5. The electrochemical cell should be connected to the instrument (M lab potentiostat/ galvanostat) which was connected to a personal computer by suitable cable and controlled by computer desktop.
6. The potentiostat and computer were switched on in order to begin the measurments. The operation program involved sending a set of commands from the computer to the potentiostat.
7. The first programmed step in this measurement was opened circuit potential (ocp) over a potential range about ± 200 mv from the opened circuit. The scan rate was 10 mv.

2.7 Characterization Techniques used in research:

Several techniques that were used in this studs where it was useful to provide knowledge of the chemical composition of extracts, the active groups in it. Other techniques to understand the proportions of elements in the alloy, and the effective inhibitor on the alloy; these techniques are as follows:

2.7.1 Special tests for alloy:

a. X-Ray Diffraction (XRD) Powder:

XRD measurement operates via a diffractometer as shown in figure (2.7). The basic of XRD involves interaction of incident light (accelerating electrons) and the crystalline sample. The accelerating electrons have a sufficient energy to reach out the inner shells once the radiation hit the target it will be diffracted at specific angle called (2θ) according to the crystalline content of the substance the greater its crystalline content the greater its intensity.

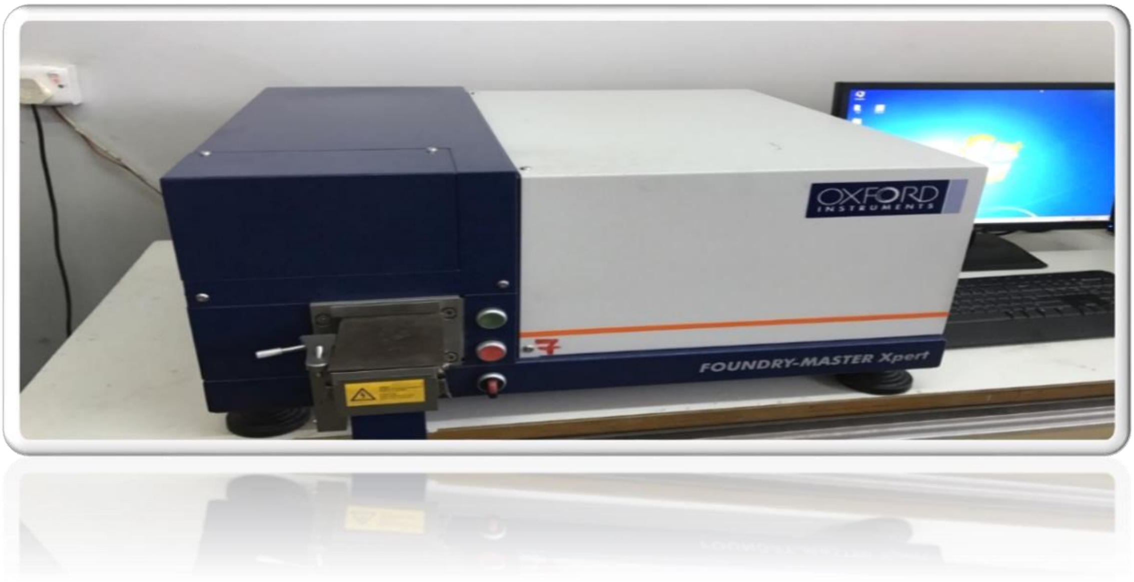


Figure **(2.7):** X-Ray Diffractometer

b. Scanning Electron Microscope (SEM):

SEM is defined as an analytical tool that measures topography of the surface using electron beams that are energetic; it produces an image using electrons that interact with the atoms in the sample and produce various signals having information about the topography and composition of the surface. The electron beam is generally scanned by the use of a raster scan, and the location of the beam is merged with the signal to create the image. In general, SEM made mainly supplies images based on the topographical in formation,(60)

As shown in Figure (2.8)

Figure **(2.8)**: Scanning Electron Microscope

2.7.2 Special tests for the inhibitor:

a. Gas Chromatography Mass Spectroscopy (GC-MS):

It is defined as a chemical analysis device that is used to separate and distinguish the chemicals in sample. The device uses a long and narrow tube known as the tube of the chapter where the injection of the sample inside separate the chemical composition of the sample, moving at varying speeds depending on the different chemicals and physical properties of each substance. When chemicals are released by the column, they are detected and marked electronically. The function of the column is to separate and concentrate the different sample components in order to amplify the signal that is detected, as shown in Figure (2.9).

Figure **(2.9):** showing Gas Chromatography Mass Spectroscopy

b. Fourier Transform Infrared Spectroscopy (FTIR):

The importance of the use of this spectroscopy lies in its ability in determining the functional groups in organic compounds under study. In addition, the infrared spectroscopy, it is possible to identify the presence of several compounds such as alcohols, alkanes and other materials. The infrared spectroscopy measures the interacting infrared radiation with a molecule and then measure the vibration of atoms of this groups. By scanning the sample over wave numbers range (4000-400)cm^3. Depending on the amount and intensity of transmitted light it is possible to determine the functional group of compounds.

Figure **(2.10)**: Fourier Transform Infrared Spectrophotomete

3.1 Analysis of FTIR spectra of Olive and Eucalyptus leaves:

Fourier transform infrared method have been used to analysis the complex nature of leaves extracts, which proved the presence of different organic compounds. Many studies have been reported that olive and eucalyptus leaves contains different natural compounds (61).

Fig. (3.1) shows the spectra of olive leaves. A wide broad peak at 3255.84 cm^{-1} of O-H band confirms the presence of alcohols compounds and carboxylic acids. The sharp mid-intense peak at 1685.79 cm^{-1} attributed to carbonyl group C=O which lead to presence of aldehydes, ketones and carboxylic acids.

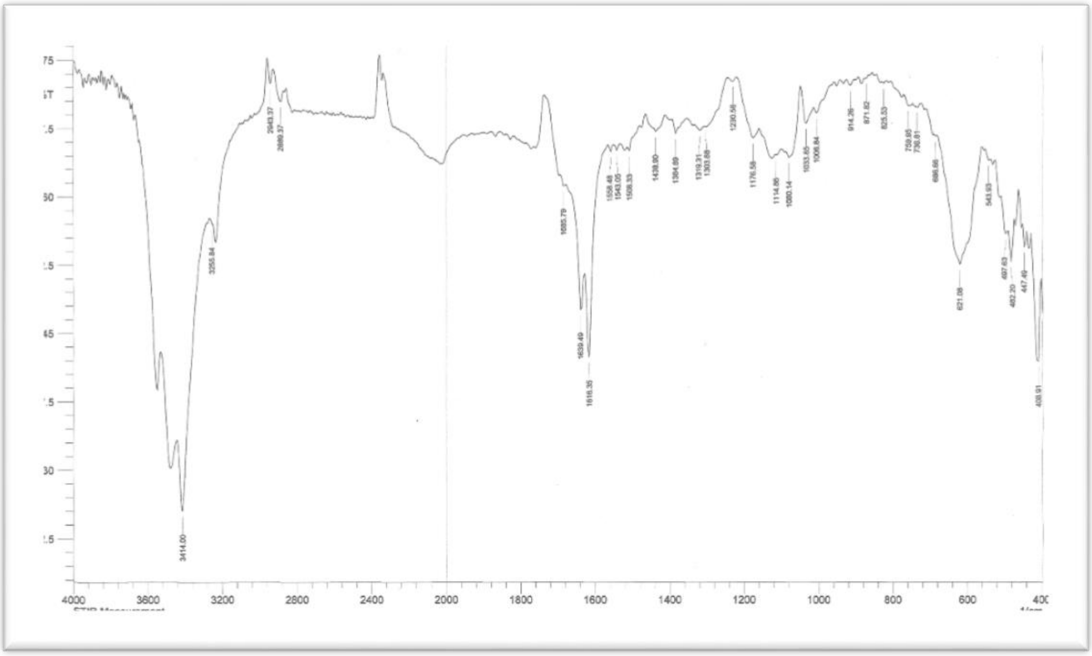


Figure (3.1): shows the FTIR spectrum for Olive leaves powder.

The other important peaks have been listed in the table below.

Table (3.1): The main FTIR bands in Olive leaves powder

No.	Peak number (cm^{-1})	Bond	Group assignment
1	3414	N-H	Amines and amides
2	3255.84	O-H	Alcohols and carboxylic acids
3	2889.37	C-H	Alkanes
4	1685.79	C=O	Carbonyl compounds
5	1639.94	C=C	Alkenes
6	1616.35	C=N	Nitro Compounds
7	1176.58	C-N	Amides
8	1114.86	C-O	Ethers

The FTIR spectrum for olive leaves powder's spectrum, the spectrum has some similarities in compare with eucalyptus leaves powder spectrum. Figure (3.2) shows the FTIR spectrum for Eucalyptus leaves powder.

A wide broad peak at 3236.55 cm^{-1} of O-H band confirms the presence of alcohols compounds and carboxylic acids. The sharp mid-intense peak at 1751.36 cm^{-1} and this attributed to carbonyl group C=O which indicates the presence of aldehydes, ketones and carboxylic acids

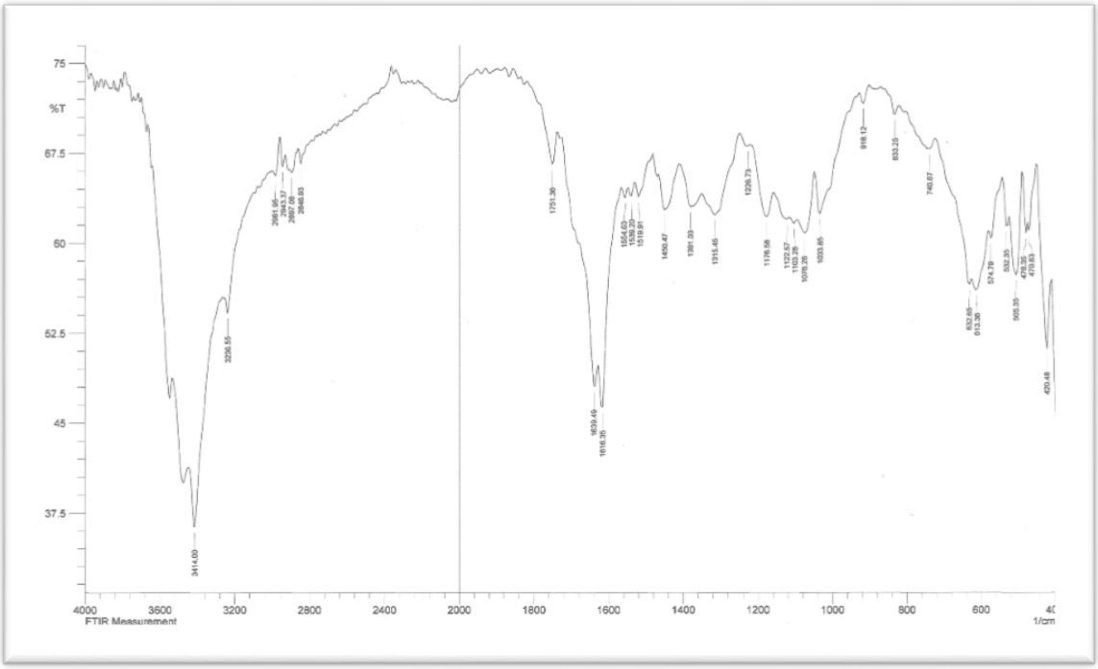


Figure (3.2): shows the FTIR spectrum for eucalyptus leaves powder.

The other important peaks have been listed in Table (3.2).

Table (3.2): The main FTIR bands in Eucalyptus leaves powder

NO.	Peak number (cm^{-1})	Bond	Group assignment
1	3414	N-H	Amines and amides
2	3236.55	O-H	Alcohols and carboxylic acids
3	2897.08	C-H	Alkanes
4	1751.36	C=O	Carbonyl compounds
5	1639.49	C=C	Alkenes
6	1616.35	C=N	Nitro Compounds
7	1176.28	C-N	Amides
8	1122.57	C-O	Ethers

The spectra of both extracts have the presence of different compounds (unsaturated compounds, nitrogen and oxygen containing compounds) which can be expected as good corrosion inhibitors.

3.2 Gas Chromatography Mass Spectroscopy (GC-MS):

The spectral of both extracts have elucidated the presence of different compounds (unsaturated compounds, nitrogen and oxygen containing compounds) which can be expected as good corrosion inhibitors.

Figure (3.3) shows the GC-MS spectrum of methanolic extract of Olive leaves, and table (3.3) demonstrates the chemical structure, nomenclature, retention times, and molecular weight.

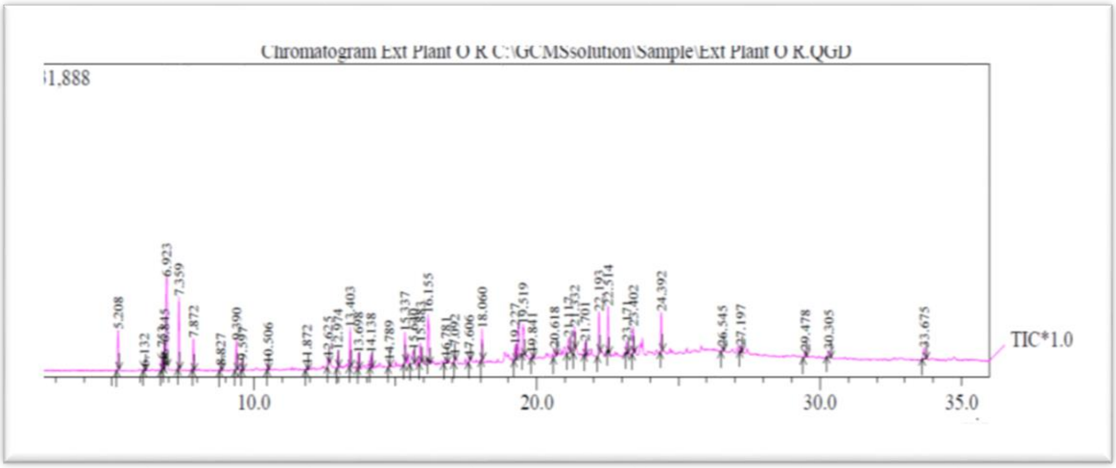
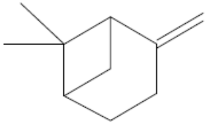
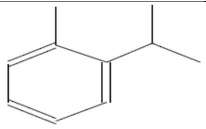
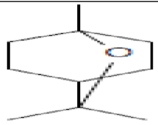
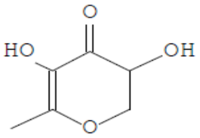
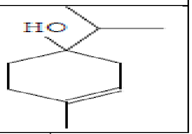
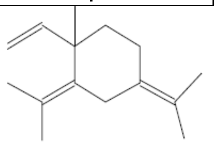
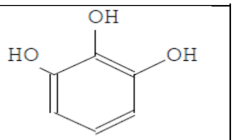
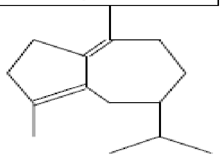
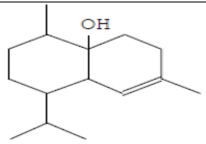
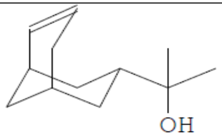
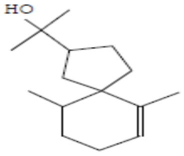
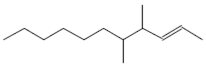
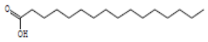
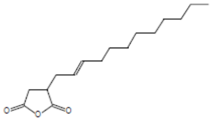
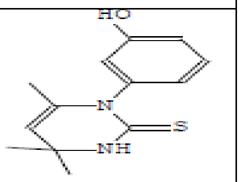
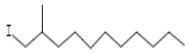
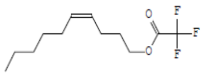
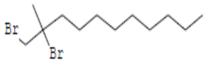
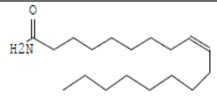
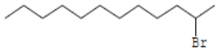


Figure **(3.3)**: Chromatogram of methanolic extract of Olive leaves.

Twenty identified active compounds have the most abundance percentages in the methanolic extract of olive leaves more than other existed compounds that they did not appeare in the spectrum.

Table **(3.3)**: Major identification compounds in methanolic extract of Olive leaves.

NO.	**Name of compound**	**RT (min)**	**Chemical formula**	**M. Wt (g/mole)**	**Structure**
1	6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane	5.208	$C_{10}H_{16}$	136	
2	1-Isopropyl-2-methylbenzene	6.753	$C_{10}H_{14}$	134	
3	p-Menthane, 1,8-epoxy-	6.925	$C_{10}H_{18}O$	154	
4	3,5-Dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one	8.825	$C_6H_8O_4$	144	
5	p-Menth-1-en-4-ol,	9.392	$C_{10}H_{18}O$	154	
6	1-Methyl-2,4-bis(1-methylethylidene)-1-vinylcyclohexane	11.875	$C_{15}H_{24}$	204	
7	1,2,3-Benzenetriol	12.625	$C_6H_6O_3$	126	
8	5-Isopropyl-3,8-dimethyl-1,2,4,5,6,7-hexahydroazulene	12.975	$C_{15}H_{24}$	204	
9	1-Isopropyl-4,7-dimethyl-1,3,4,5,6,8a-hexahydro-4a(2H)-naphthalenol	14.792	$C_{15}H_{26}O$	222	
10	2-Bicyclo[3.3.1]non-6-en-3-ylpropan-2-ol	15.642	$C_{12}H_{20}O$	180	
11	2-(6,10-Dimethylspiro[4.5]dec-6-en-2-yl)-2-propanol	15.883	$C_{15}H_{26}O$	222	

12	(2E)-4,5-Dimethyl-2-undecene	16.783	$C_{13}H_{26}$	182	
13	Palmitic acid	17.092	$C_{16}H_{32}O_2$	256	
14	2,5-Furandione, 3-dodecenyl	17.608	$C_{16}H_{26}O_3$	266	
15	2(1H)-Pyrimidinethione, 3,4-dihydro-1-(m-hydroxyphenyl)-4,4,6-trimethyl	19.225	$C_{13}H_{16}N_2OS$	248	
16	1-Iodo-2-methylundecane	19.842	$C_{12}H_{25}I$	296	
17	(Z)-4-Decen-1-ol, tri fluoro acetate	20.617	$C_{12}H_{19}F_3O_2$	252	
18	1,2-Dibromo-2-methylundecane	21.117	$C_{12}H_{24}Br_2$	326	
19	Oleic acid amide	23.175	$C_{18}H_{35}NO$	281	
20	2-Bromo dodecane	26.542	$C_{12}H_{25}Br$	248	

For the eucalyptus leaves, the chromatogram of methanolic extract of the leaves is shown in Figure (3.4). The spectrum confirmed the presence of fifteen phytochemicals compounds which have been listed in Table (3.4) along with chemical structures, molecular weight and retention times.

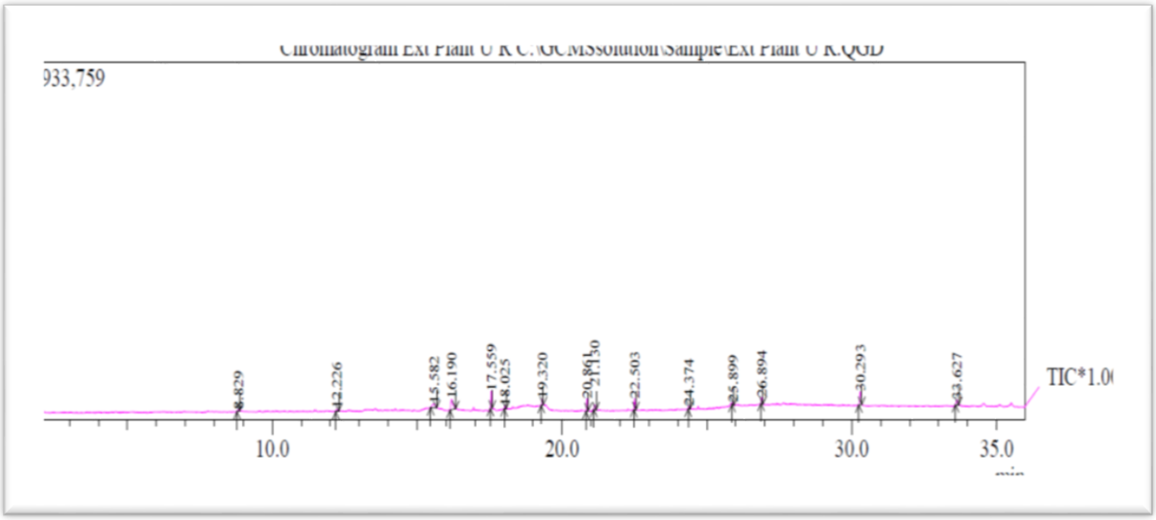
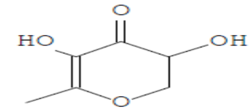
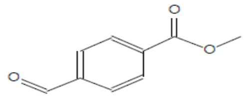
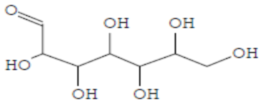
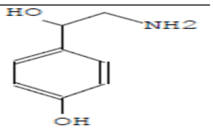
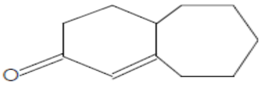
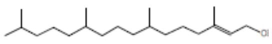
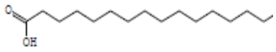
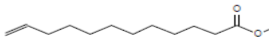
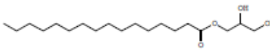
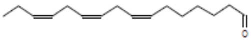
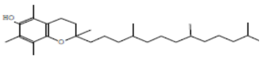
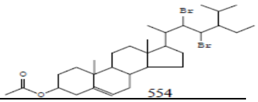


Figure **(3.4)**: Chromatogram of methanolic extract of Eucalyptus leaves.

Table **(3.4)**: Major identification compounds in methanolic extract of Eucalyptus leaves.

NO.	Name of compound	RT (min)	Chemical formula	M.Wt (g/mole)	Structure
1	3,5-Dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one	8.825	$C_6H_8O_4$	144	
2	p-Carbo methoxy benzaldehyde	12.225	$C_9H_8O_3$	164	
3	d-Glycero-d-ido-heptose	15.583	$C_7H_{14}O_7$	210	
4	Benzyl alcohol, .alpha.-(aminomethyl)-p-hydroxy	16.192	$C_8H_{11}NO_2$	153	
5	3,4,4a,5,6,7,8,9-Octahydro-2H-benzo[a]cyclohepten-2-one	17.558	$C_{11}H_{16}O$	164	
6	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	18.025	$C_{20}H_{40}O$	296	

7	n-Hexadecoic acid	19.317	$C_{16}H_{32}O_2$	256	
8	9,12,15-Octadecatrien-1-ol, (Z,Z,Z)	21.133	$C_{18}H_{32}O$	264	
9	Methyl 11-dodecenoate	22.500	$C_{13}H_{24}O_2$	212	
10	2,3-Dihydroxypropyl palmitate	24.375	$C_{19}H_{38}O_4$	330	
11	cis-7,10,13-Hexadecatrienal	25.900	$C_{16}H_{26}O$	234	
12	Vitamin E	30.292	$C_{29}H_{50}O_2$	430	
13	22,23-Dibromostigmast-5-en-3-yl acetate	33.625	$C_{31}H_{50}Br_2O_2$	612	

The mass spectra of methanolic extract of both olive and eucalyptus provides another evidence on the natural organic compounds that exist in the leaves. The qualitative measurements (GC-MS and FTIR) of the leaves confirmed that the olive leaves have more natural active organic compounds than eucalyptus leaves and this means that the olive leaves may have more active corrosion inhibitor than the eucalyptus leaves due to the large number of hetero atoms (N, S, O, P).

These atoms are responsible for corrosion inhibition as they have free lone pair (electronic density) which makes them capable of forming a coordinate bond with d-orbitals of a metal that is vacant.

3.3 The curves of polarization:

Figures (3.5-3.7) show the polarization curves in the presence and absence of various concentrations of olive and eucalyptus leaves extracts (50,100,200,400) ppm for copper alloy over temperature range (293-313)k.

Parameters of corrosion gained from polarization curves are corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (ba), and cathodic Tafel slope (bc) as shown in tables (3.5-3.7).

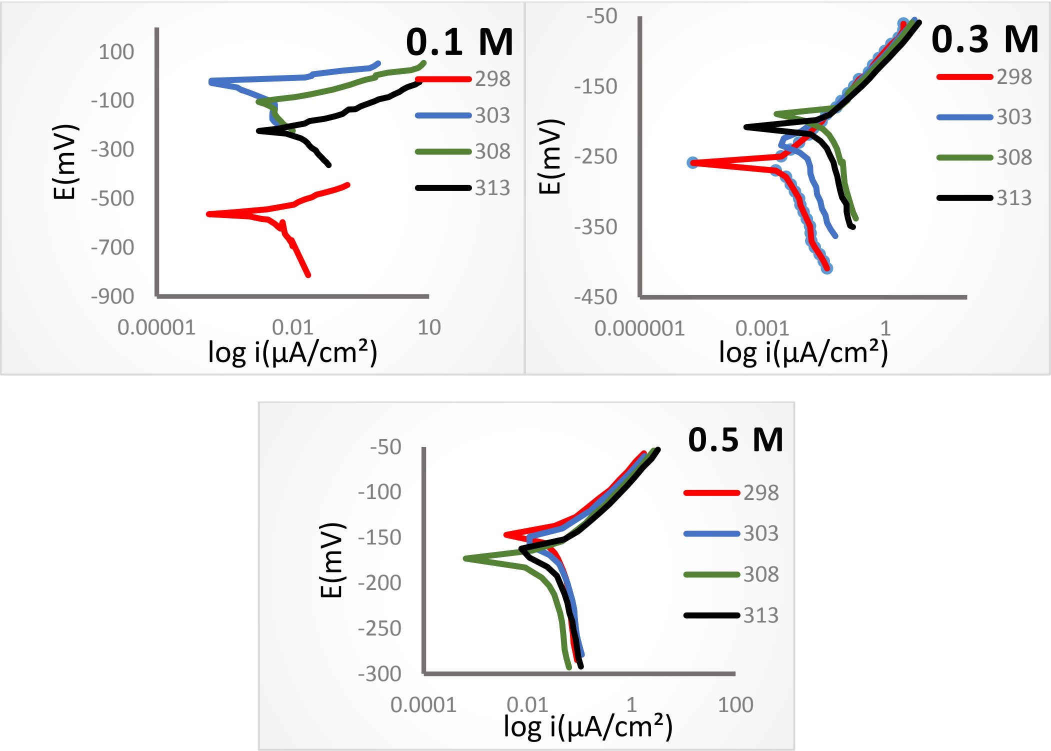


Figure (3.5): Polarization curves for copper corrosion in acid solution (HCl) at temperature range (298-313) K and different concentrations.

Table (3.5): Data of curve of polarization for cupper corrosion in various concentration of HCl over the range of temperature (298-313) K.

Con.HCl (M)	T (K)	- E_{corr} (mV)	i_{corr} ($\mu A.cm^{-2}$)	-b_c ($mV.dec^{-1}$)	+b_a ($mV.dec^{-1}$)	Weight loss $g.m^{-2}.d^{-1}$))
0.1	298	−12	1.6	−264	10.6	0.45
	303	−104	3.43	−587	36.9	0.98
	308	−218.7	4.32	−96	43.9	1.23
	313	−217.7	7.6	−252.9	61.8	2.16
0.3	298	−260	4.35	−185.8	69	1.24
	303	−235	8.67	−165	65	2.47
	308	−191.9	31.5	−161	55	8.97
	313	−207	32.95	−236	62.7	9.38
0.5	298	−145.9	32	−216	45	9.11
	303	−158.9	35.1	−196.4	56.9	9.99
	308	−193	37.8	−590	75.3	10.7
	313	−177.7	44.8	−315.8	66.8	12.7

General E_{corr} increase with the increases of temperature and with increase of acid concentration with some variation because corrosion reaction is heterogeneous reaction .

The corrosion current density (i_{corr}) is a kinetic parameter which represents the rate of corrosion process. The data in table (3.5) indicated that (i_{corr}) for copper increases with the increase of temperature and with increases of acid concentration .

The cathodic (bc) and anodic (ba) Tafel slopes which were obtained from the slope of the cathodic and anodic Tafel regions in the polarization curves of copper in HCl solution (0.5 M). Over the temperature range (298-313) K. Tables (3.5) – (3.7) show a difference in anodic Tafel slope that is feasibly due to rate determining step (r.d.s) variation of metal dissolution reaction.

Weight loss increased with the increase of temperature and with increased of acid concentration.

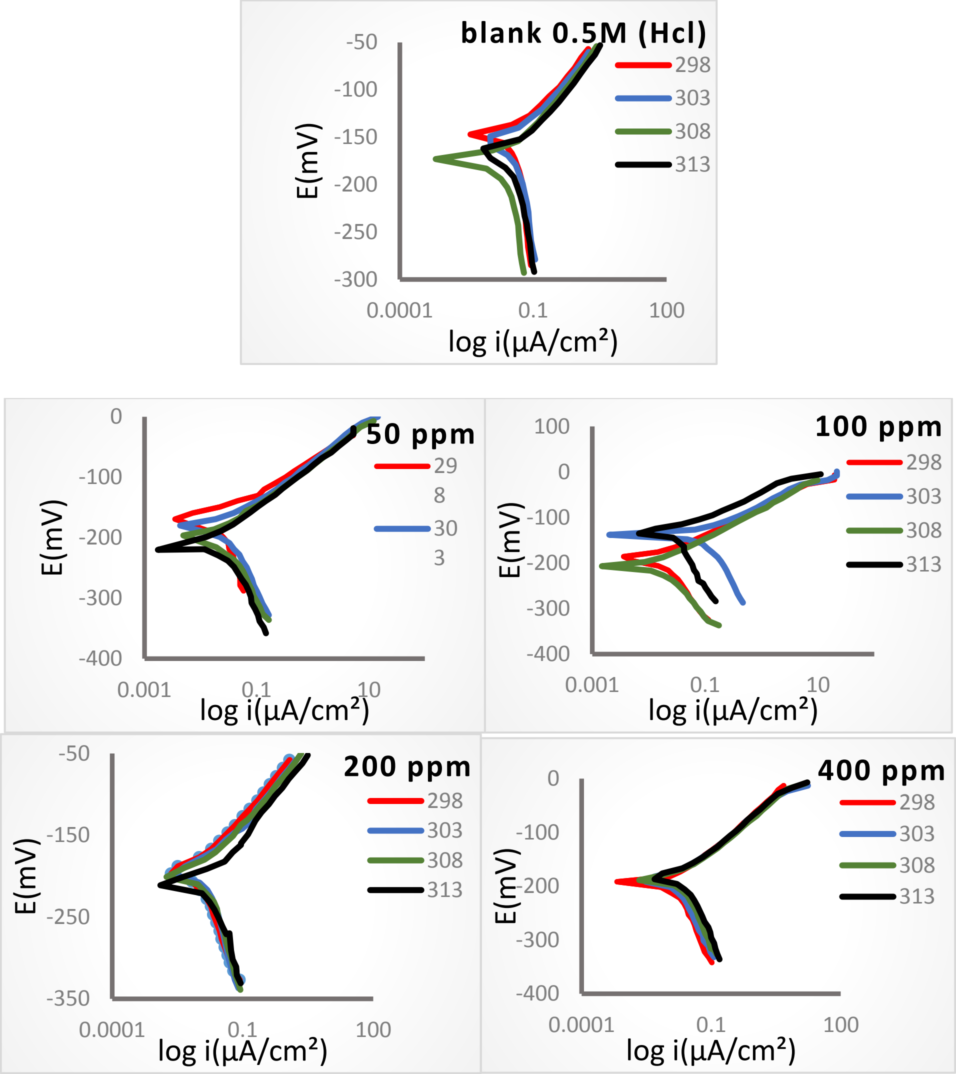


Figure **(3.6):** Curves of polarization for copper corrosion in acid solution 0.5M (HCl) at temperature range (298-313) K and in the presence of various Eucalyptus leaves concentrations.

Table (3.6): Corrosion standards for Cu and its alloys in HCl(0.5)M solution over range of temperature (298-313)K of different Eucalyptus leaves concentrations.

Inh. (Ppm)	T (K)	$-E_{corr}$ (mV)	i_{corr} ($\mu A.cm^{-2}$)	$-b_c$ ($mV.dec^{-1}$)	$+b_a$ ($mV.dec^{-1}$)	Weight loss $g.m^{-2}.d^{-1}$)
0	298	−145.9	32	−216	45	9.11
	303	−158.9	35.1	−196.4	56.9	9.99
	308	−193	37.8	−590	75.3	10.7
	313	−177.7	44.8	−315.8	66.8	12.7
50	298	−169	18	−205	56.8	5.35
	303	−164.5	21	−118	55	6.1
	308	−188.6	23	−189	66.8	6.4
	313	−221	30	−282	68.6	8.6
100	298	−167	16	−102	48	4.6
	303	−162	19.5	−105	53	5.6
	308	−214	22	−163	78	6.3
	313	−160	26	−184	49	7.4
200	298	−160	10.6	−68.2	67.7	3.02
	303	−198	14	−176.4	67.9	4.01
	308	−201	16.7	−195	71.4	4.75
	313	−210	23.3	−215.7	74.4	6.64
400	298	−193	6.6	−81	45	1.88
	303	−188	8.4	−83	50.7	2.38
	308	−185	9.9	−78	45.7	2.82
	313	−187	14.2	−87.3	62.1	4.03

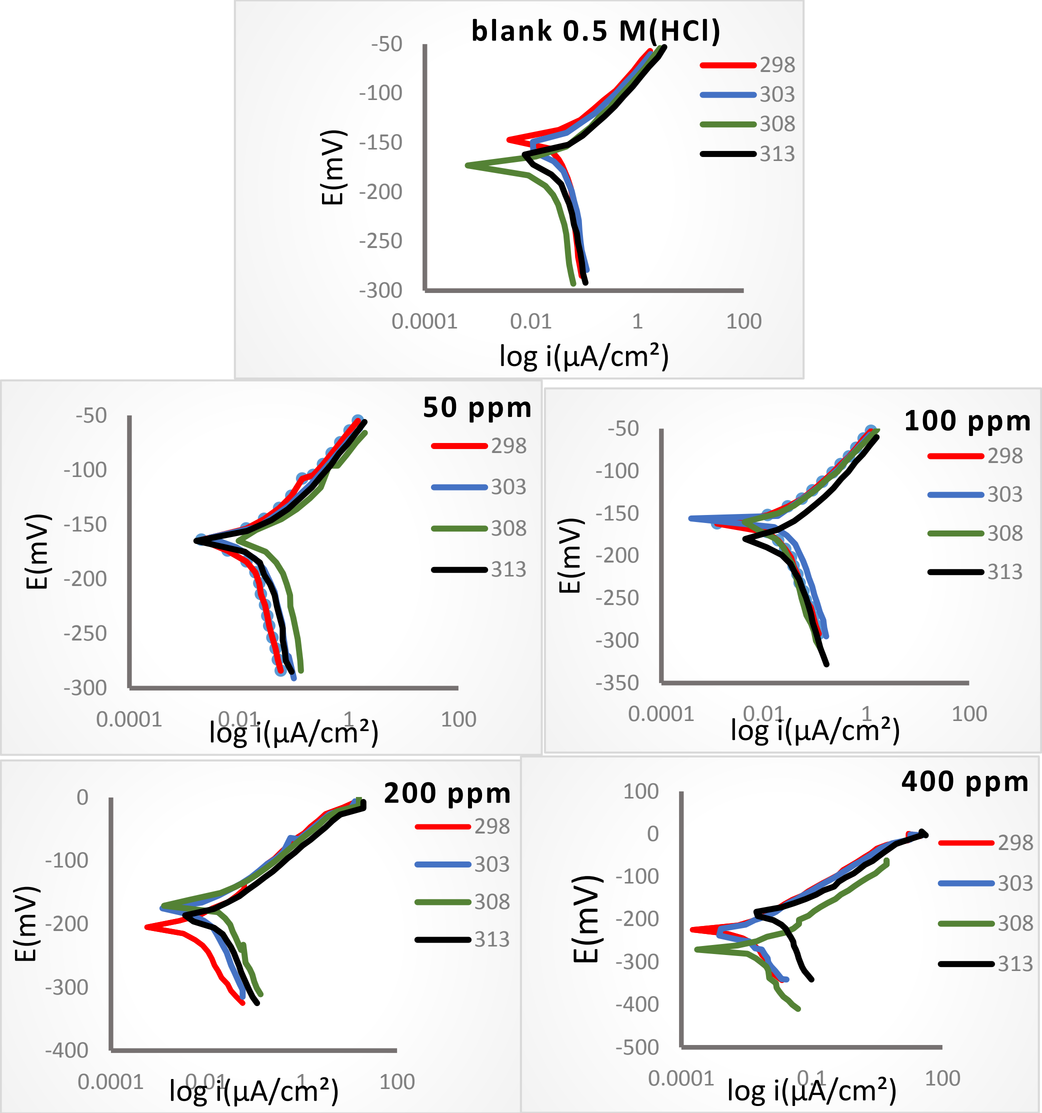


Figure *(3.7)*: Curves of polarization for corrosion of copper in acid solution 0.5M (HCl) at temperature range (298-313) K and in the presence of various Olive leaves concentrations

(3.7): Corrosion standards for Cu and its alloys in HCl solution over temperature range (298-313) K of different Olive leaves concentrations.

Inh. Ppm	T (K)	$-E_{corr}$ mV	i_{corr} ($\mu A.cm^{-2}$)	$-b_c$ ($mV.dec^{-1}$)	$+b_a$ ($mV.dec^{-1}$)	Weight loss $g.m^{-2}.d^{-1}$
0	298	−145.9	32	−216	45	9.11
	303	−158.9	35.1	−196.4	56.9	9.99
	308	−193	37.8	−590	75.3	10.7
	313	−177.7	44.8	−315.8	66.8	12.7
50	298	−167	11.2	−130	49	3.2
	303	−162.5	21.5	−175	51	6.11
	308	−163	22.8	−78	41	6.5
	313	−165	27.7	−212.5	55	7.2
100	298	−164	10.1	−78	44	2.9
	303	−160	13.8	−62	44.8	3.9
	308	−161	17.9	−181	53	5.1
	313	−181	21.4	−138	61	6.1
200	298	−206	4.1	−109	62	1.2
	303	−174	8.79	−150	49	2.5
	308	−165	12.8	−98.8	45.6	3.6
	313	−187	15.6	−157	59	4.4
400	298	-226	1.6	-79	50	0.5
	303	-232	2.18	-82.6	60	0.6
	308	-271	3.5	-125.8	60.9	0.9
	313	190.6	10.5	-89	46	3.1

The rate of corrosion rose by increasing the temperature in all inhibitor concentrations.

3.4 Corrosion coefficients:

The corrosion behavior of corrosion of copper in the acid medium is tested with a different concentration of hydrochloric acid (HCl) (0.1, 0.3, 0.5)M. The effect of various acid concentrations on the alloy and the effect of temperature change gives an idea of the acid effect and temperature on the corrosion degree as shown in Table (3.5) shows that increasing of acid concentration leads to the rising of the process of the corrosion process. This rise in corrosion is because of increasing the aggressive ions concentration such as chloride ions that can attack the alloy surface and begin to degrade it leading. .

As for the increase in temperature, the rate of corrosion begins to increase rapidly, but in the most common cases, many metals when exposed to heat. The rate of corrosion remains low in first, followed by a sudden and rapid increase. This can be explained by the temperature increase which resulted in a rise in the oxidative solution strength.(62)

3.5 Surface coverage (θ) and Inhibition Efficiency (IE %)

The calculation of the inhibition efficiency (IE %) is made by the use of the following relation: (63).

$$\mathrm{IE}\% = [1 - \frac{i}{i^{\circ}}] \times 100 \;\ldots\ldots\; (3.1)$$

Where i and i° are the current densities of corrosion in presence and absence of inhibitors in the corrosion medium respectively. The coverage of surface (θ) is calculated by the use of the relation (64).as shown in Tables (3.8). .

$$\theta = \frac{\mathrm{IE}\%}{100} \;\ldots\ldots.\; (3.2)$$

Table (3.8): Surface coverages (θ) and Inhibition efficiencies (IE %) of Olive and Eucalyptus leaves at different concentration with the range of temperature (298-313) K in 0.5M HCl.

Inh.	T (K)	50(ppm)		100(ppm)		200(ppm)		400(ppm)	
		IE %	θ	IE%	θ	IE%	θ	IE%	Θ
Eucalyptus leaves	298	43.8	0.438	50	0.5	66.8	0.668	79.4	0.794
	303	40.2	0.402	44	0.44	60	0.6	76	0.76
	308	39.2	0.392	42	0.418	56	0.56	74	0.74
	313	33	0.33	41.9	0.419	47.9	0.479	68	0.68
	298	65	0.65	68.4	0.684	87.2	0.872	95	0.95
	303	40.2	0.402	60.7	0.607	74.9	0.749	93.8	0.938

Olive leaves	308	39.7	0.397	52.6	0.526	66.1	0.661	90.7	0.907
	313	38	0.38	52.2	0.522	65.2	0.652	76.6	0.766

The above results showed that the efficiency of inhibition was inversely proportional to the temperature where the highest efficiency at (298)K.

It was also found that the olive leaves gave a higher efficiency compared to those provided by the eucalyptus leaves in the same degree of at constant temperature; pH with maximum inhibition efficiency (IE%) in(298) K by Olive is (95%) and is (79%)by Eucalyptus. .

The IE% values were recognized to rise with increasing the inhibitors concentration and reduce with the rise of temperature (65). In addition, the surface coverage data have an essential role in the evaluation of the inhibitors properties and it is useful when discussing adsorption properties with the aid of isotherm adsorption as it can describe the additions of molecules of inhibitor that are on the surface in the metal, interacting with them(66).

The surface coverage and inhibition efficiency depend on many factors such as the inhibitor concentration, inhibitor chemical structure, environment, and temperature. The IE% and θ values are greatly affected by these factors. The IE% values were identified to rise with increasing the inhibitors concentration and decrease with rise of the temperature.(67)

3.6 Copper Corrosion Activation Energy:

The energy of activation is calculated to copper corrosion in hydrochloric acid for the process of corrosion in presence and absence of inhibitors that were evaluated from equation of Arrhenius. There is a relationship between the rate of corrosion and temperature, expressed by the mathematical equation: (68.69)

$$\log i_{\mathrm{corr}} = \frac{-\mathrm{Ea}}{2.303\mathrm{RT}} + \log\mathrm{A} \ldots\ldots (3.3)$$

Where (Ea) is the of activation energy, (R) is the constant of gas (8.314), and (A) is constant of Arrhenius. Log i_{corr} values are plotted against the values of 1/T as indicated in figures (3.5). (Ea) and (log A) values were estimated from intercepts and stopes of the plots when (1/T=zero). Through the use of the alternation form of Arrhenius, the relationship can be obtained (ΔH) and (ΔS) of activation:

$$\ln\left(\frac{i_{corr}}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{act}}{R}\right) - \left(\frac{\Delta H_{act}}{RT}\right) \ldots\ldots (3.4)$$

Where (h) is "planks constant"($6.626*10^{-34}$ J.S), and(N) is "Avogadro's number" ($6.022*10^{23}$ mol^{-1}); there is a possibility to draw $\ln\left(\frac{i_{corr}}{T}\right)$ vs. $\left(\frac{1}{T}\right)$, where the slope of the straight line shows the value $\left(-\frac{\Delta H_{act}}{R}\right)$ and the intercepts shows the value$\left(\ln\frac{R}{Nh} + \frac{\Delta S_{act}}{R}\right)$. As shown in the figures (3.8-3.9),Table (3.9) the results of Ea, log A, ΔS and ΔH for copper in acidic media (HCl) in presence and absence of two inhibitors.

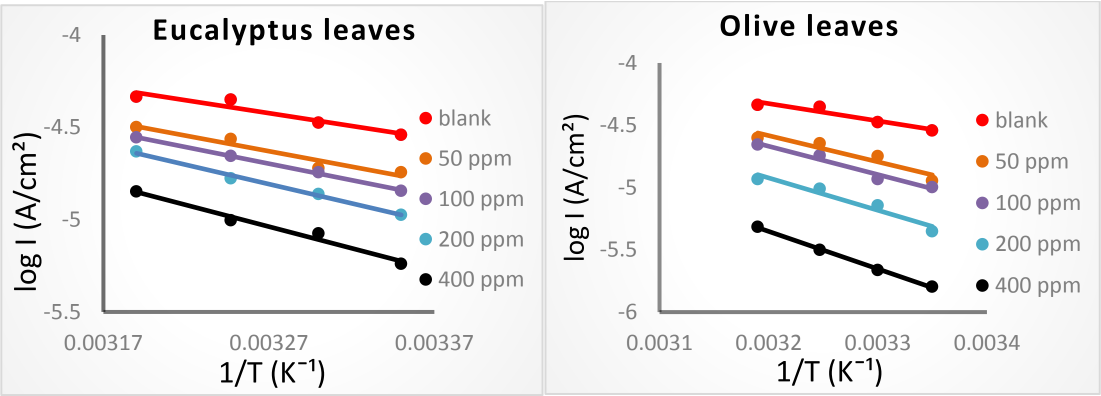


Figure *(3. 8)*: Plots of Arrhenius of log i_{corr} versus 1/T for the corrosion of copper in 0.5 M HCl with different concentrations of inhibitors (Eucalyptus and Olive leaves).

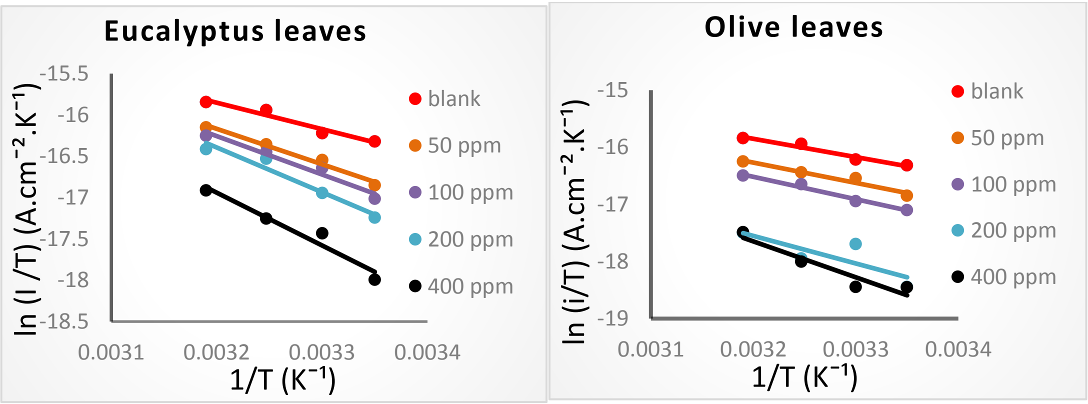


Figure *(3.9)*: Plots of Arrhenius of ln (i_{corr}/T) versus 1/T for the copper corrosion in 0.5 M HCl with different concentrations of inhibitors (Eucalyptus and Olive leaves).

Table (3.9): Activation energy (Ea), activation enthalpy (ΔHa), and the activation entropy (ΔSa) for the copper corrosion in 0.5 M HCl and in the inhibitors presence (Olive and Eucalyptus leaves).

Inh.	**Conc. (ppm)**	**E_a (KJ. mol^{-1})**	**A (molecules.cm^{-2}.s-1)**	**-ΔS_a (KJ.K^{-1}.mol^{-1})**	**ΔH_a (KJ. mol^{-1})**
Blank	–	26.6	7.98×10^{23}	-0.244	26.6
Eucalyptus leaves	50	32	4.25×10^{24}	-0.217	35.6
	100	34.3	8.56×10^{24}	-0.209	38.6
	200	39.9	6.26×10^{25}	-0.189	45
	400	44.8	2.5×10^{26}	-0.168	53
Olive leaves	50	40.3	8.62×10^{25}	-0.238	29.5
	100	43.5	2.41×10^{26}	-0.230	32.6
	200	49.7	1.48×10^{27}	-0.214	40.2
	400	57.7	1.17×10^{28}	-0.176	52.3

It can be noted from the above values that the activation energies (E_a) rose with the inhibitor presence and this rise incrementally increases the extract concentration. It was also noted that the energy of activation of olive leaves are higher than the energy activation of the leaves of eucalyptus.

The increase in the activation energy (Ea) of constant Arrhenius coefficient indicates a high reaction rate, while the decrease in the activation energy indicates of the Arrhenius coefficient is stabilized indicates a low reaction rate. There is also a clear difference in the values of the activation energies and the Arrhenius coefficient where the corrosion reaction begins with sites that have low activation cards and then spread to the sites that have higher activation energies (70). This means that adding the inhibitors rises the barrier of the energy of the copper corrosion process in the acidic solution containing chlorine ions, and that the corrosion process will also occur and that the inhibitors delays it. In addition, the increase in temperature leads to chemical changes in the inhibitor molecules, which results in increasing the electrons density in the inhibitor molecules the adsorption centers and then in improving the inhibition efficiency, where inhibitor concentration is increased(71) .

The positive sign of activation enthalpy (ΔH_a) values in presence and absence of the inhibitors reflects nature that is endothermic of the process of copper corrosion. The increase of positivity with increasing inhibitory concentration suggests the difficulty of copper corrosion in presence of olive and eucalyptus leaves extracts.(72).

(ΔS_a) values were negative in presence and absence of both negativity and inhibitors that decrease with the rise of inhibitors concentrations. This can be explained as an increase in randomness (freedom degree) when the corrosion reaction turns from reactants to the state of transition (activated complex). This means that the determining step of the rate is association instead of dissociation.(73)

3.7 Thermodynamic of Corrosion:

Thermodynamic parameters of adsorption from thermodynamic aspect metals and their temporary unstable from of pure metals have great tendency to convert to a high thermodynamically stable form which represent, as ores or natural minerals. That is the main reason metals are exited in many forms such as oxides or hydroxides, and other forms, according to their existing environment that results in the phenomenon that is known as corrosion. (74)

The coverage of the surface (θ) of the working electrode (copper) surface by the inhibitor and the inhibitors concentration (olive and eucalyptus leaves extract) (C_{inh}) were tested by being fit to different isotherms. Nevertheless, the best fit was gained with isotherm of Langmuir as illustrated in Figures (3.10) which is provided by the equation below (75.76).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{adc}} + C_{inh} \;\ldots\ldots(3.5)$$

Where k_{ads} is the equilibrium constant of the adsorption/adsorption

Process.

From calculated values of K_{ads}, calculation of adsorption Gibbs free energy has been done using the following equation (77).

$$\Delta G^{\circ}_{ads} = -RT\ln(55.5K_{ads})\ldots\ldots(3.6)$$

Where T is absolute temperature, R is constant of gas, and the value (55.5) indicates the water molar concentration in g/L. The calculation of adsorption standard enthalpy can be achieved based on the van 't Hoff formula;

$$\ln K_{ads} = -\frac{\Delta H_{ads}}{RT} + constan \ldots\ldots (3.7)$$

A plot of ln K_{ads} values versus 1/T values provides a straight line as indicated in figure (3.11) the straight line slope is equal $\frac{-\Delta H_{ads}}{R}$.

The values of $\Delta G°ads$ in the inhibitor presence are negative that is associated with the process of exothermic adsorption. $\Delta S°ads$ of the process of inhibition can be calculated from the equation below [(78)].

$$\Delta S°_{ads} = \frac{\Delta H°_{ads} - \Delta G°_{ads}}{T} \ldots\ldots (3.8)$$

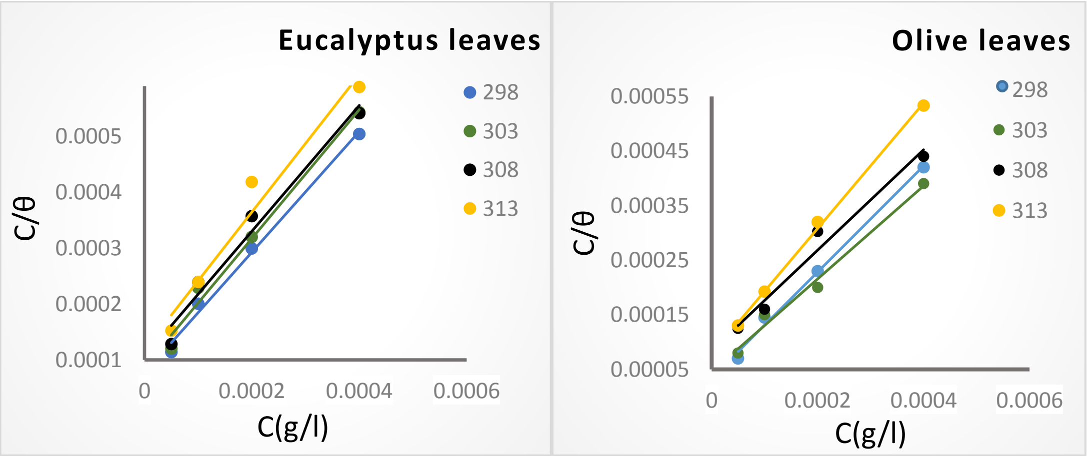


Figure ***(3.10)***: Isotherm plots of Langmuir for the (Olive and Eucalyptus leaves) adsorption on copper in 0.5 HCL.

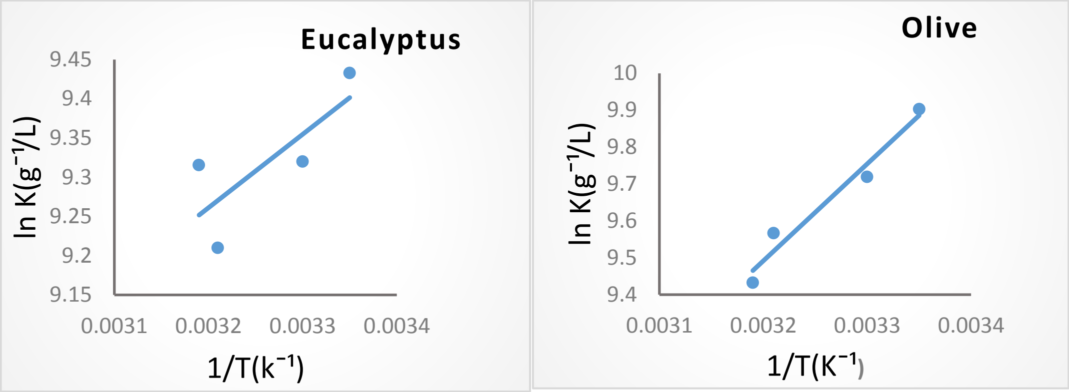


Figure ***(3.11)***: Van't Hoff formula of Olive and Eucalyptus leaves on copper in 0.5M HCL.

Table ***(3.10)***: showing thermodynamic parameters for adsorption of (Olive and Eucalyptus leaves) on copper in 0.5M HCl.

Inh.	**T (K)**	**K_{ads} ($g^{-1}.L$)**	**$-\Delta G^{o}_{ads}$ ($kJ.mol^{-1}$)**	**$-\Delta H^{o}_{ads}$ ($kJ.mol^{-1}$)**	**ΔS^{o}_{ads} ($J.K-1.mol^{-1}$)**
Eucalyptus leaves	298	12500	-33	-7.71	0.084
	303	11111	-33.6		0.085
	308	10000	-34		0.0854
	313	11111	-34.7		0.086
Olive leaves	298	20000	-34.4	-21.9	0.04194
	303	16666	-34.6		0.04191
	308	14286	-34.8		0.04188
	313	12500	-35		0.04185

The high values of (K_{ads}) refers that the two inhibitors (olive, eucalyptus leaves extracts) molecules possess strong adsorption ability on to copper surface. The negative and large values of ΔG°_{ads} indicates the table adsorbed film and spontaneity that are formed by inhibitor molecules.(79)

Generally, (ΔG°_{ads}) of (-20 J.mol^{-1}) values or less negative correspond the physisorption in which the action of inhibition is because of the electrostatic interaction between the charged metal and the charged molecules.

On the other hand, the values which around (-40 KJ.mol $^{-1}$) or mor negative correspond to the process of chemisorption. Which can be attributed to sharing of charge or transfer from molecules of inhibitor to the surface of the metal to form a covalent coordinate bond. So, from the values of (ΔG°_{ads}) obtained from this study the conclusion that is drawn is that the two extracts adsorption on the surface of copper occurs through both chemical and physical adsorption. (80)

ΔH°_{ads} Negative values reflect the adsorption exothermic nature of Olive and Eucalyptus leaves extracts on copper surface. The positive values ΔS°_{ads} indicates increase in randomness or degree of freedom accompany of adsorption process of both inhibitors.

Generally, the first step of adsorption plant extracts as inhibitors on the metal surface is usually supposed to replace one or more of the molecules of water absorbed on the surface of the metal, which results in decrease in disorder of inhibitor molecules and increase of disorder of the solution. The increase of entropy of adsorption occurred as the reaction goes from solution to metal/ solution surface.(81)

$$\mathrm{Inh}_{(sol)} + \mathrm{H_2O}_{ads} \leftrightarrow \mathrm{Inh}_{ads} + \mathrm{H_2O}_{(sol)} \;\ldots\ldots\; (3.9)$$

3.8 Tafel Slopes and Transfer Coefficients:

The values of anodic and cathodic transfer coefficients (α_a, α_c) were calculated from equations (1.2) and (1.3) are listed in tables (3.11 – 3.12).

The values of anodic and cathodic slopes that gained from the curves of polarization are put in a list in tables (3.6, 3.7).

Table *(3.11)*: Values of transfer coefficient (α_c , α_a), for copper corrosion in 0.5M HCl solution in the presence and absence of olive leaves at temperature range (298-313) K.

Conc. (M)	T (K)	$+b_a$ (mV.dec^{-1})	$-b_c$ (mV.dec^{-1})	α_c	α_a
Blank	298	45	−216	0.137	0.656
	303	56.9	−196.4	0.153	0.528
	308	75.3	−590	0.052	0.405
	313	66.8	−315.8	0.098	0.464
50	298	49	−130	0.227	0.603
	303	51	−175	0.172	0.589
	308	41	−78	0.391	0.744
	313	55	−212.5	0.146	0.564
100	298	44	−78	0.379	0.671
	303	44.8	−62	0.484	0.670
	308	53	−181	0.169	0.576

	313	61	–138	0.225	0.508
200	298	62	–109	0.271	0.476
	303	49	–150	0.200	0.613
	308	45.6	–98.8	0.309	0.669
	313	59	–157	0.198	0.526
400	298	50	-79	0.374	0.591
	303	60	-82.6	0.363	0.500
	308	60.9	-125.8	0.243	0.501
	313	46	-89	0.348	0.674

Table *(3.12)*: Values of transfer coefficient (α_c, α_a), for copper corrosion in 0.5M HCl solution in the presence and absence of Eucalyptus leaves at temperature range (298-313) K.

Conc. (M)	T (K)	$+b_a$ ($mV.dec^{-1}$)	$-b_c$ ($mV.dec^{-1}$)	α_c	α_a
Blank	298	45	–216	0.137	0.656
	303	56.9	–196.4	0.153	0.528
	308	75.3	–590	0.052	0.405
	313	66.8	–315.8	0.098	0.464
50	298	56.8	–205	0.144	0.520
	303	55	–118	0.254	0.546
	308	66.8	–189	0.161	0.457
	313	68.6	–282	0.110	0.452

100	298	48	−102	0.289	0.615
	303	53	−105	0.286	0.566
	308	78	−163	0.187	0.391
	313	49	−184	0.169	0.633
200	298	67.7	−68.2	0.433	0.436
	303	67.9	−176.4	0.170	0.442
	308	71.4	−195	0.156	0.427
	313	74.4	−215.7	0.144	0.417
400	298	45	−81	0.365	0.656
	303	50.7	−83	0.362	0.592
	308	45.7	−78	0.391	0.668
	313	62.1	−87.3	0.355	0.499

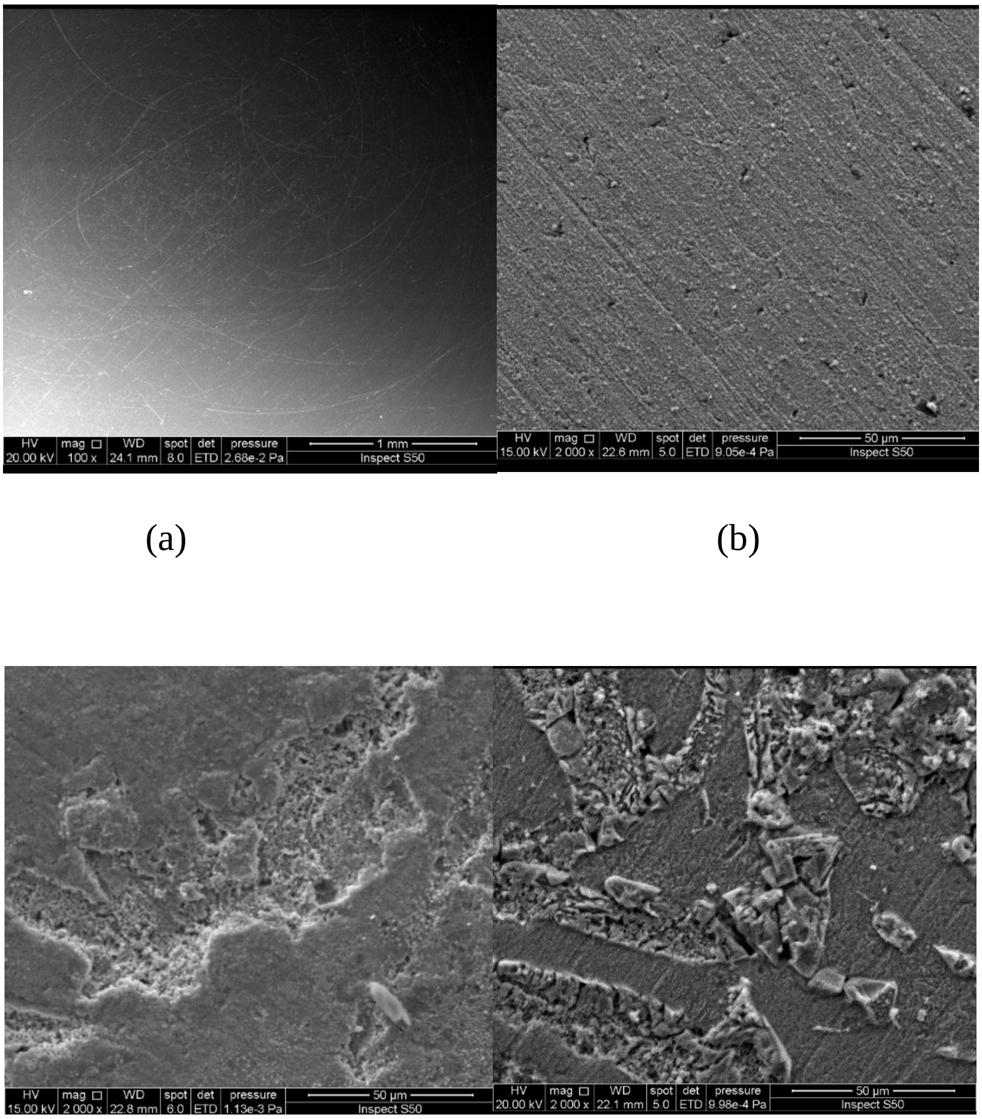
Tables (3.5) – (3.7) display the cathodic (bc) and anodic (ba) Tafel slopes which were obtained from the slope of the cathodic and anodic Tafel regions in the polarization curves of copper in HCl solution (0.5 M). Over the temperature range (298-313) K. Tables (3.5) – (3.7) show a difference in anodic Tafel slope that is feasibly due to rate determining step (r.d.s) variation of metal dissolution reaction. (82)

3.9 Surface examination study:

Scanning Electron Microscope (SEM):

The scanning electron microscope (SEM) images of pure copper specimens was submerged in the corrosive medium (0.5M) HCl for in the presence or absence of inhibitor system as illustrated in Figure (3.12).

The micrographs (a) show a smooth polished surface before immersed in the acidic media. The (SEM) (b) micrographs of copper surface was submerged in the corrosive medium. The micrographs (c-d) shows (SEM) image of copper surface after submerging (for the same time interval) in the corrosive solution additionally consisting (400 ppm)of inhibitors (olive and eucalyptus leaves).



(a) (b)

(c) (d)

Figure(3.12): Scanning electron micrographs of (a) Polished copper (b) copper in 0.5 M HCl solution (c) copper in 0.5M HCl solution and in presence of 400 ppm olive leaves extract (d) copper in solution of 0.5M HCl and in presence of the extract of eucalyptus leaves represented by 400 ppm.

The images were taken for the sample of copper to enhance the current search results, showing the microscopic images of the sample after corrosion in the acidic medium. Showing the copper surface damage and its strength in the inhibitor absence while (olive and eucalyptus leaves) inhibitors presence is relatively better as shown in figure (3.12). This dependes on the inhibitors concentration, the inhibitor molecules on the metal surface and their absorption created a protective layer that led to the appearance of the surface in smooth manner and the layer formed which is responsible for inhibiting corrosion .

Conclusions

The conclusions that could be drawn from the experimental results and the related discussions may listed as follow:

1. Copper suffers corrosion in acidic medium.
2. The corrosion parameters such as corrosion current density, weight loss and penetration loss and increased by increasing the temperature and decreased by increasing the inhibitors concentration.
3. The Fourier transform infrared spectroscopy (FTIR) and (GC-MS) for olive and eucalyptus leaves are proved the presence of many natural organic compounds, and these compounds having large number of hetero atoms that responsible for the inhibition performance of those inhibitors. According to obtained GC-MS spectra the number of phytochemicals were found that the leaves of olive contain more natural organic compounds than the leaves of eucalyptus and therefor the olive leaves act as a better inhibitor of eucalyptus leaves.
4. The values of the activation energies (E_a) are increased by increasing the concentration of the inhibitor and by increase the temperature. The values of the activation energies (E_a) are higher with the presence of the inhibitor than in the absence of it, indicating that the inhibitors raise the energy barrier to more values, (ΔH_a) values were positive and increasing with inhibitor concentration due to endothermic nature of corrosion process, and the negative values of (ΔS_a) indicated that decreasing of degree of freedom as reactants going into the transition state of activated complex.

5. (ΔG_{ads}) values were large and negative which indicated that the adsorption of inhibitors is spontaneous. The large values of (K_{ads}) approved the stability and strength of the adsorbed large that formed by adsorption of those inhibitors. The negative values of(ΔH_{ads}) indicates exothermic nature of adsorption process. The positive sing of (ΔS_{ads}) indicated that increasing on degree of freedom accompanied the adsorption process.
6. The efficiency of inhibition is higher for olive leaves than it for eucalyptus leaves. where the inhibitory efficiency in (298) K for Olive is (95%) and (79%) for Eucalyptus.

4.2 suggestion for further work:

It is useful to make some suggestions for the development of this work in the future as shown in the following points:

1. The corrosion medium may also be extended to other acids especially oxidizing acids.
2. Further studies may be required using another natural derivatives as green corrosion inhibitors for copper.
3. An attempt may be made to protect copper surface by coating with nano materials prior to the electrochemical investigation.

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الملخص:

تتضمن الرسالة دراسة كهروكيميائية لتاكل النحاس في محلول حامضي من حامض الهيدروكلوريك وبتراكيز مختلفة وضمن مدى من درجات الحرارة (298,303,308,313) باستخدام الطريقة الاستقطابية. وقد اوضحت النتائج العملية مايلي:

1- تزداد كثافة التيار(i_{corr}) بزيادة تركيز المحاليل الحامضية وزيادة درجة الحرارة حيث تبلغ اعلى قيمة لها (44.8) في محلول (0.5) من حامض الهيدروكلوريك بدرجة حرارة 313.

2- اثبتت تقنيات التشخيص الطيفية لكل من مستخلص اوراق اشجار الزيتون واليوكاليبتوز ان كلا المستخلصين يحويان انواع عديدة من المركبات العضوية وان هذة المركبات هي المسؤولة عن الفعالية التثبيطية لاوراق الزيتون واليوكاليبتوز.

3- ان قيم كفاءة التثبيط والمساحة السطحية المغطاة بالمثبط تزداد مع زيادة تركيز المثبطين وتقل مع زيادة درجة الحرارة كما اظهرت النتائج ان كفاءة التثبيط لاوراق الزيتون اعلى من اوراق اليوكاليبتوزز

4- امكن حساب حركيات التاكل من قيم تيار التاكل واعتمادها على درجات الحرارةز اظهرت النتائج ان قيم طاقات التنشيط تزداد مع زيادة تركيز المثبط اي ان المثبط قام بزيادة الحاجز الطاقي لتفاعل التاكل. ووجد ان قيم الانثالبي(ΔH_a) موجبة في وجود وعدم وجود المثبط مما يدل على ان التفاعل ماص للحرارة. وان قيم الانتروبي (ΔS_a) سالبة مما يؤكد على نقصان في عدد درجات الحركية من خلال تكوين المعقد المنشط.

5- اظهرت الحسابات الثرموديناميكية لعملية امتزاز المثبطات على سطح النحاس ان قيم طاقات كبس الحرة (ΔG_{ads}) كلها سالبة مما يدل على تلقائية العملية وان قيمها تتراوح بين (33-35) كيلوجول\مول مما يؤكد ان عملية الامتزاز للمستخلصات النباتية على سطح النحاس هي من نوع كيميائي وفيزيائي. كما اظهرت الحسابات ان قيم الانثالبي (ΔH_{ads})هي سالبة مما يدل على ان عملية الامتزاز باعثة للحرارة وقيم الانتروبي (ΔS_{ads}) موجبة مما يدل على زيادة عشوائية للنظتم اثناء حدوث عملية الامتزاز.

6- ثم دراسة وفحص سطح الفلز بواسطة المجهر الالكتروني الماسح(SEM) واظهرت الصور ان جزيئات المثبطات كونت طبقة حماية جيدة على سطح النحاس.

وزارة التعليم العالي والبحث العلمي

جامعة بغداد

كلية التربية للعلوم الصرفة / ابن الهيثم

قسم الكيمياء

حماية بعض السبائك النحاسيه من التاكل في اوساط حامضية بوساطة مثبطات صديقه للبيئة

رسالة مقدمة الى

كلية التربية للعلوم الصرفة/ ابن الهيثم جامعة بغداد

كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

ريام حسين مراح

بكلوريوس 2016 /جامعة بغداد

باشراف

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1441هـ 2019م