An-Najah National University

Faculty of Graduate Studies

A combined electrochemical and theoretical study into the effect of curcumin as a corrosion inhibitor for mild steel in 1 M HCl.

By

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This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Chemistry, Faculty of Graduat Studies, An-Najah National University, Nablus - Palestine.

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Dedication

This research is dedicateted to My beloved family, My parents , My brother

My wife and My sweet son.

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First of all ,I am thankful to my lord «Allah » for directing me to accomplish this research successfully.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

A combined electrochemical and theoretical study into the effect of curcumin as a corrosion inhibitor for mild steel in 1 M HCl.

أقر بأن ما أشتملت عليه الرسالة انما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد وأن هذه الرسالة ككل أو جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة علمية أو بحثية.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degrees or qualifications.

Student's Name:

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التوقيع:

Date :

التاريخ:

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List of Abbreviations				
Symbol	Abbreviation			
MS	Mild Steel			
WL	Weight Loss			
MD	Modeling Dynamic			
PDP	Potentiodynamic Polarization			
EIS	Electrochemical Impedance Spectroscope			
Or	Organic compound			
SEM	Scanning Electron Microscopy			
AFM	Atomic Force Microscopes			
DFT	Density Functional Theory			
Ε	Poantial			
Ι	Electrical crurent			
$\eta_{\scriptscriptstyle WL}(\%)$	Percentage weight loss			
IE%	Efficience			
C _R	Corrosion Rate			
COSMO	Cnductor Screening MOdel"			
C _{dl}	Double layer Capacitance			
R _{ct}	Inhibitor Resistance			

X List of Abbreviations

A combined electrochemical and theoretical study into the effect of curcumin as a corrosion inhibitor for mild steel in 1 M HCl.

By

Ahmad Jawad abed Alqader Alami Supervisor Prof. Shehdeh Jodeh Co- Supervisor Dr. Othman Hamed Abstract

The effect of natural curcumin on the mild steel (MS) dissolution in 1.0 M HCl at different temperature (303-333) K has been investigated, the inhibition efficiency decreases with increases in temperature, but increases with increasing concentration of curcumin. Also experimental techniques such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) methods, weight loss measurements, and computational studies. The curcumin showed high inhibition activities and its adsorption on mild steel surface have become studied was found to follow the Langmuir adsorption model. Potentiodynamic polarization results revealed that natural curcumin acts as a mixed-type inhibitor. The results from EIS analysis reveals an increase in charge transfer resistance confirming the inhibitive ability of curcumin. The electronic properties derived from, DFT method and molecular dynamic (MD) simulations were used to give further insights into the action mode of curcumin. Theoretical results correlate well with the experimental results. Surface morphology of the MS surface in

absence and presence of natural inhibitor was examined using SEM images, and AFM the average surface roughness was $2.3 \mu m$:1.2 μm favoring the curcumin treated MS.

Chapter One Introduction

Chapter One Introduction

I.1. Definition of corrosion

Corrosion is the breaking down of the material due to the reaction with its environment, where the material (metal) reacts in the presence of water and oxygen [1]. Corrosion can either be chemical or electrochemical corrosion in nature. The distinction between chemical and electrochemical depends upon the mechanism causing it. Chemical corrosion is the direct result of exposure of material (e.g. with dry air or oxygen) and is controlled by the kinetics of chemical corrosion, whereas the electrochemical corrosion occurs in the presence of an electrolyte and it is said to be the dissolution of a metal through the oxidation process [2, 3]. Therefore with metallic materials and aqueous solution, the reactions are normally electrochemical in nature. Corrosion is said to be a thermodynamically feasible process because it involves negative change of Gibbs free energy [4]. Therefore corrosion is a reaction that involves the transfer of metal ions into the solution at active area (anode), passage of electron from the metal to an acceptor at less active area (cathode), an ionic current in the solution and an electronic current in the metal [5, 6].

Corrosion does not only occur in metals and their alloys, but it can also occur in all types of natural and man-made materials including biomaterials and nanomaterials. However, among many metals, corrosion is mostly experienced in iron and steel [7. 8]. The terms corrosion and rusting are often utilized interchangeably: the word "rusting" normally applies to ferrous material, iron and steel and the word corrosion is commonly used because it is inclusive of nonferrous metal as well [8]. Corrosion can be classified as either dry or wet corrosion. In most practical occasions the liquid can also contain aggressive ions such as Cl^- , SO_4^{2-} , I^- etc., which are responsible for accelerating the rate of corrosion. In the case of dry corrosion, the environment is normally gaseous and high temperatures and reactive gases are often evolved [4]. In wet corrosion (also known as "electrochemical corrosion") the electrochemical reaction which causes corrosion is: *e.g.* Iron:

$$Fe_{\text{lattice}} \rightarrow Fe_{\text{aq}}^{++} + 2e$$

Atmospheric corrosion can be regarded as special type of wet corrosion due to the fact that the corrosion processes evolve in a wet film on the metal surface formed by condensation from the atmosphere. In the case of dry corrosion (also known as chemical corrosion or high temperature oxidation) the corrosion reaction is *e.g.* Iron [9, 10].

$$Fe_{\text{lattice}} \rightarrow Fe_{\text{oxyde}}^{++} + 2e^{-}$$
 (1)

The corrosion process normally involves two simultaneous changes, namely, the anodic change where oxidation takes place, and four various factors influence the electrochemical reaction namely:

✤ Cathode

✤ Electrolyte

✤ Anode

✤ Electronic circuit

In the presence of moisture, iron reacts with oxygen to form Iron oxide (rust) with the formula, $Fe_2O_3.(H_2O)_x$ where *x* represent the amount of water that is present in rust which also determines the color of that rust.

In this reaction iron undergoes oxidation, and it loses electrons according to the following reaction;

$$Fe \rightarrow Fe^{++} + 2e^{-}$$
 (3)

Iron then reacts with oxygen to form iron hydroxide according to the reaction below:

$$Fe^{+2}_{aq} + 2OH_{aq}^{-} Fe(OH)_{2(s)}$$
(4)

Iron (+2) hydroxide is further oxidized by oxygen to iron (+3) according to reaction:

$$Fe(OH)_2 + dissolved(O) \rightarrow rust(Fe_2O_3)$$
 (5)

Reduction reaction occurs when the electrons that are released from the process are taken up by hydrogen ions into water where a gas is produced as in reaction:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

Rusting will then occur due to the water drop on iron surface and this is possible because of more oxygen being dissolved from the air near the edges of the drop [4. 10]. Figure **I.1** shows example of rusting of an iron ore.



Figure 1.1: Iron oxide (rust)

1.2. Types of corrosion

Corrosion occurs in various widely differing forms. However, there are various forms of corrosion categorized according to different criteria, such as type of attack, mechanical stress, its shape, size, and its specific functions of metal, atmospheric conditions and the corrosion producing agent present [8,11].

1. Group 1: Can be identified by visual perception (*i.e.* by naked eye) namely:

• **Crevice corrosion:** It takes place at localized areas of contact with the metal with the other or metal with a non-metal. It is typically encountered with metals and alloys which are depended on the surface oxide film for corrosion protection. For crevice corrosion to take place, a certain

induction period is needed to create local corrosion cell between the inside and the outside crevice [1, 4, 12].

• Uniform corrosion: This is characterized by direct attack on the surface of the material, and it often occurs on the environment here there is essentially low corrosion rate or correctly maintained [1, 9, 12].

• **Petting corrosion:** This is a form of localized attack that causes small holes to form in the metal. It is known as a white or grey powdery similar to dust, which blemishes at the surface. Petting corrosion is said to be stimulated by low-velocity, stagnant-type conditions were concentrated "bubbles" of corrosives could form. It cake up to months or years before its effects can be seen [1, 9].

• **Filiform corrosion:** It is often seen by a thin threadlike attack continuing along the surface beneath a surface layer. Filiform corrosion is a special form of crevice corrosion where the chemistry build up takes place under a protection film that has been breached [1, 4, 8].

• **Galvanic corrosion:** Also known as bimetallic corrosion, it occurs when two or more dissimilar conducting materials are connected electrically and are exposed to an electrolyte. The forming of galvanic corrosion results in one of the metal in the couple being the anode and corrodes faster than it would all by itself, while the one being the cathode corrodes slower than it would [1, 4, 8-9].

• **Lamellar corrosion:** It is a form of corrosion that normally start from sites of initiation along parallel planes to the surface, generally at grain boundaries, forming corrosion product that force metal way from the body of the material, thus giving it a layer appearance [1, 4, 9].

2. Group 2: Can be identified via examination namely:

• Erosion corrosion: Is an increase rate of corrosion attack on the metal as result of a relative movement of corrosive fluid and the metal surface. It can be incited by faulty workmanship. Erosion corrosion is often the result of wearing a way of a protection scale or coating on the metal surface [1, 9, and 12].

• **Cavitation corrosion:** A special form of corrosion that is enhanced through the formation and collapse of a gas or vapor at or near the metal surface. In this form of corrosion, pits are normally localized close to each other or grown together along smaller or large areas, making a rough, spongy surface. It is said to take place at high flow velocities and fluid dynamic conditions which results in large pressure variations, mostly in the case after turbines, propellers and pump rooters [1.8].

Dealloying corrosion: Also known as selective leaching, occurs when the alloy losses its element and retains its resistance component [8, 9, 12].

• **Intergranular corrosion:** Also referred to as intercrystalline corrosion or interdendritic corrosion, it is a localized attack in on or adjacent to the grain boundaries of the metal or alloy [4, 8, 12].

• Fretting corrosion: This refers to corrosion resulting from the damage of two metal surfaces rubbing together at a point [8.9].

Group 3: Can only be identified with the aid of a microscope namely:

 \Rightarrow Environmental cracking: It is caused by many conditions that usually result in the following form of corrosion damage:

• Stress Corrosion Cracking (SCC): This type of corrosion forms a crack under mechanical stress in the presence of corrosion media. The stress is caused by applied load, residual stress from the manufacturing process. It may also occur in combination with hydrogen embrittlement [1, 4, 8, 9].

• **Corrosion fatigue:** This special type of corrosion occurs as result of the combined action of an alternating or cycling stress and a corrosive environment [11.7].

• **Hydrogen Embrittlement (HE):** This is a process that results from a decrease of the toughness or ductility of metal due to the presence of atomic hydrogen [1, 4, 9].

1.3. Rate of corrosion

Corrosion process involves the degradation of materials due to environmental factors such as water, air and temperature: thus a material loses its original properties and weight loss is encountered during that process. It is very essential to know the corrosion rate of a certain material

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in order to effectively use metals in outdoors structures. The rate of corrosion of metals can be expressed as mg/s and is usually measured either by gravimetric methods or by electrochemical methods.

Corrosion rate is strongly dependent upon the material being corroded. The known electrochemical technique that has qualitative ability concerning corrosion rate is called the polarization resistance, this is a laboratory based technique which relies on the application of a small electrical perturbation to the metal. The way in which corrosion rate is predicted is based upon the given sufficient qualitative information about the electrochemical reaction taking place [13].

Like most chemical reactions to take place, there must be change caused by the surrounding conditions or reaction within the substance itself. There are several factors that stimulate the rate of corrosion namely:

• **Material:** This depends on the chemical composition of an alloy (i.e. the chemical elements within a particular metal). As in the case of a metal, the metal with lower electrode potential is more reactive and is susceptible to corrosion and the metal that has high electrode potential are less reactive and less susceptible for corrosion. It also depends on the crystal structure and grain boundary composition. One of the most elements for this factor is the surface conditions, because corrosion rate is strongly depended upon the surface [10, 11, 12].

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• **Temperature:** At high temperatures most chemical reactions speed up, and therefore the rate of corrosion increases. This is due to the fact that the temperature of corrosive material regulate the solubilities of certain species in the fluid such as oxygen (O_2), and carbon dioxide (CO_2) [4, 8, 12].

• Water velocity: This is also one of the factors that affect the rate of corrosion. Water (H_20) is a molecule which contains particles which are in motion, and so at extremely high velocities those particles tend to remove the protective oxide layer and thus expose the metal to corrosion [1, 8, 9].

• Environmental: This is dependent upon on hydrogen-ion concentration, the influence of oxygen in solution adjacent to the metal [1, 4, 12].

• Anodic or Cathodic area: The relative sizes of cathode and anode mostly affect the rate of corrosion. Metals having smaller anodic area and the larger cathodic area exposed to corrosive atmosphere are said to have more intense and faster corrosion occurring at the anodic area due to the oxidation taking place at the anode causing electron liberation [4, 8, 12].

• Hydrogen ion concentration of the solution: As the concentration of the hydrogen ions is increased in a given environment (when the pH of the medium is decreased), the rate of corrosion increases [14]. The corrosion rates are normally slow in alkaline environment. Acidic environment are often aggressive than the environments which have low concentrations of hydrogen and high pH values [14. 15].

1.4. Effects of corrosion

Corrosion is considered to be a major problem experienced in industries and in our everyday life.it is therefore a potent force, affecting lives, jobs and the economy in our everyday life. Below are some effects of corrosion; [1, 11].

\diamond Economic effects: Useful manufacturing equipment most of which are made from metals are degraded by corrosion. Because of corrosion, industries do lose huge amounts of money in maintaining and repairing of equipment, replacing corroded equipment, and overdesigning of material [1, 4, 9].

\diamond Safety effects: There are various uses of metals in construction industries as in the construction of bridges and huge buildings. when corroded, metals can result in failure or breakdown and thus causing harm or injuries to human beings. Corrosion also affects our traveling from home to work or anywhere, this is due to the fact that we use vehicle (including cars, planes, train and ships) which are made from metal and, so any damage due corrosion of this metal can cause accidents leading to injuries and deaths. Some failures in corrosion can result in explosions, fire, collapsing of structures [1, 4, 9].

✤ Health effects: The water we use may be contaminated as a result of leaching of contents from the corroded structures such as plumbing system and thus resulting in the malfunctioning of our body system i.e. causing diseases [8, 12]. ♦ Cultural effects: The statues of our heroes (e.g. political or social heroes, musical legends and many more) are made from metallic products. And these statues are considered to be very important by many nations since they pride themselves about those heroes. Since those statues are made from metal, they can be attacked by corrosion and therefore impacting the cultural beliefs of that nation [12].

1.5. Mechanism of metal corrosion

Normally for a corrosion process to take place, there are some conditions that must exist such as: a chemical potential difference between adjacent sites on a metal surface (or between alloy) of different composition, an electrolyte ought to be available in order to allow solution conductivity and as a source of material to be reduced at the cathode and lastly an electrical path through the metal or between metal must be present so as to permit electron flows [16, 17]. The electrolytic corrosion (an electrochemical reaction made of both anodic and cathodic reaction) is composed of two half-cell processes occurring at the anode (anodic half-cell reaction) and the cathode (cathodic half-cell reaction). The combined two half-reactions are known as redox reaction [16]. The cathodic half reaction involves the reduction reaction where the ions at the interface between the metal and the solution accepting the electrons from the metal whereas the anodic half reaction cell is the oxidation reaction involving the metal releasing electron. A typical example of electrochemical corrosion of metal in

contact with water is illustrated below. In this process, a metal goes under oxidation process and losses the electron in the equation below.

$$M \to M^{++} + 2e^{-} \tag{6}$$

A metal ion in contact with water or solution forms positively charged ions. Ions moves away from the metal and further oxidation takes place. The reduction reaction which occurs at the cathode, involving the acceptance of electron from the metal by species is solution, can be in the form of hydrogen-evolution or oxygen reduction, hydrogen ion under reduction process by the excess of electron at the cathode surface and there is the evolution of hydrogen gas.

$$2H^+_{(aq)} + 2e^- \qquad H^-_{2(g} \tag{7}$$

Cathodic reaction decreases when hydrogen is not removed from the surface, and this reduces the corrosion rate. The reaction in equation (7) is associated with the environment of low pH values (acidic conditions). When air is present, the reduction of oxygen is most likely to occur, according to the following equation:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{8}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^- \tag{9}$$

The reaction in equation (7), the hydrogen evolution, or the oxygen reduction with the formation of water in equation (8), take place in acidic

media. In some instances, oxygen reduction with formation of hydroxyl ion is likely to occur in neutral or alkaline environment.

1.5.1. Mild steel

Steels are said to be mild, medium-or high-carbon steel, according to the percentage of carbon they contain (mild steel contains approximately 0.05–0.25% carbon). The surface of the metal in air (except for gold) is covered with film oxide, which prevents the anodic dissolution. Mild steel has been widely employed under different conditions in chemical and allied industries in the treatment of alkaline, acid and salt solution, and therefore gets corroded when exposed to different environmental factors such as temperatures, water and air [18-20].

Iron in steel is said to be unstable under atmospheric conditions, and because of this behavior will deteriorate to a more stable state called iron oxide (Fe_2O_3). At ordinary atmospheric conditions, iron is at the lowest energy state known as an oxide, which is a type of rust. In the process, oxygen acts as catalyst facilitating the formation of iron oxide. This reaction is said to be very slow at ordinary temperatures, and tend to proceed faster when water is present. This simple process is shown in **Figure. 1.2** below [3].



Figure 1.2. Process involved in the formation of iron oxide in the electrochemical cell

1.6. Corrosion control

There are different corrosion prevention techniques that are known and are discussed as follows [1].

• **Material selection:** It is of vital importance to understand the corrosive attack that occurs on the metal. There are no materials that are resistant to corrosion in all environments. Therefore there is a need for materials to be frequently matched to the environment that we encounter in service [5, 9-11].

• **Protective Coatings:** Protective coatings are the most commonly applied corrosion control technique. They act as sacrificial anode or release substance that inhibits corrosive attack on substrate. There are two broad groups of coatings for corrosion protection namely:

• *Metallic coatings:* They provide a layer that alters the surface properties of the work piece to those of the metal being applied.

• *Inorganic coatings:* This type of coating can be produced by chemical action with or without electrical resistance. It includes porcelain, enamels, chemical-setting silicate cement lining and glass coatings [3, 12].

• <u>Cathodic</u> Protection: It uses electrochemical properties of metal in ensuring that the metal of interest is of the cathode of an electrolyte cell. Cathodic protection also reduces the rate of corrosion of a metallic structure by simply decreasing its corrosion potential, causing the metal to be closer to an immune state. This is an electrical means of corrosion control [4. 9-11].

• **Corrosion inhibitors:** A corrosion inhibitor is a substance that when added to the environment in minute concentrations decreases the rate of corrosion on the metal [2, 8]. They reduce the rate of corrosion by

- Adsorption of ions or molecules onto the metal surface.
- Increase or decrease the anodic or cathodic reaction.
- Decreasing the diffusion rate for reactants to the surface of the metal.
- And also by decreasing the electrical resistance of the metal surface [6].

Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are also

sometimes used as additives to prevent steel from flash rusting during wet abrasive blasting. Inhibitors can be classified as (1) passivators, (2) organic inhibitors which include slushing compounds and pickling compounds and (3) Vapour-phase inhibitors [11].

• **Over-design:** Over-design of structures simply refers to the common use of heavier structural member of thicker plates than actually required in anticipation of corrosion losses. The design and material selection are done in connection with each other. In this process, both the individual components, interactions between them and the relation to other structures and the surroundings are taken into consideration [4].

There are other corrosion protection methods which are not stated above. Therefore for this research purpose natural curcumin is used as corrosion inhibitor for corrosion of mild steel in acidic medium.

1.7. Previous Studies

Many studies have investigated of corrosion in acid medium. Recent studies on green inhibitors have shown that are more effective and highly environmentally benign compared to organic and inorganic inhibitors . Published research shows that, useful organic steel corrosion inhibitors are specially those containing hetero atoms or unsaturated functional groups that are able to interact with steel such as N, O, P, S and aromatic rings.

• We want to present some of previous studies comparing with our study.

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• The use of these natural products such as :

extracted compounds from leaves or seeds as corrosion inhibitors has been widely reported by number of publications such as: Oxandra asbecki[84], Neolamarckia cadamba[85], vanillin[86], Argemone Mexicana[87], Schinopsis lorentzii[88], Gum Arabic[89], adhatoda vasica[90], Aloe vera [91]

• Jodeh etal 2016 studies the inhibition performance of sulfamerazine (SFM) for corrosion of mild steel in HCl [92].

The corrosion inhibition characteristics of SFM on MS were investigated by WS ,EIS, and PDP was used as basis for studying the corrosion inhibition behavior of the compound.

The results show that the inhibition efficiency decrease with decrease in SFM concentration in the 1M HCl solutions but increases with decrease in temperature.

Langmuir isotherm best fits the data obtained suggesting chemical and physical adsorption as the adsorption mechanism between the SFM and the MS substrate.

Study the density functional theory was employed for theoretical calculations, the result obtained from experimental measurements and those from theoretical calculations are in good agreement.

Concentration/inhiber	SFM(%)	Curcumin(%)
5×10 ⁻³	93	93
1×10 ⁻³	91	90
5×10^{-4}	84	85
1×10^{-4}	76	78

 Table.1.1: comparison the efficiency between SFM and Curcumin at various concentration .

The efficiency of SFM and Curcumin are vary closed, but the curcumin is the better than SFM because protection the anodic and cathodic at the same time.

• Ouici etal (2015) studies the Corrosion Inhibition of Mild Steel in Acidic Media Using Newly Synthesized Heterocyclic Organic Molecules:Correlation Between Inhibition Efficiency and Chemical Structure [93].

The corrosion inhibition of mild steel in 5% HCl solutions by some new synthesized organic compounds namely (2-MMT), (3-MMT) and (2-HMT), the inhibition efficiency obtained by these compounds increased by increasing their concentration. The inhibition efficiency follows the order 2-MMT >3-MMT >2HMT.



The corrosion inhibition characteristics of three type on MS were investigated by WS ,EIS, and PDP was used as basis for studying the corrosion inhibition behavior of the compound.

Based on the marked decrease of the cathodic and anodic current densities upon introducing the inhibitor in the aggressive solution, 2- MMT, 3-MMT and 2-HMT can be considered as a cathodic inhibitor any time with a slight anodic trend, meaning that the addition of triazoles reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction.

• Electrochemical Study on Newly Synthesized Chlorocurcumin as an Inhibitor for Mild Steel Corrosion in Hydrochloric Acid[94].

A new curcumin derivative, i.e., (1E,4Z,6E)-5-chloro-1,7-bis(4-hydroxy-3methoxyphenyl)hepta-1,4,6-trien-3-one (chlorocurcumin), was prepared starting with the natural compound curcumin. the molecules can be considered a mixed-type inhibitor, adding chlorocurcumin to HCl solution

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reduces the anodic dissolution of mild steel and retards the cathodic hydrogen evolution.

The corrosion inhibition of mild steel in 1 M HCl by chlorocurcumin has been studied using (PDP) and (EIS).

he inhibition efficiency increases with the concentration of the inhibitor but decreases with increases in temperature.

The efficiency of chlorocurcumin at 1×10^{-4} M is 36% but the efficiency of our study 78%.

• Oguzie etal.(2005) studied the Corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue (MB) dye[95].

This study was investigated by gravimetric techniques at 303 and 333 K as well as thermometric technique. MB was shown to be an inhibitor in the acidic corrodent.

Inhibition efficiency increased with MB concentration but decreased with rise in temperature, with maximum value of 94–95% obtained for 5.0 mM MB at 303K.

Corrosion inhibition is attributed to the adsorption of MB on the mild steel surface via a physical adsorption mechanism.

These results were further corroborated by kinetic and activation parameters for corrosion and adsorption processes evaluated from experimental data.

• Taibi Ben Hadda etal (2014) studies the adsorption and Inhibition Effect of Curcumin on Mild Steel Corrosion in Hydrochloric Acid[96].

In this study the corrosion of mild steel using the curcumin in 1M HCl, Coupons were cut into $1.5 \times 1.5 \times 0.05$ cm³ dimensions having composition (0.09% P, 0.01% Al, 0.38% Si, 0.05% Mn, 0.21% C, 0.05% S. , and the remainder iron). The experimental results suggest that this compound is an efficient corrosion inhibitor and the inhibition efficiency increases with the increase in inhibitor concentration. In addition they did is theoretical study ,and the theoretical study based on enol form of curcumin and their result are support their experimental results.



Figure 1.3. Enol form structure of curcumin

In our study we are going to look at the effect of curcumin on MS using the following:

• The piece of steel we will use a thinner, because thinner steel used in electronic device, and it very important to know how the curcumin prevent the oxidation of these thin steel piece so we can improve their efficiency in this product ,the dimensions is $1 \times 1 \times 0.04$ cm³ having composition (0.370)

% C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu, and the remainder iron).

• The study the rate of corrosion of steel at different temperature at 30, 40, 50 and 60 °C with and without curcumin by determining the activation energy (Ea), activation enthalpy (Δ Ha) and activation entropy (Δ Sa).

• Using SEM and AFM to improve the effectiveness of inhibitor.in our study the theoretical study done by using DFT and MD simulations based on keto form. The curcumin have two structure (enol), and (Keto), the previous study take the enol form, in other hand our study take keto form of curcumin and their result are support their experimental results.



Figure 1.4. Keto form structure of curcumin

1.8. Research Aim and Objectives

1.8.1. Aim

• The main aim of this study is to investigate the inhibiting effect of natural curcumin keto form structure as corrosion inhibitor of mild steel in acidic medium.

- Study the corrosion in thinner piece of MS.
- This study employs gravimetric method, electrochemical techniques and quantum chemical methods.

1.8.2. Objectives

The objectives of this research are to:

• Employ gravimetric(WL measurement) and electrochemical techniques (PDP,EIS) to study the corrosion inhibition process.

• Find the inhibiting potential of the inhibitor and the effect of their concentrations and the temperature on the corrosion rate using thermodynamic, kinetic and adsorption principles.

• Study the $E_{HOMO,}E_{LUMO}$, and gap energy using theoretical methods (DFT and Molecular dynamic simulations) to optimize the geometry, calculate the quantum chemical descriptors and determine the relationship between inhibition efficiency and structural properties of tested compound.
Chapter Two Experimental

Chapter Two Experimental

2.1. The inhibitor used in this study

The inhibitor curcumin used in this work and all chemicals were purchased from Aldrich Chemical Company (Curcumin \geq 80%, curcuminoid content \geq 94%) and used without any further purification unless otherwise specified. The inhibitor molecule is represented in **Figure.2. 1**. As can be seen, they have different active groups, which can act as adsorption centers.



Figure 2. 1: structure of curcumin.

2.2. Test solution

An aggressive solution of hydrochloric acid of 1.0 M concentration was prepared by dilution with double distilled water of 12.076 M HCl (analytical grade). The concentration of inhibitor used was varied from 1×10^{-4} to 5×10^{-3} M, and the volume of the electrolyte employed was 80 mL in all studies. The carbon steel specimens employed in this study was purchased from(Metal Samples company USA) having composition: (0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu, and Fe balance).

2.3. Weight loss tests, electrochemical measurements and surface observation.

The samples of carbon steel used in the gravimetric method are in the form of a square of dimensions 1 cm \times 1 cm \times 0.04 cm dimensions. were suspended for 6 hours in a beaker containing 100 ml of 1 M Hydrochloric acid solution without and with addition of various concentrations of the curcumin, in the absence of agitation maintained at a constant temperature 303K. At the end of the experiment, the sample is removed from the solution and then cleaned with distilled water. The surface analysis of MS samples in the aggressive solution and with the optimal concentration of curcumin (5 \times 10⁻³ M) for 6 h at 303 K was performed using scanning electron microscopy (SEM) and Atomic Force Microscopy(AFM). The gravimetric tests were performed by triplicate at same conditions.

The experimental device allowing the plotting of the polarization curves and impedance diagrams is a Voltalab PGZ 100 potentiostat / galvanostat driven by a computer and associated with "Voltamaster 4" software ,the SEM model "JEOL JSM 6510 lv",and the AFM model" Apha300 RA Correlative Raman" were used also . For all the tests we used a thermostated double cell wall (Tacussel type CEC / TH) containing three electrodes; a working electrode consisting of a carbon steel rod is coated in an epoxy resin, which makes it possible to delimit a flat surface of 1 cm² in contact with the solution and which avoids any infiltration of electrolyte. The latter is introduced into a polytetrafluoroethylene sample holder disposed opposite the platinum auxiliary electrode and a saturated calomel KCl electrode (SCE) as the reference electrode. The electrode is maintained at its free corrosion potential for 30 minutes under normal aeration conditions. The measurements are carried out at 303K in a 1M solution of dilute hydrochloric acid. The intensity-potential curves are obtained in potentiodynamic mode with a scanning speed of 1 mV / s. This speed allowed quasi-stationary conditions to have a good reproducibility of the results. The recording of these curves took place within a potential interval of between -800 and -200 mV/SCE. The direction of polarization appears to have an effect on the corrosion current. To eliminate as much as possible this phenomenon, we have chosen the direction that begins from the cathodic potential (-800 mV) and tends towards the anodic potential (-200 mV) passing through Ecorr. The measurement of the electrochemical impedances was carried out under the same conditions as the plotting of the polarization curves at 100 kHz to 10 MHz using a sinusoidal perturbation potential of 10 mV.

2.4. Theoretical calculations and dynamic simulations.

Unlike the situation with experimental results, there are no statistical errors in the results obtained using computational methods. Some molecular properties obtained using computational methods have shown correlation with corrosion inhibition efficiency[21]. There are several computational methods that are utilized in the study of the properties of molecules. These methods may be classified into molecular mechanics and quantum chemical approaches. Molecular mechanics is based on the assumption that molecules can be described by using only classical physics concepts and laws[22,23]. The atoms making a molecule are considered as if they were spheres having a mass and connected by springs. Each spring has its own force constant and the set of force constants associated with all the springs is called the force fIeld of the molecule. In the force field, one or more parameters sets are included. These parameter sets fit the equations and atom types to experimental data. The internal structure of atoms is not considered and, therefore, electrons are not considered explicitly. Individual atoms are viewed as being of different types according to their characteristics in the given molecular context. The energy of the molecule is approximated by a sum of terms describing how the potential energy of the molecule varies with the position of the particles in space[22–24].

Without considering electrons explicitly, the computational procedures are simplified to a great extent because computations related to electronic interactions are avoided. For this reason, molecular mechanics is capable of handling large-size molecular systems, such as large organic molecules, biological macromolecules and polymers[23]. As far as the size of molecules is concerned, molecular mechanics is the only technique, available to computational chemists, that is capable of handling molecules with thousands of atoms.

The discovery of the molecular properties of the studied inhibitor have been executed by calculation of quantum chemical methods. In the last years, it has been found that Density functional theory (DFT) has become the most widely used methodology for theoretical calculations because accuracy is high with in short time. (DFT) has become a proficient technique to predict chemical reactivity of molecules, clusters and solids[25]. In this study, quantum chemical calculation were carried out on the natural curcumin using DMol³ module of Materials Studio package[26]. DMol³ is designed for the realization of large scale density functional theory (DFT) calculations[27–29]. Quantum chemical parameters were calculated using the gradient-corrected functional method (GGA) with a Double Numeric Plus polarization (DNP) basis set (version 3.5) and a Becke One Parameter (BOP) functional[30]. The solvation effects (aqueous phase) was included in DMol³ calculations by COSMO[31] controls.

The ionization energy (I) and the electronic affinity(A) were determined by the values of the energies of the HOMO and LUMO orbital[32]:

$$I = -E_{HOMO} \tag{1}$$

$$A = -E_{LUMO} \tag{2}$$

The values of I and A are exploited in order to find the values of the electronegativity (χ) and the global hardness (η) of the inhibitory molecule[33]:

$$\chi = \frac{I+A}{2} \tag{3}$$

$$\eta = \frac{I-A}{2} \tag{4}$$

Chemical Softness is the reciprocal parameter of global hardness, it is determined from the equation[34]:

$$\sigma = \frac{1}{\eta} \tag{5}$$

The number of transferred electrons (ΔN) is calculated by application of the Pearson method using the equation[35]:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \tag{6}$$

Where χ_{inh} and χ_{Fe} denote the absolute electronegativity of inhibitor molecule and iron, η_{inh} and η_{Fe} denote the absolute hardness of inhibitor molecule and iron respectively. A theoretical value of $\eta_{Fe}=0$ and $\chi_{Fe}=7eV$ (since for bulk metallic atoms I = A) had been considered in order to calculate the ΔN values[36,37]. Recently, it has been reported that the value of $\chi_{Fe} = 7$ eV is theoretically not acceptable as electron-electron interactions had not been considered, only free electron gas Fermi energy of iron is considered[38–40]. Hence, the researchers are recently using work function (ϕ) of the metal surface instead of χ_{Fe} , as it is more appropriate measure for its electronegativity[38–40]. Thus, Eq. 6 is rewritten as follows:

$$\Delta N = \frac{32}{\frac{\phi - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}} \tag{7}$$

The obtained DFT derived ϕ values for Fe₁₁₁, Fe₁₁₀ and Fe₁₀₀ surfaces are 3.88, 4.82 and 3.91 eV, respectively[38,39]. In this study, we use only Fe₁₁₀ surface due to its higher stabilization energy and packed surface.

The local reactivity of inhibitor molecules were obtained by condensed Fukui functions[41]. Finite difference approximations have been used to get Fukui functions in favor of electrophilic and electrophilic attacks as[42]:

$$f_k^- = P_k(N) - P_k(N-1)$$
(8)

$$f_k^+ = P_k(N+1) - P_k(N)$$
(9)

Here, gross charge of the atom k is denoted by P_k . The $P_k(N + 1)$, $P_k(N)$ and $P_k(N - 1)$ are the charges of the anionic, neutral and cationic species, respectively.

Currently, MD simulation has been emerged as a very popular exploratory technique to studies of interaction between concerned metal surfaces and inhibitor. As earlier observed for the three kinds of Fe surfaces (111, 110 and 110), Fe_{111} and Fe_{100} surfaces have relatively open structures, with a vacuum layer on the topside. In this present investigation, calculations were carried out using Materials studio package[43]. in a 10 x 10 super

cell using the COMPASS force field and the Smart algorithm with NVT ensemble has been employed to study the interactions between the inhibitor molecules and the surface of $Fe_{110}[43]$. Herein, Fe_{110} surface has been preferred as it has a packed surface and high stability compared to other Fe surfaces[44]. The Temperature was fixed at 303 K. More detail of modeling dynamic simulation is referenced from the published articles[45,46].

Chapter Three Result and discussion

Chapter Three Result and discussion

Introduction

Corrosion reflects the reactivity of most industrial materials with respect to the environments in contact with which they are placed during their use. It is estimated that 25% of the world's annual steel production is destroyed, which is about 150 million Ton/Year .[47–49].

Widely used acid solutions in the industry, the main areas of application are being picking and cleaning by acid, stimulation of oil wells, and the elimination of localized deposits (tartar not uniformly spread, rust, bacterial deposits, etc.). The high reactivity of acid solutions with steel leads to the use of inhibitors to prevent corrosion which are indispensable in order to limit the attack of metallic materials. Of the commercially available acids, hydrochloric acid is the most frequently used and is increasingly replacing sulfuric acid. Acid inhibitors require a electron rich through which the molecule can attach to the metal surface, including the organic groups (N, NH₂, S and OH)[50–52].

The inhibition of corrosion by these organic compounds results from their adsorption on the surface of the metal. These adsorption phenomena can be described by two major type ,chemisorption and physisorption. These two types of adsorption reaction are affected by the nature, the metal

charge, the inhibitor structure and the type of electrolyte[53–55].

Natural Curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione] is polyphenol extracted from the roots of Curcuma longa L. (Zingiberaceae) and commonly used as a spice and food-colouring material [54]. It is also used for long time as a naturally occurring medicine to treat various diseases associate with inflammation. Curcumin exhibits multiple pharmacological activities including antioxidant, anticarcinogenic and antiinflammatory in different models of rodents. In recent years, curcumin has been reported to reduce the inflammatory response by regulating the production of inflammatory molecules in vitro models [55, 56].

In the present investigation, we have evaluated the efficiency of the natural curcumin as a corrosion inhibitor in 1.0 M Hydrochloric acid using electrochemical techniques such as EIS and PDP in addition to WL measurements. SEM analysis were used to confirm the adsorption of tested inhibitor. We have correlated the observed inhibition efficiency by DFT calculations and MD simulations to better understand the inhibition mechanism of tested compound.

3.1. Electrochemical study

3.1.1. Polarization curves

Tafel plots were employed as a reliable tool in order to study the behavior of the mild steel in (1.0M)HCl. The PDP curves for natural curcumin is shown in **Figure 1** while **Table 1** lists the PDP parameters for the tested inhibitor.



Figure. 3.1. PDP curve of mild steel in 1.0 M HCl in blank and with different concentration of the natural curcumin at 303K.

On the basis of these results, it appears that the cathodic curves have a wide range of linearity with a slight modification of the Tafel cathodic slopes indicate that Tafel's law is well verified[14,56]. We also note that the addition of the compounds is accompanied by a marked decrease in the cathodic branches when the concentration of the inhibitors is increased. The inhibitor appears to be adsorbed first on the steel surface before acting simply by preventing its active positions [57,58]. Same behavior has also been observed in many studies concerning carbon steels in the same medium with different organic inhibitors. In the same way, in the anodic branches, in the densities of the current densities. As **Table 1** shows, the

values of β c and β a have not any significant change in presence of tested inhibitors, as a result, anodic and cathodic reactions are not effected and the inhibition action of natural curcumin is mainly attributed to the geometric blocking effect meaning the reduction the zone of reaction on the mild steel surface by blocking the active reaction sites while the mechanism of corrosion reaction remains unaffected during corrosion inhibition process[57]. The electrochemical parameters that are collected in **Table 3.1** derived from these curves.

Table.3.1. The parameters of PDP of the mild steel at different concentrations of the natural curcumin in 1.0 M Hydrochloric acid and efficiency of inhibition at 303 K.

Inhibitors	Concentration	$-E_{\rm corr}$	$-eta_{ m c}$	eta_{a}	<i>i</i> _{corr}	$\eta_{_{\mathrm{PDP}}}$	θ
	(M)	(mV	(mV	(mV	(μΑ	(%)	
		SCE ⁻¹)	dec^{-1})	dec^{-1})	cm^2)		
HCl	1.0	496	150.19	132.2	564	-	-
	5×10^{-3}	488	161.2	114	37	93	0.93
Curcumin	1×10 ⁻³	494	165.3	111	56	90	0.90
	5×10^{-4}	489	183.4	117	85	85	0.85
	1×10 ⁻⁴	487	159.7	112	123	78	0.78

The efficiency values of inhibition are calculated by following expression[57]:

$$\eta_{\rm PDP}(\%) = \left[1 - \frac{i_{\rm corr}}{i_{\rm corr}^{\circ}}\right] \times 100 \tag{10}$$

where i_{corr} and i_{corr}° are the current densities of corrosion with presence and absence natural curcumin, respectively. Generally, it can be shown that depending on the concentration, with increases in concentration of inhibitor,the (E_{corr}) values stay unchanged, and the current densities of corrosion (i_{corr})

decrease significantly. These observations confirm the mixed character of the tested inhibitor and clearly show The anodic dissolution rate is reduced by this inhibitor, and the reduction of H + protons[59,60].

3.1.2. Measurements of electrochemical impedance spectroscopy

The acquisition of (EID) at the corrosion potential and for different concentrations aims to complete the understanding of the corrosion and inhibition mechanisms of MS in acidic medium. The **Figure 2** show the representative plots of tested curcumin. In this investigation, the spectrum pattern is similar with and whithout of the inhibitor. The spectra are in the form of a single capacitive loop. generally ,for all diagrams the attendence of a single capacitive loop indicates that by charge transfer process the reaction of corrosion can be controlled on a heterogeneous and irregular solid surface electrode[61]. This capacitive loop is also attributed to the formation of protective thin film layer on the surface of the metal during

the corrosion inhibition process. The EIS spectra can be fitted with the equivalent circuit model of the form in **Figure 3**.



Figure. 3. 2. Nyquist curves for MS in 1 M hydrochloric acid for selected concentrations of curcumin at 303K.



Figure. 3. 3. The electrochemical equivalent circuit used to fit the impedance spectra.

Table 2 lists the values of EIS parameters obtained by fitting the EIS spectra, together with the values of the efficiency of inhibition calculated by by this relation [57]:

$$\eta_{EIS}(\%) = \left[\frac{R_{\text{ct(inh)}} - R_{\text{ct}}}{R_{\text{ct(inh)}}}\right] \times 100 \tag{1}$$

where, R_{ct} and $R_{ct(inh)}$ are charge transfer resistances absence and presence inhibitor, respectively.

The double layer capacitance (C_{dl}) calculated by CPE parameter values n and Q using the relation [60]:

$$C_{\rm dl} = \sqrt[n]{Q \times R_{\rm ct}^{\rm l-n}}$$
(2)

to measure homogeneity surface by CPE where Q is the magnitude and n is the exponential term of a CPE [62].

Table 3. 2. Electrochemical impedance spectroscopy corrosionparameters of mild steel in 1M HCl at different concentrations of thecurcumin at 303 K.

Inhibitors	Concentration	$R_{\rm ct}$		$Q \times 10^{-4}$	$C_{ m dl}$	$\eta_{ m EIS}$	θ
	(M)	$(\Omega \ cm^2)$	п	$(S^n\Omega^{-1}cm^{-2})$	$(\mu F \ cm^{-2})$	%	
Blank	1.0	29.35	0.89	1.7610	91.86	-	-
	5 x 10 ⁻³	617	0.89	0.2737	16	95	0.95
Curcumin	1 x 10 ⁻³	533	0.85	0.4124	21	94	0.94
	5 x 10 ⁻⁴	289	0.83	0.6872	31	89	0.89
	1 x 10 ⁻⁴	165	0.87	0.7322	37	82	0.82

According to the obtained parameters, it is found by adding the curcumin decreases the value of the double layer capacitance C_{dl} and increase that of the R_{ct} . the main reason in decreasing of C_{dl} to adsorption of the curcumin molecules to make protective layer. [57,63]. It is observed that the values of Q decrease when the concentration of curcumin increases and are lower than those measured in the absence of the inhibitor. This result suggests that Q values are mainly influenced by inhibitor concentration. The values of IE (%) calculated by EIS method are agree with the polarization measurements.

3.2. Weight loss measurements

3.2.1. Concentration effects

The mild steel gravimetric measurements were carried out in acidic solution (1M Hydrochloric acid) with and without of various concentrations of the curcumin for 6h at 303 K. The values of the η_{WL} (%), and corrosion rates (W) derived from the WL measurements after 12 h of immersion time are listed in **Table.3.3**.

Inhibitors	Concentration (M)	$(\text{mg cm}^{-2} \text{ h}^{-1})$	$\eta_{_{ m WL}}$ (%)
HC1	1	1.135	-
	5 x 10 ⁻³	0.075	93
Curcumin	1 x 10 ⁻³	0.102	91
	5 x 10 ⁻⁴	0.192	83
	1×10^{-4}	0.260	77

 Table 3. 3. WL data of mild steed in 1.0 M hydrochloric acid for

 different concentration of the natural curcumin at 303 K.

The following equations were used to calculate the efficiency of curcumin η_{WL} (%) and the surface coverage (θ)[63]:

$$\eta_{WL}(\%) = \left[\frac{W^{\circ} - W}{W^{\circ}}\right] \times 100 \tag{3}$$

$$\theta = \left[\frac{W^{\circ} - W}{W^{\circ}}\right] \tag{4}$$

Where *W* and *W*[°] are the corrosion rates in presence and in absence of different concentrations of natural curcumin, respectively, θ is a surface coverage degree of tested natural curcumin. On the basis of these data, the rate of corrosion of MS increases with decreasing the curcumin concentration. In addition, increasing concentration of natural curcumin the efficiency of protection increases. The adsorption of natural curcumin at the mild steel interface the hydrochloric acid, the corrosion inhibition attributed [60,63].

3.2.2 Effect of temperature

In the present study, temperature effect was studied in the rang of 303-333 K. The results are shown in **Table.3.4**. From these results, it can be seen that as temperature increased there is a decrease in IE%, which may be explained by desorption of curcumin from MS surface. In addition, it is apparent from the results that the value of the (C_R) increases on increasing temperature for uninhibited as well as inhibited solutions[64]:

Table 3.4. WL measurements parameter of MS in 1M HCl containing 5×10^{-3} M of curcumin at various temperatures.

Inhibitor	TemperatureCR		η_{w}	θ
	(K)	$(mgcm^{-2}h^1)$	(%)	
	333	10.029	-	-
BLANK	323	5.032	-	-
	313	2.466	-	-
	303	1.135	-	-
	333	2.2204	77	0.77
Curcumin	323	0.8542	83	0.83
	313	0.2761	88	0.88
	303	0.0756	93	0.93

The density of current depend to temperature, can be represented by Arrhenius equations and transition state equations [65,66]:

$$C_R = k \exp\left(\frac{-E_a^*}{RT}\right) \tag{16}$$

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^*}{R}\right) \exp\left(-\frac{\Delta H_a^*}{RT}\right)$$
(17)

Where:

h:Plank's constant.

N : Avogadro's number.

 ΔH_a^* enthalpy of activation

T: temperature.

 E_a^* :activation energy.

 ΔS_a^* : entropy of activation.

R: gas constant.

k : Arrhenius constan



Figure. 3. 4. Arrhenius plots for mild steel in 1 M Hydrochloric acid in the without and with of $5*10^{-3}$ of tested curcumin at various temperatures.



Figure. 3. 5. Transition state plots for mild steel in 1 M HCl in the without and with of $5*10^{-3}$ of tested curcumin at various temperatures.

The apparent E_a^* determined from the slopes of ln (I_{corr}) vs 1/T graph given in **Figure.3.5**. The curve ln (I_{corr}/T) as a function of 1 / T **Figure.3.5-b** is a straight line whose slope is ($\Delta H_a^*/R$) and the ordinate at the origin is (ln(R/N A h) + ($\Delta S_a^*/R$)) and thanks to this law, parameters parameters ΔH_a^* and ΔS_a^* were obtained and cited in the **table 3.5**.

Inhibitor	Ea	$\Delta \mathbf{H_a}$	ΔS_a	$\mathbf{E}_{\mathbf{a}}$ - $\Delta \mathbf{H}_{\mathbf{a}}$
	(kJ/mol)	(kJ/mol)	$(Jmol^{-1} K^{-1})$	
Blank	60.79	58.16	-51.84	2.6

91.97

37

2.6

94.59

Curcumin

Table 3.5. Activation parameters for MS corrosion in 1M HCl in the without and with 5×10^{-3} M of curcumin at various temperatures.

The values of activation parameter (E_a^*) and transition state Parameters $(\Delta H_a^*, \Delta S_a^*)$ were calculated by fitting Arrhenius plots **Figure.3.5-a** and transition state plots **Figure3.5-b**, respectively. The increased value of the (E_a^*) in the presence of curcumin is attributed to the presence of inhibitor, creation of energy barrier of reaction of corrosion [67,68]. The positive values of ΔH_a^* this mean the dissolution of MS is endothermic in hydrochloric acid solution, and the positive values of ΔS a reveals that the adsorption process is accompanied by a increase in the entropy which acts as a driving force for adsorption of the inhibitor on the mild steel surface. The value of ΔS a increases in the presence of the inhibitor and is generally interpreted by increases in the disorder, as the reactants are converted to activated complexes[69].

3.3. Adsorption isotherm

The adsorption isotherm give clear information regarding the interaction between surface of MS and curcimin. From the above results, we can conclude that the coverage ratio of the surface θ (IE% / 100), calculated using the weight loss measurements, increases the concentration of

curcimin which is attributed to adsorption increases of curcimin on the surface of MS. As is known, the adsorption of any inhibitor is displacement the water molecules on the surface of the metal[60]:

$$Or_{(sol)+n}H_2O_{(ads)} \longrightarrow Or_{(sol)+n}H_2O$$

Where Or $_{(ads)}$ and Org $_{(sol)}$ are organic molecules respectively in the adsorbed on the surface of the MS and solution . H₂O (ads) is the water molecule adsorbed to the surface MS, and n the number of H₂O molecules replaced by an curcumain unit. Different adsorption isotherms were examined for this adsorption behavior of the studied compound such as Frumkin , Temkin and Langmuir and we found that the experimental data fit well to Langmuir isotherm **Figure 6** expressed by the following equation[57,60]:

$$\frac{C_{\rm inh}}{\theta} = \frac{1}{K_{\rm ads}} + C_{\rm inh}$$
(5)

Where C_{inh} is curcumain concentration, K_{ads} is equilibrium constant of adsorption-desorption.

Calculated the free energy of adsorption ΔG_{ads}° using the K_{ads} values by the Equation 9 [70]:

$$\Delta G_{\rm ads}^{\circ} = -RT \ln(K_{\rm ads} \times C_{\rm solvent}) \tag{6}$$

Where C_{solvent} : is the molar concentration of solvent (For H₂O is 55.5 mol L⁻¹).



Figure. 3.6. Langmuir adsorption of curcumain on the MS surface in 1.0 M Hydrochloric Acid at 303K.

Table 3.6. Adsorption parameters of curcumin on the MS surface in1.0 M Hydrochloric Acid at 303K.

Inhibitor	Slope	$K_{ads}(M^{-1})$	ΔG_{ads}°
			(kJ/mol)
Curcumin	1.06	70610	-38

The K_{ads} has a high value which indicates the capacity of curcumin adsorption on the MS is high. The standard free energy ΔG_{ads}° of adsorption has negative value, reflect the reaction is spontaneous of the adsorption of curcumin on MS surface and the strong Generally; we define as (physical adsorption) if the standard free energy ΔG_{ads}° has the values of -20 kJ/mol or less negative are associated with an electrostatic interaction between the charged of curcumin and the charged mild steel surface ,and if values more negative than -40 kJ /mol that mean the charge transfer of curcumin to ΔG_{ads}° surface or the sharing the charge between the curcumin and the charged MS surface to make covalent bond with high binding energy. [60,63]. In this study, the value of ΔG_{ads}° the natural curcumin adsorption on the mild steel surface suggests that interaction of curcumin with MS involves physical and chemical adsorption [63].

3.4. Scanning Electron Microscopy

The scanning electron microscopy device was model DO-2010, the analysis was carried out with and without of 5×10^{-3} M (the optimal concentration) of natural curcumin for 6h. The surface morphology without inhibitor Figure.3. 7a is highly damaged due to rapid corrosion attack in acidic solution. However, the mild steel surface containing curcumin Figure.3.7. b is significantly improved, which reveals that the corrosion process is reduced[71].



Figar. 3. 7. SEM images of mild sreel : (a) in 1.0 M Hydrochloric Acid and (b) in 1.0 MHCl and 5×10^{-3} M of curcumin after 6h of immersion time at 303 K.

3.5. Atomic Force Microscopy.

In order to continue study of interaction between nature curcumin and surface of MS, the AFM micrographs of the mild steel surface is after 6h immersion time without and with 5×10^{-3} M of curcumin in 1 M HCl shown in **Figure 3.8**. It is observed the surface of MS strongly is damaged and corroded without curcumin, because that aggressive attack by Hydrochloric acid solution with average surface roughnesses of 2.3 µm. However, in the presence of curcumin, the AFM micrograph the presence of the natural curcumin molecules on the surface of the mild steel makes adsorption and formation of a protective film which shows a noticeable improvement in the surface morphology. The calculated average surface roughnesses with natural curcumin was 1.2 µm.



Figure. 3. 8. AFM images of MS in blank and in blank + 5×10^{-3} M of inhibitor after 6h of immersion time at 303 K.

3.6. Molecular modelling

The interaction of corrosion inhibitors and metal surfaces depend on the molecular properties of the inhibitor. These molecular properties include the geometry of the molecule, the electronic properties such as partial atomic charges, frontier molecular orbitals, electronegativity and electronic energy [72,73]. These molecular properties are associated with the presence of particular groups on organic molecules, including the presence of heteroatoms, it bond, aromatic systems and electron density [74,75]. It is reported that the molecules with these functional group have high tendency to act as corrosion inhibitors[74]. (HOMO) Highest occupied molecular orbital and (LUMO) Lowest unoccupied molecular orbital - The LUMO and LOMO orbitals have an important role in the reactivity of inhibitors with the metal surface. Highest occupied molecular orbital is referred to as the orbital that could act as an donate electron, because it is the outermost (highest energy) orbital with electrons, while Lowest unoccupied molecular orbital could act as the electron acceptor, because it is the innermost (lowest energy) orbital having a capability to accept electrons[76,77]. In the interaction between the mild steel surface and the natural curcumin, it is considered that the corrosion inhibitor give electrons to the vacant or d orbital partially filled of the MS surface. In this way, the corrosion inhibitors are considered to be electron donor while the metal surfaces are often considered as electron acceptors. Therefore, molecules with electron donating ability (e.g. molecules with heteroatom, it-electrons and aromatic functional groups) are preferred for interaction

with metal surfaces. Also a corrosion inhibitor with high HOMO energy is preferred to a corrosion inhibitor with low HOMO energy for the interaction with the mild steel surface.

Charges on the atoms of the molecules of corrosion inhibitors have an important role in determining selectivity. This means that the metal surface interact with specific regions on the organic inhibitors. Usually the more negative the charge on the natural curcmain , the greater the density of electron and therefore the greater the tendency of that particular atom to give electrons to the mild steel surface[78]. The interactions between the metal surface and the organic molecule usually occur on the regions with more negative charges. Since heteroatorns π -bond and aromatic systems have high electron density: the metal surface is most likely to interact with these regions of organic molecules[79].

In this regard, (DFT) calculations were performed using DFT electronic structure program DMol³ implemented in Materials Studio Software. The (HOMO) and (LUMO) derived from the optimized molecular structure are represented in **Figure.3.9**.



Figure.3.9. Optimized molecular structure and frontiers orbitals distributions of the tested natural curciman.

55

As can be shown from the **Figure.3. 9**, the (LUMO) orbital is distributed around heteroatoms and phenyl ring, meaning the good ability of the tested natural curcumin to accept electron from the metallic surface. In case of the (HOMO, the electron density distributed in the second part of tested inhibitor. The quantum chemical calculations such as; $E_{(LUMO)}$, $E_{(LOMO)}$, ΔN and ΔE are represented in **Table.3.7**.

Low value of the difference between HOMO and LUMO energies known as energy gap (ΔE) will facilitate the adsorption of an natural curcumin [49,80]. A number of researchers have reported excellent correlations of this parameter with experimental efficiencies of natural curcumin [81]. The (ΔE) is low explains the stability of interaction between the natural curcumin and mild steel surface. ΔN is a value to measurment the capacity electron transfer between chemical compound and metal ,if $\Delta N > 0$ the electron transfer from the curcumin to mild steel and vice versa if $\Delta N <$ 0[82,83]. The obtained values in the present investigation indicates that the natural curcumin has positive ΔN values as represented in **Table.3.7**, meaning the high capacity of this curcumin to donate electrons to the metal surface.

Table. 3.7. The computed quantum chemical parameters for naturalcurcumin using DMol³ method.

Inhibitor	$E_{(LUMO)}$	$E_{(\text{HOMO})}$	ΔE_{gap}	ΔN_{110}
	(eV)	(eV)	(eV)	
Curcumin				0.681
	-1.946	-4.379	2.433	

The Fukui function is a index of reactivity to measure the region of molecule which can donate or accept electrons in a reaction. [79,79].. In the simpler version, the Fukui functions are estimated and interpreted from the computation of a change of the electronic density due to the removal (resulting in an cation) or addition (resulting in an anion) of one electron from (or to) the whole molecule. The nucleophilic, f_k^+ (*i.e.*, when there is a gains of electrons), electrophilic f_k^- (*i.e.*, when there is a loss of electrons) were calculated for each atom in tested compound[57]. As can be seen from the **Table 6**, the C (14), C (16) and O (27) are the sites attack as nucleophilic. In case of the electrophilic attack, while the C (11), O (7) and O (26) are the atoms which preferred for the electrophilic attack **Figure.3.9**. These results are consistent with the electron distribut between HOMO-LUMO orbitals.

Atom	f^+	f^-
C ₁	-0.012	0.027
C_2	0.009	0.028
C ₃	0.010	0.017
C_4	0.017	0.041
C 5	0.009	0.037
C ₆	0.013	0.015
O ₇	0.023	0.073
O ₈	0.008	0.034
C ₉	-0.008	-0.023
C ₁₀	0.034	0.010
C ₁₁	-0.015	0.050
C ₁₂	0.009	0.013
C ₁₃	-0.018	-0.008
C ₁₄	0.050	0.005
C ₁₅	0.029	0.001
C ₁₆	0.081	0.012
C ₁₇	-0.020	0.007
C ₁₈	0.034	0.006
C19	0.012	0.008
C ₂₀	0.047	0.020
C ₂₁	0.022	0.010
C ₂₂	0.031	0.007
O ₂₃	0.047	0.029
O ₂₄	0.016	0.013
C ₂₅	-0.018	-0.008
O ₂₆	0.042	0.092
O ₂₇	0.087	0.019

Table.3.8. The Fukui indices of the natural curcumin calculated usingDMol³.

3.7. MD simulations

Molecular Dynamic (MD) simulations have been done to further study the interactions between tested natural curcumin and Fe_{110} surface in presence of all concerned species, *like* water molecules, Cl^- , H_3O^+ and one molecule of investigated compounds. From the final configurations of tested

inhibitors **Figure 1-2**, its clearly observed that the curcumin molecule move to the Fe₁₁₀ surface to almost parallel or flat disposition. The adsorption of ths reaction can be occurred on the iron surface through the oxygen atoms, methoxy groups and π -bonds present in their molecular structure. The Fe₁₁₀ binding energy of adsorption of this compound is is found to be 647.04 kJ mol⁻¹. The higher positive values of binding energy is an indication of an effective adsorption and consequently the formation of natural curcumin layer adsorbed on Fe₁₁₀ surface, the conclusion of this simulations of natural curcumin can be easly1 adsorbed on Fe₁₁₀ surface. The deduction seems reasonable because the high inhibition efficiency calculated from experimental results.





Figure . 3. 10 Side and top show the adsorption of the natural curcumin on the iron surface in solution
4. Conclusion.

In this investigation, the natural curcumin was found to give best efficiency to prevent corrosion of mild steel in 1M Hydrochloric acid. the efficiency of inhibition increases with increasing concentration of the natural curcumin. The PDP results show that tested compound acts as cathodic and anodic inhibitor. The diameter of capacitive loops and resistance of charge transfer are highest with all concentrations of tested inhibitor. The adsorption of natural curcumin follows the Langmuir adsorption isotherm. The surface examination study by SEM showed the complete adsorption of natural curcumin in meld steel surface. The roughness study by AFM showed the improvement in the surface. The theoretical study using DMol³ method and MD simulations gives a better overview on the reactivity of tested compound towards mild steel and are in good agreement with the experimental results obtained by WL measurement, electrochemical studies, and surface examination.

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دراسة كهروكيميائية ونظرية في تأثير الكركم كمثبط للتآكل كربون الحديد في وسط حمضي

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> اشراف أ. د. شحدة جودة د . عثمان حامد

قدمت هذه الاطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء، في كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس – فلسطين. دراسة كهر وكيميائية ونظرية في تأثير الكركم كمثبط للتآكل كربون الحديد في وسط حمضي

يشكل تأكسد الحديد (صدأ) عيب من العيوب الأساسية للحديد الكربوني (الفولاذ) خصوصا في المصانع التي تستخدم المعدات الصناعية المكونة من الفولاذ والتي يتم غسلها في الحمض ،حيث يوجد لتأكل الحديد مشاكل كثيرة ومختلفة، وأثار التأكل على الفولاذ يشكل خطر على أمنة وفعالية هذه المعدات وفي أغلب الأحيان تكمن الخطورة في فقدان كتلة من المعدن ،حيث هنا يتم البحث عن بدائل قد تكون مكلفة مثل تغير نوع المعدن او قد تكون خطيرة مثل طلاء الفولاذ بمادة ضارة في البيئة.

لتجنب هذه التكلفة او المخاطرة العالية في أستخدام مادة ضارة للبيئة تم البحث عن مادة طبيعية لمنع تعرض الفولاذ الى الهواء او الماء،حيث تم استخدام الكركم الطبيعي لعمل طبيقة رقيقة على سطح الفولاذ لمنع تفاعل الفولاذ مع الهواء .

تم أستخدام الكركم الطبيعي الموضوع في 1.0 M HCl على درجة حرارة 303 كلفن، وتم اجراء بعض التجارب لتحقق من مدى فعالية الكركم، حيث تم فحص مقدار التغير في نقصان في كتلة المادة قبل وبعد استخدام الكركم واعطى نتائج جيد، ثانيا فحص المعاوقة في الكيمياء الكهربائية من حيث منع انتقال الألكترونات .

تبين ان للكركم قدرة عالية جدا على التثبيط والأمتزاز على سطح الفولاذ، حيث انه يتبع نموذج لانغموير الامتزازي، والنتائج التي تم الوصول اليها من التحليل الطيفي للماوقة الكهروكيمائية كشفت عن قدرة الكركم في مقاومة نقل الشحنة، وايضا من خلال الدراسة النظرية كان تطابق جيد مع التجربة العملية.