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Study of the Inhibition Effect of Walnut Shell Extract
on the Corrosion of Carbon Steel (XC70) in an Acidic
Medium

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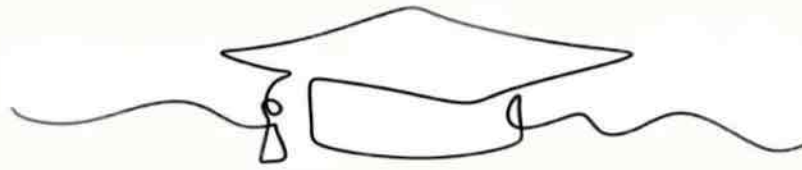
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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿وَأَنْزَلْنَا الْحَدِيدَ فِيهِ بَأْسٌ شَدِيدٌ وَمَنَافِعُ لِلنَّاسِ﴾

صَدَقَ اللَّهُ الْعَظِيمُ



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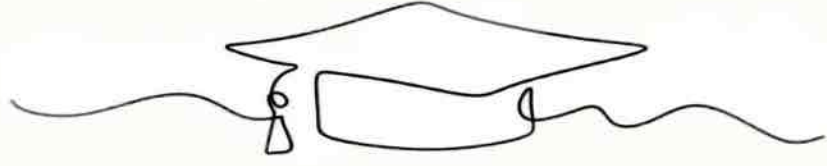
«Praise to Allah, who has guided us to this; and we would never have been guided if Allah had not guided us»

First, we would wish to thank Allah for giving us the strength, the audacity and the endurance to realize this work.

Second, we would like to express our deepest and sincere gratitude for our supervisor **Zerrouki Hayet** for the guidance, the thoughtful comments and the unfailing support all along our journey to make this humble work. We are truly grateful for all his/her efforts in revising and correcting this paper, and for all advices that he/she provided.

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Dedication

أمي التي لم تسمح لليتم أن يكسرني ليس مجرد إهداء... بل شهادة حقّ في وجه التعب
إلى أمي... منذ أن غاب أبي تحت التراب، وأنتِ دفنتِ ضعفكِ معه، وقررتِ أن لا يدفن
رأيتُ في عينيكِ دمعاً تخفيها، وخوفاً تكتمينه، وثقلُ مسؤوليةٍ لم يكن يوماً لكِ .معه مستقبلي
ومع ذلك، حملتها وحدك... وحدك

تبتسمين لي... وتبكين في صمتٍ لا يسمعه .كنتِ توقظينني للأمل، وتنامين على القلق
لم تكوني أمّاً فقط، كنتِ وطناً حين شعرتُ بالضياع، وسنداً حين انكسر ظهري، وصوت أبي .أحد
حين اشتقتُ إليه.

.هذا النجاح... هو عرقُ جبينك، هو لياليك الطويلة، هو دعواتك التي سبقتني إلى السماء
أمي... لم أدرك معنى القوة إلا حين رأيتُ امرأةً فقدت زوجها ولم تفقد إيمانها، فأدّت
.الدورين... وأدّت أكثر

لو كان :أهدي هذا التخرج، وأقول...إلى روح أبي الطاهرة، وإلى أمي التي وقفت مكانه
النجاح يُمنح لمن يستحقه، لكان اسمكِ على هذه الشهادة قبلي

سارة بربر

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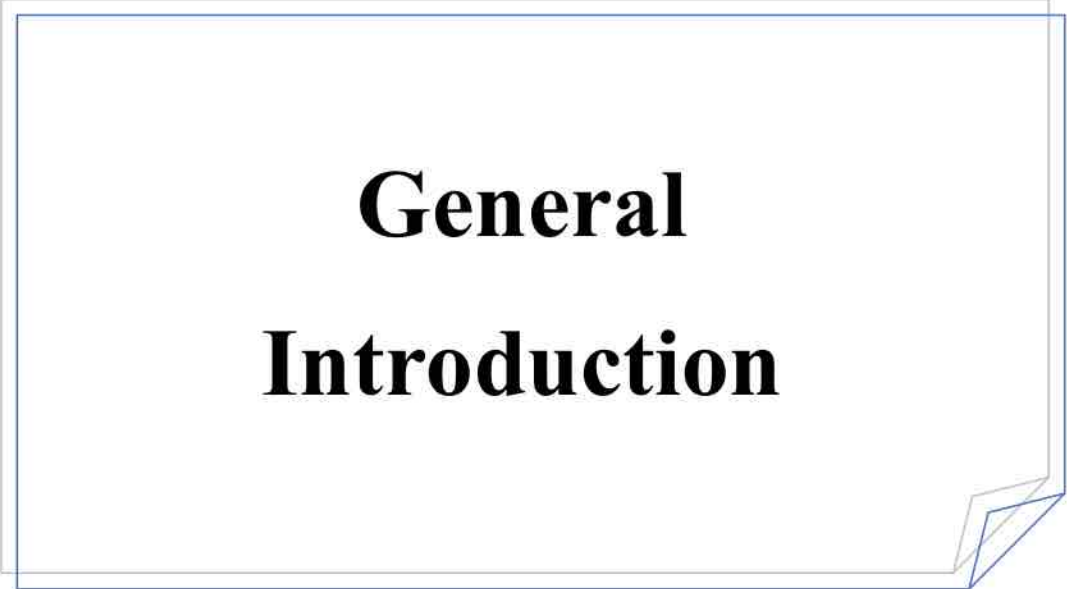
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General Introduction

Introduction:

Metal corrosion is considered one of the most significant technical and economic challenges facing various modern industrial sectors due to its direct impact on structural integrity, operational continuity, and resource efficiency. Corrosion mainly results from chemical or electrochemical reactions between the metal and the surrounding environment, particularly in acidic media characterized by high aggressiveness and a strong ability to accelerate the degradation of metallic materials. This deterioration leads to the loss of the metal's mechanical and chemical properties, adversely affecting its service life and increasing maintenance, repair, and replacement costs. Therefore, the study of this phenomenon has become an urgent scientific and practical necessity in the fields of engineering and industry [1].

Carbon steel, particularly the XC70 grade, occupies an important position among the most widely used materials in industrial and engineering applications due to its favorable mechanical properties, such as hardness and toughness, as well as its low cost and ease of forming and manufacturing. However, this type of steel remains highly susceptible to corrosion, especially when exposed to acidic media such as hydrochloric or sulfuric acid, where electrochemical reactions leading to metal dissolution are significantly accelerated. Consequently, this high corrosion susceptibility is considered one of the major limitations restricting its long-term use, which necessitates the search for effective solutions to improve its resistance under such conditions [2].

In this context, corrosion inhibitors have emerged as one of the most effective methods used to reduce metal degradation. These substances function by decreasing the reaction rate between the metal surface and the acidic medium through the formation of a protective film or by modifying the electrochemical reaction mechanism. Although many conventional inhibitors have proven effective, their use faces challenges related to high costs and adverse environmental and health effects. Therefore, researchers have increasingly focused on developing safer and more sustainable alternatives based on naturally available and environmentally friendly materials [3].

Among these promising alternatives, plant extracts have emerged as a rich source of active organic compounds such as phenols, tannins, and flavonoids. These compounds possess a strong ability to adsorb onto the metal surface, forming a protective film that reduces corrosion. Walnut shell extract is considered one of the natural materials that has attracted increasing attention in recent studies due to its rich chemical composition, which qualifies it as an effective and environmentally friendly corrosion inhibitor. These compounds can interact with the steel surface to

form a protective barrier that limits reactions with the acidic medium, thereby enhancing the corrosion resistance of the metal [4].

Accordingly, the present study focuses on evaluating the effectiveness of walnut shell extract as a natural inhibitor for the corrosion of carbon steel (XC70) in an acidic medium, while also seeking to understand its mechanism of action and assess its efficiency in comparison with conventional inhibitors. In addition, the study aims to analyze the behavior of this extract under specific experimental conditions in order to determine its potential for industrial application as a sustainable economic and environmental alternative. To achieve this objective, the study has been divided into three interconnected chapters. The first chapter is devoted to the theoretical framework of corrosion and corrosion protection methods, while the second chapter discusses corrosion inhibitors and their relationship with carbon steel. The third chapter presents an applied study on the effect of walnut shell extract on inhibiting the corrosion of XC70 steel in an acidic medium, thereby providing a comprehensive scientific evaluation of this promising approach [5].

References

- [1] Jones, Denny A. Principles and Prevention of Corrosion. 2nd Edition, Upper Saddle River, New Jersey: Prentice Hall, 1996.
- [2] Fontana, Mars G. Corrosion Engineering. 3rd Edition, New York: McGraw-Hill Book Company, 1986.
- [3] Sastri, V. S. Green Corrosion Inhibitors: Theory and Practice. Hoboken, New Jersey: John Wiley & Sons, 2011.
- [4] Rani, B. E. A., & Basu, B. B. J. "Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview." International Journal of Corrosion, Volume 2012, Article ID 380217, 15 pages, 2012. <https://doi.org/10.1155/2012/380217>
- [5] Umoren, S. A., & Solomon, M. M. "Effect of Plant Extracts on Corrosion Inhibition of Metals in Acidic Media." Journal of Industrial and Engineering Chemistry, Volume 21, Pages 81–100, 2017. <https://doi.org/10.1016/j.jiec.2014.09.033>

Chapter One Theoretical Framework of Corrosion



I.1 Introduction:

Metals are considered among the most essential materials upon which humanity has relied in various fields of life, owing to their unique mechanical and physical properties that have made them fundamental to industries, infrastructure, and engineering applications. Steel, particularly carbon steel, is one of the most widely used metals due to its strength, toughness, and relatively low cost compared to other materials. However, despite its great importance, this material faces significant challenges related to its interaction with surrounding environmental factors, as it gradually undergoes changes that affect its structure and properties. One of the most significant of these challenges is the phenomenon of corrosion, which particularly affects steel [1]. This chapter aims to present the basic definitions and fundamental concepts related to corrosion and the methods used for its protection.

I.2. Definition of Corrosion

Corrosion is defined as the progressive deterioration of materials, particularly metals, resulting from chemical or electrochemical reactions with the surrounding environment, whether atmospheric air, moisture, or a chemical medium, and it can occur at all temperatures. This reaction leads to metal degradation and the formation of a porous rust layer that weakens the mechanical structure, reduces thickness, and causes pitting. The severity of corrosion may further increase due to the movement of solid particles that remove protective layers [2].

Corrosion is also described as a change in the properties or the dissolution of a material (metal) resulting from its interaction with the surrounding environment. The driving force behind metal corrosion is a natural process that tends to return the metal to its original state in nature, namely its ore state. According to the international standard ISO 8044, corrosion is defined as a physicochemical interaction between the environment and the metal that results in changes in the characteristic properties of the metal [3].

Based on the above, corrosion can be defined as a natural phenomenon involving the degradation or deterioration of materials, especially metals, as a result of their chemical or electrochemical interaction with the surrounding environment, leading to the gradual loss of their physical and mechanical properties [3].

I.3. Physical and Chemical Factors Affecting Corrosion

The extent of corrosion depends on the following:

- The properties of the metal.
- The nature of the corrosive environment [4].

Corrosion-related factors associated with the metal:

- Electrochemical potential for metal oxidation.
- Presence of another metal or material acting as a cathode.
- Electrochemical overpotential of the metal.
- Purity of the metal.
- Physical state of the metal.
- Relative surface area of the metal acting as an anode and a cathode.
- Relative size (volume) of metal atoms and corrosion products such as oxides.
- Solubility of corrosion products formed during the corrosion process.

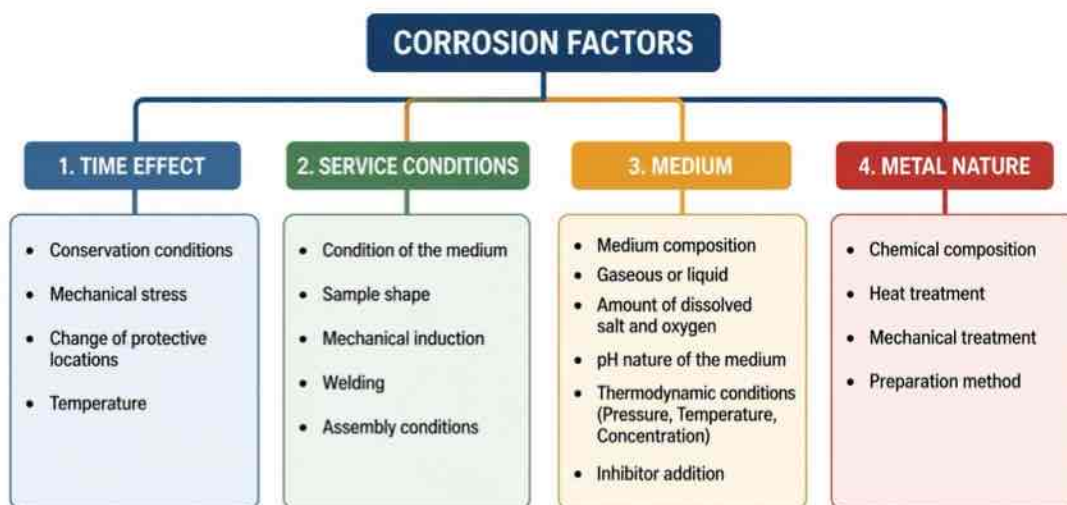


Figure I - 1: Diagram illustrating corrosion factors

I.3.1 Classification of Corrosion Factors

Corrosion phenomena depend on a vast number of factors, which can be classified into four primary groups .

 Factors of the Corrosive Environment	 Metallurgical Factors	 Factors Defining Operating Conditions	 Time-Dependent Factors
Concentration of the reactant	Composition of the alloy	Surface condition	Aging
Oxygen content	Fabrication processes	Shape of the parts	Mechanical stress
pH of the medium	Impurities	Use of inhibitors	Modification of protective coatings
Temperature	Heat treatment	Assembly processes	—
Pressure	Mechanical treatment	—	—

Figure I - 2: The Main Factors Affecting Corrosion.

The corrosion rate of a metal within an aggressive medium depends simultaneously on the characteristics of two fundamental parameters: temperature and pH. These parameters exert a direct influence on corrosion kinetics, as well as an indirect influence via the aqueous phase (such as condensation water or production water). Furthermore, hydrodynamic flow conditions, the nature of the passive film formed on the metal surface, and the global pressure exert a direct influence through the partial pressure of CO_2 [Boum, 17].

Effect of Temperature

Generally, an increase in temperature accelerates corrosion phenomena. This behavior is attributed to the restriction of the thermodynamic stability domains of metals and the acceleration of reaction and mass transport kinetics. Nevertheless, the extent of this influence varies significantly depending on the nature of the corrosive environment to which the material is exposed [Boum, 17].

Effect of Acidity (pH)

The susceptibility of a material to corrosion is highly dependent on the pH of the electrolyte. A high concentration of protons (H^+) within the solution increases the chemical aggressiveness of the medium, thereby altering the equilibria of chemical and electrochemical reactions. Consequently, the corrosion rate increases proportionally with a decrease in the pH of the medium [Boum, 17].

Electrochemical Corrosion

This is the most frequent mode of corrosion. It involves electronic transfers between a metal and an electrolytic solution in contact with it.

From a practical standpoint, the coupling of one or more oxidation reactions of the metal at the anode with one or more reduction reactions of species in solution at the cathode leads to a "mixed" corrosion potential. This is also referred to as free potential or open-circuit potential, located within a domain of the potential-pH diagram (Pourbaix diagram) where the metal is active. The entire surface of the metal assumes this potential value and becomes the site of corrosion described by the reaction:

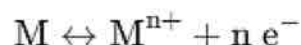


Where Red denotes the reduced species and Ox^{n+} represents the associated oxidant.

Corrosion can only take place if the electrons released by the oxidation of the metal are captured by another redox couple corresponding to the reduction reaction driving the corrosion process.

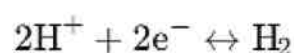
In wet (aqueous) corrosion, the essential driving factors are water, protons H^{+} (in a deaerated medium, where the dissolved O_2 concentration is considered negligible compared to that of H^{+} ions) and dissolved oxygen (in an aerated medium, where the reduction current of dissolved O_2 is higher than that of H^{+} ions). Thus, within these different environments, the reactions taking place are:

Oxidation reaction of a metal M into its ions M^{n+} :

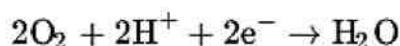


Reduction reaction of the oxidizing agent (the driving force of corrosion):

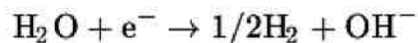
- In an acidic and deaerated medium:



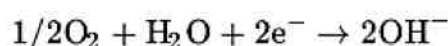
- In an acidic and aerated medium:



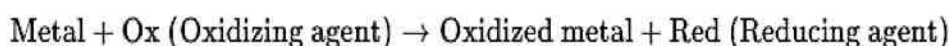
- In a neutral or basic and deaerated medium:



- In a neutral or basic and aerated medium:



- The overall corrosion reaction can be outlined as follows



Biological Corrosion

It results from the action of bacteria or products derived from bacterial activity—such as organic acids or gases like CO₂ and SO₂ — on the metallic material. Buried pipelines are highly susceptible to this type of corrosion [Robe, 99].

I.4. Types and Forms of Corrosion

I.4.1. Types of Corrosion

Corrosion is classified, based on the nature of the surrounding environment with which the metal interacts, into three main types:

I.4.1.1 Chemical Corrosion: This type of corrosion arises from the direct chemical reaction between the metal (or alloy) and the surrounding environment. It occurs through a direct chemical effect, where the metal combines with non-metallic elements or compounds such as water vapor, oxygen, chlorine, or others, to form a non-metallic compound. It relies on the oxidation of the metal and its return to the oxidizing medium at the same site, with microscopic dimensions reaching the order of an atomic diameter (Angstrom). It does not involve electron exchange due to the absence of a conductive electrolyte; therefore, it is limited to non-conductive or weakly conductive media. Most metals tend to bond with oxygen, reacting with it even in completely dry air. [5]

I.4.1.3 Electrochemical Corrosion: This is defined as the destruction of a metal surface upon contact with a chemical element, accompanied by the emergence of an electric current within the

metal. The essence of this type of corrosion is the mutual interaction between the metal and its surrounding medium, such as mud or water, resulting in metal degradation alongside the generation of an electric current. When the metal comes into contact with polarized water, surface atoms are displaced from their positions under the influence of the field strength of water molecules, which—due to their small size—penetrate into the bulk of the metal.

This form of corrosion is characterized by occurring through electrochemical reactions that consistently take place at phase boundaries and can be divided into two primary reactions: anodic and cathodic. At the anodic pole, metal oxidation occurs, meaning its dissolution into the solution as ions with the release of electrons that remain trapped on the metal surface. These electrons are then transferred through the metal to the cathodic pole, where they are consumed in a reduction reaction.

I.4.1.3 Biological Corrosion

This type of corrosion is prevalent in soils and oil wells. It is a degradation process resulting from the activity of microorganisms. It accounts for less than one quarter of the total corrosion phenomena. These microorganisms mainly include bacteria and fungi, and in some environments algae may also be present. Heat, moisture, and nutrients are among the most important conditions required for their growth and activity. [5]

I.4.2 Forms of Corrosion

This classification of corrosion is based on the appearance of the corroded metal, its visual characteristics, and the mechanism by which it occurs.

I.4.2.1 Uniform (General) Corrosion

This type refers to the gradual and uniform deterioration of the metal surface, resulting in a progressive reduction in thickness. It is the most common form of corrosion and is characterized by an even attack distributed over the entire surface exposed to the corrosive medium (such as the uniform rusting of steel sheets). In this case, the corrosion rate remains relatively constant and can be predicted in engineering applications. [6]



Figure I - 3: Uniform (General) Corrosion

I.4.2.2 Pitting Corrosion:

It is the process of forming deep pits or holes on a non-corroded surface. These pits can take multiple shapes, and this type is common in saltwater environments, occurring frequently in stainless metals; its occurrence requires the presence of chloride ions. [7]



Figure I-4: Pitting Corrosion

I.4.2.3 Intergranular Corrosion:

This occurs when the metal is in a specific metallurgical state that causes the grain boundary region to become more active than the grain regions themselves. Most alloys suffer from this type of corrosion, such as austenitic stainless steel alloys. [7]

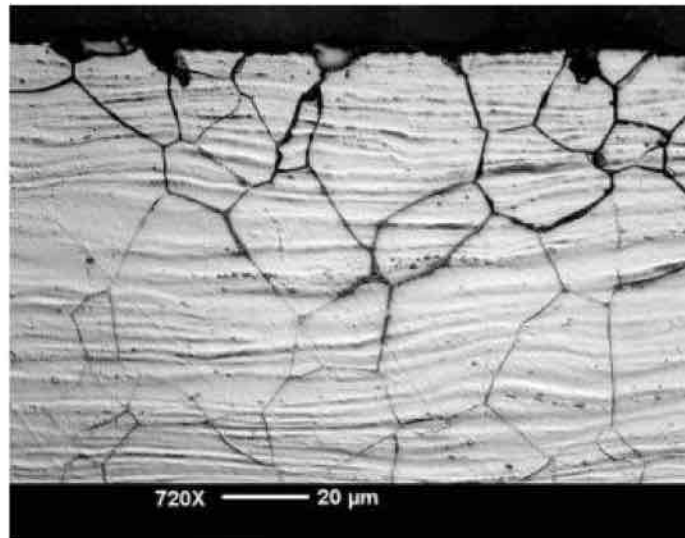


Figure I- 5: Intergranular Corrosion

I.4.2.4 Galvanic Corrosion:

This type of corrosion occurs when two metals with different potentials are in contact or connected.



Figure I- 6: Galvanic Corrosion

An electrical potential difference is created in an electrolytic corrosive medium, where one of the two metals acts as an anodic region while the other acts as a cathodic region. This phenomenon can be explained by the electrochemical series; the greater the potential difference between the two metals, the more severe the corrosion affecting the metal with the lower electrochemical potential. [6]

I.4.2.5 Selective Corrosion:

This type of corrosion occurs only in alloys composed of two or more metallic elements. Corrosion is initiated due to localized variations in composition; consequently, the more cathodic constituent remains protected, whereas the more anodic constituent undergoes corrosion. The corrosion resistance of the alloy depends on its chemical composition and increases with a higher concentration of the more cathodic metal in the alloy. [8]



Figure I- 7: Selective Corrosion

I.4.2.6 Crevice Corrosion: This type of corrosion occurs in small gaps existing between two metals, such as rivet or bolt gaps. In these crevices, the oxygen concentration is limited (acting as an anode), while the external surface (acting as a cathode) has a high oxygen concentration; this differential aeration leads to the corrosion of these gaps. [8]



Figure I-8: Crevice Corrosion

I.4.2.7 Filiform Corrosion: Filiform corrosion occurs under painted or coated surfaces when water penetrates the coating. This type of corrosion begins when small defects occur in the paint and spreads, leading to structural weakness. [9]

I.4.2.8 Stress Corrosion: Stress corrosion is defined as a slow cracking process of a metal immersed in a corrosive medium under the influence of internal and external stresses. This type of corrosion is similar to pitting corrosion in its occurrence within passive alloys. [10]



Figure I- 9: Stress Corrosion Cracking (SCC)

I.5 Electrochemical Principles of the Corrosion Process

The electrochemical principles of the corrosion process are based on the formation of microscopic electrochemical cells on the metal surface.

Corrosion is a redox process occurring within a cell composed of an anode (oxidation), a cathode (reduction), an electrolyte (a conductive medium such as water), and an electronic path (the metal itself). Electrons flow through the metal from the anode to the cathode, while ions migrate through the electrolyte to complete the circuit, leading to the gradual degradation of the metal. [11]

Vibration corrosion is a form of erosion-corrosion that combines electrochemical reactions with mechanical movement, thereby accelerating metal damage. Vibrations generate disturbances in the liquid medium, causing cavitation and the formation of high-speed gas bubbles that strip away protective layers. This exposes the metal to the corrosive environment and increases the rate of weight loss. [11]

- **Mechanism of Vibration-Induced Corrosion:**

- Simultaneous electrochemical corrosion occurs as degradation results from electrochemical reactions, while vibrational motion contributes to the mechanical effect.

- **Destruction of the Protective Layer:** Fluid scouring and solid corrosion products (driven by vibration) lead to the removal of surface protective layers, which hinders ion exchange.
- **Increase in Corrosion Rate:** As a result of surface exposure, corrosion products continue to detach, increasing the corrosion rate and leading to metal failure (particularly in turbines and boilers).[11]

I.6 Corrosion Protection Methods

The protection of metals against corrosion represents a fundamental topic in the field of materials science and engineering due to the severe damage caused by corrosion, which affects both structural integrity and operational efficiency. To minimize this phenomenon, various methods and techniques have been developed according to the nature of the metal and the surrounding environment. These approaches aim to extend the service life of materials and preserve their physical and chemical properties, as illustrated through the different corrosion protection methods adopted.

I.6.1 Protection by Appropriate Material Selection and Design

Protection against corrosion through proper material selection and suitable design involves several important aspects. These include the geographical nature of the environment, where the effects of air, water, and soil vary according to their characteristics and location. It also includes chemical environments that require the use of specific metals capable of resisting corrosion in seawater compared with atmospheric environments. In addition, consideration must be given to the contact between metals and non-metallic materials such as wood and plastics.

Temperature also plays a significant role, since the corrosion rate of iron increases when the temperature exceeds 300°C in the presence of high relative humidity. Furthermore, the design must take into account the different stresses experienced during the service life of the equipment, including forming stresses, thermal stresses generated during manufacturing, vibration stresses, as well as testing and operating loads.

From a structural and geometrical perspective, welding is considered one of the best methods for joining similar metallic parts, provided that the welded joints are free from protrusions and crevices. Likewise, horizontal surfaces such as building roofs, pipelines, and tank bottoms should

be designed in a way that prevents the accumulation of water and dust by ensuring suitable drainage systems.

This method mainly relies on selecting materials with high corrosion resistance according to the surrounding medium, whether air, water, or chemical environments. [12]

I.6.2 Cathodic Protection

Cathodic protection is defined as a method used to prevent corrosion and rust on the external surfaces of buried or submerged ferrous metallic equipment by making them act as negative electrodes within an electrical circuit. It is also considered an effective corrosion protection technique that utilizes the electrochemical properties of metals to make the structure to be protected function as the cathode of an electrolytic cell.

Cathodic protection is widely used to protect steel pipelines, storage tanks, steel structures, ships, offshore oil-loading platforms, and metallic casings of oil wells. This protection is achieved by making the metallic structure to be protected act as a cathode relative to the surrounding soil or electrolyte. An electric current flows from the positive electrode (anode) through the surrounding soil or electrolyte toward the buried steel structure, thereby completing the electrical circuit and protecting the steel from corrosion [13].

This method is commonly applied for the protection of buried pipelines, storage tanks, and marine structures.

In this method, the metal to be protected is electrically connected to another more active metal, such as zinc, aluminum, or magnesium. The more active metal acts as the anode and corrodes preferentially, thereby protecting the main metallic structure from corrosion [13].

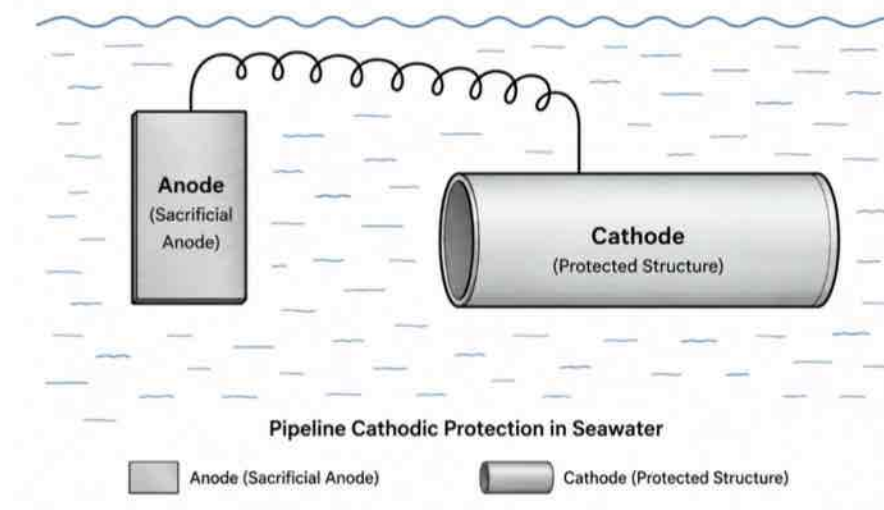


Figure I-10: Cathodic protection based on the sacrificial anode principle.

Impressed Current Cathodic Protection (ICCP): An external direct current (DC) power source, known as a rectifier, is used to provide the metal with the electrons required for protection. The negative terminal of the power source is connected to the metal structure to be protected, whereas the positive terminal is connected to an inert anode [13].

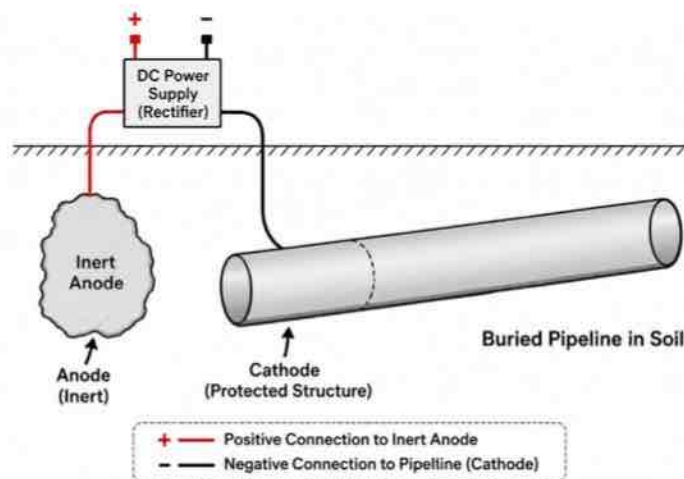


Figure I-11: Impressed current cathodic protection (ICCP) system.

I.6.3 Anodic Protection

Anodic protection is based on making the metal act as an active anode by applying a high electrical potential, which leads to the formation of a stable protective oxide layer on its surface. This method is commonly used for steel in acidic environments. It differs from cathodic protection

in that the metal is converted into an anode resistant to corrosion rather than being made a cathode [14].

I.6.4 Protection by Coating

Protection by coating is considered one of the most important methods of corrosion control. It is based on forming an insulating layer that covers the metal surface and prevents its direct contact with the corrosive environment, thereby reducing the chemical reactions responsible for corrosion.

Coating materials possess several properties that make them effective in corrosion protection, the most important of which are their strong adhesion to the metal surface, high resistance to moisture and water, and good electrical resistance.

Protective coatings are classified into several types, including metallic coatings, which involve covering the metal with a thin layer of another metal that is more resistant to corrosion. They also include organic coatings composed of pigments, binders, plasticizers, and solvents, as well as inorganic coatings that involve techniques such as hot-dip coating and electrodeposition. In addition, thermal insulating coatings are also used. All these coating systems aim to improve corrosion protection and extend the service life of metals [15].

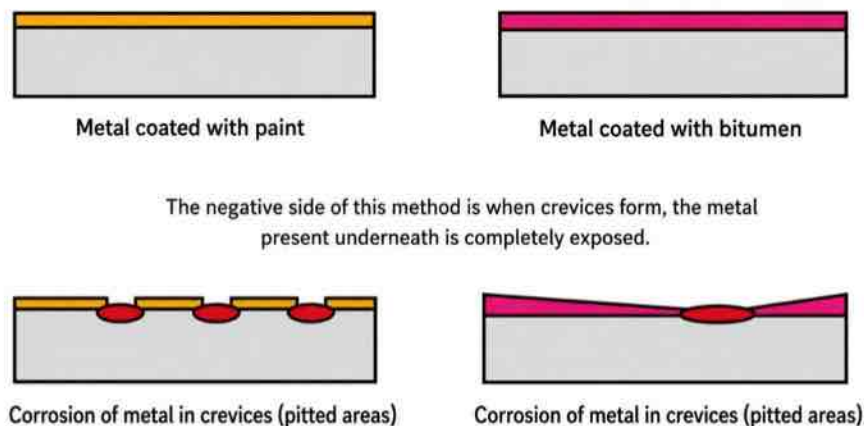


Figure I-12: Coating protection against corrosion.

I.6.5 Protection by Corrosion Inhibitors

Protection by corrosion inhibitors is considered one of the effective methods for preventing metal corrosion. These chemical substances are added in low concentrations to the corrosive

environment in order to form a protective layer on the metal surface, thereby reducing the rate of electrochemical reactions or preventing direct contact between the metal and the corrosive medium, such as water or oxygen.

Corrosion inhibitors act through several mechanisms, including adsorption, where inhibitor molecules adhere to the metal surface to form a hydrophobic protective film, the formation of a dense oxide layer, or the precipitation of insoluble compounds. These inhibitors are widely used in the oil, gas, and water industries [16].

The main types of corrosion inhibitors include:

- **Oxide Film Inhibitors:** These oxidize the metal surface to form a dense protective film, such as chromates used on steel.
- **Precipitation Inhibitors:** These react with ions in the medium to form an insoluble protective layer, although their adhesion is generally weaker.
- **Adsorption Inhibitors:** These are organic compounds containing hydrophilic and hydrophobic groups, commonly found in amines and sulfur-containing compounds [16].

REFERENCES

- [1] Darwish, S. *Study of the Corrosion Behavior of Carbon Steel in Aqueous Media*. Master's Thesis, Faculty of Science, University of Aleppo, Syria, 2005.
- [2] Al-Saedi, S. A. K. S. "Use of Composite Coatings to Inhibit Chemical Corrosion in Metallic Petroleum Storage Tanks." *Journal of Petroleum Research and Studies*, Vol. 3, No. 26, 2020, p. 2.
- [3] Dekmouche, M. *Preparation and Physicochemical Characterization of Certain Dithiolethione Compounds and Their Associated Salts for the Application of Their Inhibitory Efficiency in Metal Corrosion Studies*. PhD Dissertation, Kasdi Merbah University, Ouargla, Algeria, 2014.
- [4] Wasel, M. M. A. *Principles of Industrial Chemistry*. 1st Edition, Dar Al-Fajr Publishing and Distribution, Cairo, Egypt, 2005, pp. 181–188.
- [5] Bouzidi, H. *Corrosion Inhibition of Copper in Hydrochloric Acid Medium Using an Aqueous Extract of Eucalyptus Leaves*. Master's Thesis, Materials Physics Specialization, Faculty of Exact Sciences and Natural and Life Sciences, Mohamed Khider University of Biskra, Algeria, 2022/2023, p. 5.
- [6] Al-Khazraji, Q. K. *Corrosion: Causes, Types, and Protection Methods*. Dar Degla Publishing House, 2009.
- [7] Khleifallah, F. Master's Thesis, University of Biskra, Algeria, 2024, p. 27.
- [8] Hache, A. *La Corrosion des Métaux*. 3rd Edition, Presses Universitaires de France, Paris, France, 1959, p. 6.
- [9] Huang, Y.-H. et al. "Improvement of Stress Corrosion Cracking Resistance by Low Cycle Fatigue of a CrNiMoV Steel." *npj Materials Degradation*, 2023.
- [10] Vakili, M. et al. "Analysis and Mitigation of Stress Corrosion Cracking in Stainless Steels in the Oil and Gas Sector." *Surfaces*, 2025.
- [11] Ahmed, M. A. L., & Jassim, A. H. "Comparison Between Corrosion in Static and Vibrating Media for Medium Carbon Steel CK45." *Journal of Engineering and Development*, Vol. 17, No. 4, October 2013, p. 12.

- [12] Damlouh, S., & Bajra, A. K. Contribution to the Study of Carbon Steel Corrosion Inhibition Using Peppermint Oil in an Acidic Medium. Master's Thesis, Chemical Engineering Specialization, Faculty of Applied Sciences, Kasdi Merbah University, Ouargla, Algeria, 2022, pp. 12–13.
- [13] Qabasa, M. A., Qabasa, A. M., & Al-Arousi, M. F. "Design of a Cathodic Protection System Using Sacrificial Anodes." *International Journal of Science and Technology*, No. 17, 2019, p. 8.
- [14] Naami, K. Study of the Effect of Certain Plant Extracts on the Corrosion Inhibition of Carbon Steel in an Acidic Medium. Master's Thesis, Water Chemistry Specialization, Faculty of Mathematics and Material Sciences, Kasdi Merbah University, Ouargla, Algeria, 2020, pp. 13–14.
- [15] "Types of Corrosion Inhibitors and Their Mechanisms of Action." Accessed on April 09, 2026.
- [16] Nantong Reform Petrochemical Co., Ltd. Types of Corrosion Inhibitors and Their Mechanisms of Action, 2023.
- [Boum, 17] Boumegue, F., & Iabbassen, D. Study of zinc corrosion inhibition in hydrochloric acid using Nettle plant extract. Graduation Thesis, Abderrahmane Mira University – Bejaia, 2017.
- [Robe, 99] Perin, R., & Scharff, J. P. *Industrial Chemistry*. 2nd edition, 1999, p. 240.

Chapter Two:
Effect of Corrosion Inhibitors
on Carbon Steel

II.1 Introduction:

The use of metals has significantly increased in countries with the development of technology and economic growth. Metal consumption under the influence of environmental conditions is considered a major problem for industrial companies (Ayşe TOSUN, Mübeccel ERGUN, 2006). Equipment damaged annually due to corrosion processes is estimated to cost billions of dollars. Therefore, it is essential to study this phenomenon and identify the factors responsible for its occurrence in order to develop effective methods to control it. [1]

Corrosion is considered one of the most important research topics today due to the urgent need to protect the world's metal resources. It is defined as a phenomenon that leads to the deterioration or destruction of metallic structures through chemical or electrochemical reactions. [2] This process results in significant material losses due to the replacement of damaged equipment and systems. To reduce these losses, various protection methods are used, among which corrosion inhibitors are the most effective. These substances act by reducing the corrosion rate to a minimum level, since corrosion cannot be completely eliminated but can be significantly controlled. [2]

Carbon steel is one of the most widely used types of steel in engineering applications, accounting for approximately 85% of total steel usage. It is widely utilized due to its availability in daily life and its low cost compared to other metals. In addition, it can be used in different environments, including acidic, alkaline, and saline media. The properties of carbon steel depend mainly on its carbon content, which is generally less than 1%. It is used in manufacturing parts for marine, land, and air transport systems, as well as in oil pipelines, building structures, and bridges due to its good mechanical properties. However, carbon steel is susceptible to various types of corrosion in certain environments, which makes it necessary to apply corrosion protection methods. Several preventive techniques have been developed, among which the use of corrosion inhibitors is one of the most important. Therefore, this chapter aims to clarify the concept of corrosion, the types of corrosion inhibitors, their mechanisms of action, and their effects on carbon steel in different environments. [2]

II.2. Classification of Corrosion Inhibitors

II.2.1 Inorganic Inhibitors

Inorganic inhibitors are chemical compounds used to reduce metal corrosion by forming a protective layer on the metal surface or by modifying electrochemical reactions. These inhibitors include phosphates, chromates, silicates, and molybdates. They act by slowing down the corrosion process through several mechanisms, mainly surface adsorption, passivation, and inhibition of anodic and cathodic reactions. [7].

II.2.2 Organic Inhibitors

Organic inhibitors are chemical compounds that contain carbon atoms and function by reducing or slowing down metal corrosion. They act through adsorption on the metal surface, forming a protective insulating layer that prevents the metal from interacting with the corrosive medium. [4]

II.2.3 Cathodic Inhibitors

Based on their protective effect, cathodic inhibitors are generally less effective than anodic ones. Their action is based on the local alkalinization of the medium, which leads to the formation of insoluble products on cathodic areas, thereby isolating part of the surface from the solution. For example, calcium bicarbonate can be formed, releasing calcium carbonate in an alkaline medium as a poorly soluble precipitate. Cathodic corrosion inhibitors, depending on their composition and environment, do not increase destructive processes even when present in insufficient amounts. [5]

II.4. Mechanism of Action of Corrosion Inhibitors

The primary mechanism of organic inhibitors is adsorption on the metal surface, where their molecules are adsorbed on the anode, cathode, or the entire surface, forming a thin film that is impermeable to water and ions. This layer reduces the interaction between the metal and corrosive species such as H^+ and Cl^- ions, thereby slowing down the oxidation and reduction processes responsible for corrosion. [8]

II.4.1 Electrochemical Control of Reactions

Inhibitors are generally classified into: [9]

Chapter II : Effect of Corrosion Inhibitors on Carbon Steel

- **Anodic inhibitors:** These slow down the metal oxidation process (electron loss) by forming an oxide or sparingly soluble salt layer on the anodic sites.

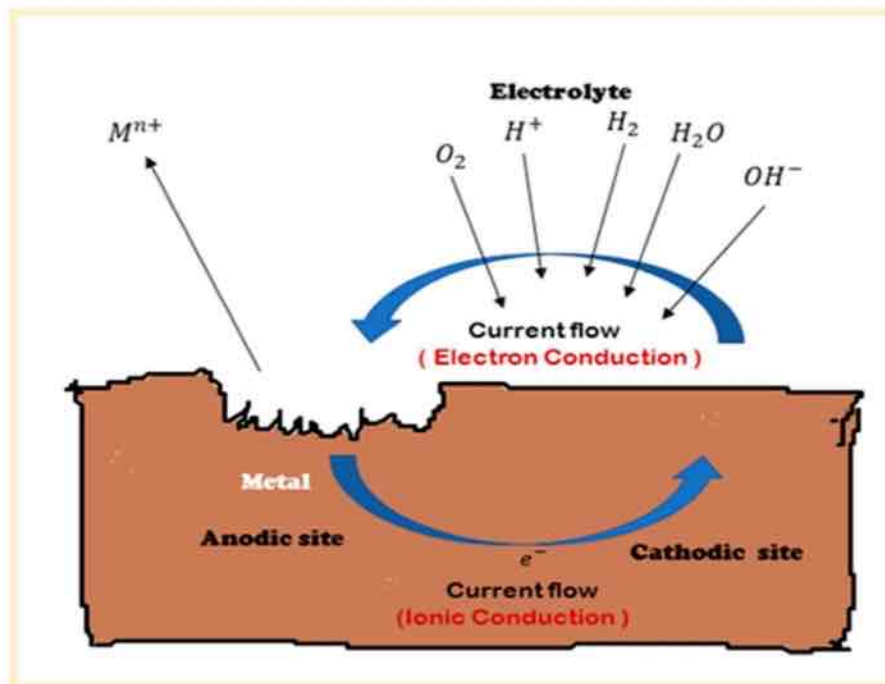


Figure II-1: Electron loss process (metal oxidation)

- **Cathodic inhibitors:** These reduce the reduction reactions (oxygen or hydrogen ion reduction).

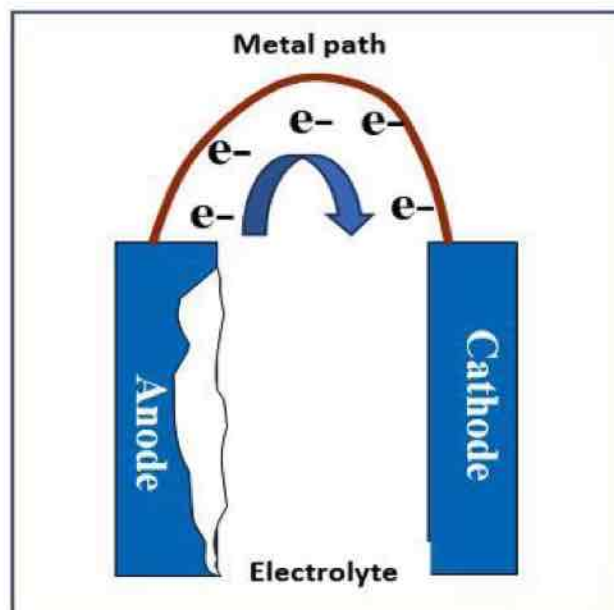


Figure II-2: Electron gain process (O_2 or H^+ reduction)

Chapter II : Effect of Corrosion Inhibitors on Carbon Steel

- **Mixed inhibitors:** These affect both anodic and cathodic reactions simultaneously, significantly reducing the overall corrosion rate.

The Corrosion Cell :

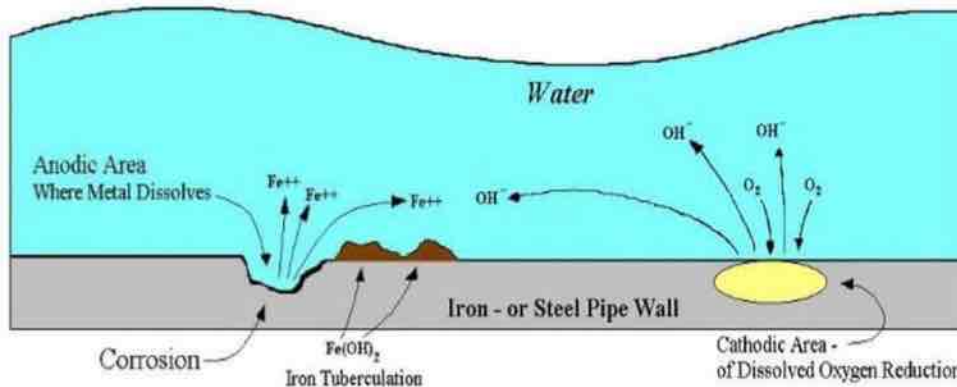


Figure II-3: Simultaneous anodic and cathodic reactions

II.4.2 Modification of Surface and Medium Properties

Some low molecular weight inhibitors, such as surfactants, act by modifying the surface tension of water or the medium, which facilitates the formation of a protective layer that prevents the penetration of corrosive agents. [10]

II.5. Effect of Corrosion Inhibitors on Carbon Steel

II.5.1 Definition of Carbon Steel

Carbon steel, or plain carbon steel, is defined as an iron–carbon alloy in which iron is the main component and carbon is the primary alloying element. [11] It is classified as carbon steel when it mainly consists of iron and carbon, with small amounts of other elements such as manganese, phosphorus, and sulfur, and without significant additions of alloying elements such as chromium, nickel, or copper. Carbon steel is generally classified into three main categories[12] :

- Low carbon steel (mild steel): ~0.04%–0.3% carbon, characterized by high ductility and weldability.
- Medium carbon steel: ~0.3%–0.6% carbon, offering a balance between strength, hardness, and ductility.
- High carbon steel: ~0.6%–1.5% carbon, characterized by high hardness and low ductility.



Figure II-4: Carbon steel

II.5.2 Properties of Carbon Steel

Carbon steel is characterized by several properties:

- **Mechanical properties:**

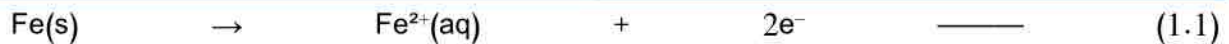
As carbon content increases, the strength and hardness of steel increase after heat treatment, but ductility decreases and brittleness increases. Low carbon steel is soft and easy to machine, while high carbon steel is used for tools, springs, and metal meshes requiring high resistance to deformation. [13]

- **Physical and chemical properties:**

Carbon steel is generally more prone to corrosion than stainless steel; however, high carbon steel may show improved corrosion resistance when appropriate heat treatments are applied. Increasing carbon content slightly lowers the melting point compared to pure iron and reduces weldability without pre-treatment. [14]

II.5.3 Corrosion Mechanism of Carbon Steel

Corrosion of steel is an important issue in daily life, as metals such as iron and aluminum undergo different forms of degradation, causing significant problems in industries and factories. This occurs due to oxidation and reduction reactions on the metal surface, leading to material deterioration. The following reactions describe the electrochemical processes of iron corrosion: [15]



Equation (1.1) represents the oxidation process occurring at the anode, while equation (1.2) represents the reduction process occurring at the cathode. [15]

A corrosion cell consists of three electrodes: the working electrode (anode), the calomel electrode, and the hydrogen electrode (cathode), in addition to an electrical conductor. This reaction is known as a half-cell reaction. [15]

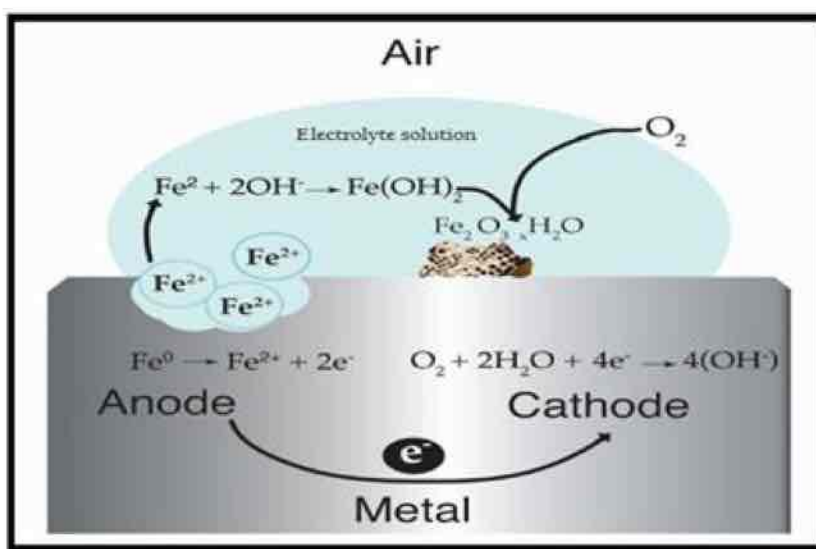


Figure II-5: Carbon steel corrosion mechanism

II.6. Mechanism of Inhibitor Action on Steel Surface (Factors Affecting Inhibition Efficiency)

Corrosion inhibitors act on the carbon steel surface through adsorption and the formation of a protective layer at corrosion sites, thereby reducing or preventing oxidation and reduction reactions responsible for iron corrosion.

II.6.1 Adsorption on Metal Surface

Adsorption is a surface phenomenon that occurs because surface atoms are not fully bonded, making them capable of attracting surrounding molecules. There are two types of adsorption. The mechanism of corrosion inhibition is based on direct or indirect adsorption of inhibitor molecules on the metal surface, reducing its contact with the aggressive medium. Most metals are naturally unstable and tend to react chemically and electrochemically with aggressive environmental agents

such as Cl^- and H^+ ions. Inhibitor adsorption on active sites (high-energy regions) leads to the formation of a protective film that isolates the metal surface from the corrosive environment and prevents corrosion. [16]

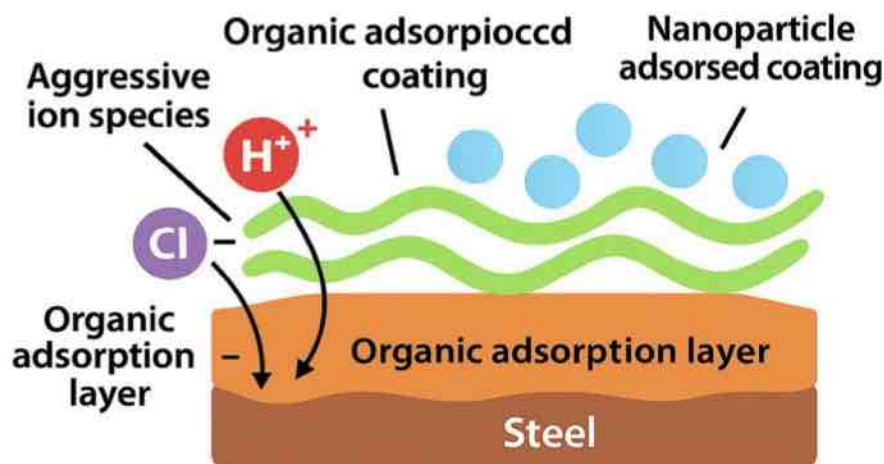


Figure II-6: Adsorption on the Metal Surface

Inhibitor molecules (usually organic compounds containing heteroatoms such as N, O, S, or P) adsorb on carbon steel via chemical bonds or Van der Waals interactions, covering anodic and cathodic sites. The presence of free electron pairs (e.g., nitrogen or oxygen lone pairs) increases adsorption strength on iron, thereby improving inhibition efficiency. [17]

II.6.2 Formation of Protective Film

Many inhibitors form a thin film on carbon steel, which may be:

- An oxide or insoluble salt film (e.g., chromate or phosphate inhibitors) that shifts the corrosion potential toward passivation[17] .
- An adsorbed organic film (e.g., plant extracts or Schiff base compounds) that acts as a physical barrier preventing the access of H^+ and Cl^- ions to the steel surface. [16]

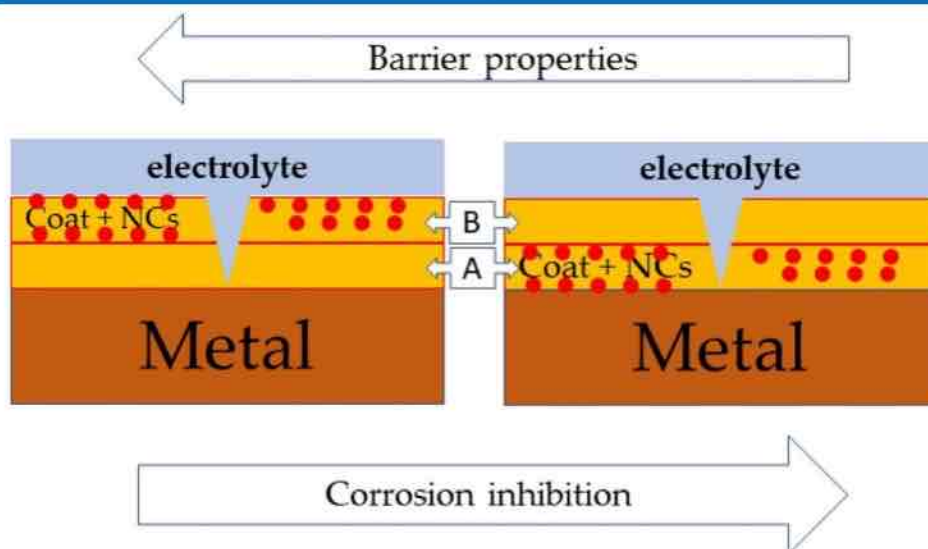


Figure II-7: Formation of protective film

II.6.3 Formation of Protective Film

On carbon steel surfaces in acidic media such as HCl and H₂SO₄, corrosion results from simultaneous anodic and cathodic reactions. Inhibitors reduce these reactions through anodic, cathodic, or mixed mechanisms. [18]

- **Anodic inhibition** reduces iron dissolution ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) by blocking active anodic sites or forming a protective layer. This shifts the corrosion potential toward more positive values, indicating partial passivation.
- **Cathodic inhibition** reduces reduction reactions such as hydrogen evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) or oxygen reduction, decreasing overall corrosion rate.
- **Mixed inhibition** affects both reactions simultaneously, commonly observed with organic compounds such as hydrazone derivatives and Schiff bases. Polarization curves typically show reduced anodic and cathodic currents with slight changes in corrosion potential, confirming mixed-type inhibition and a significant decrease in corrosion current density. [18]
- An oxide or insoluble salt film (e.g., chromate or phosphate inhibitors) that shifts the corrosion potential toward passivation[17] .

II.6. Conclusion

It can be concluded that corrosion inhibitors are an effective and essential method for reducing the corrosion of carbon steel, especially in acidic media. Their efficiency mainly depends on their chemical nature and interaction mechanism with the metal surface. These inhibitors function

Chapter II : Effect of Corrosion Inhibitors on Carbon Steel

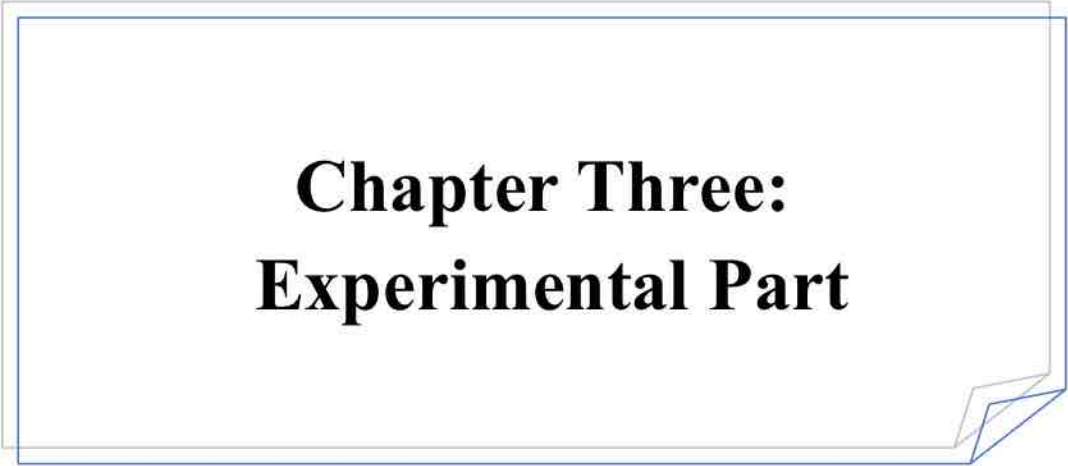
through adsorption and the formation of a protective layer that isolates the metal from the aggressive environment, as well as by directly affecting electrochemical reactions through anodic, cathodic, or mixed inhibition. The selection of an appropriate inhibitor depends on several factors such as cost, toxicity, and stability, which encourages the use of environmentally friendly inhibitors. Therefore, understanding their mechanisms and factors affecting their efficiency is essential for developing more efficient and sustainable corrosion protection systems for carbon steel.

References

- [1]Corrosion Study: Concept, Types, and Protection Methods. Future University. (October 31, 2022). <https://uomus.edu.iq/NewCol>
- [2]Al-Zubaidi, Basim Muhsin Mohammed. (2011). Study of the Effect of Double Salt $KAl(SO_4)_2 \cdot 12H_2O$ on the Corrosion Behavior of Low Carbon Steel. Journal of Babylon University for Pure and Applied Sciences, Vol. (19), No. (1). College of Materials Engineering, University of Babylon, Iraq.
- [3]Dr. Mohammed Ismail Ali Al-Darmali. Electrochemistry. Dar Al-Ilm wa Al-Iman Publishing and Distribution & Dar Al-Jadeed Publishing and Distribution, 2018.
- [4]Bbayya, Nour El-Iman & Oulad Boukheir, Massouda. (2021). Study of the Inhibitory Effect of Some Organic Compounds in a Corrosive Medium for a Type of Steel (Theoretical Study) [Master's Thesis]. Department of Chemistry, Faculty of Mathematics and Material Sciences, Kasdi Merbah University – Ouargla, Algeria.
- [5]Corrosion Inhibitors: Methods of Corrosion Prevention. <https://ar.unansea.com/>
- [6]E.Pardillo-Fontdevvila,R.G.alez –Rubio,A group –interaction contribution approach.A new strategy for the estimation of physico – chemical properties of branched isomers, Chem.Eng.Commun. 245- 254,1998
- [7] Al-Amiery, A.A. et al. (2023)A Review of Inorganic Corrosion Inhibitors: Types, Mechanisms, and Applications ,Tribology in Industry, Vol. 45(2), pp. 313–339
- [8]Zhang, D., Gao, L., & Zhou, G. (2022), Adsorption and corrosion inhibition performance of organic inhibitors on metal surfaces: A review. Frontiers in Energy Research, 10,
- [9] Verma, C., Ebenso, E. E., & Quraishi, M. A. (2024) Corrosion inhibitors: Classification, mechanism, and applications in different environments. Journal of Molecular Liquids, 397,
- [10] Obot, I. B., & Umoren, S. A. (2020). Surface chemistry and adsorption mechanism of corrosion inhibitors: A review. Journal of Molecular Structure, 1219, 128599.
- [11]Dr. Mohammed Hassan Abdullah. Engineering Materials Science. Dar Al-Masirah for Publishing and Distribution, Amman, 2014.
- [12]Dr. Samir Abbas Ali. Fundamentals of Materials Science. Dar Safaa Publishing, 2012.
- [13]Dr. Abdullah Abdul Karim. Materials Science and Manufacturing Technology. Dar Wael Publishing, 2015.
- [14]Dr. Ahmed Zaki Badawi. Metal Corrosion and Protection Methods. Dar Al-Kutub Al-Ilmiyyah, 2009.
- [15] Laith Baqir Jassim & Hamida Aidan Salman. Carbon Steel Corrosion Treatment. College of Education for Pure Sciences – University of Karbala, 2020.

Chapter II : Effect of Corrosion Inhibitors on Carbon Steel

- [16]Naqous, Sabrina. Study of the Inhibition of Carbon Steel Corrosion in Hydrochloric Acid Using Essential Oil of the Plant Haplophyllum tuberculatum [Master's Thesis]. Department of Process Engineering, Faculty of Applied Sciences, Kasdi Merbah University – Ouargla, Algeria.(2020) .
- [17]Laith Baqir Jassim. Inhibition of Carbon Steel Corrosion in Acidic Medium Using Different Hydrazone Derivatives [Master's Thesis in Chemistry]. College of Education for Pure Sciences, Department of Chemistry, University of Karbala, Iraq.(2019) .
- [18] Naami, Kalthoum. Study of the Effect of Some Plant Extracts on the Inhibition of Carbon Steel Corrosion in Acidic Medium [Master's Thesis]. Department of Chemistry, Faculty of Mathematics and Material Sciences, Kasdi Merbah University – Ouargla, Algeria. Defense date: September 30, 2020. Academic year: 2019–2020.



Chapter Three: Experimental Part

III.1 Introduction:

In this chapter, the effect of time and temperature on the corrosion rate of XC70 steel in an acidic medium (HCl) was investigated at different temperatures of 35°C, 40°C, and 45°C over a period of 15 minutes. The variation of corrosion rate with time was monitored using a chemical titration technique with potassium permanganate solution (KMnO₄). In addition, the efficiency of walnut shell extract as a natural corrosion inhibitor was evaluated by studying its ability to reduce the corrosion rate of XC70 steel in the acidic medium and its contribution to improving the metal's resistance to corrosion..

III.2. Materials and Reagents Used

III.2.1 Equipment Used:

Mechanical polishing device



Figure III-1: Mechanical polishing device

- Electronic balance with a sensitivity of 0.0001 g



Figure III-2: Electronic balance with high sensitivity

- Cylindrical funnel (graduated funnel)
- Rotary evaporator

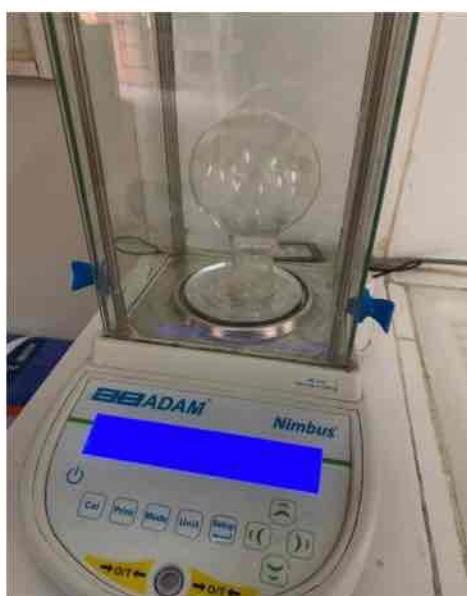


Figure III-3: Rotary evaporator

- Reflux apparatus
- III.2.2 Laboratory Tools:
- Abrasive papers(2500 ,1200 ,800 ,600 ,400)



Figure III-4: Abrasive papers (400, 600, 800, 1200, 2500)

- Beakers (100 mL, 200 mL)
- Flask (1000 mL)
- Funnel
- Filter paper

III.2.3 Chemicals Used:

- Methanol
- Acetone
- Distilled water
- Hydrochloric acid (HCl)
- Potassium permanganate (KMnO₄)
- Walnut shells



Figure III-5: Walnut shells

III.3 Studied Metal:

The studied material consists of XC70 steel samples cut from a pipeline used for oil transportation in the production and refining area of the Berkawi basin. This type of steel is widely used in the petroleum industry due to its mechanical properties and good resistance.

The chemical composition of XC70 steel is presented in the following table:

Table (III -1) : Chemical composition of XC70 steel

Element	C	Mn	Si	P	S	Fe
Percentage	0.85%	0.80%	0.35%	0.025%	0.025%	97%

III.3.1 Sample Preparation:

- Cutting samples in cold conditions according to the required shape
- Mechanical polishing using abrasive papers (400-600-800-1200-2500) under running water



Figure III-6: the steel sample after polishing

III.4. Study of Time and Temperature Effect on Corrosion Rate Using Titration Method

III.4.1 Effect of Time on Steel Corrosion:

The variation of XC70 steel corrosion rate in HCl medium was studied as a function of time using KMnO_4 titration. The effect of walnut shell extract as a natural inhibitor was also evaluated.

III.4.2 Preparation of KMnO_4 Solution:

A volume of 10 mL of 0.02 M potassium permanganate solution was taken and diluted with distilled water to a final volume of 200 mL to obtain a diluted solution used for titration..

III.4.3 Experimental Procedure:

- XC70 steel samples were immersed in HCl solution with different concentrations of walnut shell extract.
- Every 5 minutes, a 5 mL sample was withdrawn from the solution.
- Titration was performed using KMnO_4 until a stable light pink color appeared (equivalence point).
- The experiment lasted 55 minutes, and titration volumes were recorded at each interval.

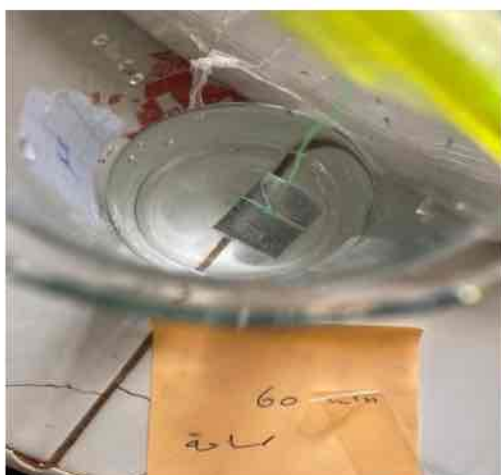


Figure III-7: Steel in acidic medium



Figure III-8: Titration of the medium

III.4.4 Corrosion Rate Determination:

A The corrosion rate was calculated using:

$$V_{\text{corr}} = \Delta m / (S \times t)$$

Where:

Δm : mass loss

S: total surface area of the sample

t: immersion time

Table (III -2) : Corrosion rate and KMnO_4 consumption versus time

Time (minute)	volume(KMnO_4) mL	Corrosion Rate
5	0.6	9.31×10^{-4}
10	1.1	8.54×10^{-4}
15	1.3	6.73×10^{-4}
20	1.4	5.43×10^{-4}
25	1.5	4.66×10^{-4}
30	1.6	4.15×10^{-4}
35	1.8	3.99×10^{-4}
40	2	3.88×10^{-4}
45	2.1	3.63×10^{-4}
50	2.2	3.42×10^{-4}
55	2.2	3.10×10^{-4}

The obtained results were plotted as shown in Figure III-9

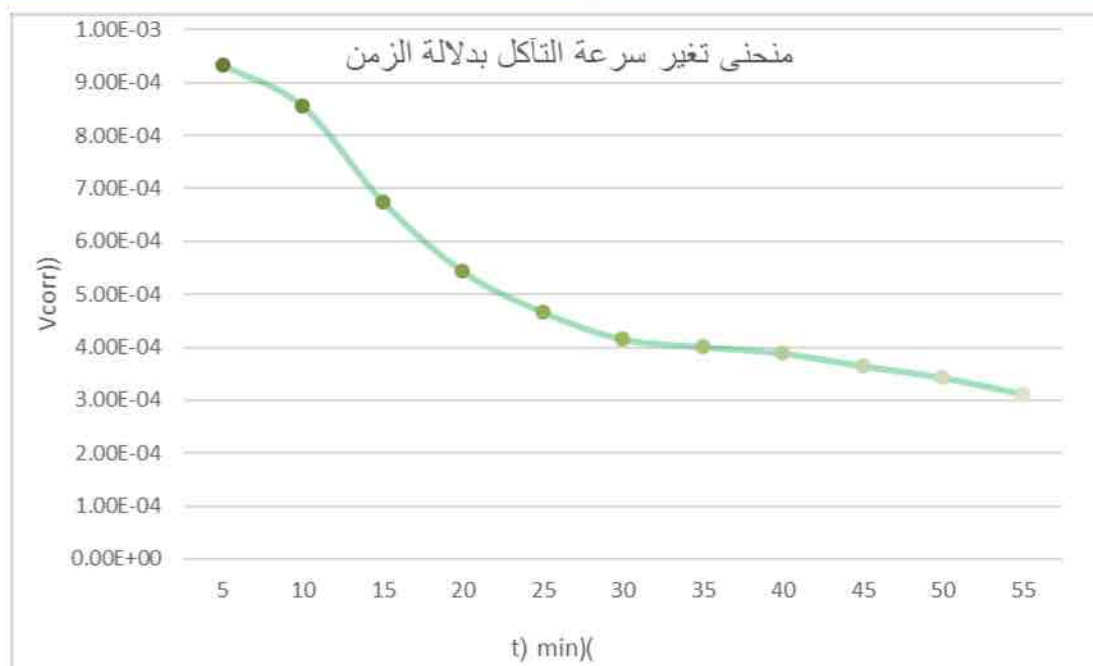


Figure III.9: Corrosion Rate as a Function of Time

The graph shows that the corrosion rate decreases gradually with time, which is attributed to the formation of a corrosion product layer on the steel surface that inhibits further reaction.

III.4.5 Effect of Temperature:

The effect of temperature on the corrosion rate of XC70 steel in HCl was studied at different temperatures for a fixed immersion time of 15 minutes..

III.4.6 Experimental Procedure:

- HCl solutions of identical concentration were prepared.
- Temperatures were adjusted to 35°C, 40°C, 45°C, 50°C, and 60°C using a thermostatic water bath.
- Steel samples were immersed separately at each temperature for 15 minutes.
- 5 mL of solution was withdrawn for KMnO_4 titration.
- Fe^{2+} concentration was determined and corrosion rate calculated

Table (III -3) : Corrosion rate versus temperature

Température (°C)	KMnO ₄ Volume (mL)	Corrosion Rate after Multiplication by (M × 5/2)
35	0.6	5.59×10^{-6}
40	0.8	7.44×10^{-6}
45	1.05	9.77×10^{-6}
50	1.3	1.21×10^{-5}
60	1.8	1.68×10^{-5}

The results show that corrosion rate increases with temperature due to the acceleration of electrochemical reactions



Figure III.10: Corrosion Rate as a Function of Temperature

The curve shows that the corrosion rate increases with increasing temperature. This behavior can be explained by the acceleration of electrochemical reactions in the acidic HCl medium, which leads to a higher corrosion rate of the steel.

III.5. Evaluation of Walnut Shell Extract Inhibitor

III.5.1 Selection of Inhibitor:

Walnut shells were selected as a natural corrosion inhibitor due to their content of several active organic compounds, such as polyphenols, flavonoids, tannins, and other oxygen- and nitrogen-containing compounds. These constituents are characterized by their ability to adsorb onto the steel surface and form a protective layer that reduces the interaction between the metal and the acidic medium, thereby decreasing the corrosion rate. In addition, walnut shells are a natural, readily available, low-cost, and environmentally friendly material compared to conventional chemical inhibitors. The walnut shells used in this study were collected from local markets.

III.5.2 Extract Preparation:

To prepare the plant extract and recover the active compounds, walnut shells were used as the raw material. In the first stage, the shells were thoroughly washed with distilled water to remove dust and adhering impurities, and then allowed to partially dry in air at room temperature. Oven-dried at 110°C for 3 hours



Figure III.11: Image showing the cleaning and drying of walnut

After that, the shells were subjected to thermal drying in an oven set at 110°C for three hours, in order to ensure complete removal of moisture and improve the extraction yield. They were then left to cool gradually at room temperature to prevent reabsorption of moisture.



Figure III.12: Image of grinding walnut shells

After drying, the shells were ground using an electric grinder to obtain a fine and homogeneous powder, which increases the contact surface area during the extraction process. Then, an amount of 50 g of the powder was accurately weighed using an analytical balance.

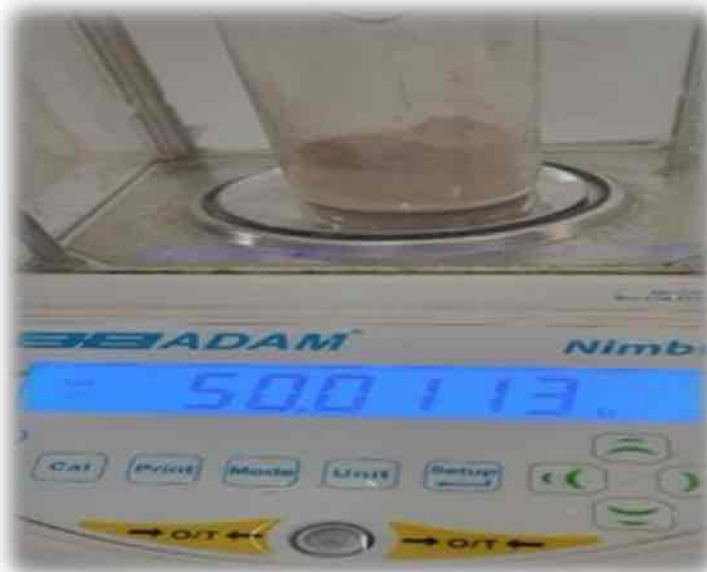


Figure III.13: Image showing the weighing of walnut shells powder

Extraction was carried out using the reflux technique, where the powder was placed in a round-bottom flask, and then a methanol/water mixture (80:20) was added. The reflux apparatus was operated under suitable thermal conditions to allow the extraction of compounds soluble in the solvent.



Figure III.14: Image of the reflux technique

Next, the liquid extract was concentrated using a rotary evaporator at 40°C in order to preserve the stability of heat-sensitive compounds. To determine the yield, the empty flask was first weighed, then the extract was added after evaporation and the flask was weighed again to calculate the final mass.

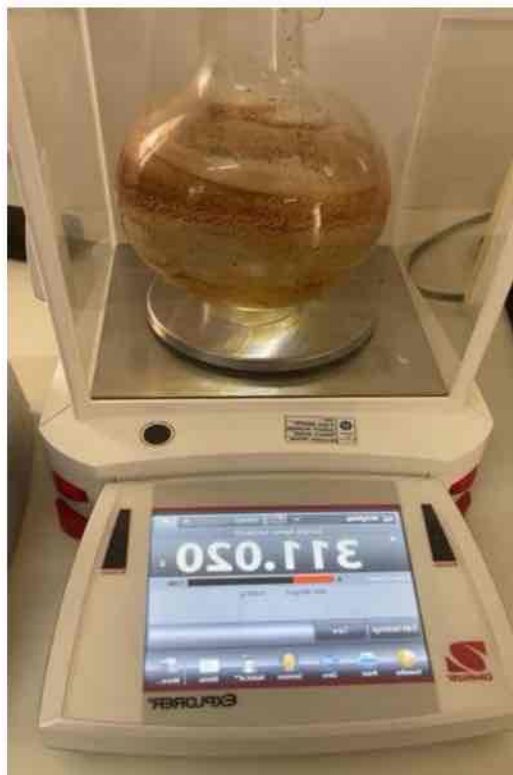


Figure III-15: The liquid extract was concentrated using a rotary evaporator at 40°C.

- Finally, the extract was stored in dark, tightly sealed glass bottles until further analysis.



Figure III-16: Image of solvent removal using a rotary evaporator

III.5.3 Extraction Yield:

The extraction yield is calculated according to the following equation:

$$R\% = (m_{\text{ex}} / m_{\text{in}}) \times 100$$

Where:

m_{ex} : final mass of the extract after evaporation

m_{in} : initial mass of walnut shells used

R%: percentage yield

The obtained yield was 7.34%.

III.5.4 Electrochemical Method:

Electrochemical measurements were carried out using a PGZ301 potentiostat/galvanostat, connected to an electrochemical cell consisting of three electrodes: a reference electrode, an auxiliary electrode, and a working electrode.

A cylindrical Pyrex glass cell with a capacity of 500 mL was used, equipped with a lid containing multiple openings that allow the insertion of electrodes and the addition of necessary accessories during the experiment, such as a nitrogen gas inlet and other auxiliary components.



Figure III-16: Schematic diagram of the electrochemical cell setup

III.5.5 Auxiliary Electrode:

The auxiliary electrode is one of the essential components of the electrochemical cell, as its role is to ensure the passage of electric current through the studied medium during electrochemical measurements. In this study, a platinum electrode was used due to its chemical inertness and high resistance to corrosion, which makes it non-participating in the chemical reactions occurring in the solution. The surface area of the auxiliary electrode is approximately 1 cm², and it was positioned inside the cell in a way that ensures uniform current distribution during the experiment..

III.5.6 Reference Electrode:

A Saturated Calomel Electrode (SCE) was used as the reference electrode in this study due to its stable and well-defined electrode potential during electrochemical measurements. This electrode contains a saturated potassium chloride (KCl) solution and is used as a stable reference for measuring the potentials of other electrodes within the cell. It also allows accurate determination of corrosion potential and various polarization parameters without being affected by changes in the corrosive medium...

III.5.7 Experimental Procedure:

Before starting the experiment, different solutions were prepared and the metal sample was carefully polished mechanically to obtain a smooth, homogeneous, and impurity-free surface. The electrodes were then inserted into the electrochemical cell and connected to the measurement device. The experimental conditions, such as scan rate and potential range, were adjusted based on preliminary tests and previous studies in this field.

After setting the experimental parameters, the device was operated to obtain electrochemical polarization curves and Tafel plots, which allow the study of corrosion behavior and the determination of the main electrochemical parameters. These curves provide several important indicators, including:

- Corrosion potential (E_{corr}) at the equilibrium current point
- Corrosion current density (I_{corr})
- Polarization resistance (R_p)
- Anodic and cathodic Tafel slopes

- Corrosion rate
- Correlation coefficient (Coef), which ranges between 0 and 1 and indicates the degree of agreement between experimental results and the theoretical model

III.6. Electrochemical Study

- Study of Corrosion Rate

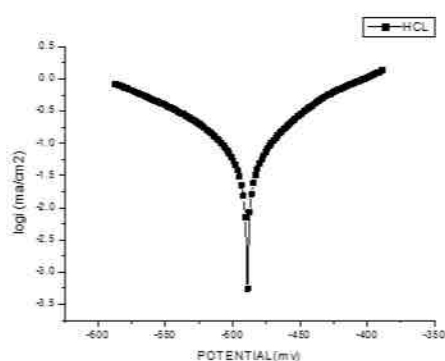


Figure III-17: Tafel curve in the absence of inhibitor

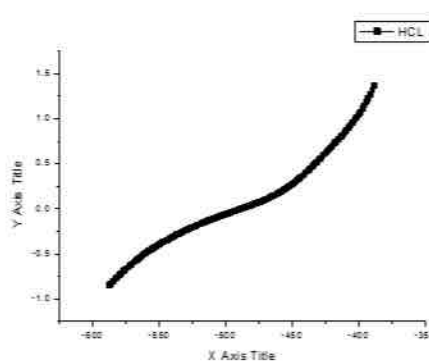


Figure III-18: Polarization curve in the absence of inhibitor

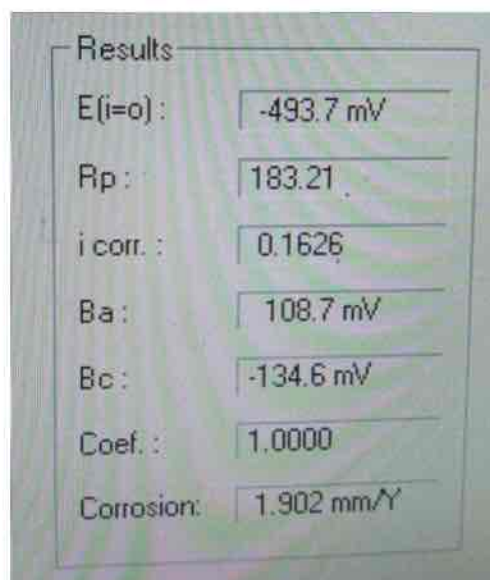


Figure III-19: Electrochemical parameters of the effect of HCl on XC70 steel

III.7. Effect of Inhibitor on Corrosion Rate in HCl (0.5 M)

III.7.1 Tafel Curves:

The following figures show polarization curves of XC70 steel in HCl with different concentrations of walnut shell extract...

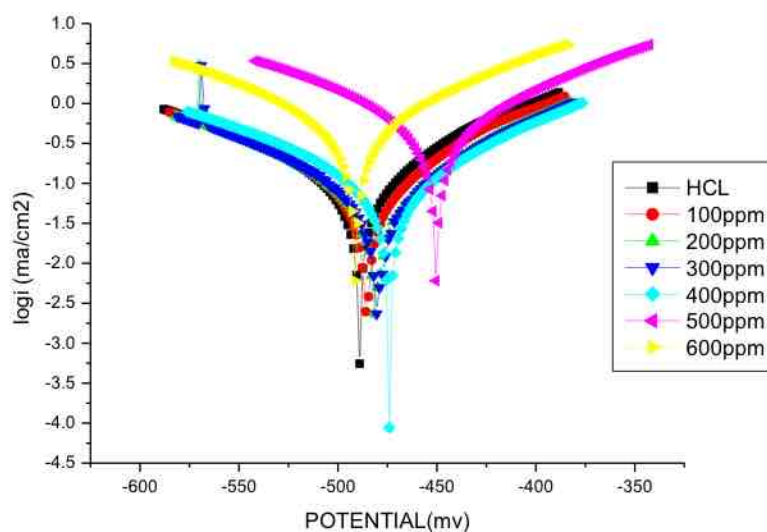


Figure III-20: Tafel Curves of XC70 Steel in HCl Medium at Different Inhibitor Concentrations.

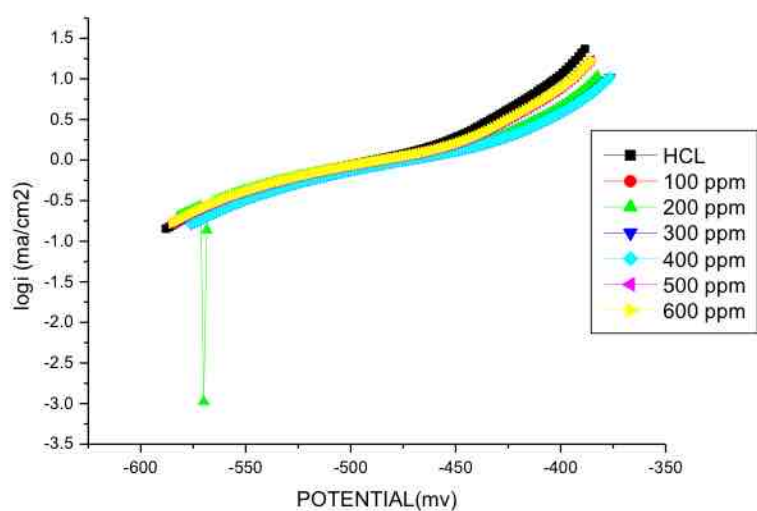


Figure III-21: Polarization Curves of XC70 Steel in HCl Medium at Different Inhibitor Concentrations.

Table (III -4) : Electrochemical Parameters of the Effect of the Inhibitor on XC70 Steel

PPm (mv)	Tafel data				
	-Ecorr (mV/SCE)	icorr ($\mu\text{A cm}^{-2}$)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	η_{Tafel} (%)
0	493.7	162.6	134.6	108.7	-
100	489.9	95.1	105.9	83.8	41.51
200	485.2	87.4	95.5	91.2	46.24
300	481.1	72.40	99.6	87.0	55.47
400	478.5	71.7	85.7	79.0	55.90
500	452.7	60.67	120.9	111.9	62.73

- XC70 steel shows a high corrosion rate in HCl without inhibitor, indicated by high corrosion current density.
- The addition of walnut shell extract reduces corrosion current density, indicating improved corrosion resistance.
- This improvement is due to adsorption of extract molecules on the steel surface, forming a protective layer.
- Increasing inhibitor concentration enhances surface coverage and improves inhibition efficiency significantly

Abstract



Abstract

This study investigated the corrosion behavior of XC70 carbon steel in 0.5 M hydrochloric acid (HCl) and evaluated the effectiveness of walnut shell extract as a natural corrosion inhibitor. Corrosion rate measurements showed that the corrosion rate decreased with immersion time due to the formation of a protective layer on the steel surface, while it increased with temperature as a result of accelerated electrochemical reactions. Walnut shell extract was prepared by reflux extraction using a methanol/water mixture, yielding an extraction efficiency of 7.34%. Electrochemical studies using Tafel polarization demonstrated that the addition of the extract significantly reduced the corrosion current density and improved the corrosion resistance of XC70 steel. The inhibition efficiency increased with inhibitor concentration, reaching 62.73% at 500 ppm. The protective effect is attributed to the adsorption of active organic compounds, such as polyphenols and tannins, onto the steel surface, forming a barrier film that limits metal dissolution. The results confirm that walnut shell extract is an effective, low-cost, and environmentally friendly corrosion inhibitor for carbon steel in acidic media.

Keywords: XC70 steel, Corrosion inhibition, Walnut shell extract, Hydrochloric acid, Tafel polarization, Corrosion rate, Natural inhibitor.

المخلص

تهدف هذه الدراسة إلى تقييم سلوك تأكل فولاذ XC70 في وسط حمضي من حمض الهيدروكلوريك (0.5 مول/لتر) ودراسة فعالية مستخلص قشور الجوز كمثبط طبيعي للتآكل. أظهرت نتائج القياسات أن معدل التآكل ينخفض مع زيادة زمن الغمر نتيجة تشكل طبقة واقية على سطح الفولاذ، بينما يزداد بارتفاع درجة الحرارة بسبب تسارع التفاعلات الكهروكيميائية. تم تحضير مستخلص قشور الجوز بطريقة الاستخلاص بالارتجاع باستعمال مزيج الميثانول/الماء، حيث بلغ مردود الاستخلاص 7.34%. كما بينت الدراسات الكهروكيميائية باستعمال منحنيات تافل أن إضافة المستخلص أدت إلى انخفاض ملحوظ في كثافة تيار التآكل وتحسن مقاومة الفولاذ للتآكل. وازدادت كفاءة التثبيط مع زيادة تركيز المستخلص لتصل إلى 62.73% عند تركيز 500 جزء في المليون. ويُعزى هذا التأثير إلى امتزاز المركبات العضوية الفعالة، مثل البوليفينولات والتانينات، على سطح الفولاذ وتكوين غشاء واقٍ يحد من انحلال

المعدن. وتؤكد النتائج أن مستخلص قشور الجوز يمثل مثبّطاً فعالاً واقتصادياً وصديقاً للبيئة لحماية فولاذ XC70 في الأوساط الحمضية.

الكلمات المفتاحية: فولاذ XC70 ، تثبيط التآكل، مستخلص قشور الجوز، حمض الهيدروكلوريك، استقطاب تافل، معدل التآكل، مثبّط طبيعي