

Ministry of Higher Education
and Scientific Research
University of Diyala
College of Science
Department of Chemistry



**Corrosion Inhibition of Aluminum and Its Alloy
(AA2024-T3) in Acidic Media Using Expired Drugs
(Aspirin and Deoxycyclin)**

A Thesis Submitted to the Council of the College of Science, University of
Diyala in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemistry

By

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

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DEDICATION

Every challenging work requires self-effort as well as guidance from the elderly, especially those who were very close to my heart.

My humble effort and my work I dedicate to my life, my mother and my father, may God have mercy on him

To the one who gave me affection, love and encouragement and made me able to achieve success, I dedicate my effort to my husband, and with all appreciation and respect, I dedicate my work to my supervisor.

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Abstract

Inhibition is a crucial strategy for reducing corrosion in aluminum and its alloys, and choosing a green inhibitor with no side effects is critical.

In this research, two expired drugs (Aspirin and Deoxycycline) were investigated to protect aluminum and its alloy (AA2024-T3) in 0.5M of H_2SO_4 solution at (293.15, 303.15 and 313.15K). Six concentrations (50, 100, 150, 200, 250 and 300 ppm) of each drug were used. Corrosion tests, inspection of inhibited surfaces, and other thermodynamic methods were used to evaluate the inhibition process. High-performance liquid chromatography (HPLC) and infrared spectroscopy was used in some inspections and testing to recover components from expired medications (FTIR).

Corrosion test (weight loss measurement) showed the good inhibition efficiencies (IE%) in 0.5M H_2SO_4 media. Aspirin gave 96.98 % at 313.15 K and 300ppm for aluminum pure, and gave 95.04 % for aluminum alloy (AA2024-T3) under the same conditions. Deoxycycline gave 93.25 % for aluminum pure at 313.15 K and 300 ppm, and gave 87.95 % for aluminum alloy (AA2024-T3), under same conditions.

The adsorption behavior of inhibitors was explained using three adsorption isotherms. The Langmuir, Freundlich and Temkin adsorption isotherm. It was found that all inhibitors follow creating a monolayer on the metal surface, the Langmuir adsorption isotherm is achieved. To define the kind of adsorption, from the values of activation energy and the enthalpy of activation adsorption found involves physical adsorption. Inspection the inhibited surface by SEM confirmed the adsorption of drug molecules on aluminum and its alloy (AA2024-T3) surface to achieve the inhibition. AFM images that showed the less roughness inhibited surfaces due to adsorption process to form a film as barriers between aluminum and its alloy (AA2024-T3) surface and environment.

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List of Abbreviation

Meaning	Abbreviation
Acetone	C₃ H₆O
Acetylsalicylic Acid	ASA
Aluminum	AL
Aluminum Alloy	AA2024-T3
Aluminum – Copper- Magnesium	Al –Cu –Mg
Aluminum Oxide	AL₂O₃
Atomic Force Microscope	AFM
Bauxite	AL₂O₃.nH₂O
Direct Current	Dc
Feldspar	K(ALSi₃O₈)
Fourier Transform Infrared Spectroscopy	FTIR
High-Performance Liquid Chromatography	HPLC
No Steroidal Anti-Inflammatory Drug	NSAID
Scanning Electron Microscope	SEM
Sulpharic Acid	H₂SO₄

List of Symbols

Symbol	Meaning	Units
CR	corrosion rate	Gmd
CR _{inhib}	Corrosion rate of inhibited	g/m ² d
CR _{unhibi}	Corrosion rate of uninhibited acid	g/m ² d
θ	Surface coverage	-
IE	Inhibition Efficiency	-
T	Absolute temperature	K
E _a	Activation energy	<i>kJ/mol</i>
N	Avogadro number	<i>moleculemol⁻¹</i>
R ²	Correlation coefficient	-
ΔH*	Enthalpy change	<i>kJ/mol</i>
ΔS*	Entropy change	<i>kJ/K . mol</i>
K _{ads}	Equilibrium adsorption constant	-
t	Exposure time	Day
A	Frequency factor	-
R	Gas constant	<i>J/K . mole</i>
C _{in}	Inhibitor concentration	Ppm
MW	Molecular weight	<i>g/mol</i>
h	Planks constant	<i>J . S</i>
n	Slope	-
ΔG ^o _{ads}	Standard adsorption free energy	<i>kJ /mol</i>
A	Surface area	m ²
ΔW	Weight loss	G
K _L	Langmuir adsorption constant	L/mg
K _F	Freundlich adsorption constant	L/mg
a	Molecular interaction parameter	-
K _T	Timken adsorption constant	L/mg

Chapter One

Introduction

And

Literature Survey

1.1 Introduction

Corrosion is described as partial or complete damage to an alloy or metal as a result of the alloy or metal's contact with a medium, whether it is a liquid or a gas. To comprehend the reason of the corrosion process, it is necessary to understand that most minerals do not exist alone in nature (they are combined with elements). Aluminum, for example, can be found in the form of ores like feldspar $K(AlSi_3O_8)$ and oxides like bauxite $Al_2O_3 \cdot nH_2O$. Because a certain amount of energy is expended in extracting minerals from their combined picture in order to retrieve them individually, the metal is in an unstable state when compared to its natural state when combined with other elements, and the new mineral state is described as the active state that qualifies the metal interact with the environment and the medium to overcome unstable state and tendencies to return to its original less energy and more stable state through the (corrosion process).[1]

Corrosion in other words, is an electrochemical reaction that occurs when metals are damaged by the environment. The rate and nature of the corrosion process are influenced by the material, the material's qualities, the environment, the chemical composition, the components, and the temperature.[2-3]

The corrosion process is usually made up of a series of electrochemical reduction/oxidation reactions. At anodic sites, the metal is oxidized to corrosion products, while at cathodic sites, some species are reduced. Other materials, such as plastics and ceramics, are susceptible to deterioration, but the term "corrosion" is typically reserved for metals.

Metallic substance corrosion can be classified into two categories:

Wet corrosion, where the corrosive state is a liquid of dissolved species, such as water. Corrosion may occur in other fluids such as molten metal and fused salts; the solvent is an electrolyte, and the mechanism is usually electrochemical.

Dry corrosion, where the corrosive atmosphere is a dry gas. The most well-known example of dry corrosion, also known as chemical corrosion, is high-temperature corrosion.

Corrosion can be split into two categories: chemical and electrochemical.

Metals reacting directly with their environment induce chemical corrosion, which results in the deposit of corrosion products on the metal surface. The electrochemical process is far more prevalent than the chemical one, and it consists of two partial reactions that occur at distinct periods, anodic and cathodic. A number of elements combine to initiate the electrochemical reaction.[4]

Alloys and metals are commonly employed in industries such as architecture, petroleum refining, vehicles, and other fields. Aluminum, for example, holds a significant place because of its high work capacity, excellent mechanical qualities, low cost, and this material has a high heat conductivity, however it has a low corrosion resistance in acidic conditions, which could result in economic losses. But the big problem with were realize that it accrue until some damage has already been done, often in the manufacture (loss of product efficiency , money due to repairs). Corrosion has a high cost associated with it because of the damage. Corrosion costs average between 3.5 and 4.5 percent in most developed countries.[5] Corrosion inhibitors must be used to protect metals.

Chemical inhibitors used as corrosion control inhibitors, such as nitrates, chromates, carbonates, phosphates, molybdates, silicates, and other hazardous compounds have demonstrated to be effective and inexpensive. These inhibitors, on the other hand, cause more issues than they solve. Their usage should be forbidden and fined as a result of the environmental risk and legislation. As a result, obtaining environmentally acceptable inhibitors from a certain supplier is preferred. Plant and medicine extracts have been valued because they are easily available and environmentally friendly. They are also a sustainable source of a wide variety of inhibitors, and they can be as effective corrosion inhibitors.[7]

There are two types of significance for corrosion research. The first is economic, which entails lowering material losses due to piping deterioration or unexpected failure, machine metal components, ship hulls, and marine structure. The second is protection, which is primarily applied to metal resources, and which incorporates comparable energy and water resource losses associated with metal structure manufacture and fabrication.[8] By taking proper preventive measures, the expenditures and harm can be reduced. The rate of corrosion can be maintained to a minimum by using the correct materials and surface treatments.

1.2 Expired Drugs

The majority of medications are not harmful until they expire, but their potency will deteriorate with time. The term "shelf life" refers to the reduction of the concentration of a drug in a drug product from 100% to 90% of its original concentration. Various methodologies for recycling active drugs from recycled drug products are being investigated.

As a result, appropriate chromatographic approaches and analytical tools may be used to isolate and eventually quantify active ingredients in order to successfully recycle them into usable synthetic intermediates or active medicines. From the standpoint of industrial applicability and commercial advantages, this solution can be both cost-effective and environmentally sustainable.[9]

1.3 Literature Survey

Abdullah(2004), The corrosion activity of aluminum by Hydrogen evolution was examined in a 2 M HCl solution in the absence and existence of four antibacterial drug molecules, weight reduction, and potentiostatic polarization methods. The efficiency of these chemicals as inhibitors is determined by their concentration and chemical composition, according to research. The molecules are adsorbed through the active areas in their structure obstructing the electrode surface was identified as the inhibitory action of these chemicals. The following is the adsorption procedure: Isotherm of Langmuir adsorption.[10]

Obot et al...(2009), Weight loss tests at 30 and 50 °C were used to investigate the inhibitory Clotrimazole (CTM) and Fluconazole (FLC), two antifungal medications, have been tested on aluminum electrochemical corrosion in a 0.1 M HCl solution. Both compounds appear to serve as inhibitors in the acidic corroding, according to the findings. Absence and inclusion of antagonists also reduced inhibition efficacy at steady acid concentrations. At all of the quantities and temperatures were studied. According to the isothermal model of Langmuir adsorption, CTM and FLC adsorb on the surface of aluminum. The obtained activation parameter is utilized to hypothesize a physical adsorption event.[11]

Bhat and Alva...(2011), The researchers looked into weight loss, dynamic effective polarization, and electrochemical impedance spectroscopy. The inhibitory effect of meclizine hydrochloride on corrosion activity of aluminum in a 1 M (HCl) medium. The findings showed that Meclizine behaved admirably as an aluminum corrosion inhibitor. This is thought to be as a result of the adsorption inhibitor on metal surface. Depend on the Langmuir adsorption isotherm model, the inhibitor adsorbs on the aluminum surface.[12]

Abdallah et al...(2012), Using potential static polarization measurements, the corrosion activity of aluminum and three aluminum–silicon alloys in various concentrations of HCl solutions, as well as its inhibition by antihypertensive drugs, was investigated. The rate of corrosion increases as the acid concentration rises. Aluminum has a lower corrosion resistance than any Al–Si alloy. The drug compounds' inhibition efficiency rises with their concentration until it reaches a critical value. The inhibition efficiency begins to deteriorate at higher additive concentrations. These compounds have an inhibitory effect since they form an insoluble complex on surface of the metal. Then there's the adsorption Langmuir adsorption isotherms.[13]

Fares et al...(2013), Polyethylene glycol (PEG) and the antibiotic ciprofloxacin were used to examine the synergistic inhibition of aluminum corrosion in acidic medium. The addition of ciprofloxacin to PEG alone result in marked in elevation the inhibition of aluminum corrosion. Ciprofloxacin was found to improve PEG inhibition efficiency from 61 to 91 percent. Addition of ciprofloxacin increases the thermo kinetic parameters of aluminum corrosion, such as the free energy of activation, enthalpy of activation, and entropy of activation, which is corresponding to the observed increase in inhibition efficiency.[14]

Abdullah and Jahdaly...(2015), Techniques such as weight loss, hydrogen evolution, galvanic static polarization, and electrochemical impedance spectroscopy were used to investigate the inhibitory effect of three antibiotic drug molecules, gentamicin, kanamycin, and amikacin, in a 1.0 M HCl solution on metal corrosion for aluminum. When the concentration of inhibitor is increased while the temperature is reduced, the inhibition efficiency improves. The antibiotic compounds studied acted as mixed form inhibitors, according to polarization measurements. The Langmuir isotherm model governs adsorption.[15]

Hameed et al...(2015), Using scanning electron microscopy (SEM) and potential dynamic polarization methods, the inhibition of pure aluminum Ampicillin was used to investigate corrosion in a 3.5 percent NaCl aqueous solution. It was discovered that Ampicillin effectively reduces aluminum corrosion in the saline solution. As the inhibitor concentration rises, the inhibition efficiency (%IE) rises as well ; When the temperature rises, further, (%IE) decreases. The inhibitor adsorption on the metal surface occurred spontaneously and followed the Langmuir adsorption isotherm.[16]

Abdel Hammed...(2015), The efficacy of expired Voltaire (EV) medication as a corrosion inhibitor for aluminum in 1 M HCl was investigated using weight loss and electrochemical techniques. The EV's inhibitory behavior is mixed-type, according to polarization curves. As the inhibitor molecules were added, the corrosion potential (E_{corr}) changed in a more noble course. Effect of temperature on inhibitor adsorption on an aluminum surface it was studied. The EV's The Langmuir isotherm was identified to govern adsorption.[17]

Sani and Amed...(2016), Gravimetric, gasometrical, and (SEM) techniques were utilized to investigate the corrosiveness inhibition potentials of Cefpodoxime projectile (CP). Cefpodoxime projectile inhibitory efficiency increases as the concentration increases, but drops as the temperature rises, according to the results of weight loss and hydrogen evolution experiments. The inhibitor's adsorption on aluminum. The Langmuir adsorption isotherm was discovered on the surface.[18]

Motawea et al...(2016), Weight loss, hydrogen evolution, The inhibitory impact was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM) techniques of expired Cidamex medication on aluminum in 1M HCl solution. Cidamex is a strong inhibitor, according to the findings, and efficiency of inhibition increased with concentration, reaching 99.6% at 300 ppm. The drug's potentiodynamic polarization curves revealed that it is an inhibitor of mixed types. This medication was adsorbed on the aluminum surface in the following way: Langmuir adsorption isotherm.[19]

Amed and Sani ...(2016), Cefuroxime axetil (CA) was examined as a corrosion inhibitor for aluminum in (HCl) solution using a thermometric, gas metric weight loss, and (SEM) technique. In an acidic media, the results demonstrated that this chemical has strong aluminum corrosion inhibitory capabilities, At 0.5 g / L, inhibitory efficiency reached 89.87 percent. The weight loss method's results were also found to be very similar to those obtained using the hydrogen evolution method and the gas metric approach, both of which mean that inhibitor performance improves as inhibitor concentration increases. Cefuroxime axetil prevented aluminum corrosion in HCl solutions through the physisorption mechanism.[20]

Yavari eh al...(2018), Quantum chemical computations, Tafel polarization, SEM, molecular dynamics process, and weight loss were used to investigate the inhibitory properties of tetracycline and streptomycin on aluminum corrosion in HCl solution. The studied tetracycline and streptomycin function as mixed-type inhibitors, according to polarization curves, inhibition efficiencies are thought to be in the tetracycline-streptomycin order. The Timken adsorption isotherm governs inhibitor adsorption.[21]

Nathiya et al...(2018), Weight loss tests, potentiodynamic polarization experiments, electrochemical impedance spectroscopy, and a research using a (SEM) were used to investigate corrosion inhibition of aluminum in 1 M H₂SO₄ using expired medications of moxifloxacin and betanesol as corrosion inhibitors. Experiments demonstrate that the medications used as inhibitors suppress aluminum corrosion and that the inhibition efficacy improves with the addition of moxifloxacin and betanesol at different temperatures. Furthermore, potentiodynamic polarization curves show that both betanesol and moxifloxacin serve as mixed form inhibitors of corrosion, but mainly anodic. The Langmuir adsorption isotherm were found for exist used to research the impact of temperature on aluminum corrosion in the existence and absence of inhibitors.[22]

Vivek et al... (2018), Spends' ability to prevent acidic corrosion of aluminum was investigated using a variety of experimental and analytical techniques. At 2000 ppm, Spends showed a 98 %inhibition effectiveness. Spends' ability to inhibit is related to its concentration in an acidic medium, according to research. The influence of temperature was also looked into, and it was discovered that it corroded Spends by raising the rate of corrosion and lowering the inhibition efficiency. Effective dynamic polarization and electrochemical impedance spectroscopy(Tafel) experiments were also used to examination the adsorption process, which revealed a complex physiosorption mechanism.[23]

Gbassi et al...(2018), At 298-318 K, the effects of Cefixime on aluminum (Al) corrosion in 1 M HCl was investigated quantum chemical methods based on density functional theory (DFT) calculations were used to calculate mass loss, Tafel polarization (at 298 K). According to the data, increasing the inhibitor concentration from 0.02 to 2 mM increases inhibition efficacy to 90.41 percent, but as the solution temperature rises, it decreases. Adsorption of the Cefixime molecule on the surface of the

corroded aluminum follows the Langmuir adsorption temperature and often occurs spontaneously through physical adsorption. Cefixime as a mixed-type inhibitor, according to potentiodynamic polarization evidence, which agrees with mass loss findings. (SEM) was used to examine the aluminum surface and indicated the presence of a preservative layer of inhibitor molecules.[24]

Diki et al...(2018), By use the weight loss and Tafel polarization methods, the inhibitory performance of Cefadroxil medication on Aluminum (Al) in 1 M hydrochloric acid solution was evaluated in the temperature range of 298-318k and the concentration range of 0.02-2mM. The findings suggest that Cefadroxil can prevent the hydrochloric acid medium from corroding. In the case of weight loss and strong dynamic polarization, In the presence of 2mM inhibitor, the highest inhibitory efficacy was 93.22% and 90.30%, respectively. It was found adsorption of the investigated inhibitor on Aluminum follows the Langmuir adsorption formula.[25]

Fayomi and Akande...(2019), Efficacy of hexamine as a corrosion inhibitor on aluminum alloy in with 3.65% NaCl at room temperature. Described in this analysis. Using potentiodynamic polarization techniques, numerical experiments, and mass loss calculations, the corrosion-preventative potential of Hexamine was investigated. Hexamine inhibits the corrosion of aluminum alloy in (NaCl) solution, according to the findings of the study. The mass loss caused by the inhibited Aluminum alloy appears to decrease with higher mass concentration of Hexamine. The testing revealed that Hexamine had a 47.1 percent inhibition efficiency, which is likely to increase as mass concentration increases. Hexamine in 3.65 % NaCl at room temperature acted as a mixed-type inhibitor, according to the polarization curve. The Langmuir adsorption isotherm was observed in the adsorption of Hexamine molecules on the Aluminum alloy.[26]

Abdullah et al...(2019), Electrochemical impedance testing, galvanic static, potentiodynamic anodic polarization, and weight loss were used to show the inhibitory action of tramadol medication (TR) on aluminum (Al) corrosion in 1MHCl solution. The inhibitory effect of drug TR is enhanced by increasing the dosage and lowering the temperature. TR drug is a mixed inhibitor, according to data derived from polarization.[27]

Vaszilcsin et al...(2019), Inhibitors of electrochemical processes can be used to shield metals and alloys from degradation, as well as to level cathodic metal deposition in galvanic technique. Drug active compounds are good inhibitors because they include structures in their molecules that contain electrons or lone pair electrons, allowing them to absorb on metal surfaces through physical or chemical interactions. Several medications have been shown to have significant inhibitory efficiency for many years, but because drugs are expensive, their practical implementation corrosion inhibitors for metals and alloys have been postponed.[28]

Narasimha ...(2019), The surface protection property of expired lifebuoy soap on the surface of Al investigated in a 3 M HCl environment using gravimetric, geometry, Tafel plot, and impedance spectroscopy techniques. The results reveal that in a 3 M HCl solution, the expired lifebuoy soap acts as a corrosion inhibitor for the AL. The protective efficacy improves as the amount of expired lifebuoy soap in the corrosive media increases. At 60o C and 0.2 g/L, the maximal protection efficiency is 96 percent. The Tafel plots validated the expired lifebuoy soap's mixed corrosion inhibition role in corrosive conditions.[29]

Fouda et al ... (2019), The effects of different thiophene derivatives on Al-Si alloy corrosion in 0.5M H₂SO₄ were examined using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Polarization experiments at various temperatures revealed that the substances under investigation are anodic inhibitors. The effects of temperature on corrosion inhibition were investigated, with thermodynamic activation and adsorption parameters measured and addressed. The inhibition happens as a result of the examined compounds adsorbing on the alloy surface without changing the corrosion mechanism. Both Tafel and kinetic thermodynamic isotherms suit the experimental results.[30]

Fayomi et al... (2019), Using potentiodynamic polarization methods, weight loss calculations, computational analyses, and structural characterization, In a 0.5 M (HNO₃) solution, the inhibitory activity of Cefadroxil (C) and Dicloxacillin (D) medicines on aluminum was investigated comprehensively. (SEM/EDS), (OPM), and (XRD) were applied to distinguish the structural properties. The corrosion protection and adsorption ability of (C) and (D) drugs on aluminum were revealed by a potentiodynamic polarization test (A). The Tafel plot confirmed that Cefadroxil and Dicloxacillin medicines have mixed inhibitory properties. It was possible to achieve a 58.9% inhibition efficiency.[31]

Akande et al... (2020), Using a three-electrode device, the inhibitory potential of Suptrim drug on aluminum 6063 alloy was investigated in the presence of (0.5M H₂SO₄) solution. For an increase in the volume concentration of the inhibitive drug, the corrosion rate (Cr) and corrosion current density (j_{corr}) decrease. The drop in (Cr) and (j_{corr}) values shows that the inhibitory drug molecules have affixed themselves to the metal surface. The inhibitory Suptrim medication (ISD) had a 52.55 percent inhibition efficacy at a mean test volume concentration of 20 ml. ISD conducts itself as a mixed-type inhibitor, as demonstrated by the similar

Ecorr values and overlapping existence of the polarization curves. The Langmuir adsorption isotherm was observed to be largely accompanied by ISD molecules adsorption on the aluminum alloy. The adsorption of ISD molecules on the aluminum alloy's surface was verified by morphology analysis using SEM micrographs.[32]

Hamza et al...(2020), The inhibition and adsorption behavior of phenylphrine medication for aluminum2024 alloy corrosion in 1 M acidic chloride solution at 293-303 Kelvin was investigated using the weight loss process. The result showed that phenylphrine inhibits the corrosion of Al 2024 alloy in a molar HCl solution. The inhibition efficacy improves as the phenylphrine concentration and temperature rise, suggesting a chemisorptions process. The phenylphrine adsorption on the Al 2024 alloy surface follow the Langmuir adsorption isotherm model. In the presence of phenylphrine in acidic solution, SEM picture reveals a smoothed surface of Al 2024 alloy.[33]

Bashir et al...(2020), On aluminum in an acidic medium, the nontoxic anticorrosion characteristics of nicotinamide were investigated. Weight loss methods, electrochemical measurements, quantum chemical calculations, Monte Carlo simulation, infrared spectroscopy, and (SEM) were among the technologies used . The impact of several parameters on corrosion inhibition efficiency was studied, and it was discovered that increasing inhibitor concentration and temperature improved inhibition efficiency. This paper examines the adsorption of inhibitor molecules on the surfaces of mineral specimens. The adsorption function was predicted using thermodynamic parameters.[34]

Hiba, B ,D...(2020), The effects of cordial myxa leaves (CML) extracts as a helpful, inhibitor on aluminum corrosion in (1MH₃PO₄) were investigation in the absence and presence of cordial myxa leaves (CML) extracts. (Temperature, Inhibitor (Effects the effects of weight loss on concentration) were investigated. The findings showed that Cordial myxa leaves(CML) extracts serve as an aluminum inhibitor in (H₃PO₄) and minimize the rate of corrosion. The efficacy of inhibition was observed to improve as the inhibitor concentration was increased, while the temperature did not. Higher inhibitor concentrations and temperatures result in greater inhibition efficiency (90.95%) was obtained. The adsorption of Cordial myxa leaf extracts followed a predictable trend (Model of Langmuir adsorption isotherm).[35]

1.4 Object of study

Due to the spread of corrosion in the industrial environment and the impact of its economic problems and its impact on the environment and human safety, as well as due to widespread worry about toxicity of corrosion inhibitors used in industry, toxic effects of these inhibitors are not limited to biological systems, but also to environmental pollution, the target of this study is to control corrosion What is caused by acidic solutions in the industrial environment through:

1. Extract and develop new natural inhibitory systems, readily available, non-toxic and inexpensive and environmentally friendly.
2. Aluminum corrosion inhibition and its alloy in acidic media using expired drugs. Using two expired drugs (Aspirin and Deoxycycline) as corrosion inhibitor to protect aluminum and its alloy (AA2024-T3) in 0.5M of H_2SO_4 acidic medium at three temperatures(293.15,303.15,313.15) using several concentrations (50,100,150,200,250,300 ppm).
3. Study the surface shape of aluminum and its alloy (AA2024-T3) by means of scanning electron microscope (SEM) and atomic force microscope (AFM) study of surface morphology.
4. Study of the active groups in inhibitors by of Fourier Transform Infrared Spectroscopy (FTIR).
5. A study of the mechanics of adsorption of corrosion inhibitors on the surface of aluminum and its alloy (AA2024-T3).

Chapter Two



Theoretical part




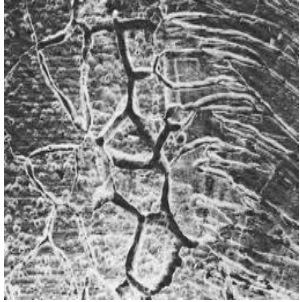
2.1 Types of Corrosion



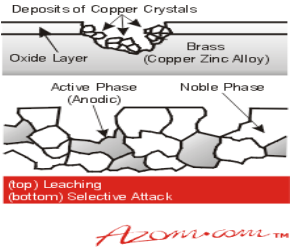
Corrosion's impact on a metal surface can take many distinct shapes, depending on the nature, state, and condition of the medium that produces the corrosion.

The corrosion types can be classified as listed in the table (2.1).

Table (2.1) Types of corrosion.

Corrosion Type	Description of condition	Case illustrations
Uniform corrosion	The term "uniform corrosion" refers to an assault that occurs uniformly across the entire surface area. Fresh or salt water, soil, and alkaline or acid salt solutions are examples of such environments, the metallic component is usually broken down into metallic ions, and the metal may be coated to prevent this type of corrosion. [36]	
Local corrosion	Means that specific areas of the metal surface are exposed to corrosion, because of the appropriate electrolyte. The regulation of this kind of corrosion is more complex than that of general corrosion.	

<p>Pitting corrosion</p>	<p>This type of corrosion is a focused attack that causes quick wall thickness penetration and appears on a metal surface as cavities or "holes." Because just a small area is affected, this type of corrosion is extremely difficult to detect and prevent.[37]</p>	
<p>Galvanic Corrosion</p>	<p>Corrosion occurs when two dissimilar metals have a potential difference. When two metals with different electrochemical potentials come into contact with the same solution, this phenomenon happens.</p>	
<p>Crevice Corrosion</p>	<p>Corrosion that is concentrated and severe. It's most common in cracks, fissures, lap joints, and behind gaskets, as well as on metals exposed to stagnant solutions in protected locations.</p>	
<p>Intergranular corrosion</p>	<p>Intergranular corrosion is a focused attack on the microstructure of metals and alloys that occurs at or near grain boundaries. With proper material selection, heat treatment, quenching, and welding processes, intergranular deterioration can be prevented.</p>	

<p>Stress corrosion cracking</p>	<p>The cracking caused by the interaction of tensile stresses and a corrosive material is known as forming. Tensile stresses can be created by cold working, welding, or heat treatment, or they can be caused by external loads, centrifugal forces, or temperature changes.</p>	 <p>The image shows two cylindrical metal tubes. The tube on the left is labeled 'Cracked tube' and has a prominent red line indicating a longitudinal crack. The tube on the right is labeled 'Comparison tube' and appears intact. A ruler is visible at the bottom for scale.</p>
<p>Erosion corrosion</p>	<p>Erosion is characterized as the slow removal of material from a stable surface. Any machinery that is exposed to flowing fluids may be subject to erosion as a result of the mechanical contact between the surface and the fluid.</p>	 <p>The image shows a cross-section of a pipe. The interior surface is heavily eroded, showing a rough, brownish, and irregular texture, contrasting with the smoother, greenish outer surface.</p>
<p>Selective leaching</p>	<p>is the corrosion-induced elimination of one part from an alloy; the procedure is known as selective leaching, de-alloying, or dezincification.[38]</p>	 <p>The diagram illustrates the process of selective leaching in brass. It shows a cross-section of the alloy with an 'Oxide Layer' on top. Below this, 'Deposits of Copper Crystals' are shown. The alloy is labeled 'Brass (Copper Zinc Alloy)'. The diagram is divided into an 'Active Phase (Anodic)' and a 'Noble Phase'. A red bar at the bottom indicates '(top) Leaching' and '(bottom) Selective Attack'. The logo 'AZOM.COM™' is visible at the bottom right.</p>

2.2 parameters effect on Corrosion

2.2.1 Temperature Effect

Over (293.15, 303.15, and 313.15) K, temperature effect on corrosion rate was examined. Temperature accelerates practically all chemical reactions, increasing the rate of corrosion, and as the temperature rises, the rate of corrosion accelerates. In most chemical reactions, however, the inhibition efficiency diminishes as the temperature rises. [39] The Arrhenius equation, in which the corrosion reaction rate is proportional to temperature, can be used to express this effect .[40]

$$CR = A e^{\left[\frac{-Ea}{RT}\right]} \dots \dots \dots (2.1)$$

Where (A) is Frequency factor (Ea) is energy of activation (KJ/mol), (R) is Gas constant (8.314 J.mol⁻¹.K⁻¹), (T) is Absolute temperature (K). From Arrhenius. Equation activation energy and frequency factor can be calculated by taking the natural (logarithm) of the previous equation:

$$\ln(CR) = \ln A - \frac{Ea}{RT} \dots \dots \dots (2.2)$$

So (lnCR) can be plotted against (1/T) with a slope of (-Ea/R) and intercept of ln (A). Temperature changes have the greatest effect when the rate determining step is the activation process. It is therefore not surprising that the activation energy of inhibited reactions at high coverages can be either larger or smaller than that of uninhibited reactions. The information in the literature shows that the relationship $\ln CR=f(1/T)$ is quite frequently, although not always linear in the presence of inhibitor.

Equation of transition state can be used to calculate enthalpy and entropy of activation as[41]

$$CR = \frac{RT}{Nh} \exp \left[\frac{\Delta S^*}{R} \right] \exp \left[-\frac{\Delta H^*}{RT} \right] \dots \dots \dots (2.3)$$

$$\frac{CR}{T} = \frac{R}{Nh} \exp \left[\frac{\Delta S^*}{R} \right] \exp \left[-\frac{\Delta H^*}{RT} \right] \dots \dots \dots (2.4)$$

$$\ln \frac{CR}{T} = \ln \left[\frac{R}{Nh} \exp \left(\frac{\Delta S^*}{R} \right) \exp \left(-\frac{\Delta H^*}{RT} \right) \right] \dots \dots \dots (2.5)$$

$$\ln \left[\frac{CR}{T} \right] = \ln \left[\frac{R}{Nh} \right] + \ln \exp \left[\frac{\Delta S^*}{R} \right] + \ln \exp \left[-\frac{\Delta H^*}{RT} \right] \dots \dots \dots (2.6)$$

$$\ln \left[\frac{CR}{T} \right] = \ln \frac{R}{Nh} + \left[\frac{\Delta S^*}{R} \right] - \left[\frac{\Delta H^*}{RT} \right] \dots \dots \dots (2.7)$$

Where;(h)is the Planck's constant (j.s), (N)is the Avogadro's number (molecule mole⁻¹),(ΔS^*)is the apparent entropy of activation (KJmole⁻¹K⁻¹),(ΔH^*) is the enthalpy of activation (KJ mole⁻¹). From equation(2.7) we can plot $\ln(CR/T)$ against $(1/T)$ and the slope of the straight line show a value $(-\Delta H^*/R)$ and intercept show a value of $(\frac{\Delta S^*}{R} + \ln R/Nh)$ from which (ΔH^*) and (ΔS^*) can be calculated.

2.2.2 Acid Concentration Effect

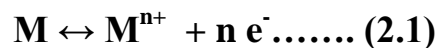
Because the amount of hydrogen ions increases as the acid concentration rises, and the term is typically defined as rising hydrogen activity by lowering the values of other elements, increasing the acid concentration improves corrosion efficiency (pH).[42]

2.2.3 Effect of inhibitor concentration

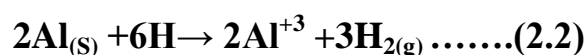
There is a relationship between the concentration of the inhibitor and weight loss in the mineral sample. There was a rise in the inhibitor concentration; whenever weight loss reduces, it continues to get closer to a low fixed value that depends on the inhibitor properties used where the study of the drugs powder for the purpose of knowing the active groups, and compounds is contained in the inhibitor; it has an inhibitory effect, and the reason is due to the multiple active groups.[43]

2.3 mechanism of corrosion

The loss of stability or stability of the metal is the primary cause of corrosion (alloy). Corrosion occurs as a result of oxidation and reduction reactions, and this form of corrosion is referred to as electrochemical corrosion. Electrochemical corrosion has the following general interaction:



Where (M) refers to the metal and ($\mathbf{M^{n+}}$) represents the ion of the metal and n stands for the number of electrons. The frontal interaction is a reaction of oxidation of an anodic reaction, the back interaction is the reaction of a cathode reaction.[44]The overall electrochemical process of corrosion of aluminum and alloy(AA2024-T3) can be written as follows:



The anodic and cathodic processes that are described by equations:



2.4 Thermodynamics of corrosion

Thermodynamics predicts which reactions are probable and whether a particular reaction will occur. This aids in the comprehension of corrosion dynamics and is crucial in the study of corrosion cells. The effect of entropy in chemical reactions is discussed in chemical thermodynamics studies, which describes equilibrium as a function of the elements and compounds present as well as the surrounding conditions (e.g., temperature, pressure, and chemical composition). It's used to determine whether or not corrosion can occur, as well as to forecast the formation of durable corrosion materials. The law of nature, which presupposes a collection state, is the most stable. Reactants have the lowest free energy of all the conditions. As a result, metal surfaces in contact with a solvent appear to be in the lowest possible free energy state. When the system hits this condition, nothing else happens. Finally, the state of equilibrium is the special lowest energy state. When a system is stable, there are no driving forces that can cause it to shift.[45]

2.5 Corrosion Protection and Control

Corrosion is controlled by taking certain measures that may relate to the metals and alloys used in terms of their choice and form of use, the medium or the environment to which these materials are exposed in terms of inference with some environmental factors affecting corrosion, and these procedures may also include means of external intervention by applying electrochemical means specific to protecting materials, Combining two or more of these strategies results in excellent corrosion control.[46]

2.5.1 Selection of Materials

Corrosion is controlled by taking certain measures that may relate to the metals and alloys used in terms of their choice and form of use, the medium or the environment to which these materials are exposed in terms of inference with some environmental factors affecting corrosion, and these procedures may also include means of external intervention by applying electrochemical means specific to protecting materials.[46] Corrosion prevention and control must be taken into account during the materials procurement phase of the design process if structures are to age in a predictable and cost-effective manner. It should be remembered that the materials procurement process is not limited to selecting the material from which to build a structure or component. Instead, it is used to choose a material framework that provides the necessary mechanical, thermal, electrical and physical properties to satisfy performance specifications while also providing the requisite resistance to environmental attack, such as corrosion.[47]

2.5.2 Design

A structure's design is important almost as crucial as the choice of construction materials because it can drastically minimize the time and expense maintenance and repair of corrosion. Mechanical and strength requirements, as well as corrosion resistance, must be addressed when constructing devices or instruments made of metals and alloys. Prior awareness of the candidate material's corrosion resistance and the atmosphere in which it operates is critical for the proper construction of any equipment. It's important to keep all situations as consistent as possible in the system. Corrosion often occurs in dead spaces or crevices, so these areas can be eliminated or reduced when designing.[48]

2.5.3 Coating

The most popular approach for avoiding corrosion is to use protective coatings. A protective coating's aim is to give a suitable barrier between the metal and its surroundings. Metallic coatings, inorganic coatings, and organic coatings are the three kinds of coatings that can be used.[48]A typical multifunctional coating can provide a nice scent, corrosion resistance, high adhesion, among other things. Barrier defense, chemical inhibition, and galvanic (sacrificial) protection are the three fundamental mechanisms by which protective coatings operate.

2.5.4 Cathodic protection

The cathode is the item to be guarded in cathodic protection, which is an electrochemical means of preventing corrosion. Cathodic protection is accomplished by providing electrons to the metal to be shielded while eliminating the corrosion current in a corrosion cell. An external power supply is used to protect the majority of pipelines and marine structures. A direct current (dc) power supply is used to power both the buried anodes and the things to be safeguarded. In most cases, the buried anode materials are inert materials and natural cathodes that safeguard steel pipes or tanks. The natural polarities of the materials are reversed with the use of dc power supply, and steel pipelines are cathodically protected.[48]

2.5.5 Anodic protection

It is an electrochemical technique to prevent corrosion of the metal in destructive environments such as hydrochloric acid and sulfuric acid. Anodic protection count on the exposure of the metal or alloy to an anodized current that leads to the formation of the bug of negative protective oxides on its surface that reduces the rate of corrosion ,and it is not very common in use except in some chemical industries ,as it is applied to some metals that have the property of negative oxides, such as metal Titanium in the acid hydrogen sulfide industries, and one of the disadvantages of this method is the possibility of corrosion due to the collapse of the negative layer, and some ions such as the chloride ion affect this energy and destroy it.[49]

2.5.6 Inhibitors

“Inhibitor is a substance that retards corrosion when added to an environment in small concentrations”. Corrosion inhibitors have been proven to be an effective and simple way to control corrosion. An inhibitor is a chemical molecule or group of compounds that, when used in small amounts in a corrosive environment, effectively delays or prevents corrosion without causing significant interactions with the other components. One important feature is that the inhibitor can be added without disrupting the process. To prevent or reduce corrosion of metal components, inhibitors used must meet the following conditions. [50-51]

1. Inhibitors must provide good corrosion protection at low inhibitor concentrations.
2. Inhibitors must safeguard all exposed materials against corrosion.
3. Inhibitors has to be able to operate in harsh situations and still be effective (higher temperature and velocity).
4. Corrosion rate should not increase dramatically if the inhibitor dosage is too low or too high.
5. The inhibitor, or its reaction products, should not leave any deposits on metal surface, especially in areas where heat transfer occurs.
6. Inhibitors should be able to protect against both uniform and localized corrosion.
7. Inhibitors should be effective for a lengthy period of time.
8. Inhibitors should not be a source of toxicity or contamination.

2.6 Inhibitors classifications

Corrosion inhibitors come in a variety of forms, including synthetic and natural compounds, and are categorized as follows:

- Organic or inorganic nature of the chemical nature.
- The anodic, cathodic, or anodic-cathodic mode of action, as well as adsorption action.
- Whether they are oxidants or not.

Inorganic inhibitors are classified as either cathodic or anodic. Organic inhibitors contain both cathodic and anodic properties, as well as the ability to absorb protective films.

2.6.1 Inorganic inhibitors

2.6.1.1 Anodic inhibitors

By preventing the anode reaction and maintaining the normal response of metal surfaces through a decreasing anodic reaction, anodic inhibitors work. Generally, the inhibitors react with the corrosion agent that has already formed on the metal surface, forming a film that is both cohesive and insoluble.[52] The cathodic current density at the initial passivation potential exceeds the critical anodic current density when the inhibitor concentrations are high enough, and the metal is passivation as a result.[53]The concentrations of inhibitors in the solution must be high enough. The wrong value of the inhibitors affects the creation of safety layer, so that it does not completely cover the metal and leave exposed areas, which leads to localized corrosion.[54] Nitrates, molybdates, sodium chromates, phosphates, hydroxides, and silicates are examples of anodic inorganic inhibitors.

2.6.1.2 Cathodic inhibitors

Cathodic corrosion inhibitors prohibit the metal from undergoing a cathodic reaction during the corrosion process. In the presence of alkalinity, metal ions in these inhibitors can trigger a cathodic reaction, it results in insoluble compounds that precipitate selectively at the cathodic sites. As a consequence , the surface résistance and diffusion restriction of reducible species, such as the diffusion oxygen and conductive electrons in these regions, increase. Cathodic inhibition is very high is caused by these inhibitors.[55] Cathodic inhibitors create an insoluble precipitate barrier over the metal, essentially shielding it.

As a result, even though the metal is fully immersed, it is constrained in its interaction with the environment, avoiding corrosion. Since cathodic inhibitors are not affected by concentration, they are far less dangerous than anodic inhibitors. Magnesium, zinc, and nickel ions are inorganic cathodic inhibitors that react with hydroxyl (OH⁻) in water to generate insoluble hydroxides (Mg(OH)₂, Zn(OH)₂, and Ni(OH)₂) which are deposited on the cathodic site on the metal surfaces which leads to its isolation from corrosion.

2.6.2 Organic inhibitor

Organic substances that are utilized as inhibitors might be cathodic in nature, or combined, but in general, they operate by a mechanism of surface adsorption known as film formation. Compounds with high inhibitory efficiency and low environmental impact are naturally produced when molecules with a strong attraction for metal surfaces are present.[56] These inhibitors provide a protective hydrophobic layer on the metal surface that adsorbs molecules and prevents the metal from dissolving in the electrolyte. It must be soluble or dispersed in the medium surrounding the metal. The existence of polar functional groups of S, O, or N atoms in the molecule, heterocyclic molecules, and pi electrons, all of which have ionizable hydrophilic or hydrophobic sections, determines the potency of these organic corrosion inhibitors. For the adsorption process to start, the polar feature is commonly thought of as the reaction core.[57] The organic acid inhibitor, which includes oxygen, nitrogen, and sulfur, binds to the metallic surface and prevents active corrosion sites from forming.[58]

Ascorbic acid, succinic acid, tryptamine, caffeine, and extracts natural substances, amines, urea, benzotriazole, aldehydes, heterocyclic nitrogen compounds, sulfur-containing compounds, and acetylene chemicals are among examples. The effectiveness of an organic inhibitor is determined by the type of organic inhibitor used:

- Chemical composition
- An aromaticity compound and conjugated bond, such as the length of the carbon chain.
- The molecule's type and number of bonding atoms or groups (either π or σ).
- Bonding strength to metal substrate, as well as the nature and charges of the metallic surface of the adsorption mode.
- A layer's capacity to compress or cross-link.
- The ability to form a complex with an atom as a solid within the metallic net work.
- Electrolyte type, such as appropriate environmental solubility.[58]

2.6.3 Mixed Inhibitors

They are the inhibitors that slow down the anode and cathodic reactions causing the corrosion process on an equal footing. To this type of inhibitors belong polyphosphates and silicates.[59]

2.7 Aluminum

Aluminum is a silvery white chemical element that belongs to the boron family. Atomic number is 13 and its symbol is Al. In usual conditions, it is not water soluble. Aluminum is the most abundant metal and the third most abundant element in the Earth's crust (after oxygen and silicon) and makes up around 8% of the Earth's solid surface by weight. Aluminum is a chemically reactive metal that does not exist in nature. Instead, it's present in over 270 different minerals in various combinations.[60] Aluminum has 59 percent of the thermal and electrical conductivity of copper, making it a good thermal and electrical conductor. Aluminum has a superconducting critical temperature of 1.2 K and a critical magnetic field of about 100 Gauss, making a superconductor (10 mS slice).[61] Corrosion resistance can be strong due to the thin surface layer of aluminum oxide that occurs when the metal is exposed to air, preventing further oxidation. Due to galvanic interactions with alloyed copper, the strongest aluminum alloys are less corrosion resistant.[62] When several aqueous salts are present, especially when different metals are present, corrosion resistance is generally considerably reduced.

2.8 Aluminum Alloy (AA2024-T3)

Aluminum alloy (AA2024-T3) (Al –Cu –Mg) is one of the best aluminum alloys it is widely used as a structural material in the aviation, automobile, and shipbuilding industries. Coatings are being utilized to protect aluminum alloys against corrosion.[63] Aluminum alloys offer a number of desirable features, including high flexibility, light weight, low melting temperatures, excellent thermal conductivity, and good surface polish, which make them ideal for casting.[64]

Anxxx(Al –Cu –Mg) series alloy, an example of a combination of some of these factors. Where they investigated the effects of welding parameters on the corrosion behavior of welded alloy (AA 2024-T3). Figure(2.1) show the principal aluminum alloys.

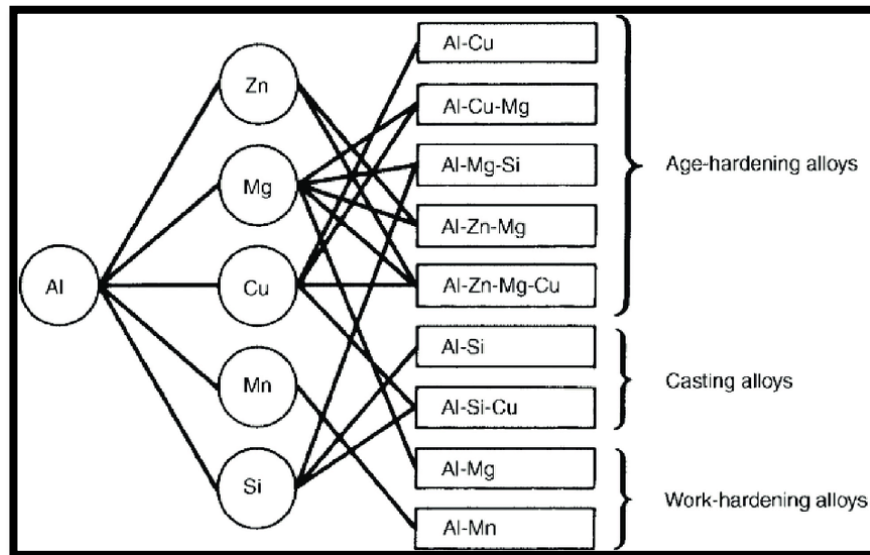


Fig.(2.1) The principal aluminum alloys.

2.9 Industrial Applications of Aluminum Alloys

Aluminum can be alloyed with a variety of elements, including zinc, magnesium, silicon, copper, manganese, and lithium. As a consequence, it may be used for a variety of purposes. Vehicle paneling, mine cages, airframes, fertilizer plants, pressure vessels, road tankers, ammonium nitrate transportation, drainage pipes, and window frames are only a few examples. The following are a few commercial uses for aluminum alloy.[65]

1. They are good heat and electrical conductors, which is why they are utilized in various chemical industries to prepare aluminum products.
2. During the reaction process, aluminum alloys harden. As a result, they are very desirable alloys in terms of weld ability and formability. They are also preferable for cryogenic applications, even in the case of annealed treatments.
3. Aluminum alloys have a good corrosion resistance. They protect it from a variety of harsh chemical treatments, allowing it to keep its brilliance and strength. It's also resistant to seawater and ocean water. As a result, it can be utilized for a variety of air cages without difficulty.
4. Because aluminum alloys are ductile, they can be transformed into any shape. Sheets or wires can be easily drawn into many shapes since they are sheets or wires.
5. A cathodic protection system made of aluminum alloy is also used (pipeline cathodic protection, oil tank, ship hull aluminum up anode , boiler anodes, aluminum rod and aluminum bracelet anodes).

2.10 Environmentally Friendly Corrosion Inhibitors

2.10.1 green inhibitors

Due to the increase in environmental awareness and the shift in the rules prohibiting conventional corrosion inhibitors due to their toxicity, green corrosion inhibitors are of interest. Because most of their extracts contain essential elements like O, C, N, and S, which are active in organic compounds and aid in the adsorb these compounds on metals or alloys to form a film that protects the surface and prevents corrosion, natural products are a good source of corrosion.

Thanks to advances in green chemistry and green chemical techniques, new synthetic methods for ionic liquids, which are new green inhibitors corrosion, as well as adsorption mechanism, how these green inhibitors act in different media, and their protective role of various metals and alloys, are now available.[66]

2.10.2 Drug inhibitors

Organic inhibitors, for the most part, are toxic and detrimental to the environment. The growing knowledge of health and environmental issues has prompted researchers to focus their efforts on developing highly effective and reliable eco-friendly inhibitors. As a result, developing low-cost, environmentally friendly corrosion inhibitors is critical.[67] Because of their low to negligible environmental effects. Drugs have some advantages over various inorganic/organic inhibitors when it comes to preventing metal corrosion. Since drugs are nontoxic, inexpensive, and have few harmful environmental effects, it was recommended that they be used instead of the typical toxic corrosion inhibitors.[68] Many experts in this field believe that pharmaceuticals are corrosion inhibitors that interact well with newly discovered green corrosion inhibitors, and that the bulk of these drugs can be made from natural materials. The following criteria are used to select some drugs that are utilized as corrosion inhibitors:

1. The major active centers of drug compounds are oxygen, nitrogen, and sulfur.
2. Environmentally friendly medications are said to be important in biological processes.
3. Some medications are simple to make.

As a result of the research findings, it has been determined that the majority of these drugs are natural products or plant extracts that have been discovered to achieve the goal of using a cheap, environmentally friendly, abundantly available, and effective high inhibition efficiency with little or no environmental impact.

2.11 Important Considerations in Selection of Inhibitors

Many considerations may be taken into account when inhibitors will be chosen as follows:

1. The magnitude of inhibition must be uniform and prevent localized corrosion.
2. Long range activity.
3. Performance of inhibitors as a function of concentration and temperature.
4. The inhibitor effect on heat transfer characteristics.
5. Pollution and toxicity problems.
6. The inhibitors are competed technically and economically with other inhibitors.[69]

2.12 Mechanism of Inhibitor

The effective mechanism of inhibitors is shown as the following:

1. Adsorption is the process of forming a coating on a metal surface.
2. encourage the development of corrosion products such as iron sulfide, a passivation species.

3. Changing the characteristics of the media, resulting in precipitates that are supposed to be removing and protecting or inactivating an aggressive element.

By adsorption, the organic molecules protect the metal from corrosion by producing a barrier between the medium and the metal. As a result, The non-polar end of the polar group molecule is trended vertically to the metal surface, producing a barrier against electrochemical and chemical damage by fluids on the metallic surface.

Because an inhibitor may be effective in one system and not in another, the following criteria should be considered:

- 1.**The inhibitory compound's chemical structure.
- 2.** Type of mediums to the corrosive environment.
- 3.** The surface nature of metal.
- 4.** Process conditions (pressure, temperature and pH).
- 5.** Thermal stability of inhibitors are limited temperature, above this temperature, the loss of their effectiveness causes degradation of the containing compounds.
- 6.** To offer the best results in metal surface protection, the inhibitor's solubility is necessary, which is determined by the length of the hydrocarbon chain.
- 7.**Surfactants are used to promote the solubility or disposability of inhibitors. [70]

2.13 Adsorption Isotherm

The relationship between the inhibitor and metal surface molecules can be interpreted by an isoadsorption model. It is known that in many corrosion systems, (Langmuir, Freundlich and Timken), are the most commonly used isotherms. The degree of surface coverage (θ) for different concentrations of the inhibitor must be determined to obtain the adsorption isotherm and the different models must be determined. To demonstrate the consistency of the model with data via equations, tests must be carried out follows:

$$\theta = \frac{IE}{100} \dots \dots \dots (2.8)$$

Where (θ) is "the degree of surface coverage" and (IE) is "inhibition efficiency". [71]

Langmuir adsorption Isotherm

In the model of Langmuir isotherm there is a set of uniform adsorption sites and many cases of strong adsorption do not fit this isotherm. Mathematically, this isotherm is given as.

$$\theta = \frac{K_L C_i}{1 + K_L C_i} \dots \dots \dots (2.9)$$

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

$$\frac{C_i}{\theta} = \frac{1}{K_L} + C_i \dots \dots \dots (2.10)$$

Can draw (C_i / θ) versus (C_i) we get values (k_L) "constant equilibrium" from the intercept.[71] Another useful equation also is:

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5 * KL) \dots \dots \dots (2.11)$$

Where; (ΔG°_{ads}) is standard adsorption free energy (kJ mol^{-1}).

Freundlich adsorption isotherm

This isotherm can be represented by the equation:

$$\theta = Kf C_i^n \dots \dots \dots (2.12)$$

Where, for a given system at a given temperature, K_F (Freundlich constant) and (n) are constants.[72] This isotherm can be written as:

$$\ln \theta = \ln(Kf + C_i^n) \dots \dots \dots (2.13)$$

$$\ln \theta = \ln Kf + n \ln C_i \dots \dots \dots (2.14)$$

Can be plotted as $\ln(\theta)$ against $(\ln C_i)$, where the slope and intercept yield the values of (n) and K_F respectively.

Timken adsorption isotherm

Timken isothermal adsorption, as defined in equation (2.15), was used to describe the adsorption of aluminum metal and aluminum alloy(AA2024-T3) surface adsorption inhibitors.

$$e^{-2a\theta} = KTC_i \dots \dots \dots (2.15)$$

$$\theta = \frac{1}{-2a} \ln KT - \frac{1}{2a} \ln C_i \dots \dots \dots (2.16)$$

Where; a is the molecular parameter of interaction, K_T is the equilibrium, (Timken adsorption isotherm) constant, (L / gm) equation (2.16) can be

plotted as surface coverage (Θ) versus ($\ln C_i$), where slope and intercept yield a and K_T values, respectively.[73]

2.14 Drugs Expiration

The drugs aren't harmful and toxic after the expired date existing on the bottle or box, but some drugs, like liquid antibiotics or insulin have fast degradation. Any drug that includes an organic component is also exposing to decay. Thus, most of drugs are remained active after the expiration date. The expiration date does not show that the drugs will be harmful or ineffective beyond that date, but the drug is still good.[74] The expiration dates don't mean that the drugs cannot remain useable for longer periods. In fact, stability has been pronounced for some drugs for periods of 10-15 years or more. But, the two important factors are affected on the shelf-life are humidity and temperature.[75] There has recently been an effort to investigate various approaches for recycling active pharmaceuticals from outdated medication goods. It is believed that when a medicine product reaches the end of its shelf life, it may contain 90% or more of the active pharmacological components. As a result, appropriate chromatographic processes and analytical techniques could be used to isolate and eventually quantify active components in order to successfully recycle them into useful synthetic intermediates or active drugs. From the standpoint of industrial application and commercial benefits, this strategy would be both cost-effective and environmentally beneficial.[76]

2.15 Kardikern (Aspirin)

Aspirin, commonly known as acetylsalicylic acid (ASA), is a ache reliever, fever reducer, and anti-inflammatory.[77] Pericarditis and rheumatic fever are some of the inflammatory disorders that aspirin is used to treat.[77] When Aspirin is taken soon after a heart attack, it reduces the risk of death. In adults at high-risk, aspirin is also used long-term to help prevent heart attacks, strokes, and blood clots. It may also reduce the risk of certain cancers, including colorectal cancer. [78] Aspirin is a non-steroidal anti-inflammatory medication (NSAID) that works in the same way as other NSAIDs but also inhibits platelet function. Table (2.2) lists the chemical properties of Aspirin and fig. (2.2) shows the Aspirin chemical structure.

Table (2.2) chemical properties of Aspirin.

Color	Weight
Molecular Formula	$C_9H_8O_4$
Molecular Weight	180.158 g/mol

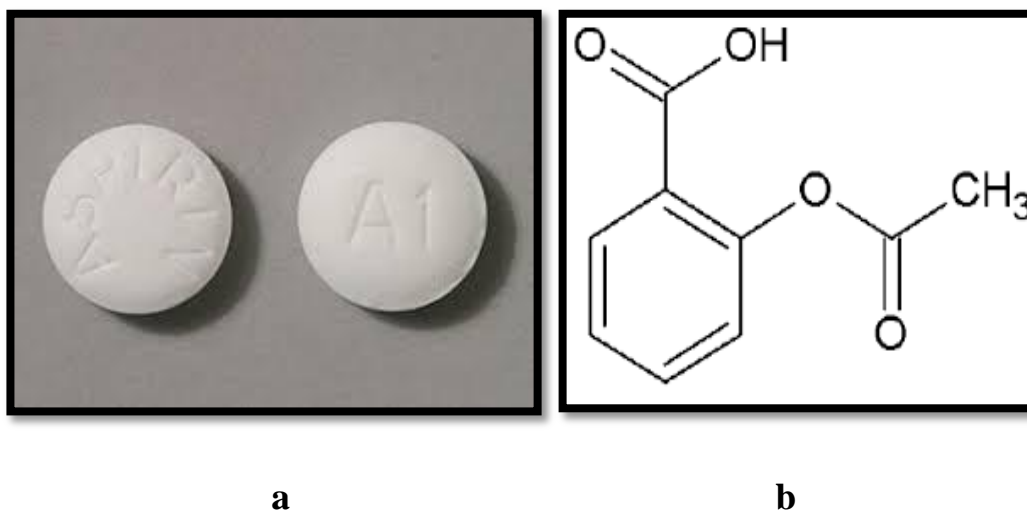


Fig. (2.2): (a) Appearance and (b) chemical structure of Aspirin.

2.16 Deoxycycline

Deoxycycline is a tetracycline-class antibiotic with a broad spectrum of action that is used to treat bacterial and parasite infections.[79] Bacterial pneumonia, acne, Chlamydia infections, Lyme disease, cholera, typhus, and syphilis are all treated with it. It is also used to prevent malaria and to treat malaria when combined with quinine. Deoxycycline can be given orally or through a venous injection. By blocking protein formation, it either slows or kills bacteria. [80]It kills malaria by attacking the apicoplast, a plastid organelle.[81] Table (2.3) lists the chemical properties of Deoxycycline and fig. (2.3) shows the Aspirin chemical structure.

Table (2.3) chemical properties of Deoxycycline.

Color	Light yellow
Molecular Formula	$C_{22}H_{24}N_2O_8$
Molecular Weight	444.4 g/mol

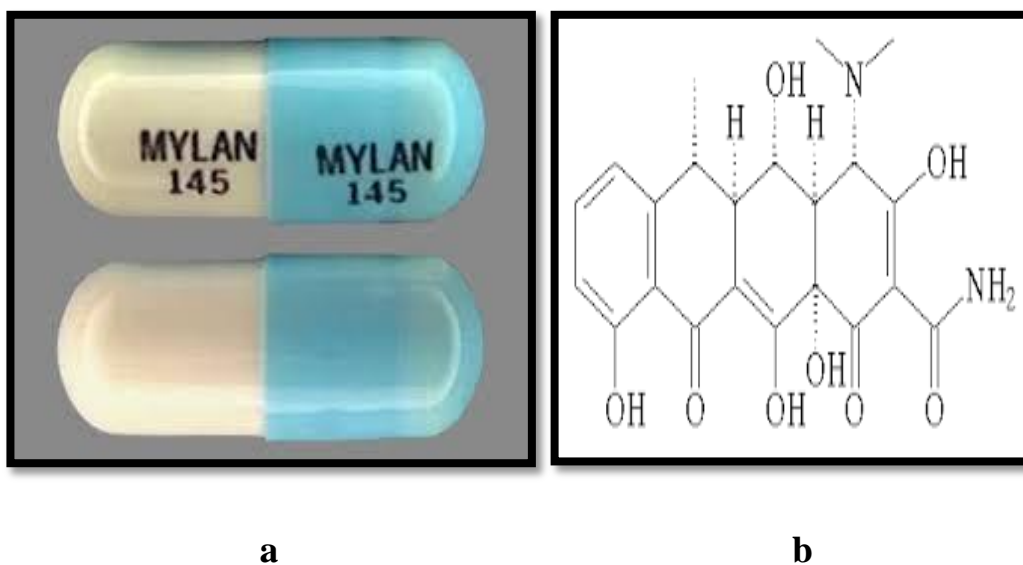


Fig. (2.3): (a) Appearance and (b) chemical structure of Deoxycycline.

Chapter Three

Experimental part

3.1 Introduction

The experimental section of this research include Selection of expired drugs and characterizing them by FTIR and HPLC techniques. Aluminum pure and aluminum alloy (AA2024-T3) was prepared for corrosion test in a corrosion media, including 0.5M H₂SO₄ solution at three temperatures (293.15, 303.15, and 313.15) K. Corrosion inhibition was studied using loss weight measurements and supported by SEM and AFM analysis.

3.2 Chemicals and Materials

3.2.1. Chemicals

3.2.1.1 Sulfuric acid

As a corrosion solution, sulfuric acid was utilized after dilution to (0.5M) and produced in Germany, Properties of sulfuric acid with the chemical formula (H₂SO₄), sulfuric acid is a strong acid. The solution is acidic enough to be corrosive also sulfuric acid has purity 96% molecular weight 98.08 g / mol and density is (1.84g / ml) , From (0.5M H₂SO₄) a solution with pH of 1.2 was prepared.

3.2.1.2 Acetone

Is a chemical with the formula (C₃H₆O), purity (99.9%) and molecular weight (58.08g / mol). It was used to dry the mineral coupons before and after each test, designed by (ROMIL) company and manufactured in Europe.

3.2.1.3 Distilled Water

Was used to prepare and clean the water samples and was obtained from. The laboratories of the Department of Chemistry / College of Science / University of Diyala.

3.2.2 Materials

Basic materials are listed in table(3.1)

Table(3.1) The mineral materials used in this study.

Material	Formula	Manufacturer	Purity
Aluminum	AL	Iraqi	% 99.7
Aluminum Alloy(AA2024-T3)	AA	America	% 93.7

The composition of the aluminum and aluminum alloy(AA2024-T3) have been determined by (optical emission spectroscopy OSE) available in central organization for standardization and quality control as shown in table(3.2).

Table(3.2)Composition of aluminum and aluminum alloy(AA2024-T3).

Composition (WT%)							
Pure aluminum				aluminum alloy(AA2024-T3)			
Si	% 0.0390	V	% 0.0066	Si	% 0.0442	V	% 0.0048
Fe	% 0.159	Bi	% 0.0111	Fe	% 0.140	Bi	% 0.0100
Cu	% 0.0067	Zr	% 0.0020	Cu	% 3.92	Zr	% 0.0020
Mn	% 0.0070	B	% 0.0036	Mn	% 0.655	B	% 0.0032
Mg	% 0.0072	Ga	% 0.0030	Mg	% 1.44	Ga	% 0.0010
Zn	% 0.0150	Cd	% 0.0020	Zn	% 0.0716	Cd	% 0.0030
Cr	% 0.0010	Co	% 0.0020	Cr	% 0.0013	Co	% 0.0020
Ni	% 0.0050	Ag	% 0.0010	Ni	% 0.0050	Ag	% 0.0010
Ti	% 0.0010	In	% 0.0050	Ti	% 0.0178	In	% 0.0050
Be	% 0.0010	Ce	% 0.0050	Be	% 0.0010	Ce	% 0.0050
Ca	% 0.0034	Hg	% 0.0050	Ca	% 0.0020	Hg	% 0.0050
Pb	% 0.0050	La	% 0.0050	Pb	% 0.0050	La	% 0.0050
Sn	% 0.0050	Al	% 99.7	Sn	% 0.0050	Al	% 93.7

3.3 Instruments Used

The instruments, used in this study are listed in the table(3.3) with their model and origin, in College of Science, Diyala University.

Table(3.3) The instruments, used in this study.

NO.	Instruments	Model	Manufacturer	Location
1	Electronic Scale	KERN & Shone GmbH, Type ACS 120-4, NO. WB12AE0308,CAPACITY 120g, READABILITY 0.1mg.)	Germany	Laboratories of Chemistry Department, College of Science, University of Diyala, Iraq
2	Thermostatic Water Bath,	THERMOSTAT Water Bath HH-2	China	
3	Distillation Device	LUZ DE AVISO AGUA INSUFICICENTE	Germany	
4	Laboratory Thermal Oven	BINDER, Hotline International	Germany	

3.4 Appliances used in characterization

The devices used are shown in table(3.4) with their model, and location.

Table(3.4) Devices, used in the Characterization.

NO.	Devices Names	Model	Location	Manufacturer
1	Fourier Transform Infrared Spectroscopy(F TIR)	(Perkin Elmer Spectrum 65 term(400- 4000cm ⁻¹)	Laboratories of Chemistry Department, College of Science, University of Diyala, Iraq	Germany
2	Atomic Force Microscope (AFM)	Scanning Probe Microscope, AA 3000 SPM 220 V-Angstrom Advanced Inc., AFM contact	The Special Laboratory of Dr. Abdul Kareem M.A. AL-Sammarraie , College of Science, University of Baghdad, Iraq	Germany
3	Scanning Electron Microscope (SEM)	TESCAN(Czech Republic)	The Special Laboratory, Tehran ,Iran College of Science, University of Sharif of Technology	Germany
4	High-performance liquid chromatography HPLC	LC-2010AHT LIQUID CHROMATOGRAPH	The Ministry of science and Technology, Baghdad, Iraq.	Germany

3.5 Preparation of Corrosion Medium

This study used corrosion media, including a 0.5M H₂SO₄ solution. These media were produced in distilled water and placed in flasks with 500 mL capacities filled with various drug concentrations, as shown in fig. (3-1).



Fig.(3.1) Preparation of corrosion medium H₂SO₄ acid and different concentrations of drugs.

3.6 Extraction of Expired Drugs

The inhibitors, which include (Aspirin and Deoxycycline), were chosen as the active ingredient from two expired medications. These medications were mashed with a pestle, combined with distilled water for 24 hours, filtered for 36 hours, and then dried for 4 hours every day in an oven at 80 degrees Celsius, as shown in fig (3-2). High performance liquid chromatography (HPLC) and FTIR techniques were employed to determine the presence of (Aspirin and Deoxycyclin) in the active substance.

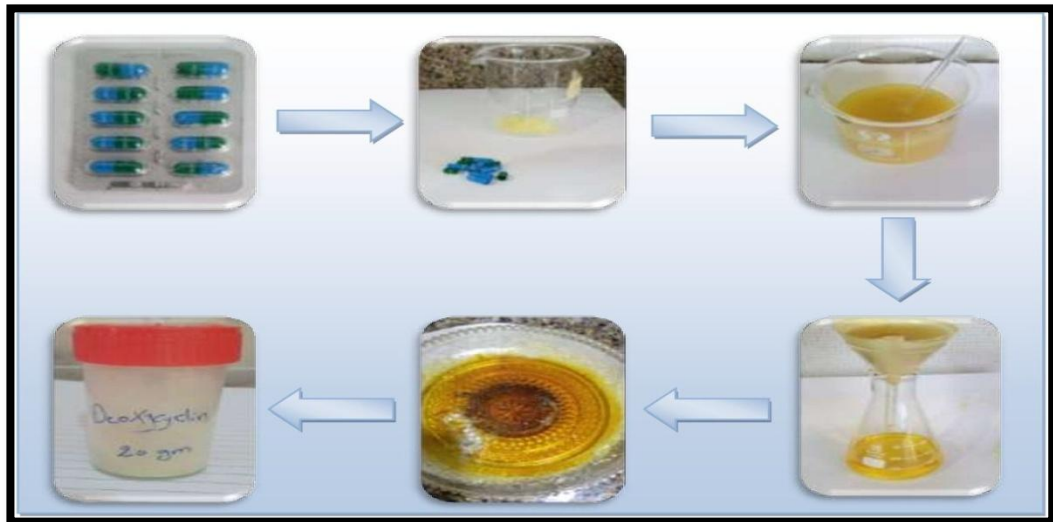
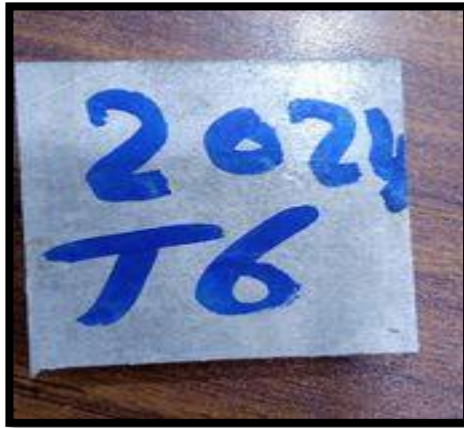


Fig.(3.2) Stages of extraction active material.

3.7 Specimens Preparation

Aluminum pure and alloy (AA2024-T3) specimens were made initially to examine the corrosion test (loss weigh). Cutting the specimen is regarded a significant parameter in corrosion resistance, and it is vital to prepare a consistent surface. Square specimens (3cmx3cmx1cm) were cut using an electrical saw into a final specimen shape with a hole drilled on one side for easy suspension in the corroding solution.

The second thing grinding and polishing the specimens were then ground with paper of various in sequence of (220,400,600,800,1000,1500 and 2000) to achieve a smooth, scratch-free surface. The samples were polished with alumina suspension .After that, distilled water was used to rinse the samples. Acetone was used to degrease the polished samples, which were then dried and stored in a plastic container. A four-digit electronic balance was used to weigh the samples, and an electronic ruler (venire) was used to measure their dimensions.[88]



(a)



(b)

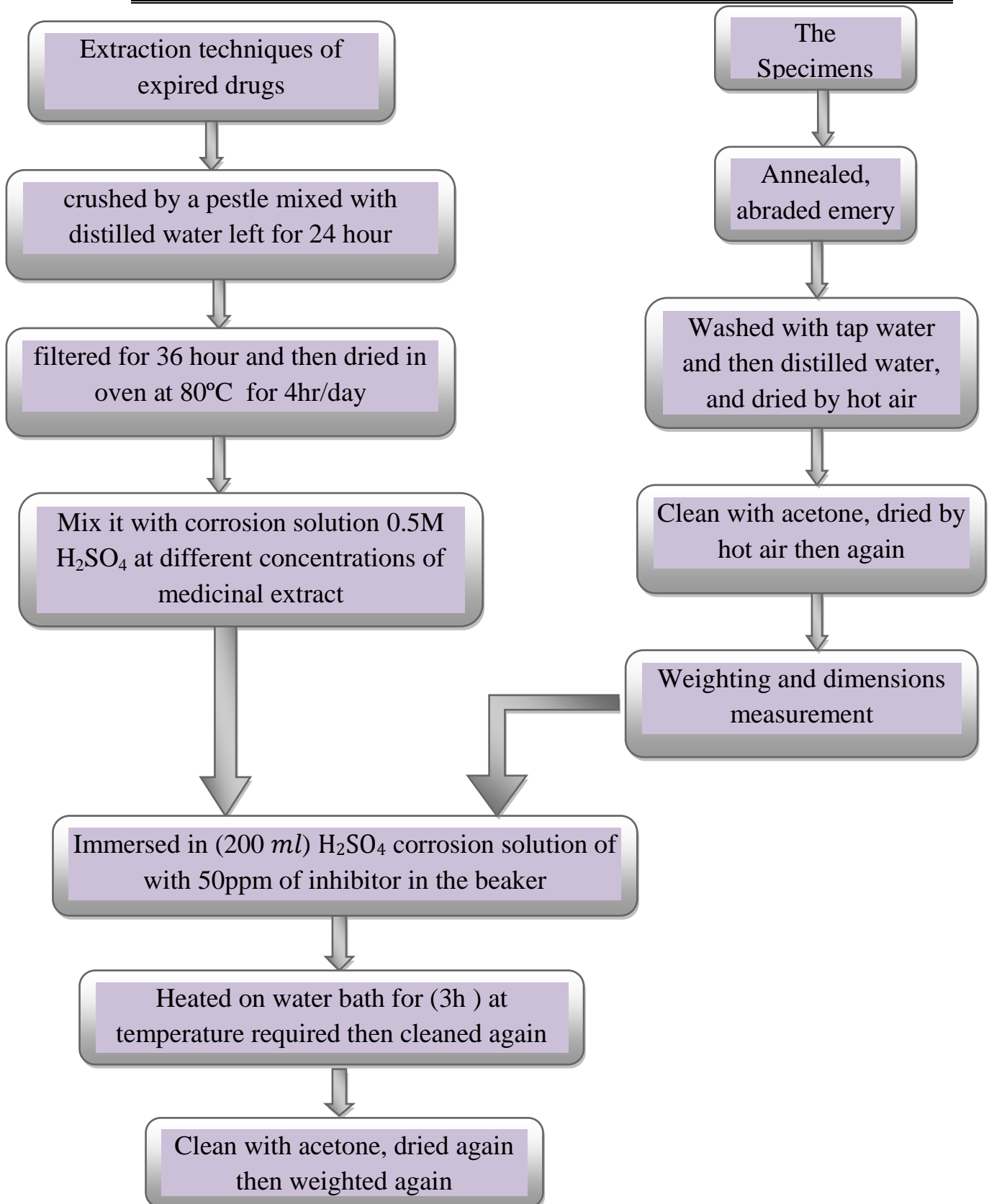


(c)

Fig.(3.3):The preparation steps of pure aluminum and aluminum alloy(AA2024-T3).

3.8 Weight Loss Measurement

To determine how much weight has been lost, aluminum and aluminum alloy (AA2024-T3) specimens were employed. The samples were immersed in 250ml of 0.5M H₂SO₂ after being washed and dried. A solution with and without inhibitor was tested for a period of time (3 hours). After cleaning, the samples were dried using an electric drier and weighed with an analytical balance. Experiments with varied inhibitor concentrations (50,100,150,200,250,300) ppm and temperatures (293.15,303.15,313.15) K were utilized to quantify weight loss, as shown in figure (3.4).



Figure(3.4): The experimental set up of corrosion study.

3.9 Analytical Methodologies

The study of the surface effects of acid on aluminum and its alloy (AA2024-T3) and the structure of the inhibitor used were carried out using the following techniques:

3.9.1 Fourier Transform Infrared Spectroscopy(FTIR)

The FTIR technology is used to determine the active groups in the drugs used after the extraction process by taking a sample from the extract and mixing it with KBr the spectra were recorded by the(Perkin Elmer Spectrum a model 65). Made in Germany Faculty of Science, University of Diyala device appears FTIR in fig.(3.5). The result was discussed to confirm the active groups in inhibitive.

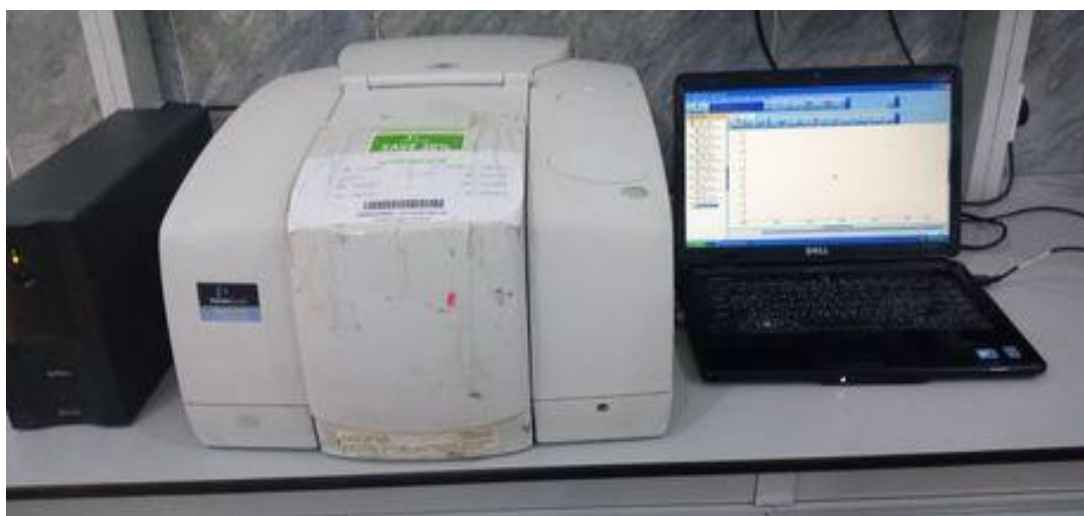


Fig.(3.5): Fourier Transform Infrared Spectroscopy(FTIR).

3.9.2 High performance liquid chromatography (HPLC)

Used to identify the active material, obtained from the assay method prepare 60% water/ 30% acetonitrile and 10% methanol as diluting solution, column (ODS_{c18} 250 x 4.6 Id)mm, 5Mm particle size ,flow rate =1ml/min (to identify the active material of aspirin). To identify the active material of Deoxycyclin method prepare 45% acetonitrile / 55% oxalic acid, column (ODS_{c18} 250 x 4.6 Id)mm, 5Mm particle size, flow rate =0.8ml/min the test shown in fig.(3.6).



Fig. (3.6): High Performance Liquid Chromatography (HPLC) instrument.

3.9.3 Scanning Electron Microscope(SEM)

After the needed studies, the surface morphology of aluminum and aluminum alloy(AA2024-T3) was evaluated using a scan electron microscopy (SEM) model(TESCAN(Czech Republic)) The Special Laboratory, Tehran ,Iran College of Science, University of Sharif of Technology, as shown in fig.(3.7).



Fig. (3.7): Scanning Electron Microscopy(SEM).

3.9.4 Atomic Force Microscopy (AFM)

A cantilever with a sharp tip (probe) at its end is used to scan the specimen surface for AFM imaging of the insulating surface structure at atomic resolution. The topography of the surface was displayed and the roughness were measured using atomic force microscopy. Figure (3.8) shows an AA3000 Scanning Probe Microscope in the College of Science at the University of Baghdad.



Fig.(3.8): Atomic Force Microscopy(AFM).

Chapter Four

Results

and

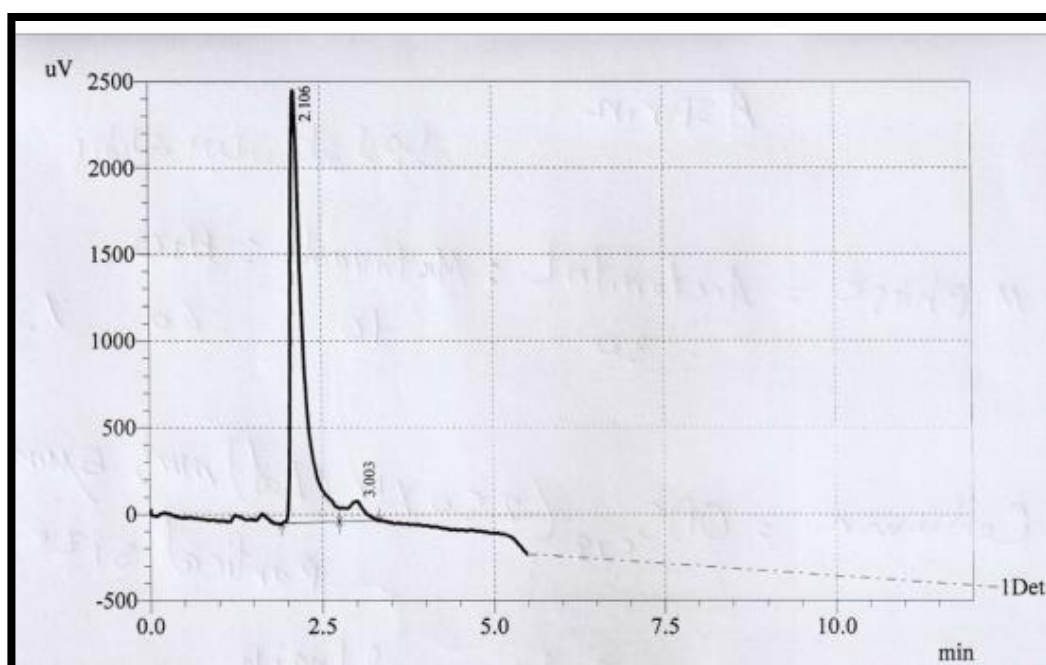
Discussion

4.1 Characterization of Extracted Materials

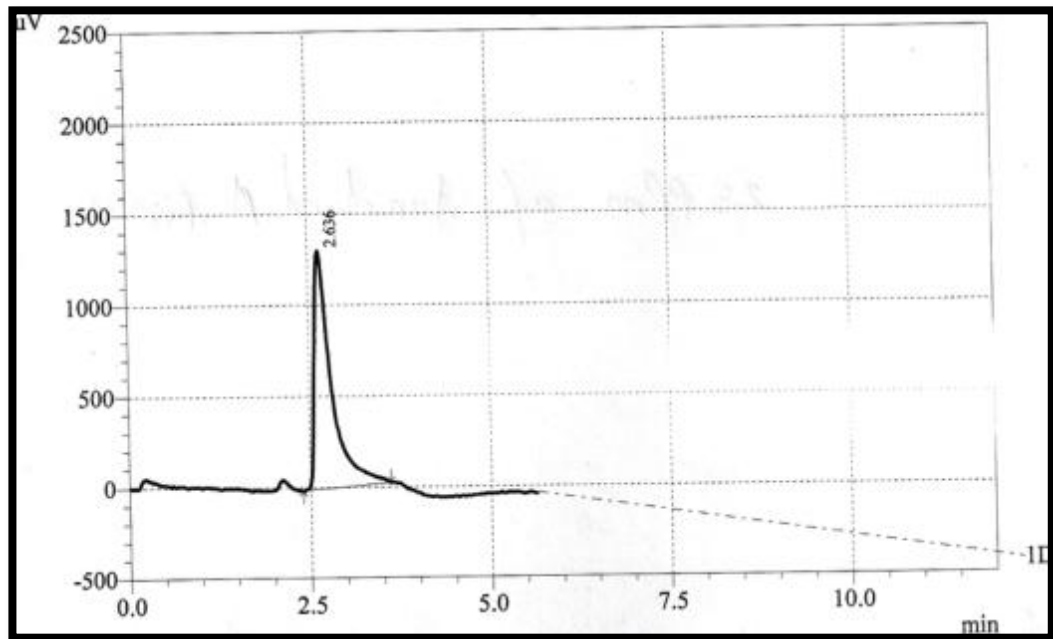
Some procedures and additives are employed in the manufacturing of pharmaceuticals to make final compressed tablets, such as active compounds, catalytic materials, tastes, and adsorbent materials. As a result, active compounds for use as corrosion inhibitors are required. As demonstrated in the experimental section, many processes were done to acquire the active components from various medications, and some inspections were undertaken to characterize these materials.

4.1.1 High performance liquid chromatography (HPLC)

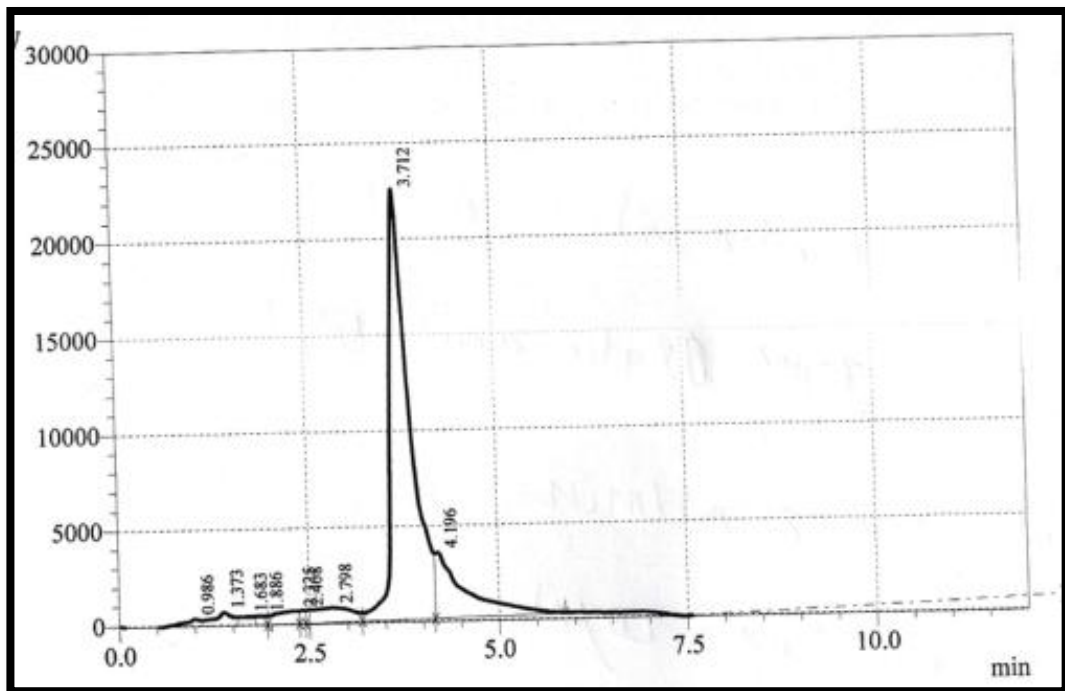
The active ingredients' composition was checked using the HPLC method. The HPLC data for the active components in Aspirin and Deoxycyclin are shown in figure (4.1). This graph shows the presence of active materials in the large curve versus the standard material in the small curve.



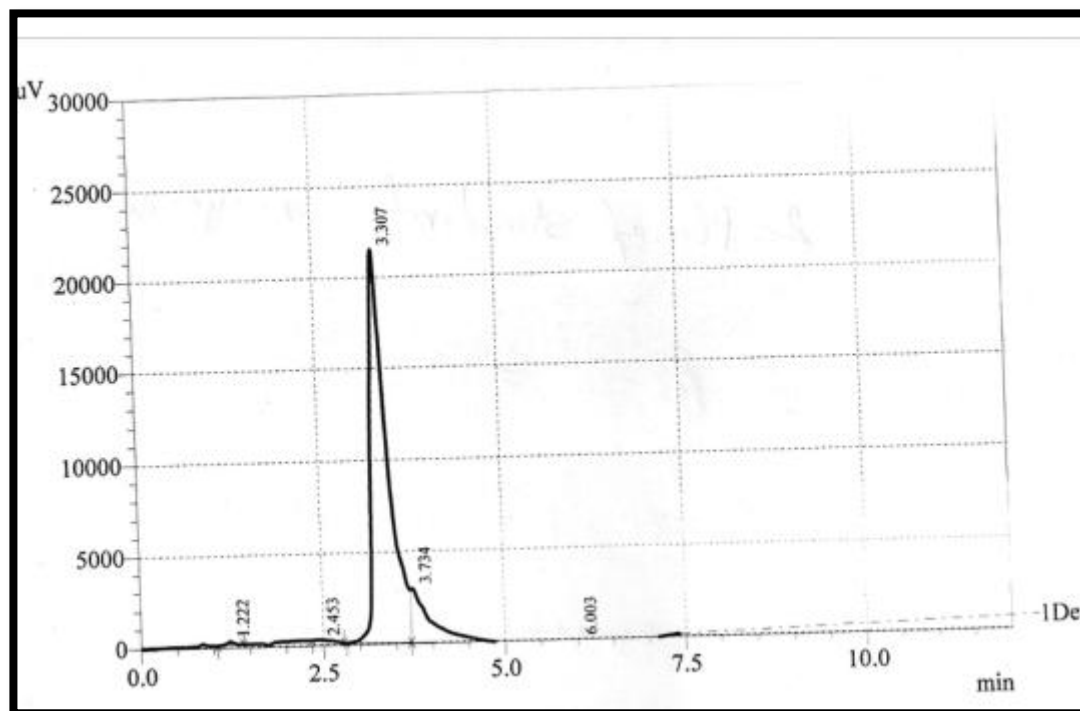
Aspirin extract



Aspirin stander



Deoxycyclin extract



Deoxycyclin stander

Fig. (4.1): HPLC analysis for the extracted active material from drugs compared with the standard material.

4.1.2 Fourier Transform Infrared Spectroscopy(FTIR)

FTIR spectra are the best tool to characterize the organic materials. figure (4.2) illustrates the FTIR spectra for the active materials. Figure (4.2,a) indicates the spectrum of the FTIR of Aspirin; Peak at 1754.7cm^{-1} is attributed to $\text{C}=\text{O}$ vibration stretch; the peak at 3492.4 cm^{-1} represent the carboxylic acid $-\text{OH}$ str., a peak at 1687.3 cm^{-1} carbonyl appears characteristic of carboxylic acids, Peaks at 1306.5 cm^{-1} represent $\text{C}-\text{O}$ str. Peak at 755.24 cm^{-1} represent ortho $\text{C}-\text{H}$ substituted aromatic ring.

Figure (4.2b) indicates the FTIR spectrum of Deoxycyclin; The peak at 3389.2cm^{-1} was attributed to (OH) stretching and 2929.2cm^{-1} was a certain to (C-H) stretching. (C=C) stretching peak was appeared at 1615.9cm^{-1} , vibration peak at 890.08cm^{-1} was a certain to (C-N) stretching. The aromatic in plane and out plan deformation peaks were appeared at $1247\text{-}1040.8\text{cm}^{-1}$, aromatic (C-H) bending was appeared at 1457.2cm^{-1} .

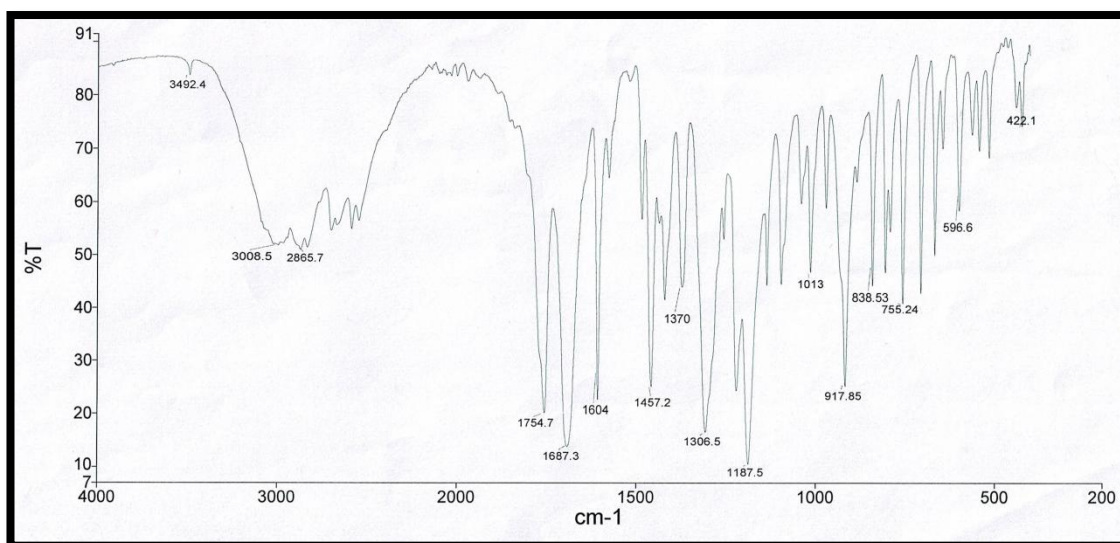


Fig.(4-2,a): FTIR spectra of Aspirin extract.

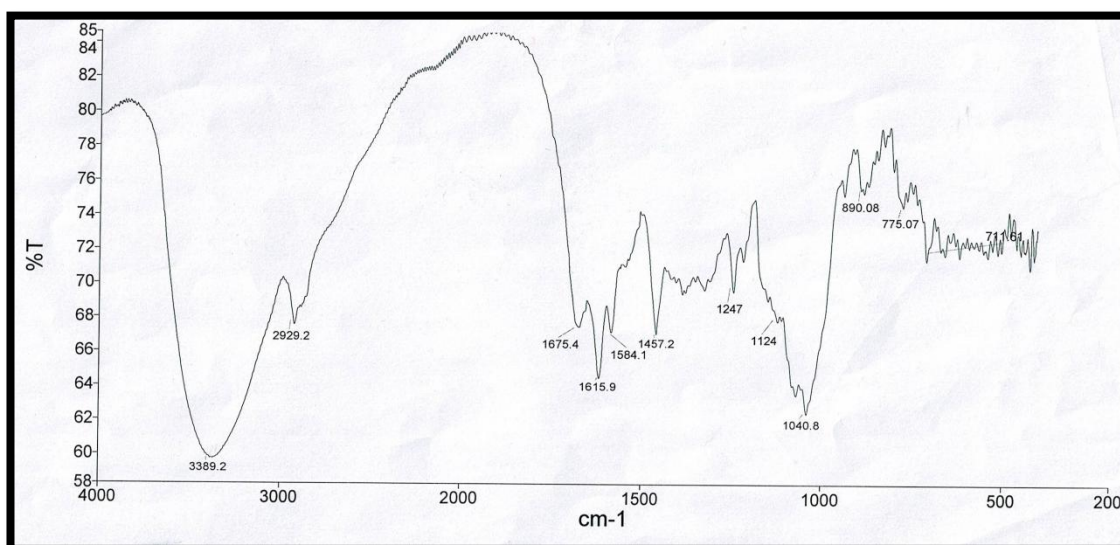


Fig.(4-2,b): FTIR spectra of Deoxycyclin extract.

4.2 Weight - Loss Measurement

The corrosion rate is calculated from change in weight of samples. (CR_{corr}) was calculated by using the following relationship.[89]

$$CR = \frac{\Delta W t}{A * t} \dots \dots \dots (4.1)$$

Where; (CR) was corrosion rate, Δw was weight loss in grams, (A) it is area of the specimen in m^2 , (t) it is time immersion in days, The corrosion rates are given in units $g/m^2 \cdot day$ symbolized by it (gmd).

From the corrosion rate, the damping efficiency ratio is calculated using the following equation.[90]

$$\%IE = \frac{CR_{inhibit} - CR_{inhibitor}}{CR_{inhibit}} \times 100 \dots \dots \dots (4.2)$$

Where; %IE the inhibition efficiency, $CR_{inhibit}$ = corrosion rate without inhibitor, $CR_{inhibitor}$ = corrosion rate with inhibitor.

The rate and efficiency of inhibition were assessed under various operating circumstances (temperature and concentration), and the findings were recorded in the tables (4.1),(4.2),(4.3) and (4.3). It is obvious that the corrosion rate increases with rising temperature and reduces with increasing inhibitor concentration. In terms of inhibition efficiency, it improves as the inhibitor's concentration rises and as the temperature rises.

Table(4.1) Show the effect of temperature on the corrosion rate, inhibition efficiency and surface coverage of aluminum pure in (0.5M H₂SO₄) in absence and presence of Aspirin extract.

Time(3h)					
Run	C _{inh} (ppm)	Temperature (°C)	CR (gmd)	θ(surface coverage)	IE%
1	Blank	20	312.042	0	0
2		30	549.086	0	0
3		40	1193.310	0	0
4	50	20	101.711	0.6740	67.40
5		30	159.175	0.7101	71.01
6		40	193.512	0.8378	83.78
7	100	20	84.574	0.7289	72.89
8		30	125.392	0.7716	77.16
9		40	176.585	0.8520	85.20
10	150	20	76.273	0.7556	75.56
11		30	99.330	0.8191	81.91
12		40	147.816	0.8761	87.61
13	200	20	60.477	0.8062	80.62
14		30	83.363	0.8482	84.82
15		40	113.804	0.9046	90.46
16	250	20	42.194	0.8648	86.48
17		30	66.179	0.8806	88.06
18		40	71.605	0.9399	93.99
19	300	20	22.461	0.9180	91.80
20		30	29.667	0.9459	94.59
21		40	35.962	0.9698	96.98

Table(4.2) Show the effect of temperature on the corrosion rate, inhibition efficiency and surface coverage of aluminum alloy(AA2024-T3) in (0.5M H₂SO₄) in absence and presence of Aspirin extract.

Time (3h)					
Run	C _{inh} (ppm)	Temperature (°C)	CR (gmd)	θ(surface coverage)	IE%
1	Blank	20	556.143	0	0
2		30	897.978	0	0
3		40	1684.030	0	0
4	50	20	230.167	0.5861	58.61
5		30	271.178	0.6980	69.80
6		40	360.243	0.7861	78.61
7	100	20	190.576	0.6573	65.73
8		30	220.942	0.7540	75.40
9		40	257.812	0.8469	84.69
10	150	20	146.096	0.7373	73.73
11		30	160.930	0.8208	82.08
12		40	196.378	0.8834	88.34
13	200	20	103.947	0.8131	81.31
14		30	117.481	0.8692	86.92
15		40	133.756	0.9206	92.06
16	250	20	80.009	0.8561	85.61
17		30	90.545	0.89.92	89.92
18		40	103.814	0.9384	93.84
19	300	20	68.436	0.8769	87.69
20		30	71.386	0.9205	92.05
21		40	83.457	0.9504	95.04

Table(4.3) Show the effect of temperature on the corrosion rate, inhibition efficiency and surface coverage of aluminum pure in (0.5M H₂SO₄) in absence and presence of Deoxycyclin extract.

Time(3h)					
Run	C _{inh} (ppm)	Temperature (°C)	CR (gmd)	θ(surface coverage)	IE%
1	Blank	20	312.042	0	0
2		30	549.068	0	0
3		40	1193.310	0	0
4	50	20	120.674	0.6133	61.33
5		30	187.305	0.6589	65.89
6		40	261.745	0.7806	78.06
7	100	20	109.791	0.6482	64.82
8		30	167.679	0.6946	69.46
9		40	246.531	0.7934	79.34
10	150	20	92.791	0.7026	70.26
11		30	145.429	0.7351	73.51
12		40	220.605	0.8151	81.51
13	200	20	79.309	0.7458	74.58
14		30	119.545	0.7823	78.23
15		40	179.811	0.8493	84.93
16	250	20	69.249	0.7781	77.81
17		30	94.970	0.8270	82.70
18		40	133.819	0.8879	88.79
19	300	20	60.730	0.8054	80.54
20		30	77.085	0.8596	85.98
21		40	80.589	0.9325	93.25

Table(4.4) Show the effect of temperature on the corrosion rate, inhibition efficiency and surface coverage of aluminum alloy(AA2024-T3) in (0.5M H₂SO₄) in absence and presence of Deoxycyclin extract.

Time(3h)					
Run	C _{inh} (ppm)	Temperature (°C)	CR (gmd)	θ(surface coverage)	IE%
1	Blank	20	556.143	0	0
2		30	897.978	0	0
3		40	1684.030	0	0
4	50	20	273.149	0.5086	50.86
5		30	371.935	0.5858	58.58
6		40	564.658	0.6647	66.47
7	100	20	242.150	0.5646	56.46
8		30	333.451	0.6287	62.87
9		40	503.537	0.7009	70.09
10	150	20	193.489	0.6521	65.21
11		30	271.571	0.6976	69.76
12		40	380.378	0.7741	77.41
13	200	20	164.711	0.7038	70.38
14		30	224.119	0.7504	75.04
15		40	339.309	0.8045	80.45
16	250	20	144.621	0.7399	73.99
17		30	202.197	0.7748	77.48
18		40	247.732	0.8529	85.29
19	300	20	122.678	0.7794	77.94
20		30	172.652	0.8077	80.77
21		40	203.033	0.8795	87.96

4.3 Effect of Different Conditions on Corrosion Rate

4.3.1 Corrosion Rates in the Absence of Inhibitor

The corrosion rate was calculated using the weight loss measurement rates in acidic solutions not inhibited at different temperatures after 3h from the time the aluminum was soaked and alloyed (AA2024-T3) in (0.5M H₂SO₄) at (PH of 1.2) . When indicated in figures (4.3) and (4.4), the rate of corrosion increased in the case of aluminum pure from (312.042 to 1193.310 gmd) and in the case of aluminum alloy (AA2024-T3) from (556.143 to 1684.030 gmd) as temperature increased from (293.15, 303.15, and 313.15 K) .

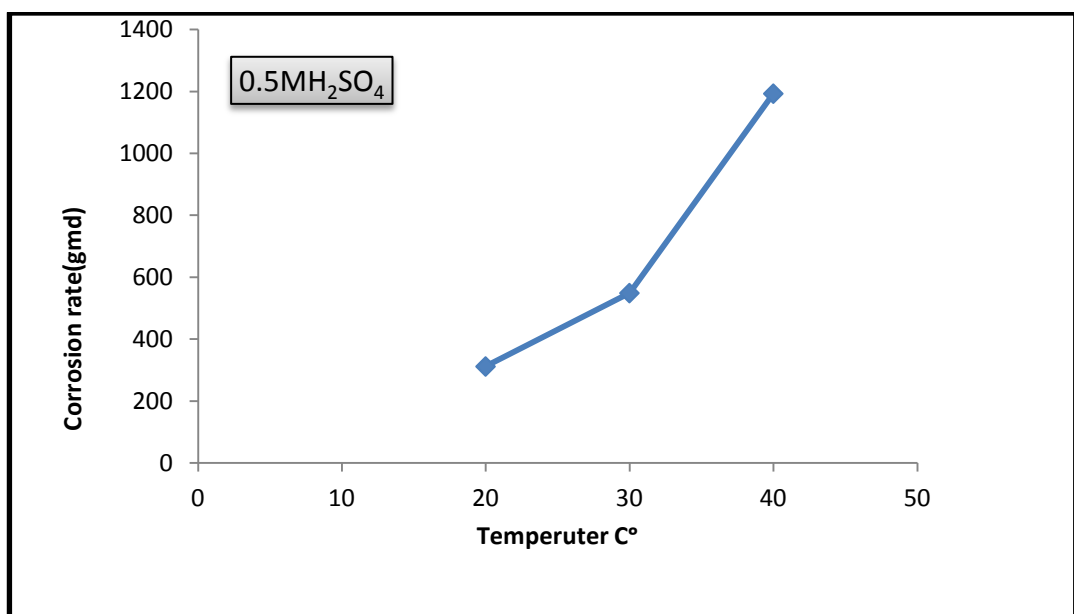
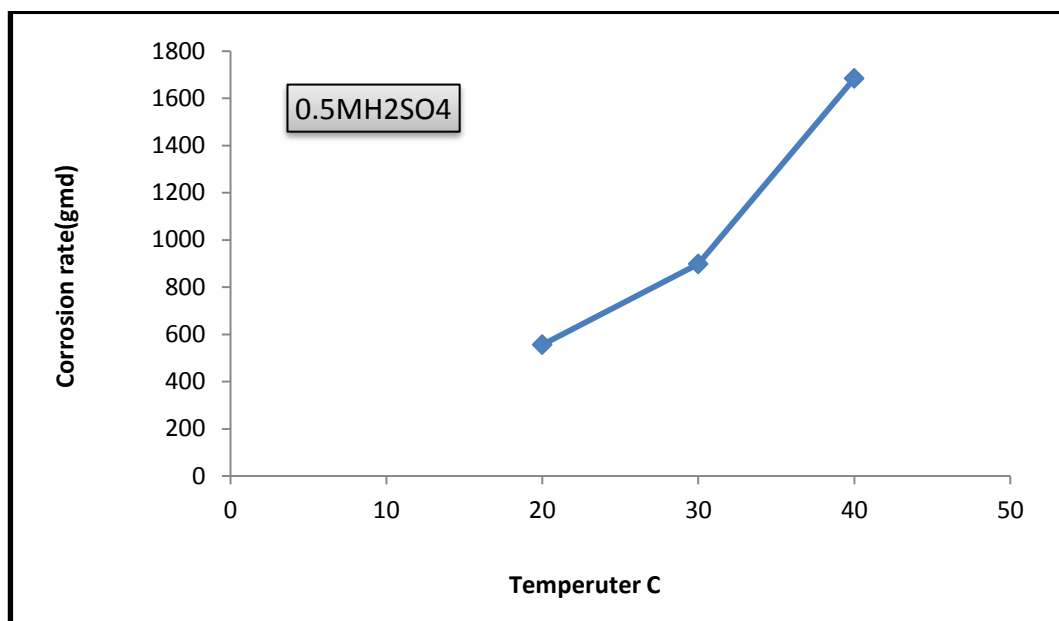


Fig.(4.3):Effect of temperature on the corrosion rate of aluminum after immersion in(0.5M H₂SO₄) for (3h).



Figure(4.4):Effect of temperature on the corrosion rate of aluminum alloy(AA2024-T3) after immersion in(0.5M H₂SO₄)for (3h).

4.3.2 Corrosion Rates Acid in the Presence of Inhibitor

As shown in tables (4.1),(4.2),(4.3) and (4.4), adding Aspirin and Deoxycyclin drug extracts significantly lowers the corrosion rate, and generally for aluminum and aluminum alloy (AA2024-T3) corrosion rate was found to increase with temperatures. The higher (Aspirin and Deoxycyclin) concentration added, the lower was the rate of corrosion in (0.5M H₂SO₄). Therefore,(Aspirin and Deoxycyclin) decreased the aluminum and aluminum alloy (AA2024-T3) corrosion rate in (0.5M H₂SO₄), which indicates that it can be used as a corrosion inhibitor for that metal as shown in figures (4.5),(4.6),(4.7) and (4.8).[91]

The effect of temperature on corrosion rate at different inhibitor concentration is expressed in figures (4.9),(4.10),(4.11) and (4.12) these figures show the rate of corrosion increases as the temperature rises at all studied inhibitor concentrations.

At inhibitor concentration of (50ppm) , the corrosion rate increases significantly when the temperature increased from (293.15, 303.15 and 313.15 K) . The effect of (100ppm) inhibitor concentration is higher than (50ppm). While at the inhibitor concentration of (150,200,250 and 300ppm).The rate of corrosion increases slightly as the temperature rises. This could be owing to the inhibitor partially desorbing from the aluminum and aluminum alloy (AA2024-T3) surface when the temperature rises and the inhibitor concentration rises.[92]

As the concentration of the inhibitor increase, the values of the inhibitor efficiency rise . Figures (4.13),(4.14),(4.15) and (4.16), show the variation of inhibitor efficiency with inhibitor concentration. It varies, it was (%67.40 - %96.98) for (50-300ppm) of Aspirin in (0.5M H₂SO₄) for aluminum pure respectively, it was (%58.61 - %95.04) for (50-300ppm) of aspirin in (0.5M H₂SO₄) for aluminum alloy (AA2024-T3) respectively, it varies, , it was (%61.33 - %93.25) for (50-300ppm) of Deoxycyclin in (0.5M H₂SO₄) for aluminum pure respectively, it was (%50 - %87.96) for (50-300ppm) of Deoxycyclin in (0.5M H₂SO₄) for aluminum alloy (AA2024-T3) respectively.[93] Figures (4.17),(4.18),(4.19) and (4.20), show the effect of temperature on inhibitor efficiency.

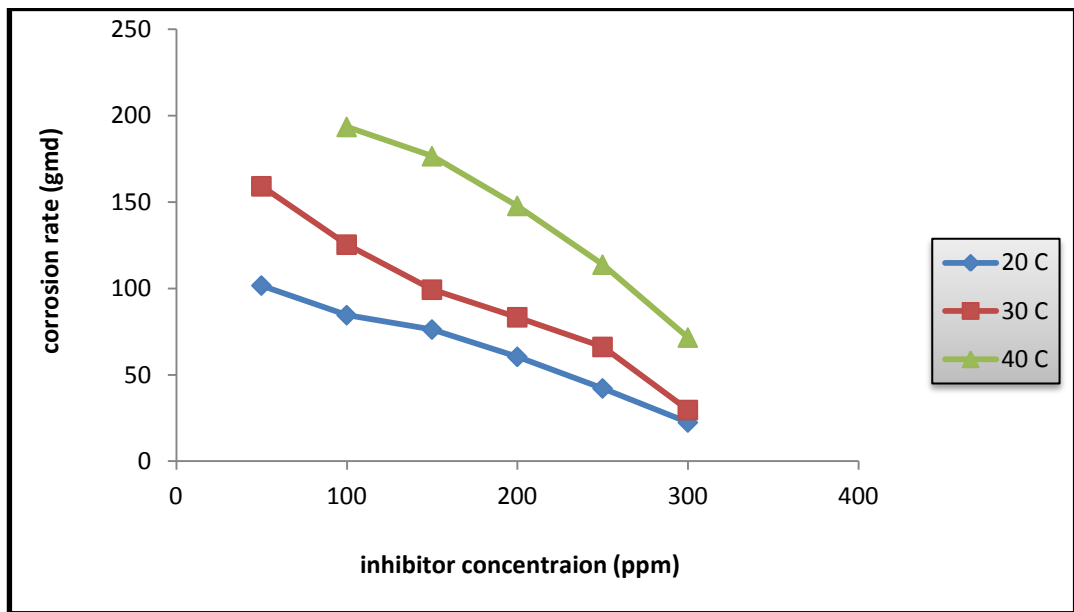


Fig.(4.5): Inhibitor concentration effects (Aspirin extract) on the corrosion rate of aluminum.

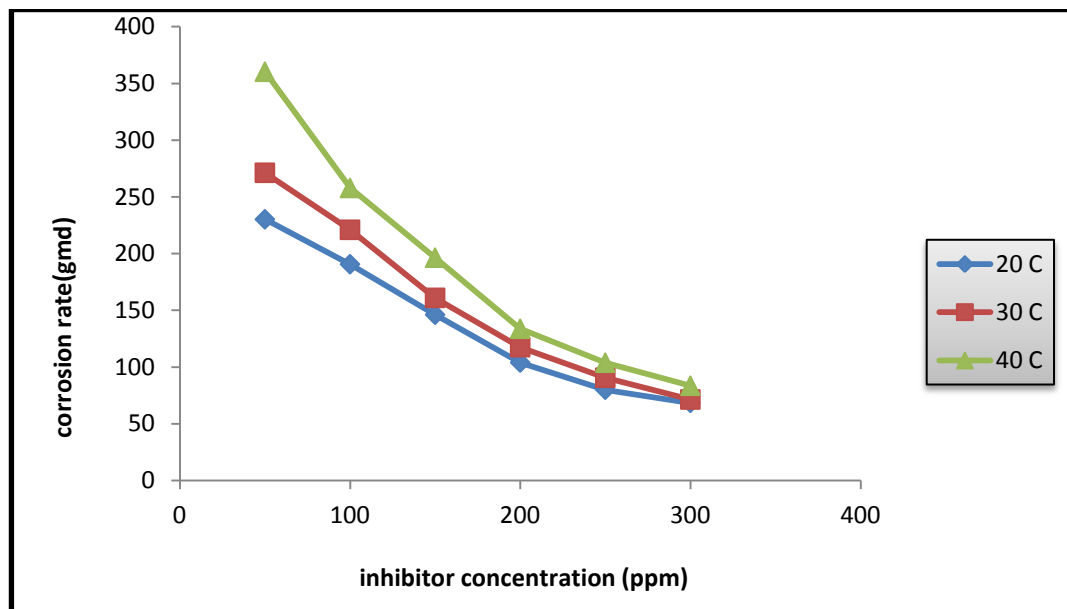


Fig.(4.6): Inhibitor concentration effects (Aspirin extract) on the corrosion rate of aluminum alloy (AA2024-T3).

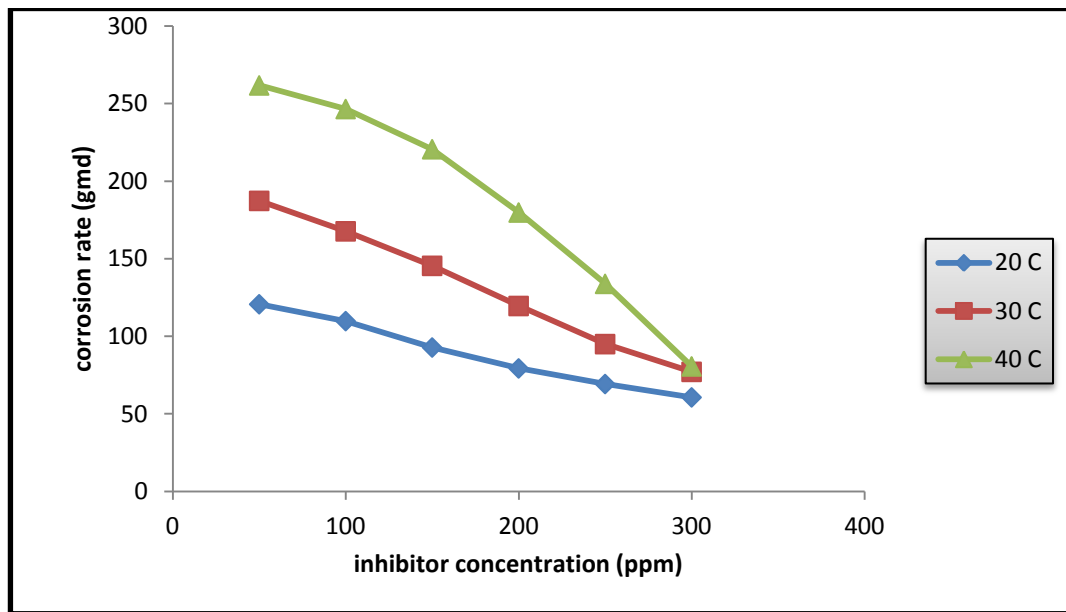


Fig.(4.7): Inhibitor concentration effects (Deoxycyclin extract) on the corrosion rate of aluminum.

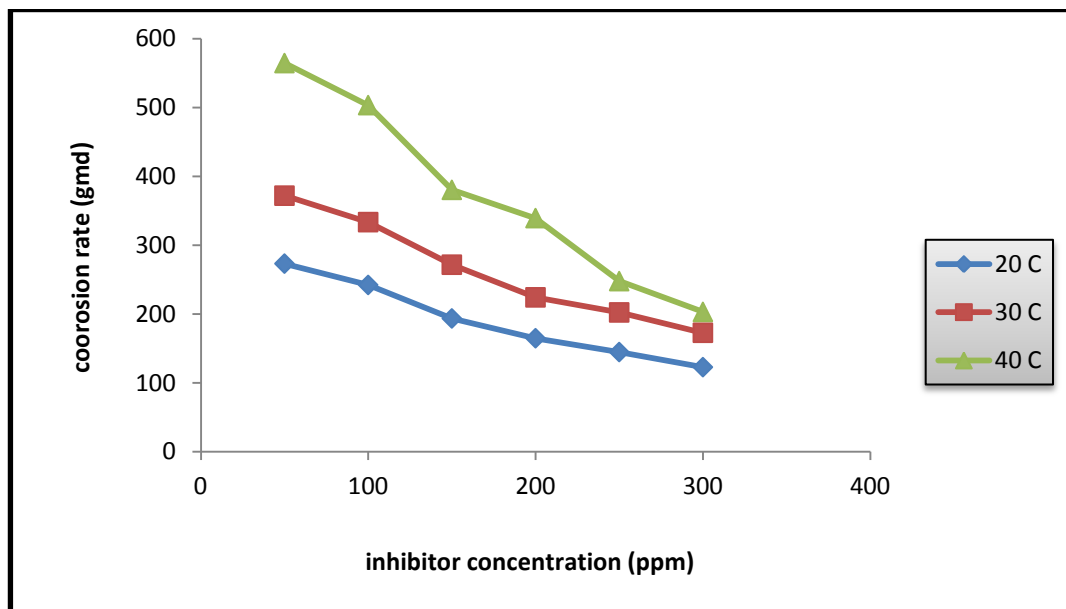


Fig.(4.8): Inhibitor concentration effects (Deoxycyclin extract) on the corrosion rate of aluminum alloy (AA2024-T3).

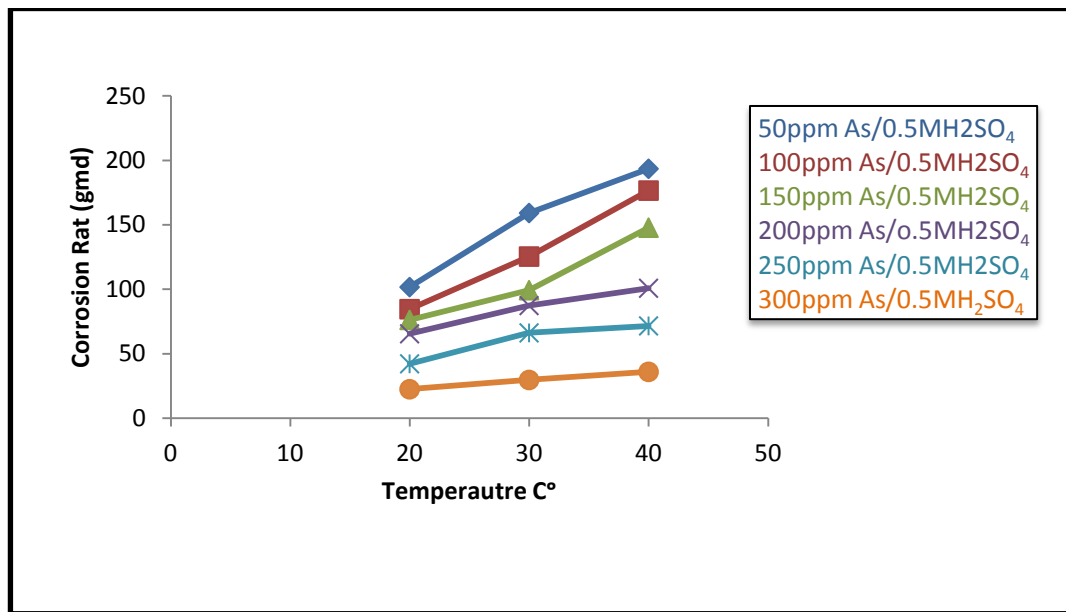


Fig.(4.9): Effect of temperature on the rate corrosion of aluminum in (0.5M H₂SO₄) at various inhibitor concentration(Aspirin extract).

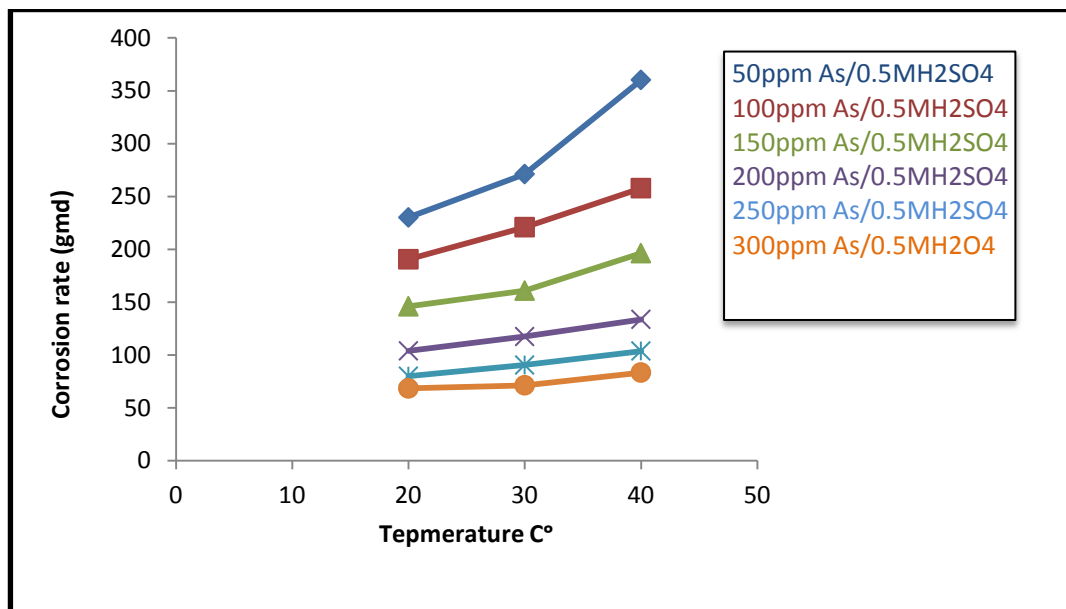


Fig.(4.10): Effect of temperature on the rate corrosion of aluminum alloy(AA2024-T3) in (0.5M H₂SO₄) at various inhibitor concentration(Aspirin extract).

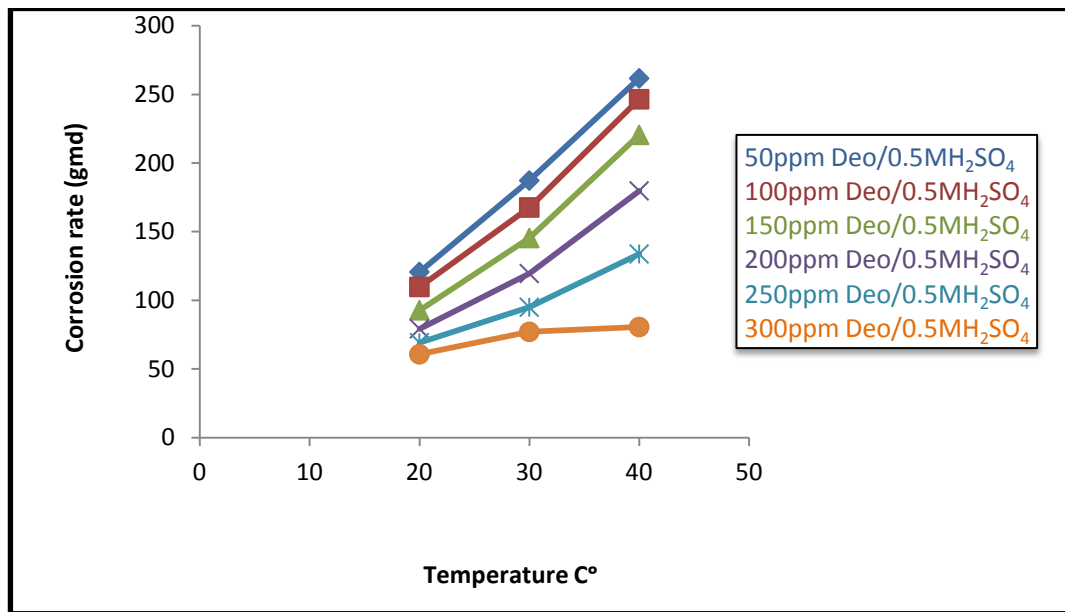


Fig.(4.11): Effect of temperature on the rate corrosion of aluminum in (0.5M H₂SO₄) at various inhibitor concentration(Deoxycyclin extract).

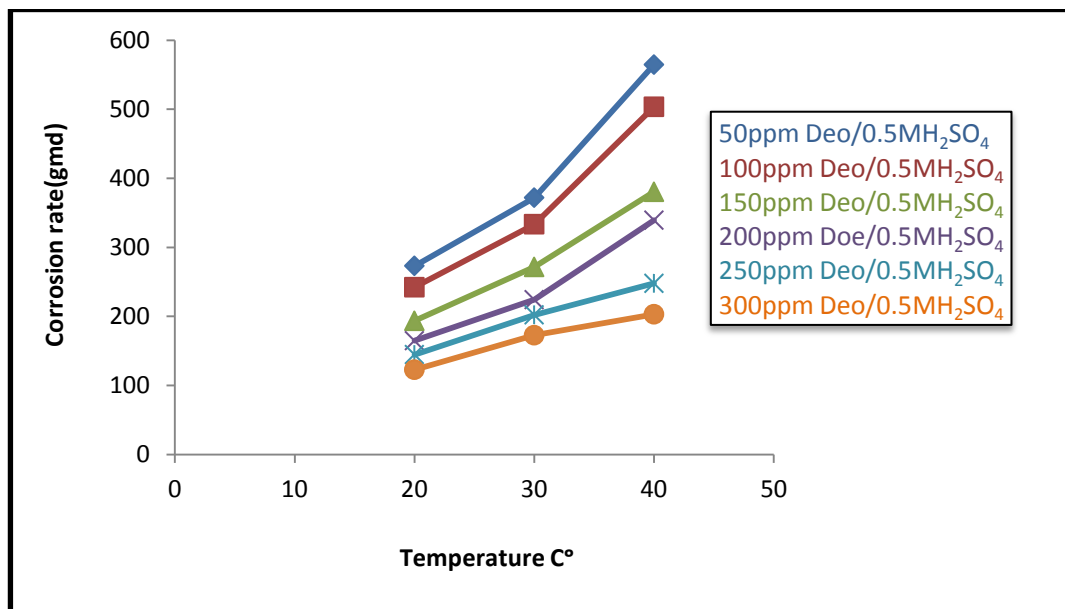


Fig.(4.12): Effect of temperature on the rate corrosion of aluminum alloy(AA2024-T3) in (0.5M H₂SO₄) at various inhibitor concentration(Deoxycyclin extract).

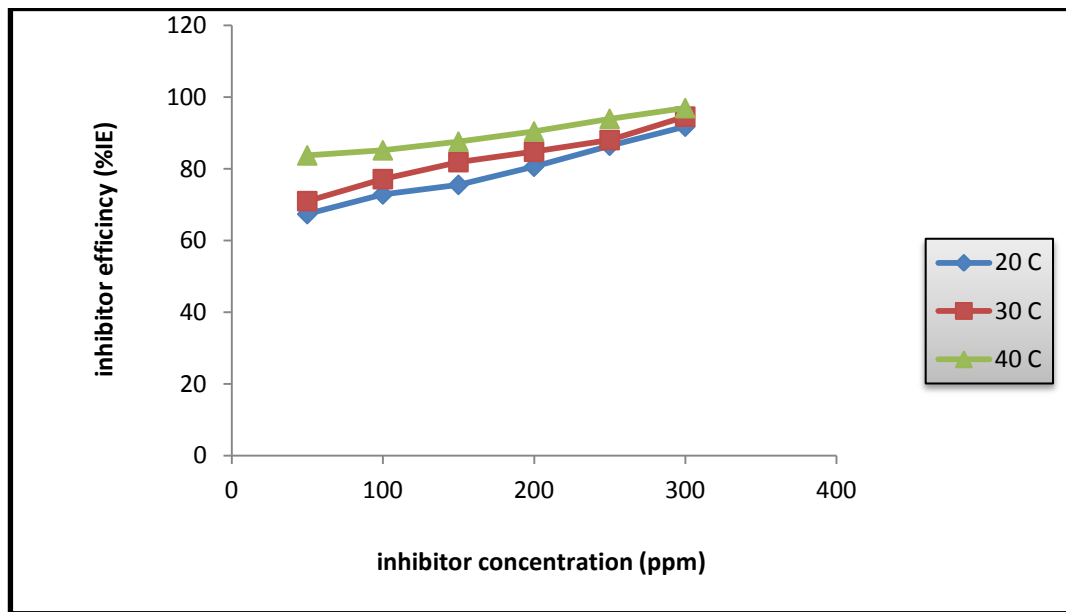


Fig.(4.13): Effect of concentration of (Aspirin extract) on inhibitive efficiency of aluminum corrosion in (0.5M H₂SO₄).

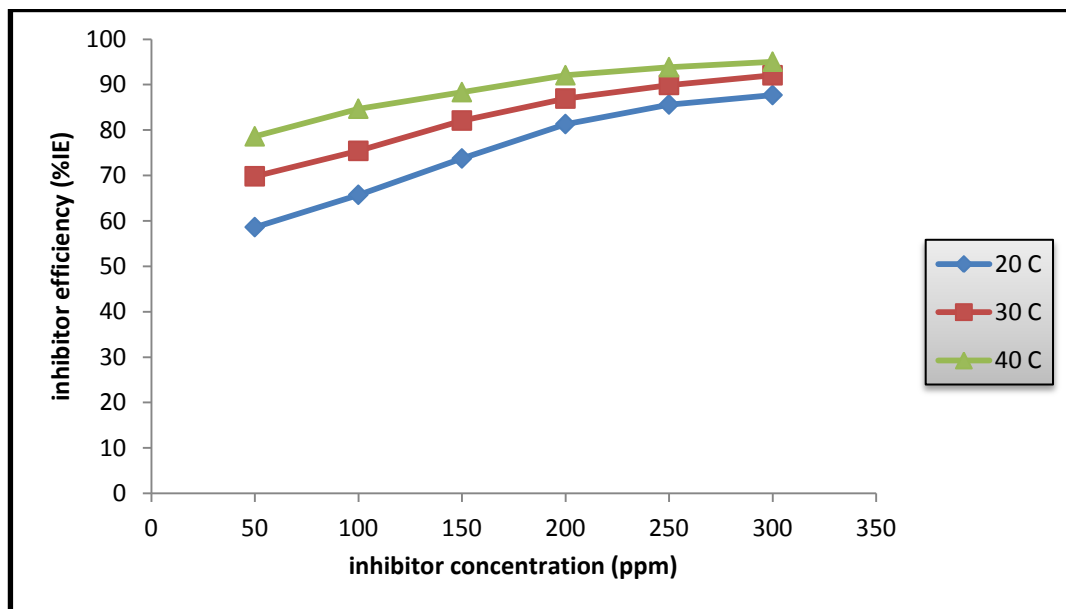


Fig.(4.14): Effect of concentration of (Aspirin extract) on inhibitive efficiency of aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

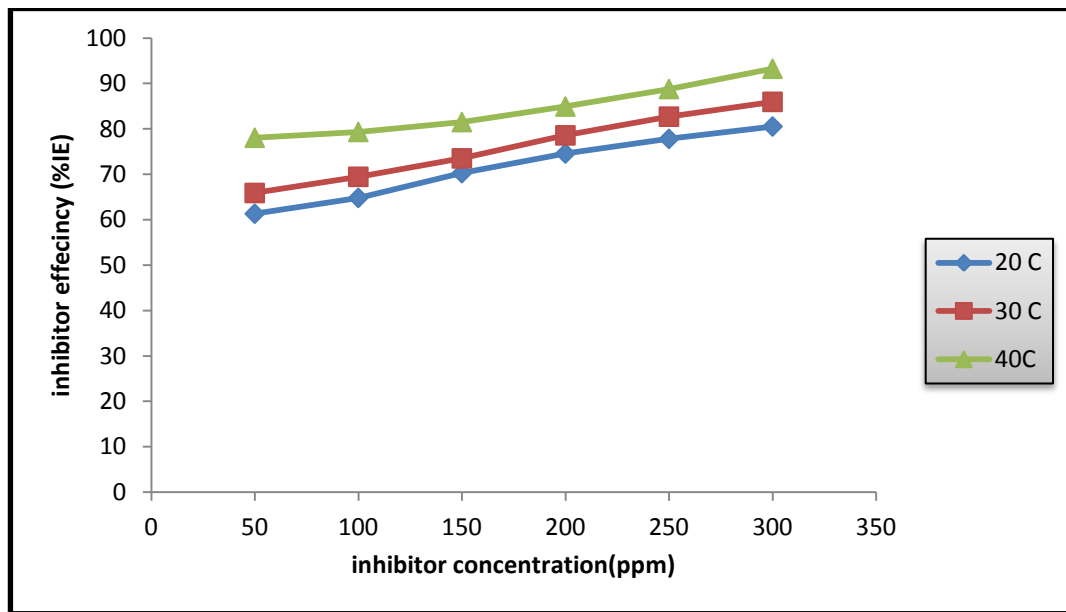


Fig.(4.15): Effect of concentration of (Deoxycyclin extract) on inhibitive efficiency of aluminum corrosion in (0.5M H₂SO₄).

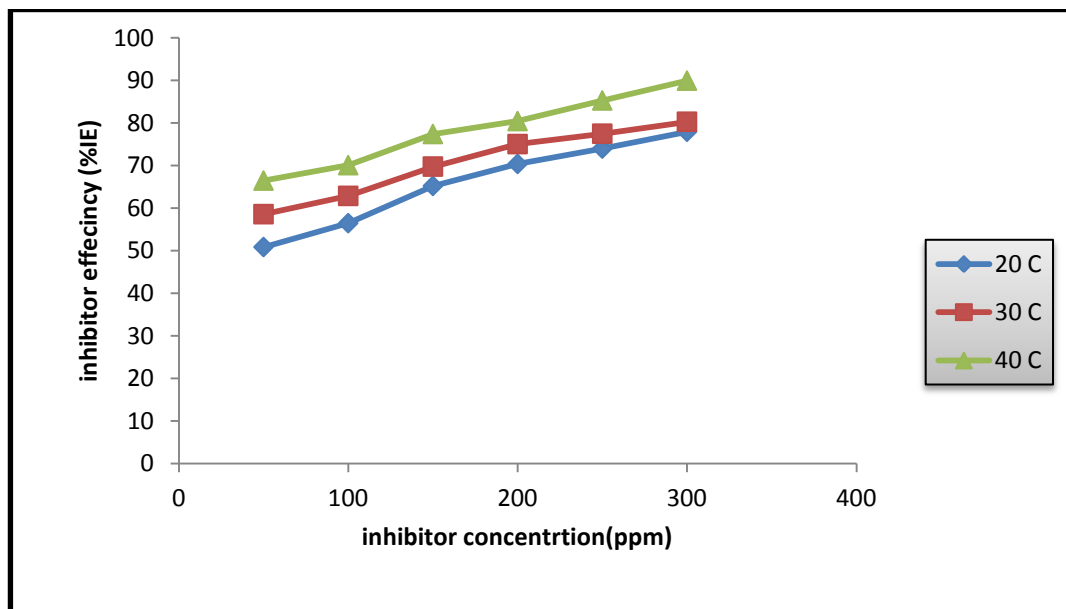


Fig.(4.16): Effect of concentration of (Deoxycyclin extract) on inhibitive efficiency of aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

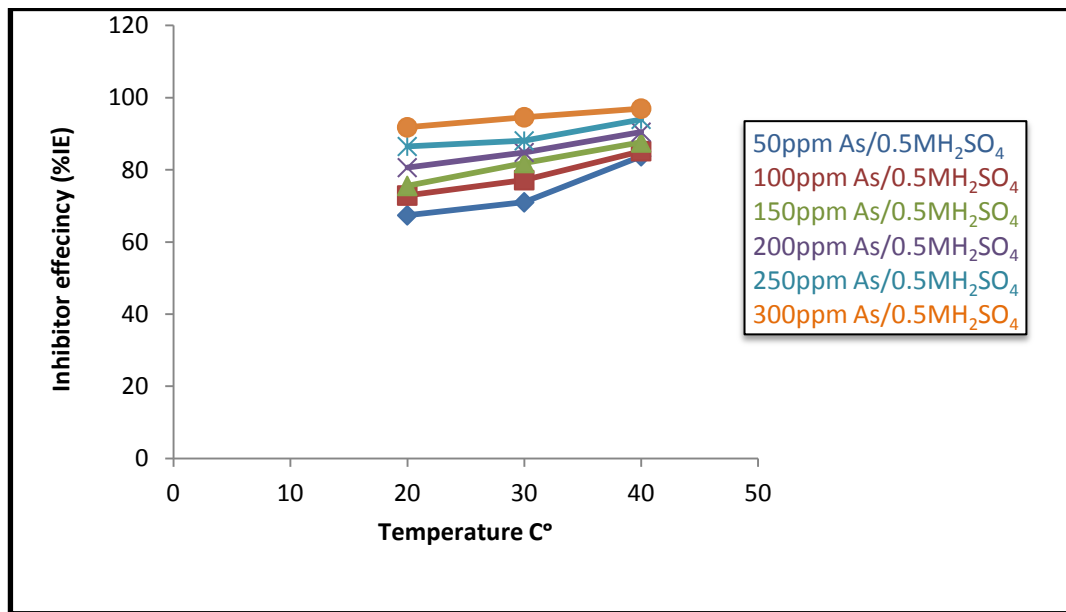


Fig.(4.17): Effect of temperature on inhibitive efficiency of (Aspirin extract) for aluminum corrosion in(0.5M H₂SO₄).

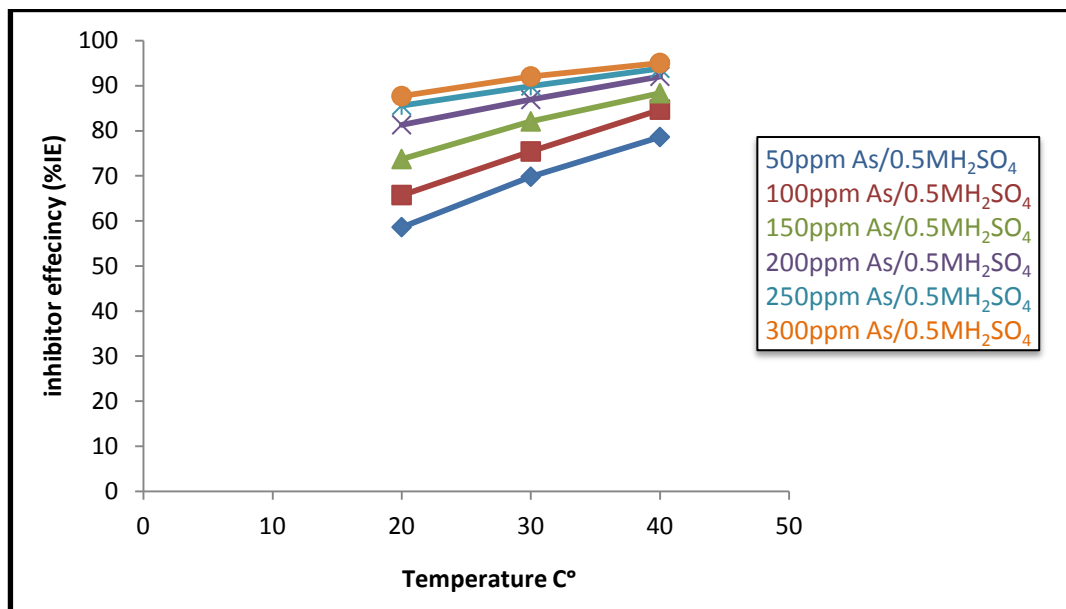


Fig.(4.18): Effect of temperature on inhibitive efficiency of (Aspirin extract) for aluminum alloy(AA2024-T3) corrosion in(0.5M H₂SO₄).

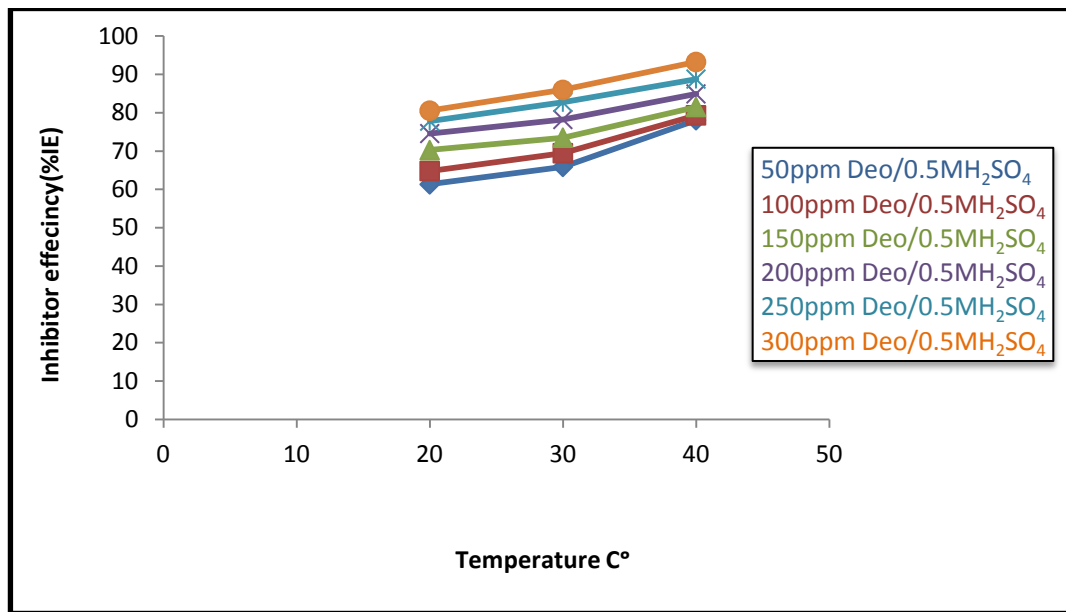


Fig.(4.19): Effect of temperature on inhibitive efficiency of (Deoxycyclin extract) for aluminum corrosion in(0.5M H₂SO₄).

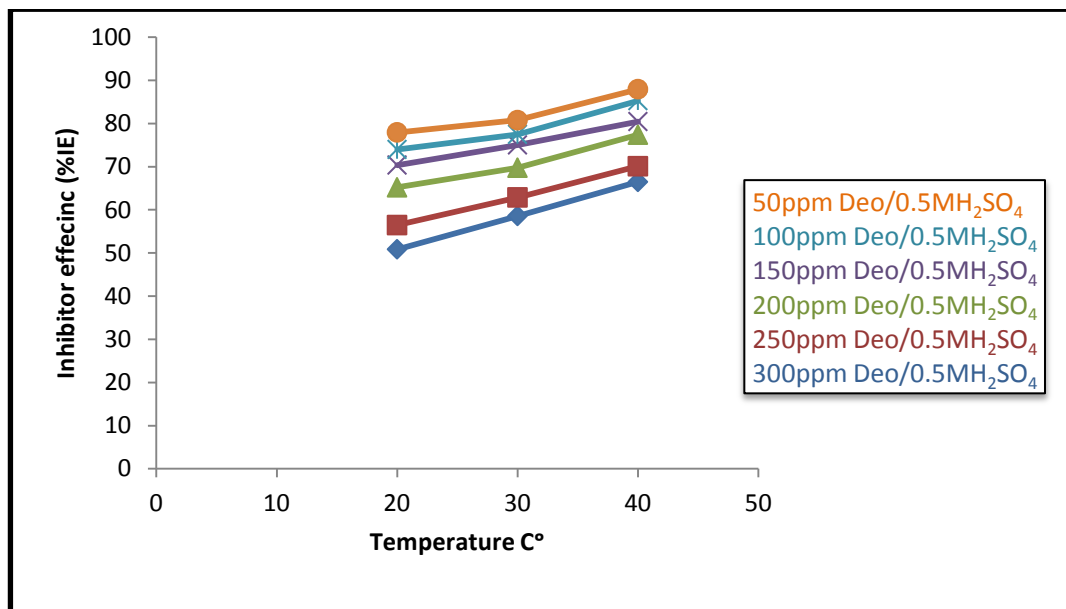


Fig.(4.20): Effect of temperature on inhibitive efficiency of (Deoxycyclin extract) for aluminum alloy(AA2024-T3) corrosion in(0.5M H₂SO₄).

4.4 Inhibitor Performance and Adsorption Studies

It has been demonstrated that raising concentrations of inhibitors ranging from 50 to 300 ppm reduces the corrosion rate to extremely low levels. Figures (4.5) to (4.8) clearly depict this condition. When the inhibitor concentration is at its maximum (300 ppm), the corrosion rate approaches its minimal value, as shown in these graphs. This could be because the inhibitor concentration (300ppm) is sufficient to cover the metal surface at the temperature range of (293.15, 303.15 and 313.15 K). For (250ppm) inhibitor concentration, the inhibitor concentration will have a less effect than in (300ppm), with the temperature has risen from (293.15 , 303.15 K) Corrosion rate values do not vary significantly as a result of this, but when the temperature increased to (313.15K), the corrosion rate values changed markedly. At inhibitor concentration of (200 and 50 ppm) shown in figures (4.5) to (4.8) and tables (4.1) to (4.4) the reduction in corrosion rate is small and it decreases at higher temperature. When analyzing adsorption characteristics, the surface coverage (θ) data is extremely important. Equation(2.8) is used to calculate the surface coverage of an inhibitor at a particular concentration. The adsorption mechanism can be studied using the corrosion rate data.

4.4.1- Langmuir Adsorption Isotherm

It is calculated by using equation (2.10). Figures (4.21) to (4.24) show plots of $(\frac{C_i}{\theta})$ versus (C_i) for (Aspirin and Deoxycyclin) extract inhibitors in (0.5M H_2SO_4) at (293.15, 303.15 and 313.15 K) according to equation(2.10). The data fit straight lines, demonstrating that inhibitors are adsorbed according to the Langmuir isotherm, it could also explain the rise in inhibitory efficiency as a result of an increase in quantity of inhibitor molecules that adsorb on the surface of aluminum and aluminum alloys (AA2024-T3), preventing active sites from direct acid attack and so

protecting metals from corrosion.[94] From the intercept of the straight-line K_L values can be evaluated which can be then substituted in equation (2.10) to calculate ΔG_{ads}° . Table (4.5),(4.6),(4.7) and (4.8) show values of K_L and ΔG_{ads}° and correlation coefficient (R^2). The equilibrium constant of the inhibitor adsorption K_L values increase with increasing temperature from (293.15,303.15 and 313.15 K). The higher K_L values clearly proved the strong adsorption of (Aspirin and Deoxycyclin) extracts molecules on aluminum and aluminum alloy (AA2024-T3) surfaces.[95] ($\Delta^\circ G_{ads}$) values indicate that the inhibitors are spontaneously adsorbed on metal surface, and that ($\Delta^\circ G_{ads}$) change values is associated with the efficiency of inhibition and ($\Delta^\circ G_{ads}$) values increasing with temperature increase, It is common knowledge that the value of ($\Delta^\circ G_{ads}$) in the order of (-20KJ/mole) or less negative are associated with an electrostatic interaction between the charged inhibitor particle and charged metal surface (physical adsorption) process is connected with a less negative outcome. In (-40 KJ/mol) or more negative involves charge sharing or transferring from inhibitor molecules to the metal surface to produce a coordinate covalent bond (chemical adsorption) process.[96] The free energy of adsorption (ΔG_{ads}°) of the studied inhibitor lie between them (- 1.0831KJ/mol) and (-0.0610 KJ/mol) in Table (4.5), (-0.4755 KJ/mol) and (-1.4447 KJ/mol) in Table (4.6),(-1.0917 KJ/mol) and (- 2.4627 KJ/mol) in Table (4.7), (-0.0110 KJ/mol) and (- 1.4127 KJ/mol) in Table(4.8), Physical adsorption is shown by the fact that it is less than (- 20 KJ/mol). Adsorption of inhibitor particle on the surface of aluminum and aluminum alloy (AA2024-T3). So it involves physical adsorption, and this assumption is supported by data obtained depending on the temperature of the inhibition process, reported in Tables (4.1) to (4.4) which show that the calculated inhibitory efficiency of the extracts increases with increasing temperature.

As a result, we may assume that inhibitor adsorption on the surface of aluminum and aluminum alloys (AA2024-T3) in (0.5M H₂SO₄) is complicated in nature and largely physical, with estimated (ΔG_{ads}) values also appearing. To make a coordinate covalent bond, molecules share or transfer to the metal surface .[94]

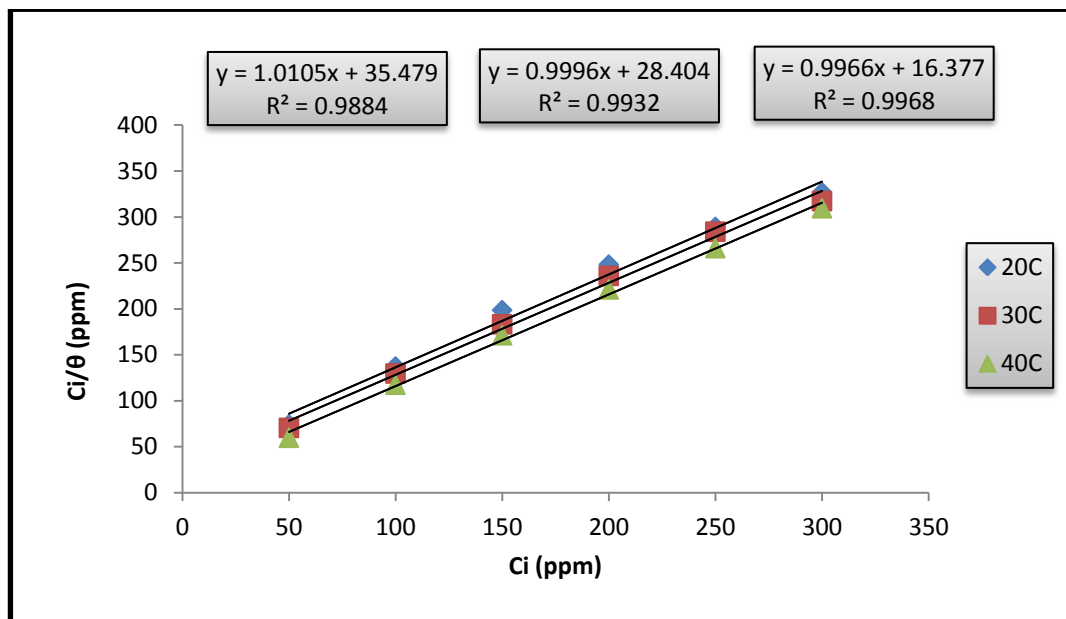


Fig.(4.21): Langmuir adsorption isotherm of (Aspirin extract) for aluminum corrosion in (0.5M H₂SO₄).

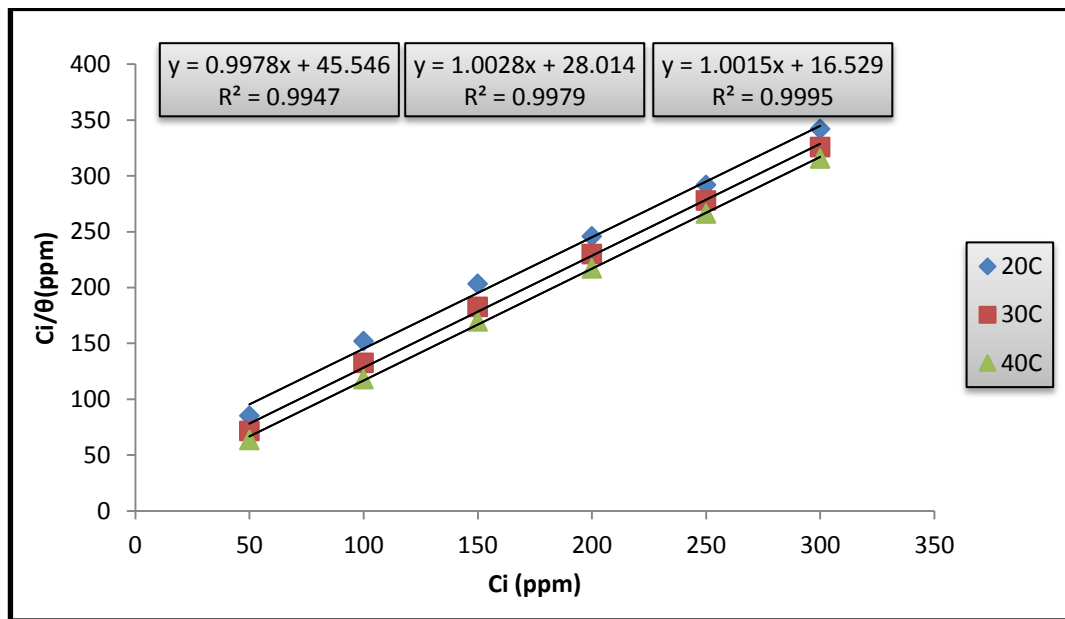


Fig.(4.22): Langmuir adsorption isotherm of (Aspirin extract) for aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

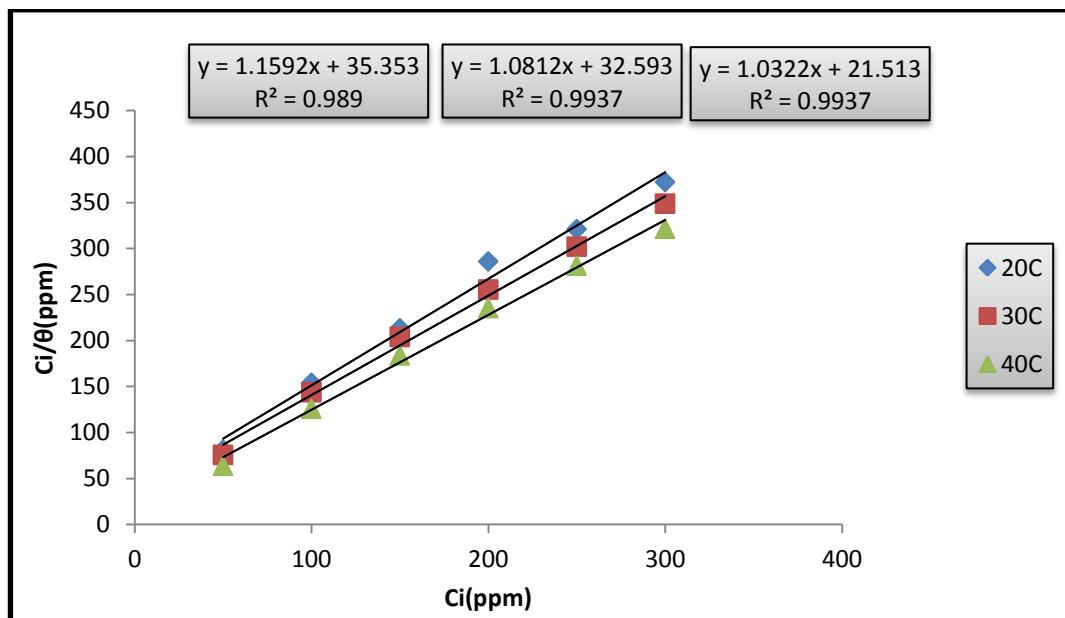


Fig.(4.23): Langmuir adsorption isotherm of (Deoxycyclin extract) for aluminum corrosion in (0.5M H₂SO₄).

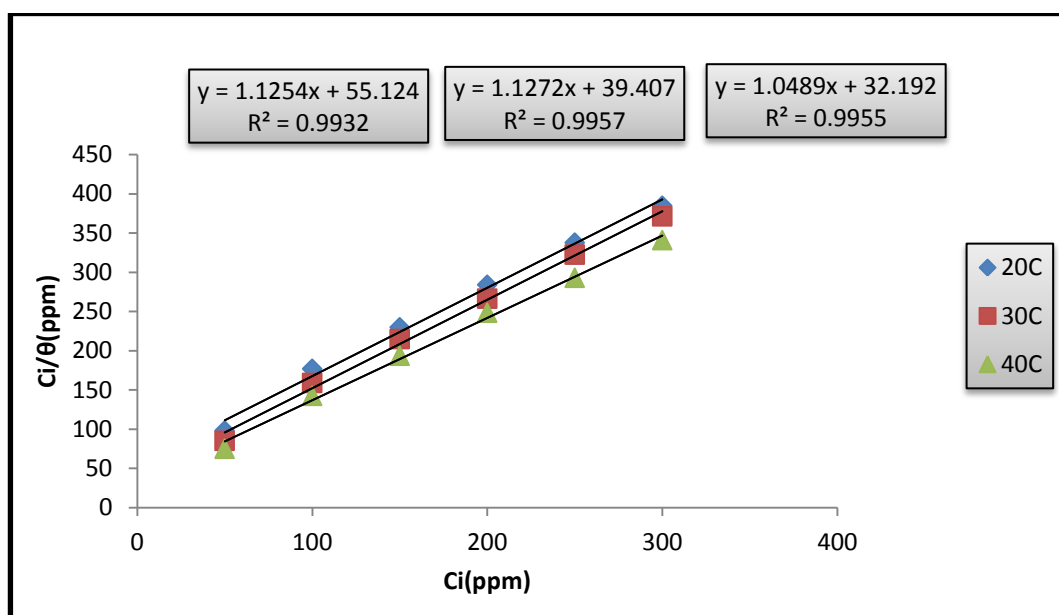


Fig.(4.24): Langmuir adsorption isotherm of (Deoxycyclin extract) for aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

Table(4.5): Show the (K_{ads}), (ΔG°_{ads}), and (R^2) for Langmuir type adsorption isotherm of(Aspirin extract) for aluminum corrosion in (at different temperatures).

Temperature(K)	K_L (L/mg)	ΔG° (KJ/mol)	R^2
293.15	0.0281	- 1.0831	0.9884
303.15	0.0352	- 1.2676	0.9932
313.15	0.0610	- 3.1750	0.9968

Table(4.6):Show the (K_{ads}), (G°_{ads}), and (R^2) for Langmuir type adsorption isotherm of (Aspirin extract) for aluminum alloy (AA2024-T3) corrosion at different temperatures.

Temperature (K)	K_L (L/mg)	ΔG° (KJ/mol)	R^2
293.15	0.0219	- 0.4755	0.9947
303.15	0.0356	- 1.7163	0.9979
313.16	0.0604	- 1.4447	0.9995

Table(4.7):Show the (K_{ads}), (ΔG°_{ads}), and (R^2) for Langmuir type adsorption isotherm of (Deoxycyclin extract) for aluminum corrosion at different temperatures.

Temperature(K)	K_L (L/mg)	ΔG° (KJ/mol)	R^2
293.15	0.0282	- 1.0917	0.9890
303.15	0.0306	- 1.3348	0.9937
313.15	0.0464	- 2.4627	0.9937

Table(4.8):Show the (K_{ads}), (ΔG°_{ads}), and (R^2) for Langmuir type adsorption isotherm of (Deoxycyclin extract) for aluminum alloy (AA2024-T3) corrosion at different temperatures.

Temperature(K)	K_L (L/mg)	ΔG° (KJ/mol)	R^2
293.15	0.0181	- 0.0110	0.9932
303.15	0.0253	- 0.8855	0.9957
313.15	0.0310	- 1.4127	0.9955

4.4.2-Freundlich Adsorption Isotherm

It is calculated by using equation (2.14) figures (4.25),(4.26),(4.27) and (4.28), show produced by plotting $(\ln\theta)$ against $(\ln C_i)$ with slope and intercept yielding the values of (n) and (KF) respectively as with data given in tables (4.9),(4.10),(4.11) and (4.12), Show equilibrium constant (KF) , slope (n) , and correlation coefficient (R^2) . Because the correlation coefficient values are low, Freundlich does not appear to apply well to this system; however, the Langmuir isotherm does apply and provides more fitness to the adsorption isotherm system because the correlation coefficient values are high.[97]

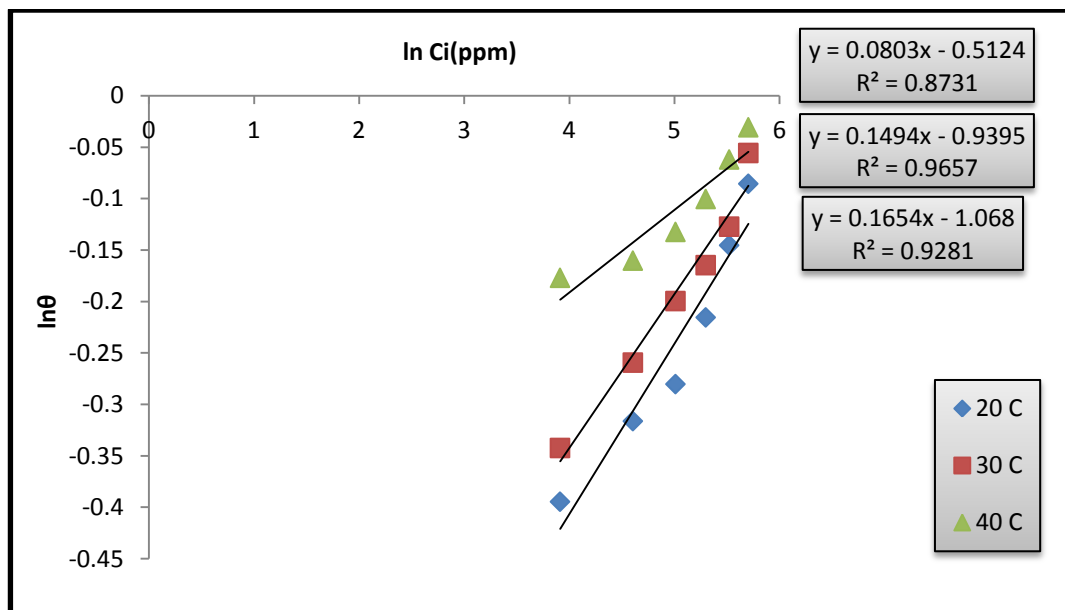


Fig.(4.25): Isotherm Freundlich adsorption of (Aspirin extract) for aluminum corrosion in (0.5M H₂SO₄).

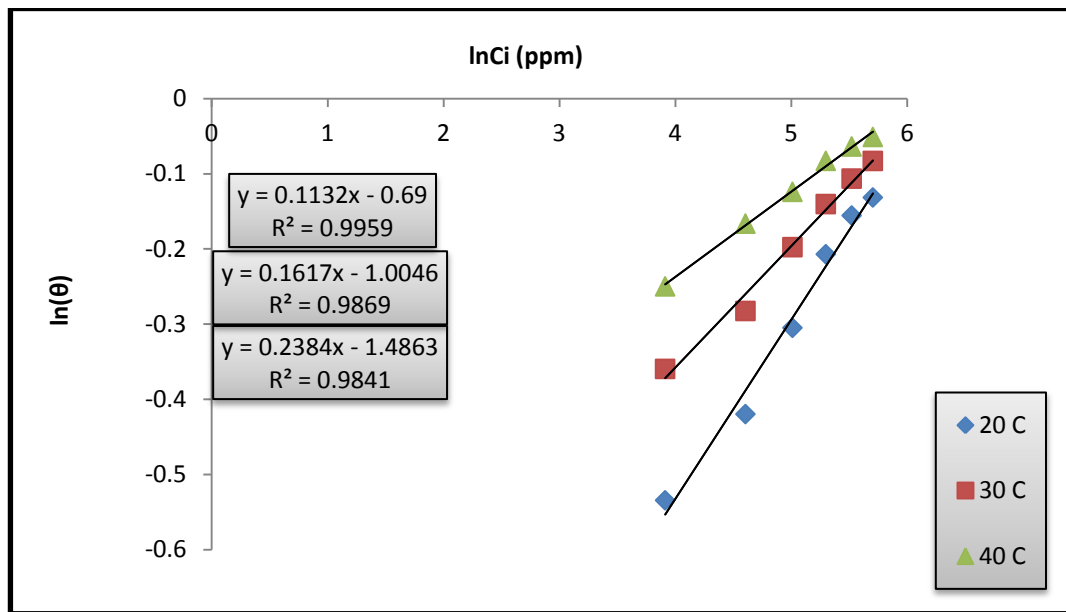


Fig.(4.26): Isotherm Freundlich adsorption of (Aspirin extract) for aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

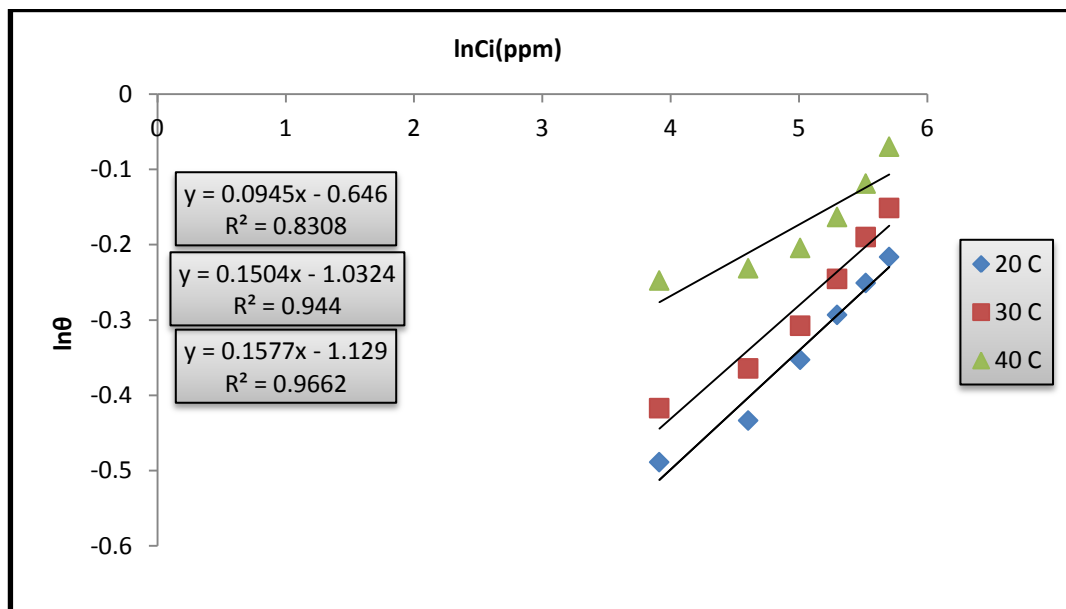


Fig.(4.27): Isotherm Freundlich adsorption of (Deoxycyclin extract) for aluminum corrosion in (0.5M H₂SO₄).

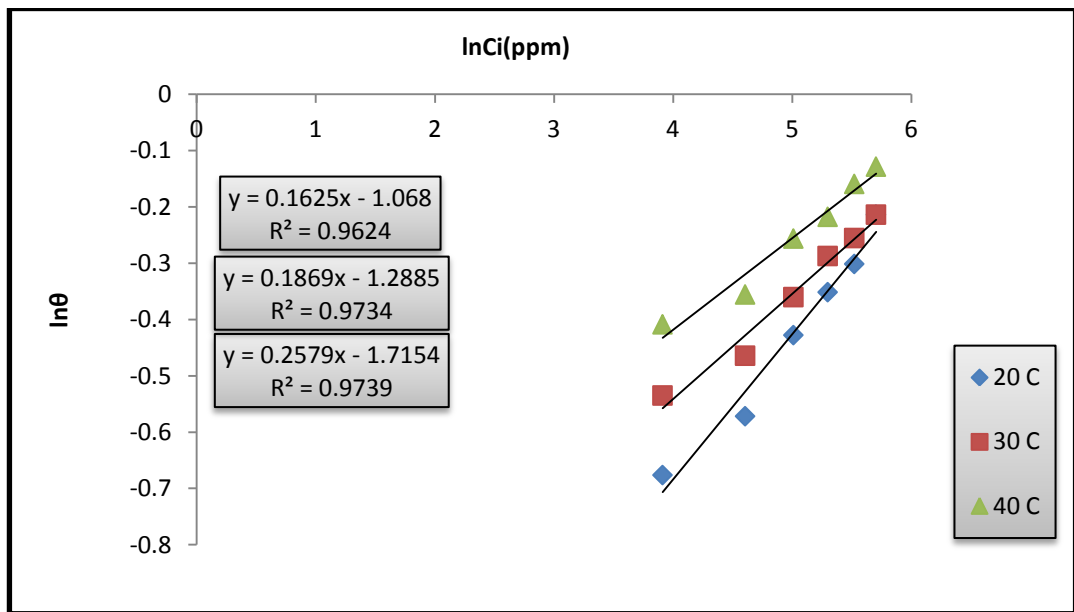


Fig.(4.28): Isotherm Freundlich adsorption of (Deoxycyclin extract) for aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

Table(4.9):Show the (K_F), slope (n), and (R^2) for Freundlich type adsorption isotherm of (Aspirin extract) for aluminum corrosion.

Temperature(K)	K_F (L/mg)	n	R^2
293.15	0.3436	0.1654	0.9281
303.15	0.3908	0.1494	0.9657
313.15	0.5990	0.0803	0.8731

Table(4.10):Show the (K_F), slope (n), and (R^2) for Freundlich type adsorption isotherm of (Aspirin extract) for aluminum alloy (AA2024-T3) corrosion .

Temperature(K)	K_F (L/mg)	n	R^2
293.15	0.2262	0.2834	0.9841
303.15	0.3661	0.1617	0.9869
313.15	0.5015	0.1132	0.9959

Table(4.11):Show the (K_F), slope (n), and (R^2) for Freundlich type adsorption isotherm of (Deoxycyclin extract) for aluminum corrosion.

Temperature(K)	K_F (L/mg)	n	R^2
293.15	0.3233	0.1577	0.9962
303.15	0.3561	0.1504	0.9440
313.15	0.5241	0.0945	0.8308

Table(4.12):Show the (K_F), slope (n), and (R^2) for Freundlich type adsorption isotherm of(Deoxycyclin extract) for aluminum alloy (AA2024-T3) corrosion.

Temperature(K)	K_F (L/mg)	n	R^2
293.15	0.1798	0.2579	0.9739
303.15	0.2768	0.1869	0.9734
313.15	0.3436	0.1625	0.9624

4.4.3-Timken Adsorption Isotherm

It is calculated by using equation (2.16) was used to describe the adsorption of the extracts (Aspirin and Deoxycyclin) on aluminum metal and aluminum alloy (AA2024-T3) surface figures (4.29),(4.30),(4.31) and (4.32), were produced by plotting surface coverage (θ) versus ($\ln C_i$) with slope and intercept yield the values of (a) and (K_T) respectively and data given in tables (4.13),(4.14),(4.15) and (4.16). show the equilibrium constant (K_T), slope (a), and correlation coefficient (R^2). Because the correlation coefficient values are smaller, it is clear that the Timken isotherm does not apply well to this system. The Langmuir adsorption isotherm is the best since the correlation coefficient values are high.[98]

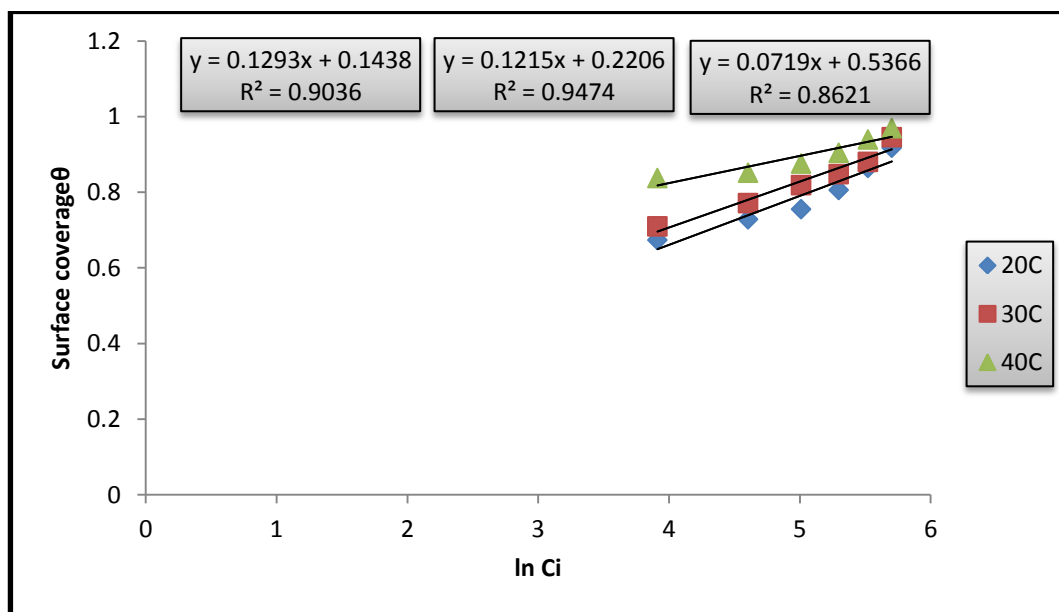


Fig.(4.29): Timken adsorption isotherm of (Aspirin extract) for aluminum corrosion in (0.5M H₂SO₄).

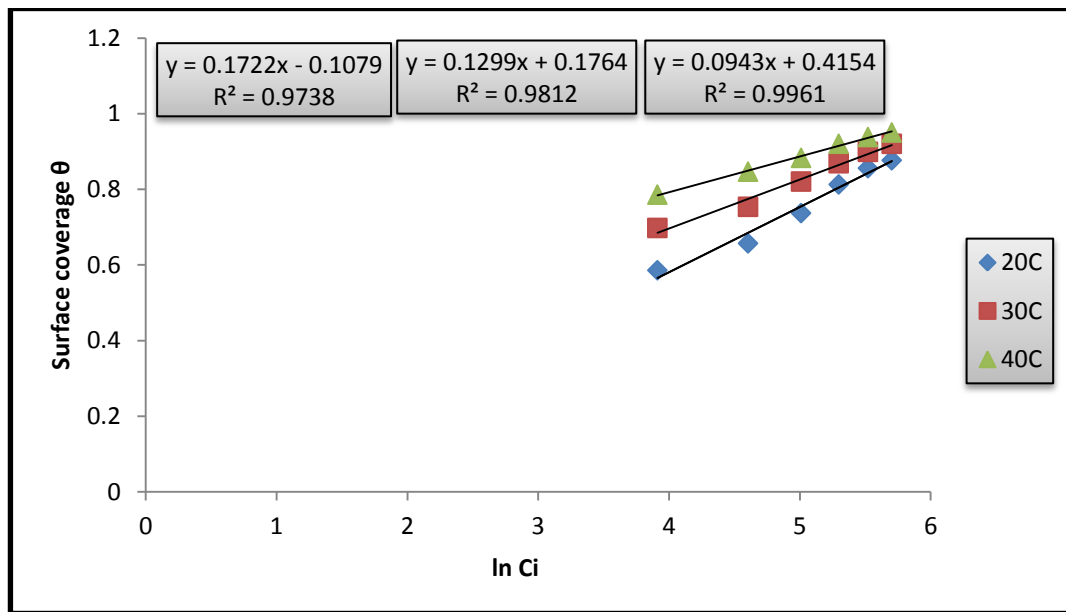


Fig.(4.30): Timken adsorption isotherm of (Aspirin extract) for aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

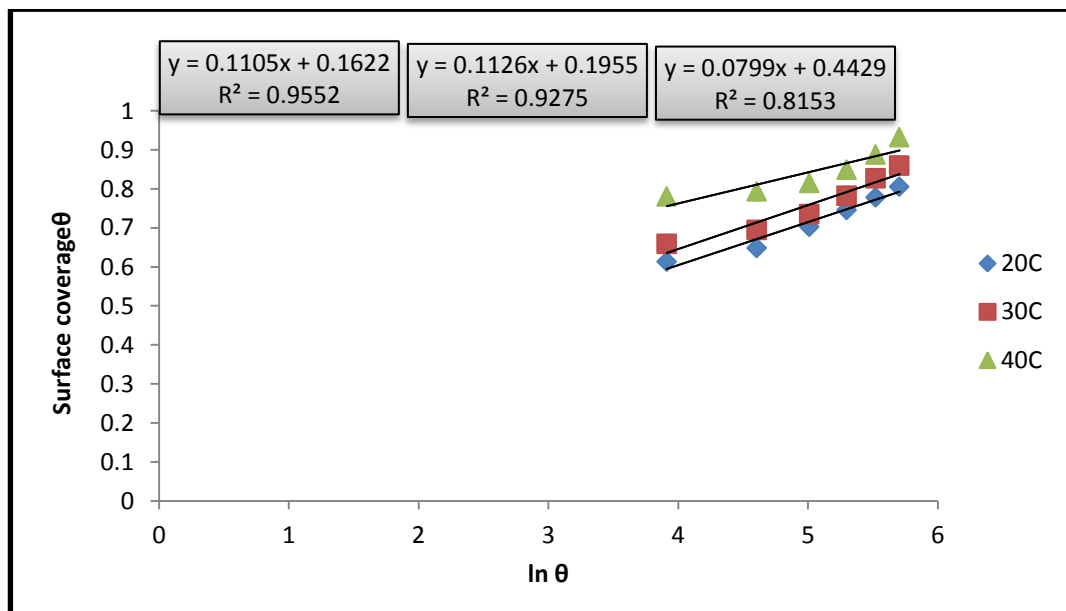


Fig.(4.31): Timken adsorption isotherm of (Deoxycyclin extract) for aluminum corrosion in (0.5M H₂SO₄).

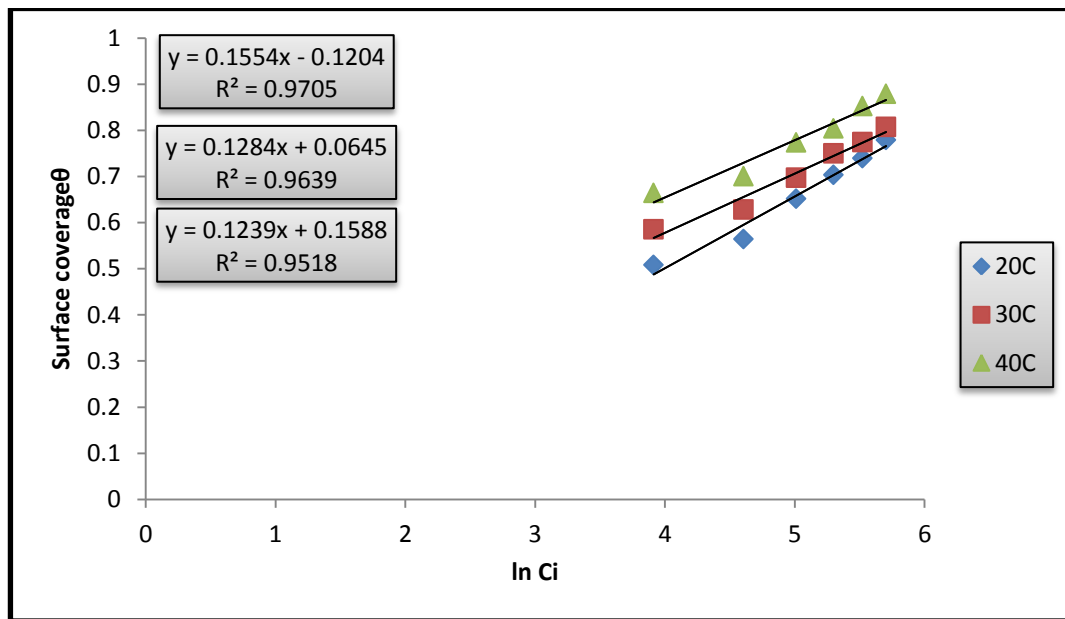


Fig.(4.32): Timken adsorption isotherm of (Deoxycyclin extract) for aluminum alloy (AA2024-T3) corrosion in (0.5M H₂SO₄).

Table(4.13):Show the (K_T), slope (a), and (R^2) for Timken type adsorption isotherm of (Aspirin extract) for aluminum corrosion.

Temperature(K)	a	K_T	R^2
293.15	3.8669	1.1546	0.9036
303.15	4.1152	1.2468	0.9474
313.15	6.9541	1.7101	0.8621

Table(4.14):Show the (K_T), slope (a), and (R^2) for Timken type adsorption isotherm of (Aspirin extract) for aluminum alloy (AA2024-T3) corrosion.

Temperature(K)	A	K_T	R^2
293.15	2.9036	1.1139	0.9738
303.15	3.8491	1.1929	0.9812
313.15	5.3022	1.5149	0.9961

Table(4.15):Show the (K_T), slope (a), and (R^2) for Timken type adsorption isotherm of (Deoxycyclin extract) for aluminum corrosion.

Temperature K	A	K_T	R^2
293.15	4.5248	1.1760	0.9552
303.1	4.4404	1.2159	0.9275
313.15	6.2578	1.5572	0.8153

Table(4.16):Show the (K_T), slope (a), and (R^2) for Timken type adsorption isotherm of (Deoxycyclin extract) for aluminum alloy (AA2024-T3) corrosion.

Temperature K	A	K_T	R^2
293.15	3.2175	1.1279	0.9705
303.15	3.8940	1.0666	0.9639
313.15	4.0355	1.1721	0.9518

4.5 Effect of Temperature and Activation Studies

The apparent activation energy values (E_a) corrosion for aluminum and aluminum alloy (AA2024-T3) corrosion process in (0.5M H_2SO_4) in the presence and without of (Aspirin and Deoxycyclin) extracts was calculated by using equation (2.2) By plotting the Arrhenius plots of ($\ln CR$) versus ($1/T$) data given in tables (4.1) to (4.4) which give straight lines with a slope of ($-E_a/R$) as in figures (4.33) to (4.36). The estimated values of (E_a) for aluminum and aluminum alloy (AA2024-T3) corrosion in the presence of (Aspirin and Deoxycyclin) extracts in (0.5M H_2SO_4) are listed in the tables (4.17) to (4.20). Activation energy of aluminum was found to be (50.308KJ/mol) in the absence of the extract and decreases to (17.834) in the presence of (As) extract and decreases to (10.883KJ/mol) in the presence of (Doe) extract. Activation energy of aluminum alloy (AA2024-T3) was found to be (41.578KJ/mol) in the absence of the extract and decreases then to (7.346KJ/mol) in the presence of (As) extract and decreases to (19.180KJ/mol) when (Deo) extract is present. Uninhibited solution (E_a) has a greater value than inhibited solution (E_a), implying that aluminum and aluminum alloy (AA2024-T3) dissolution is slow in the presence of inhibitor. As the temperature rises, various chemical changes in the inhibitor molecules occur, resulting in higher electron density at the adsorption center of the inhibitor molecules, which improves inhibition efficiency. As the inhibitor concentration rises, the value (E_a) decreases. It is obvious that the inhibitor concentration plays a role in lowering the activation energy values, indicating a stronger inhibitory impact, therefore (E_a) is lower in general when an inhibitor is present.[99]

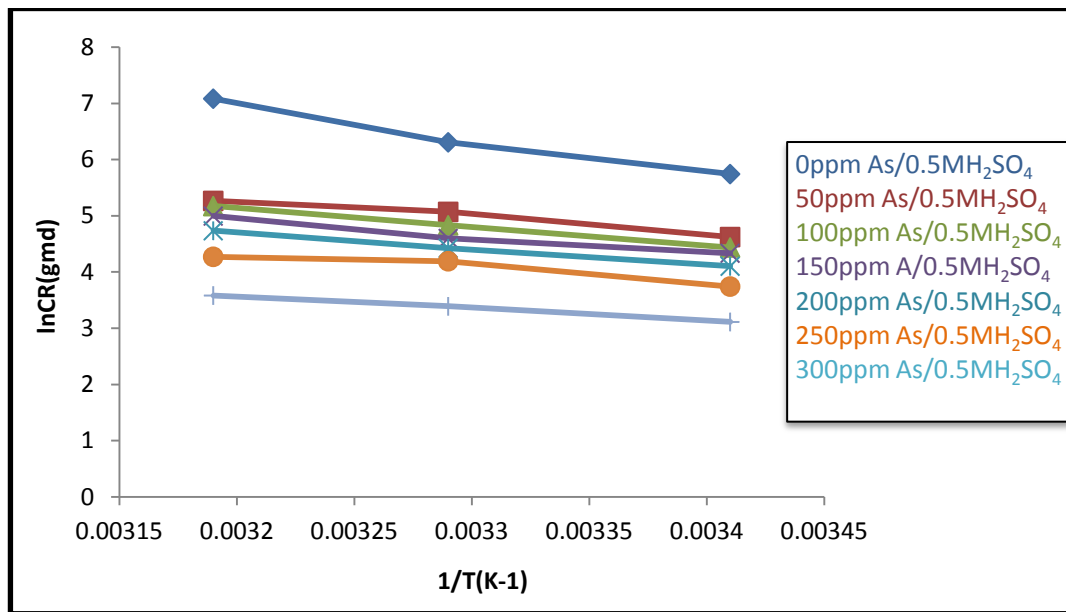


Fig.(4.33):Arrhenius plot of aluminum corrosion with various concentrations of Aspirin extract at different temperatures.

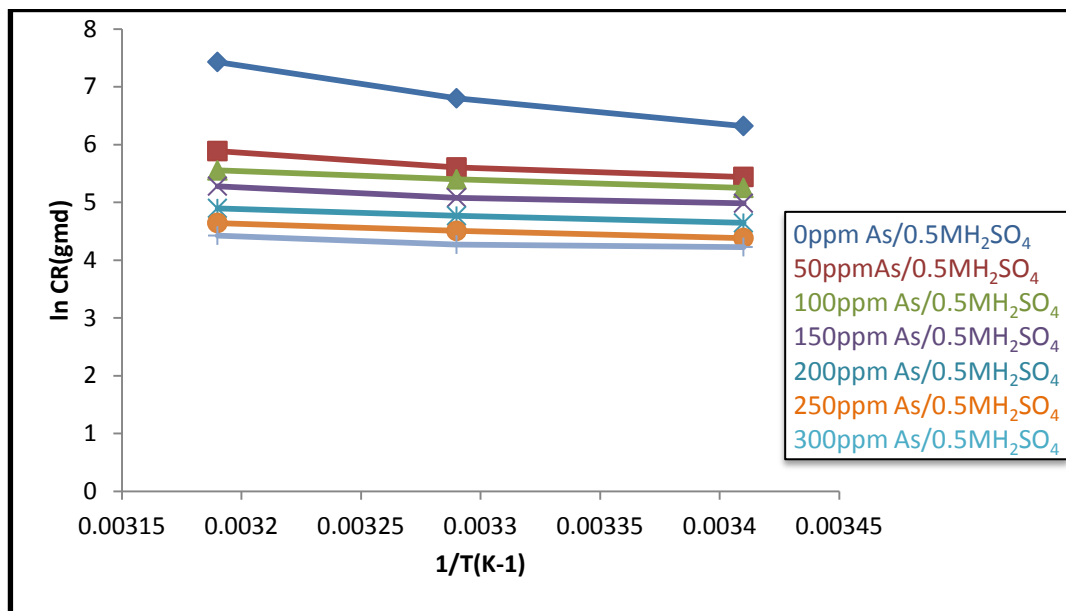


Fig.(4.34):Arrhenius plot of aluminum alloy(AA2024-T3) corrosion with various concentrations of Aspirin extract at different temperatures.

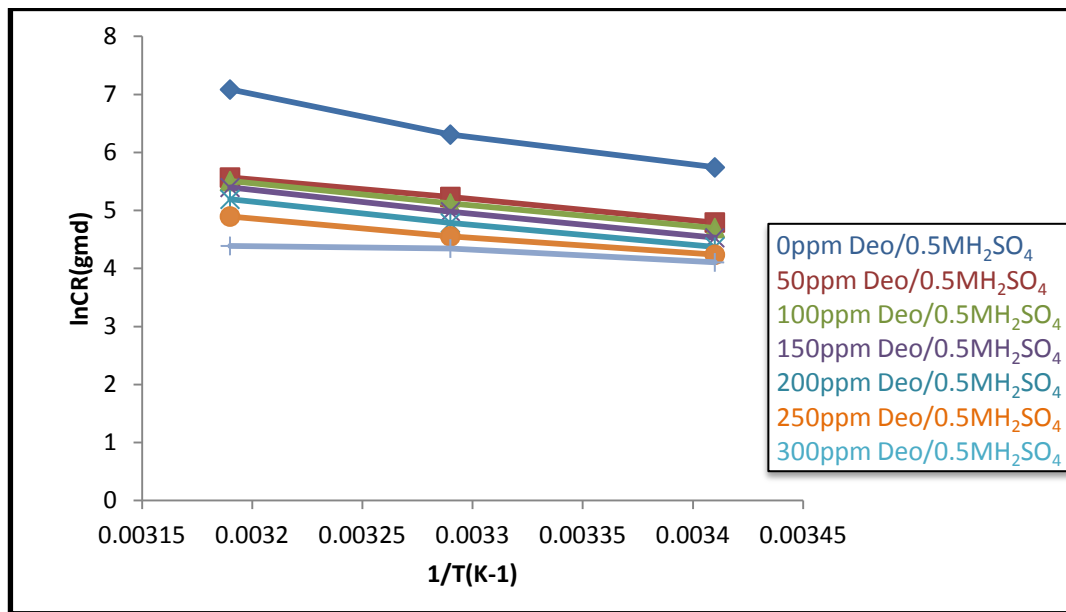


Fig.(4.35): Arrhenius plot of aluminum corrosion with various concentrations of Deoxycyclin extract at different temperatures.

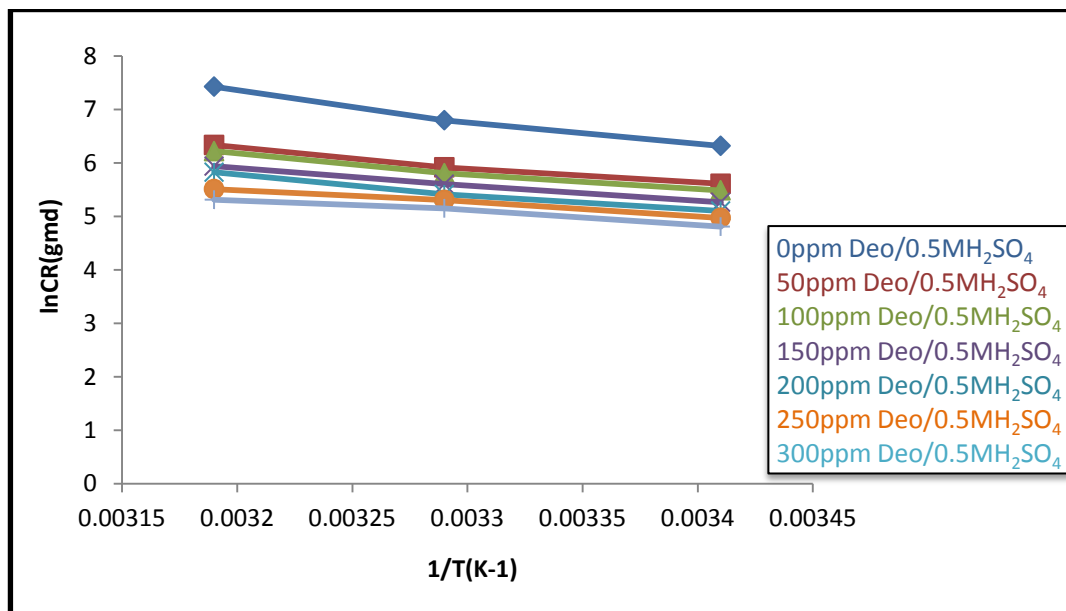


Fig.(4.36): Arrhenius plot of aluminum alloy (AA2024-T3) corrosion with various concentrations of Deoxycyclin extract at different temperatures.

**Table(4.17): Values of activation energies in existence and absence
Aspirin extract of aluminum corrosion.**

C_i (ppm)	E_a (KJ.mol⁻¹)
Blank	50.3080
50	24.5263
100	27.8020
150	24.7757
200	23.8362
250	20.3526
300	17.8345

**Table(4.18): Values of activation energies in existence and absence
Aspirin extract of aluminum alloy (AA2024)corrosion.**

C_i (ppm)	E_a (KJ.mol⁻¹)
Blank	41.5783
50	16.7443
100	11.3735
150	11.0243
200	9.4862
250	9.8022
300	7.3462

Table(4.19): Values of activation energies in existence and absence Deoxycyclin extract of aluminum corrosion.

C_i (ppm)	E_a (KJ.mol⁻¹)
Blank	50.3080
50	29.2985
100	30.5290
150	32.6740
200	30.8449
250	24.7923
300	10.8830

Table(4.20): Values of activation energies in existence and absence Deoxycyclin extract of aluminum alloy(AA2024-T3) corrosion.

C_i (ppm)	E_a (KJ.mol⁻¹)
Blank	41.5783
50	27.2366
100	27.4777
150	25.4740
200	27.1119
250	20.4274
300	19.1803

From the transition state, the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for the production of the activated complex were computed. Using experimental corrosion rates values calculated from weight loss measurements for aluminum and aluminum alloy (AA2024-T3) in the presence and absence of (Aspirin and Deoxycyclin) extracts, corrosion was seen in (0.5M H_2SO_4). Equations in(2.7) was used to compute the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*). By plotting ($\ln CR/T$) versus ($1/T$) as shown in figures (4.37) to(4.40), where (ΔH^*) and (ΔS^*) were calculated and listed in tables (4.21) to (4.24) using straight lines with slopes of ($-\Delta H^*/R$) and intercepts of ($\ln R/Nh$) $+(\Delta S^*/R)$. The change in activation enthalpy has a positive sign, denoting an endothermic activation process of the aluminum and aluminum alloy (AA2024-T3) corrosion.[100] Large and negative values of (ΔS^*) indicate that the activated complex is a bond instead of breakup move in the rate-determining phase, meaning that disordering from reactants to the activated complex is continuously reducing.[101]

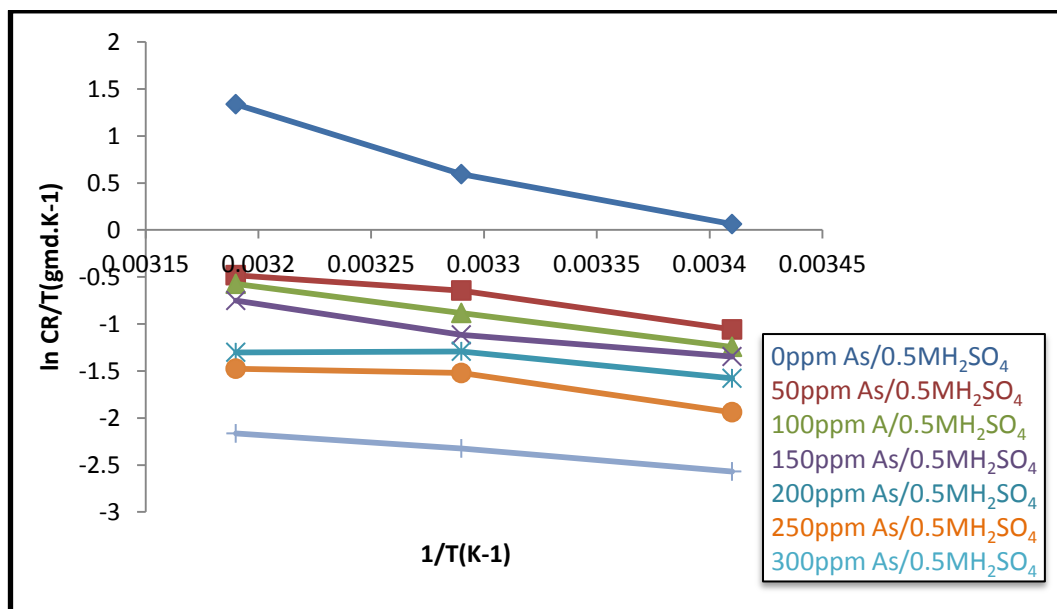


Fig.(4.37): Transition state plot for aluminum corrosion in absence and presence of various concentrations of (Aspirin) extract.

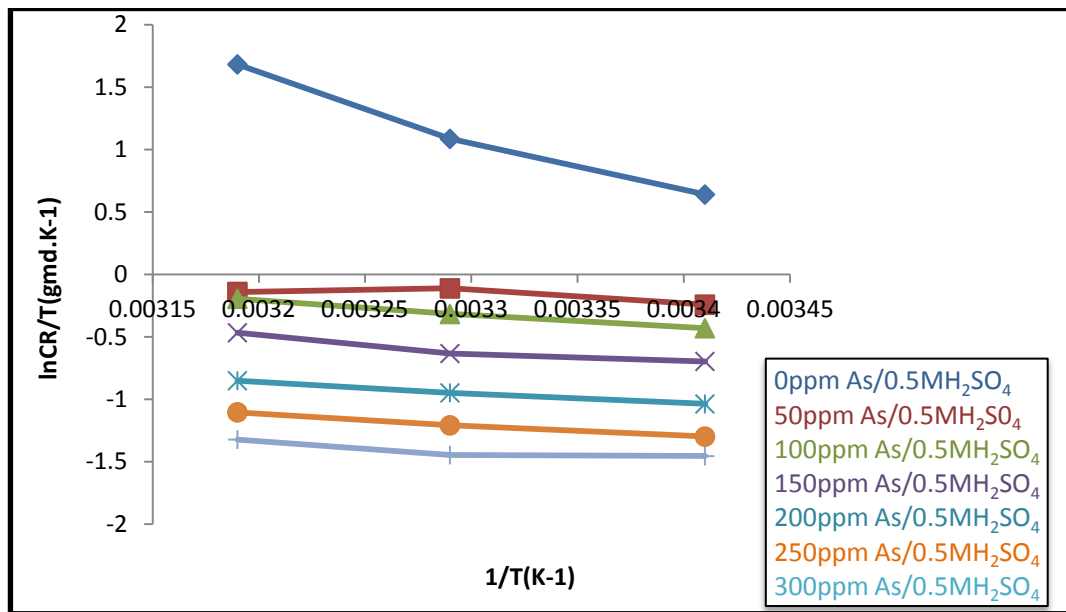


Fig.(4.38): Transition state plot for aluminum alloy (AA2024-T3) corrosion in absence and presence of various concentrations of (Aspirin) extract.

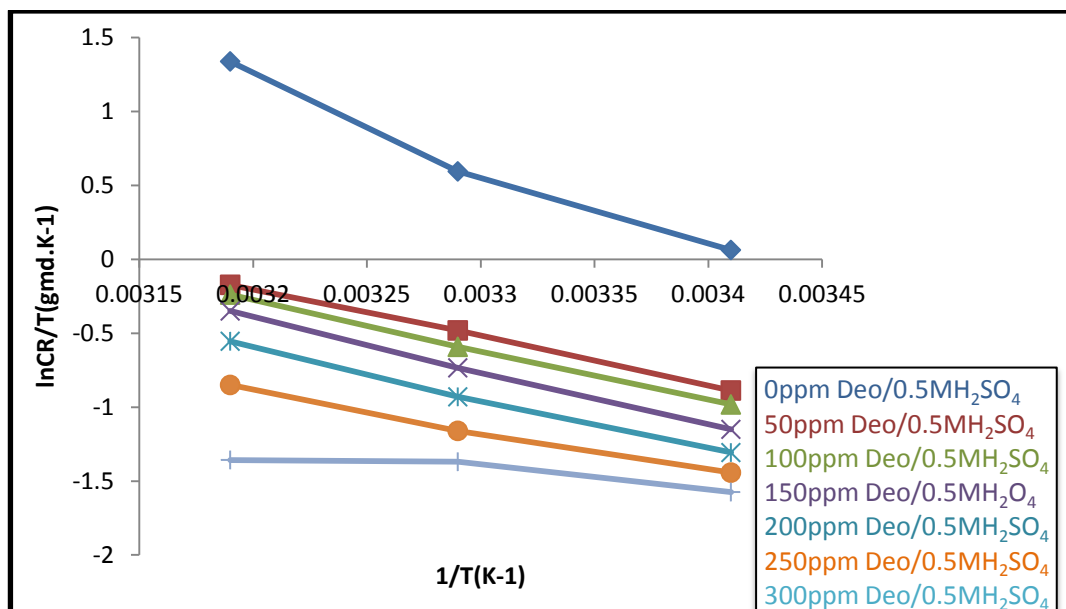


Fig.(4.39): Transition state plot for aluminum corrosion in absence and presence of various concentrations of (Deoxycyclin) extract.

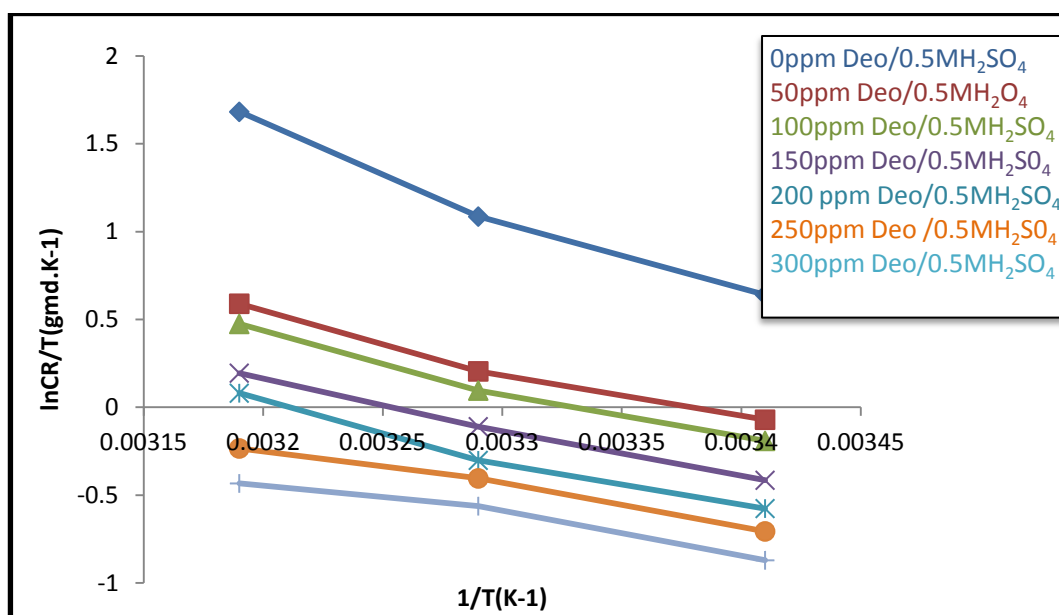


Fig.(4.40): Transition state plot for aluminum alloy (AA2024-T3) corrosion in absence and presence of various concentrations of (Deoxycyclin) extract.

Table(4.21):Enthalpy and Entropy of aluminum corrosion activation values with various concentrations of Aspirin extract.

C_i (ppm)	ΔH^* (KJ.mol ⁻¹)	ΔS^* (KJ.mol ⁻¹ .K ⁻¹)
Blank	47.8138	-0.0344
50	22.0404	-0.1309
100	25.3078	-0.1216
150	22.2898	-0.1329
200	10.7833	-0.1735
250	17.8667	-0.1523
300	15.3476	-0.1665

Table(4.22): Enthalpy and Entropy of aluminum alloy(AA2024-T3) corrosion activation values with various concentrations of Aspirin extract.

C_i (ppm)	ΔH^* (KJ.mol ⁻¹)	ΔS^* (KJ.mol ⁻¹ .K ⁻¹)
Blank	39.0924	-0.0593
50	4.0182	-0.1857
100	8.8877	-0.1708
150	8.5385	-0.1744
200	7.0037	-0.1823
250	7.3097	-0.1835
300	4.8620	-1.9323

Table(4.23):Enthalpy and Entropy of aluminum corrosion activation values with various concentrations of Deoxycyclin extract.

C_i (ppm)	ΔH^* (KJ.mol ⁻¹)	ΔS^* (KJ.mol ⁻¹ .K ⁻¹)
Blank	47.8138	-0.0344
50	27.0371	-0.1127
100	28.0348	-0.1102
150	30.1798	-0.1043
200	28.3591	-0.1118
250	22.2981	-0.1336
300	8.3888	-0.1819

Table(4.24): Enthalpy and Entropy of aluminum alloy(AA2024-T3) corrosion activation values with various concentrations of Deoxycyclin extract.

C_i (ppm)	ΔH^* (KJ.mol ⁻¹)	ΔS^* (KJ.mol ⁻¹ .K ⁻¹)
Blank	39.0924	-0.0593
50	19.2635	-0.1316
100	24.9919	-0.1119
150	22.9882	-0.1227
200	24.6261	-0.1186
250	17.9426	-0.1421
300	16.6945	-0.1477

4-6 Surface Morphology of Inhibited Aluminum and alloy(AA2024-T3)

4.6.1 Surface analysis using (AFM)

Atomic force microscopy Characterization (AFM) is a strong tool for investigating surface morphology at the nano- to micro scale, and it has emerged as a new option for studying the impact of inhibitors on the development and progression of corrosion on metals.[102,103] Figure (4.41) and (4.42) shows the 2D and 3D picture of the polished surface of aluminum and its alloy (AA2024-T3) with a slight roughness (2.69 nm) for aluminum and (1.56nm) for alloy due to the atmospheric corrosion during transfer the sample for inspection. While, figures (4.43) and (4.44) demonstrate the corroded surface in H₂SO₄ medium, for aluminum and alloy respectively these images illustrate the maximum peak-to-valley (in 3D images) for the corroded sample with average roughness (22.3 nm) for aluminum and (5.13 nm) for alloy (AA2024-T3).

These data also refer to that the greater surface roughness for the corroded surface is due to the corrosion of the aluminum and alloy in acidic environments. The AFM analysis of inhibited surface is shown in figure (4.45) and (4.46) in 0.5M H₂SO₄ medium with aspirin extract for aluminum and alloy(AA2024-T3), respectively. The AFM analysis of inhibited surface is shown in figure(4.47) and (4.48) in 0.5M H₂SO₄ medium with Deoxycyclin extract for aluminum and alloy (AA2024-T3), respectively. In these images, one can see that the roughness decreased according to the nature of molecular configuration of drugs to be adsorbed on the surface.

Figures (4.49) to (4.56) and table (4.25) to (4.32) exhibit the granularity accumulation distribution charts for different samples, these charts indicate the different distributions of particles on the aluminum and alloy surface with a different average diameter, As listed in table (4.33).The average roughness (Ra) is the average deviation from a mean line of all measured roughness profile points. The measured average departure from the mean is referred to as root mean square roughness (Rq). The data are listed in table (4.33). Also, Rq is more sensitive than Ra to small and large high deviations. The results show that the metallic surface is smoothed because of the formed adsorption of drugs by the active sites in the inhibitors. The softness of surface is attributed to form a compact protective layer of AL⁺³ – drug complex thereby inhibiting the corrosion of aluminum and alloy.

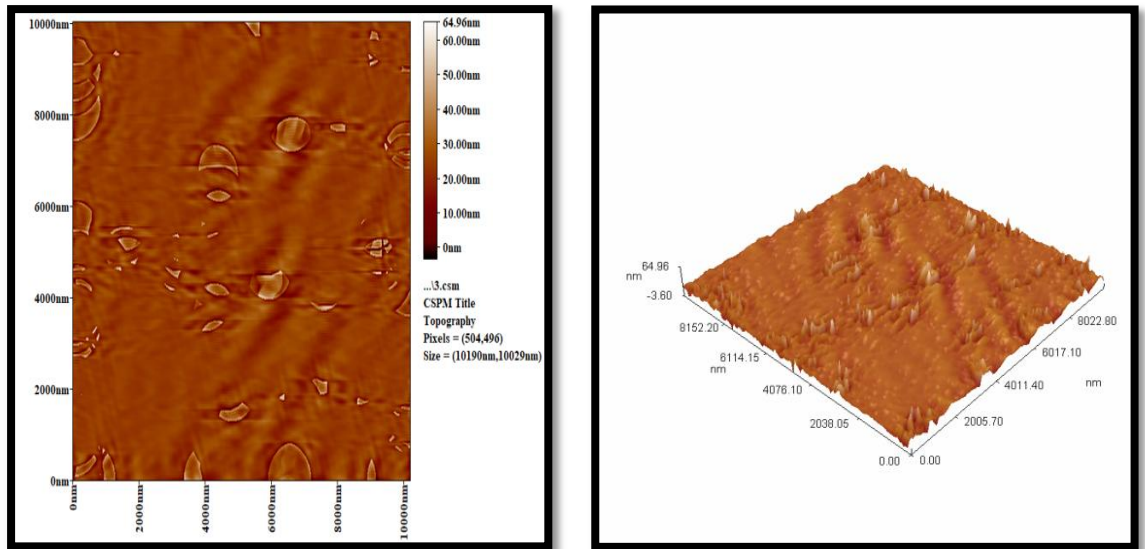


Fig.(4.41): 2D and 3D images of AFM for polished aluminum surface.

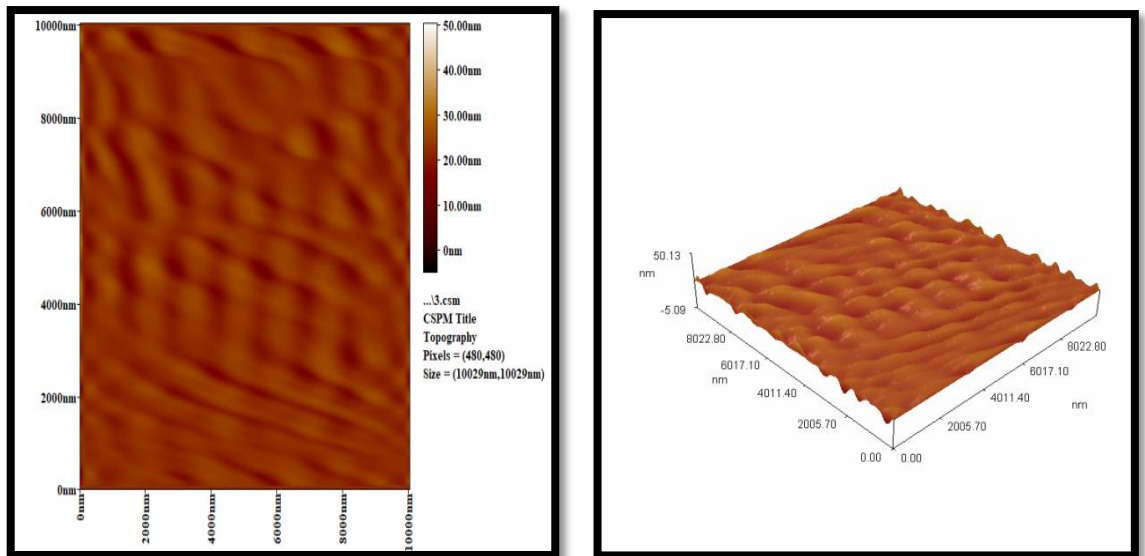


Fig.(4.42): 2D and 3D images of AFM for polished aluminum alloy(AA2024-T3) surface .

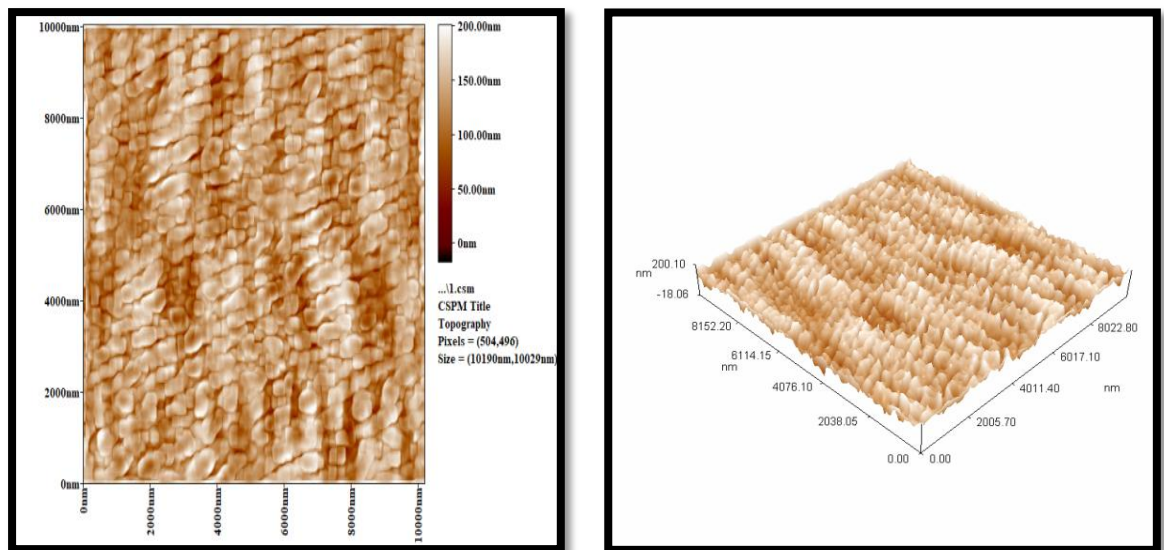


Fig.(4.43):2D and 3D images of AFM aluminum surface immersed in (0.5M H₂SO₄).

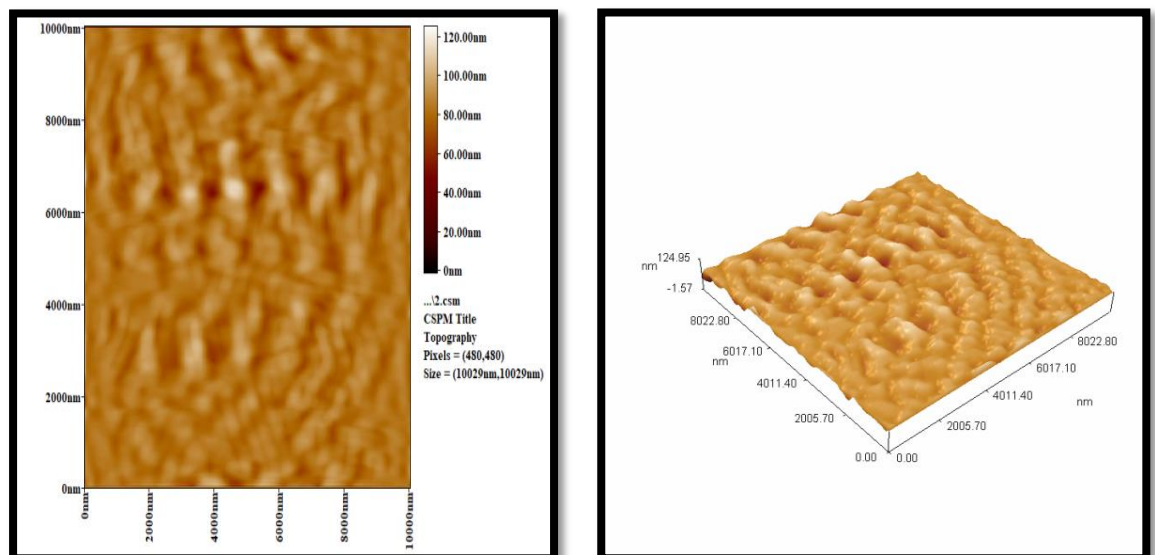


Fig.(4.44):2D and 3D images of AFM aluminum alloy(AA2024-T3) surface immersed in (0.5M H₂SO₄).

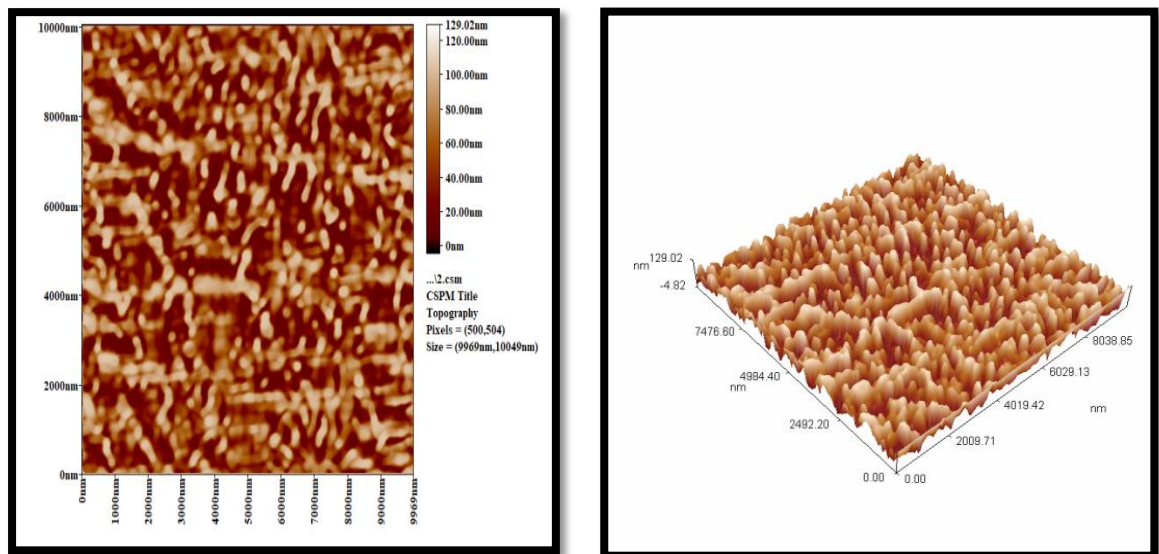


Fig.(4.45):2D and 3D images of AFM aluminum surface immersed in (0.5M H₂SO₄) presence (300 ppm) of aspirin extract.

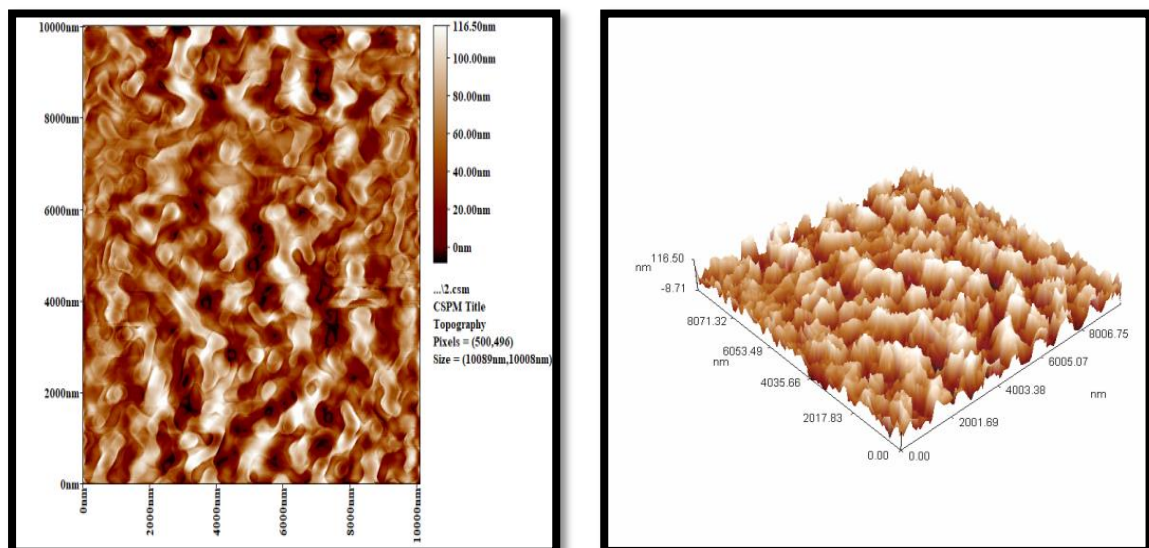


Fig.(4.46):2D and 3D images of AFM aluminum alloy(AA2024-3) surface immersed in (0.5M H₂SO₄) presence (300 ppm) of aspirin extract.

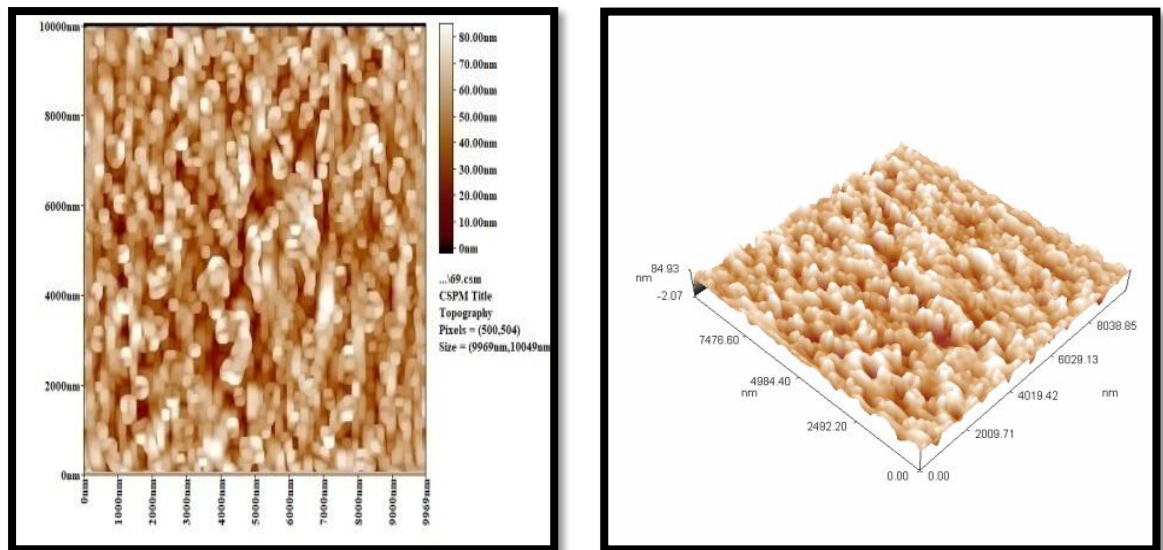


Fig.(4.47):2D and 3D images of AFM aluminum surface immersed in (0.5M H₂SO₄) presence (300 ppm) of Deoxycyclin extract.

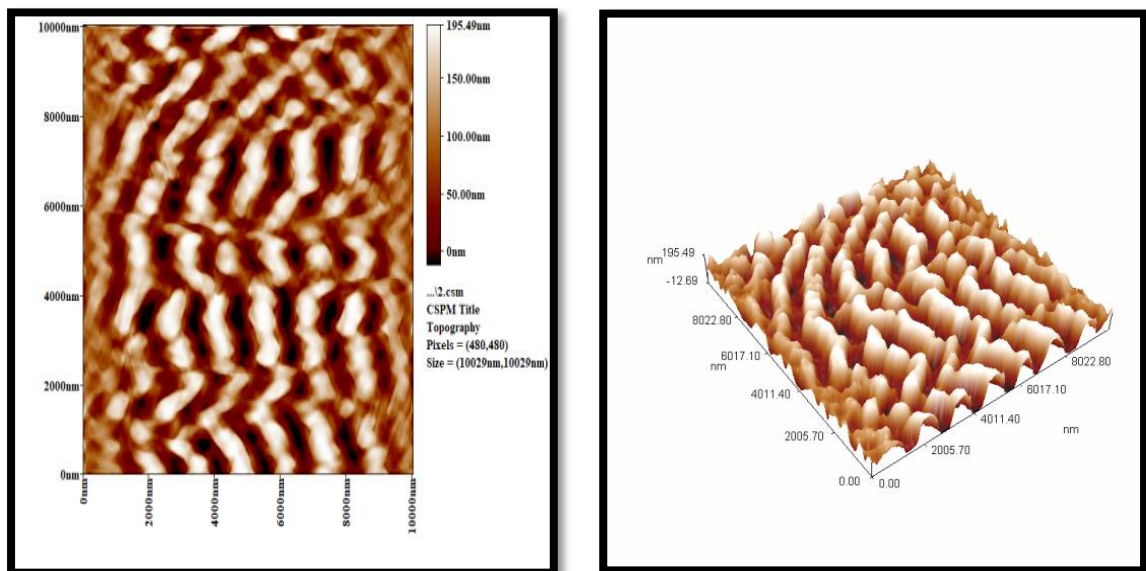


Fig.(4.48):2D and 3D images of AFM aluminum alloy(AA2024-T3) surface immersed in (0.5M H₂SO₄) presence (300 ppm) of Deoxycyclin

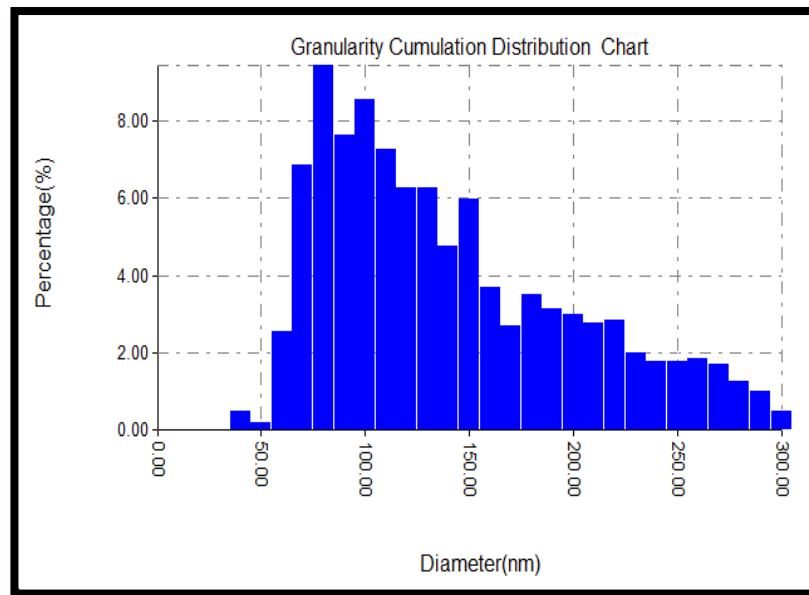


Fig.(4.49): Granularity cumulating distribution of polished aluminum surface.

Table(4.25) Granularity cumulating distribution of polished aluminum surface.

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
40.00	0.50	0.50	130.00	6.28	55.60	220.00	2.86	88.08
50.00	0.21	0.71	140.00	4.78	60.39	230.00	2.00	90.08
60.00	2.57	3.28	150.00	6.00	66.38	240.00	1.78	91.86
70.00	6.85	10.14	160.00	3.71	70.09	250.00	1.78	93.65
80.00	9.42	19.56	170.00	2.71	72.81	260.00	1.86	95.50
90.00	7.64	27.19	180.00	3.50	76.30	270.00	1.71	97.22
100.00	8.57	35.76	190.00	3.14	79.44	280.00	1.28	98.50
110.00	7.28	43.04	200.00	3.00	82.44	290.00	1.00	99.50
120.00	6.28	49.32	210.00	2.78	85.22	300.00	0.50	100.00

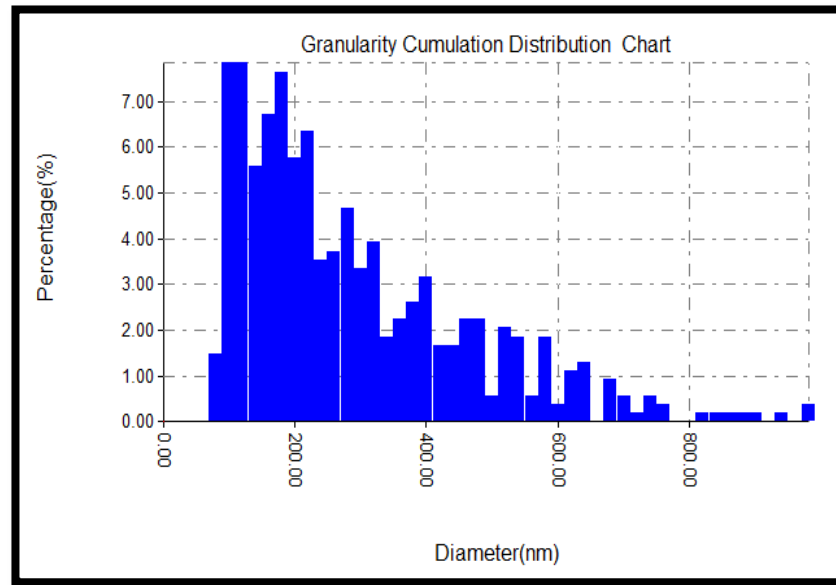


Fig.(4.50): Granularity cumulating distribution of polished aluminum alloy(AA2024-T3) surface.

Table (4.26) Granularity cumulating distribution of polished aluminum alloy(AA2024-T3) surface.

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Cumulati on(%)	Volum e(%)
80.00	1.49	1.49	360.00	2.24	72.57	640.00	95.90	1.31
100.00	7.84	9.33	380.00	2.61	75.19	680.00	96.83	0.93
120.00	7.84	17.16	400.00	3.17	78.36	700.00	97.39	0.56
140.00	5.60	22.76	420.00	1.68	80.04	720.00	97.57	0.19
160.00	6.72	29.48	440.00	1.68	81.72	740.00	98.13	0.56
180.00	7.65	37.13	460.00	2.24	83.96	760.00	98.51	0.37
200.00	5.78	42.91	480.00	2.24	86.19	820.00	98.69	0.19
220.00	6.34	49.25	500.00	0.56	86.75	840.00	98.88	0.19
240.00	3.54	52.80	520.00	2.05	88.81	860.00	99.07	0.19
260.00	3.73	56.53	540.00	1.87	90.67	880.00	99.25	0.19
280.00	4.66	61.19	560.00	0.56	91.23	900.00	99.44	0.19
300.00	3.36	64.55	580.00	1.87	93.10	940.00	99.63	0.19
320.00	3.92	68.47	600.00	0.37	93.47	980.00	100.00	0.37
340.00	1.87	70.34	620.00	1.12	94.59			

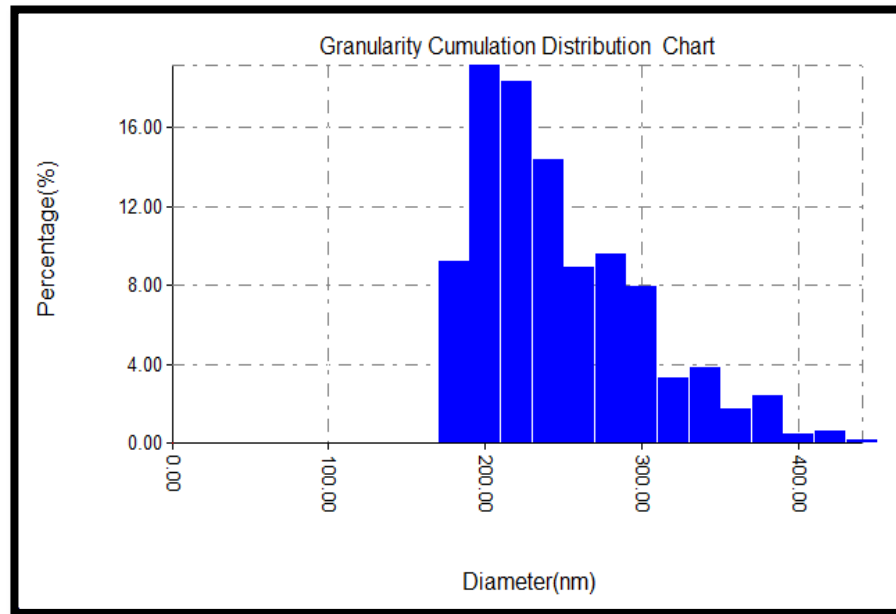


Fig.(4.51): Granularity cumulating distribution of aluminum surface immersed in(0.5M H₂SO₄).

Table(4.27) Granularity cumulating distribution of aluminum surface immersed in(0.5M H₂SO₄).

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
180.00	9.24	9.24	280.00	9.55	79.46	380.00	2.39	98.73
200.00	19.11	28.34	300.00	7.96	87.42	400.00	0.48	99.20
220.00	18.31	46.66	320.00	3.34	90.76	420.00	0.64	99.84
240.00	14.33	60.99	340.00	3.82	94.59	440.00	0.16	100.00
260.00	8.92	69.90	360.00	1.75	96.34			

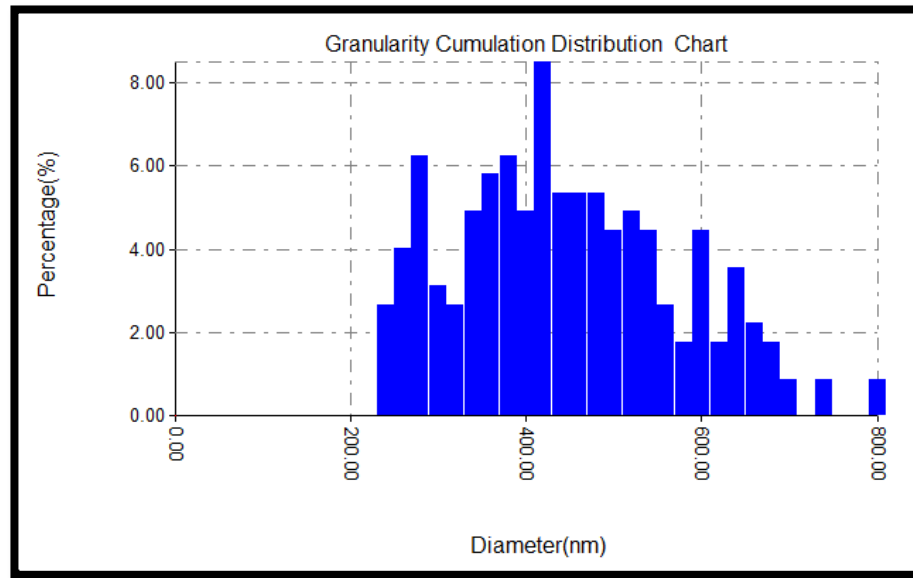


Fig.(4.52): Granularity cumulating distribution of aluminum alloy (AA2024-T3) surface immersed in(0.5M H₂SO₄).

Table(4.28) Granularity cumulating distribution of aluminum alloy (AA2024-T3) surface immersed in(0.5M H₂SO₄).

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
240.00	2.68	2.68	420.00	8.48	49.11	600.00	4.46	87.95
260.00	4.02	6.70	440.00	5.36	54.46	620.00	1.79	89.73
280.00	6.25	12.95	460.00	5.36	59.82	640.00	3.57	93.30
300.00	3.13	16.07	480.00	5.36	65.18	660.00	2.23	95.54
320.00	2.68	18.75	500.00	4.46	69.64	680.00	1.79	97.32
340.00	4.91	23.66	520.00	4.91	74.55	700.00	0.89	98.21
360.00	5.80	29.46	540.00	4.46	79.02	740.00	0.89	99.11
380.00	6.25	35.71	560.00	2.68	81.70	800.00	0.89	100.00
400.00	4.91	40.63	580.00	1.79	83.48			

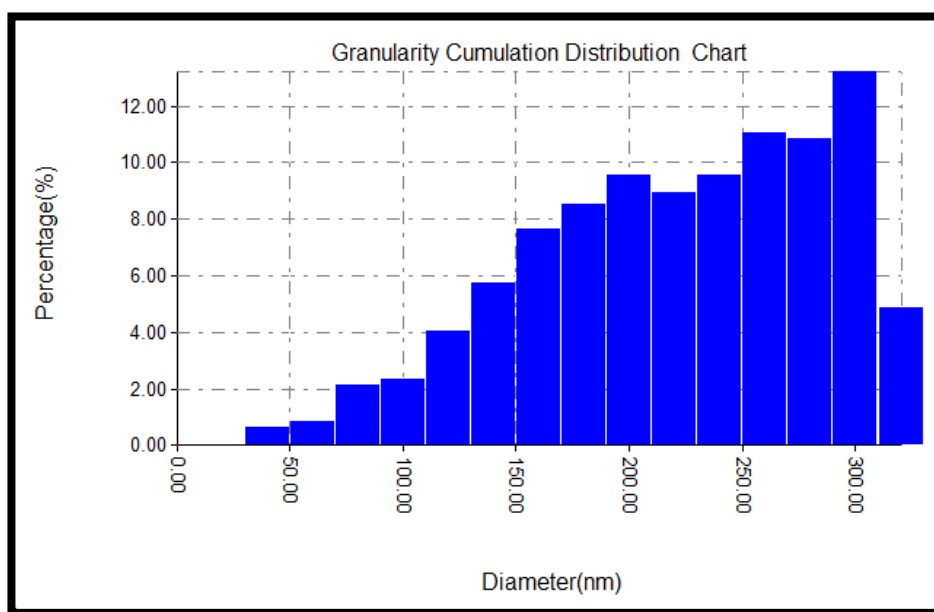


Fig.(4.53): Granularity cumulating distribution and average diameter of aluminum surface immersed in(0.5M H₂SO₄) presence of (300ppm) of aspirin extract.

Table(4.29) Granularity cumulating distribution and average diameter of aluminum surface immersed in(0.5M H₂SO₄) presence of (300ppm) of aspirin extract.

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
40.00	0.64	0.64	140.00	5.74	15.74	240.00	9.57	60.00
60.00	0.85	1.49	160.00	7.66	23.40	260.00	11.06	71.06
80.00	2.13	3.62	180.00	8.51	31.91	280.00	10.85	81.91
100.00	2.34	5.96	200.00	9.57	41.49	300.00	13.19	95.11
120.00	4.04	10.00	220.00	8.94	50.43	320.00	4.89	100.00

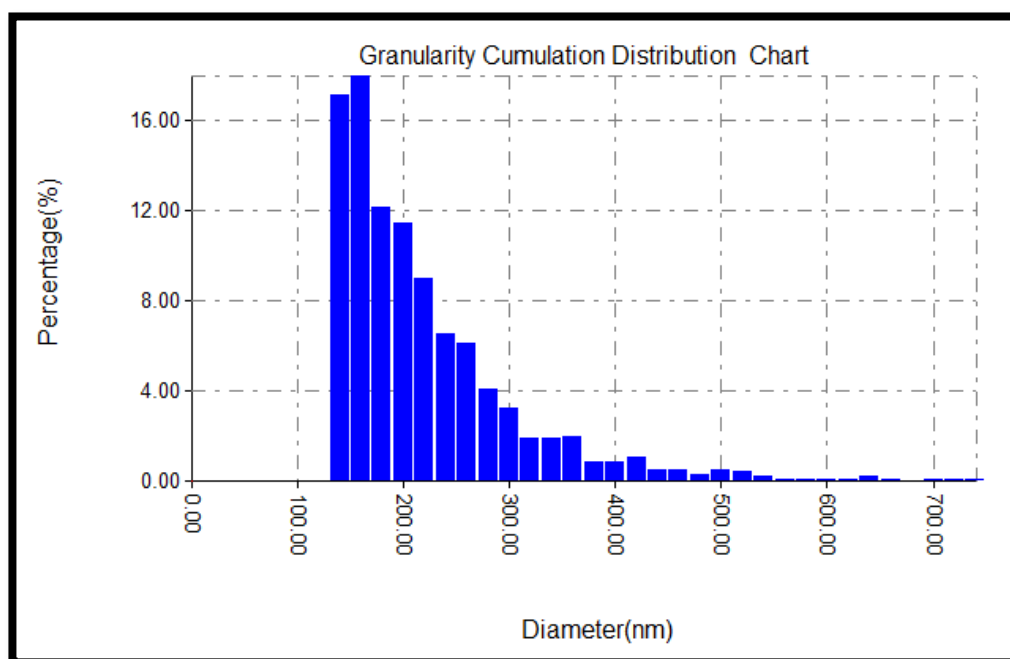


Fig.(4.54): Granularity cumulating distribution and average diameter of aluminum alloy(AA2024-T3) surface immersed in(0.5M H₂SO₄) presence of (300ppm) of aspirin extract.

Table(4.30) Granularity cumulating distribution and average diameter of aluminum alloy(AA2024-T3) surface immersed in(0.5M H₂SO₄) presence of (300ppm) of aspirin extract.

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
140.00	17.11	17.11	340.00	1.89	91.33	540.00	0.22	98.89
160.00	17.89	35.00	360.00	2.00	93.33	560.00	0.11	99.00
180.00	12.11	47.11	380.00	0.89	94.22	580.00	0.11	99.11
200.00	11.44	58.56	400.00	0.89	95.11	600.00	0.11	99.22
220.00	9.00	67.56	420.00	1.11	96.22	620.00	0.11	99.33
240.00	6.56	74.11	440.00	0.56	96.78	640.00	0.22	99.56
260.00	6.11	80.22	460.00	0.56	97.33	660.00	0.11	99.67
280.00	4.11	84.33	480.00	0.33	97.67	680.00	0.11	99.78
300.00	3.22	87.56	500.00	0.56	98.22	700.00	0.11	99.89
320.00	1.89	89.44	520.00	0.44	98.67	720.00	0.11	99.99
						740.00	0.11	100.00

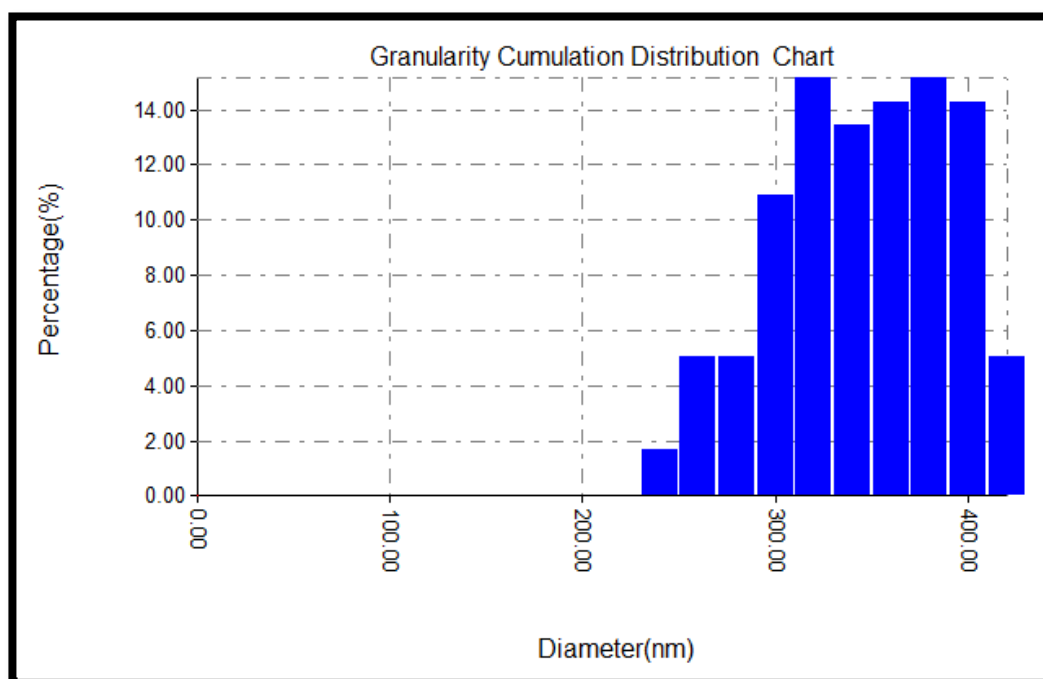


Fig.(4.55): Granularity cumulating distribution and average diameter of aluminum surface immersed in(0.5M H₂SO₄) presence of (300ppm) of Deoxycyclin extract.

Table(4.31) Granularity cumulating distribution and average diameter of aluminum surface immersed in(0.5M H₂SO₄) presence of (300ppm) of Deoxycyclin extract.

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
240.00	1.68	1.68	320.00	15.13	37.82	400.00	14.29	94.96
260.00	5.04	6.72	340.00	13.45	51.26	420.00	5.04	100.00
280.00	5.04	11.76	360.00	14.29	65.55			
300.00	10.92	22.69	380.00	15.13	80.67			

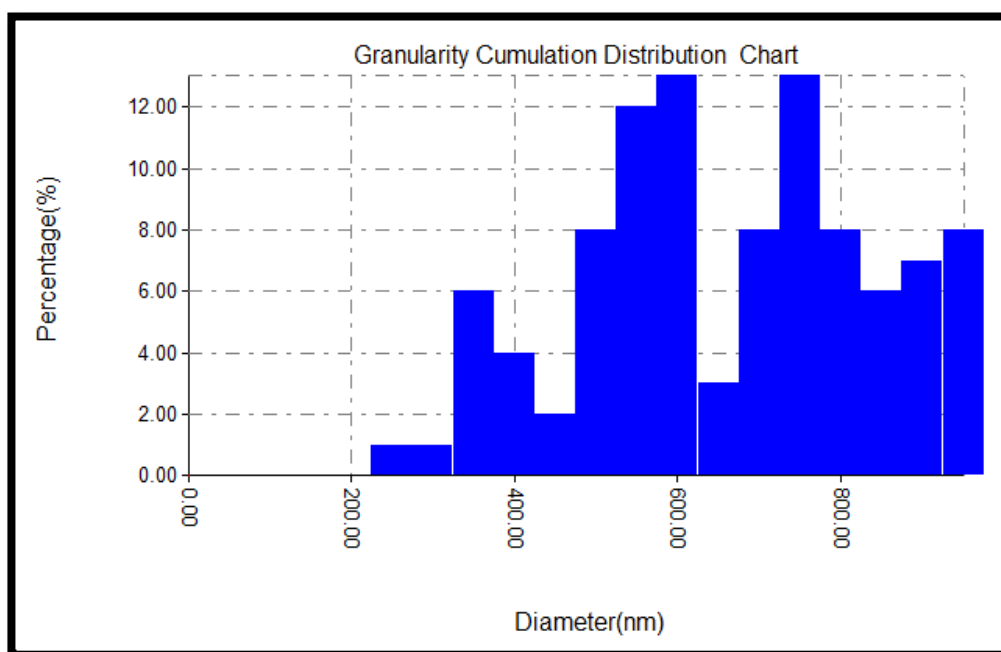


Fig.(4.56): Granularity cumulating distribution and average diameter of aluminum alloy(AA2024-T3) surface immersed in(0.5M H₂SO₄) presence of (300ppm) of Deoxycyclin extract.

Table(4.32) Granularity cumulating distribution and average diameter of aluminum alloy(AA2024-T3) surface immersed in(0.5M H₂SO₄) presence of (300ppm) of Deoxycyclin extract.

Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)	Diameter (nm)<	Volum e(%)	Cumulati on(%)
250.00	1.00	1.00	500.00	8.00	22.00	750.00	13.00	71.00
300.00	1.00	2.00	550.00	12.00	34.00	800.00	8.00	79.00
350.00	6.00	8.00	600.00	13.00	47.00	850.00	6.00	85.00
400.00	4.00	12.00	650.00	3.00	50.00	900.00	7.00	92.00
450.00	2.00	14.00	700.00	8.00	58.00	950.00	8.00	100.00

Table(4.33) Average roughness and average diameter for all cases.

Case	Ra(nm)	Rq(nm)	Average diameter(nm)
Corroded aluminum pure in H₂SO₄	22.3	27.8	238.04
Inhibited aluminum pure by aspirin	25.8	29.6	211.12
Inhibited aluminum pure by Deoxycyclin	11.6	14.8	335.40
Corroded aluminum alloy in H₂SO₄	5.13	7.38	437.76
Inhibited aluminum alloy by aspirin	24.3	29.3	211.03
Inhibited aluminum alloy by Deoxycyclin	52	60.1	638.75

4.6.2 Scanning electron microscope(SEM)

The microstructure of aluminum and aluminum alloys (AA2024-T3) was studied using a scanning electron microscope (SEM). Figure (4.57.a and b) shows scanning electron microscopy (SEM) pictures of pure aluminum and alloy specimens before they were immersed in corrosion solution. The fig.(4.58 a and b) shows images of pure aluminum and its alloy (AA2024-T3) after immersion in a corrosion solution (0.5M H₂SO₄) for (3h) .The fig.(4.59.a and b) shows images of aluminum and its alloy (AA2024-T3) after immersion in a corrosive solution (0.5M H₂SO₄) in the existence of an extract of expired aspirin.

Fig.(4.60 a and b) shows images of aluminum and its alloy (AA2024-T3) after immersion in a corrosive solution (0.5M H₂SO₄) in the presence of an extract of expired Deoxycyclin, respectively, at the best concentration (300 PPM) and highest temperature (313.15 K) depending on IE% values.

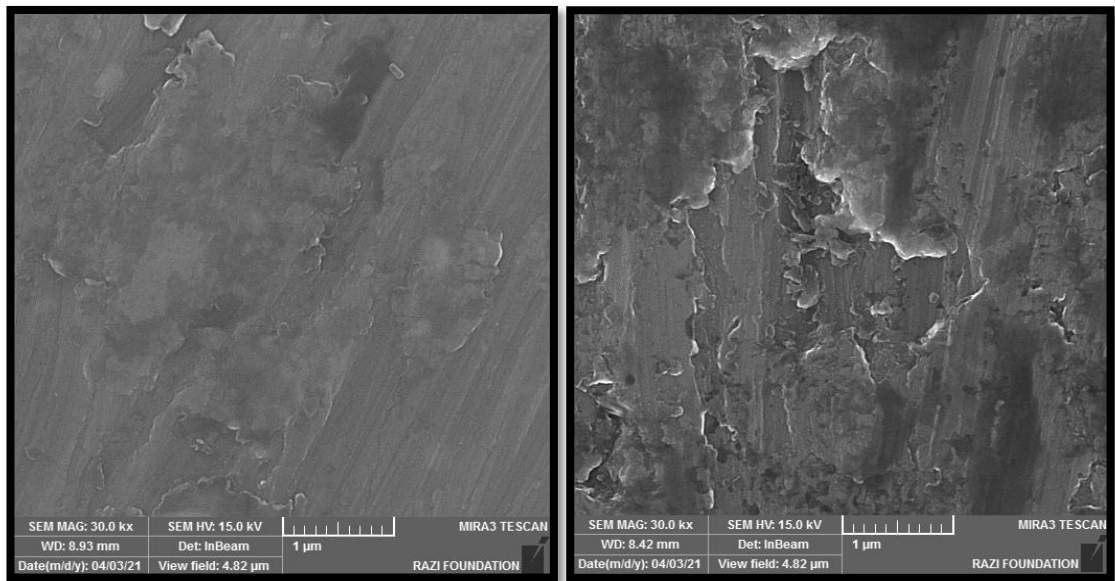
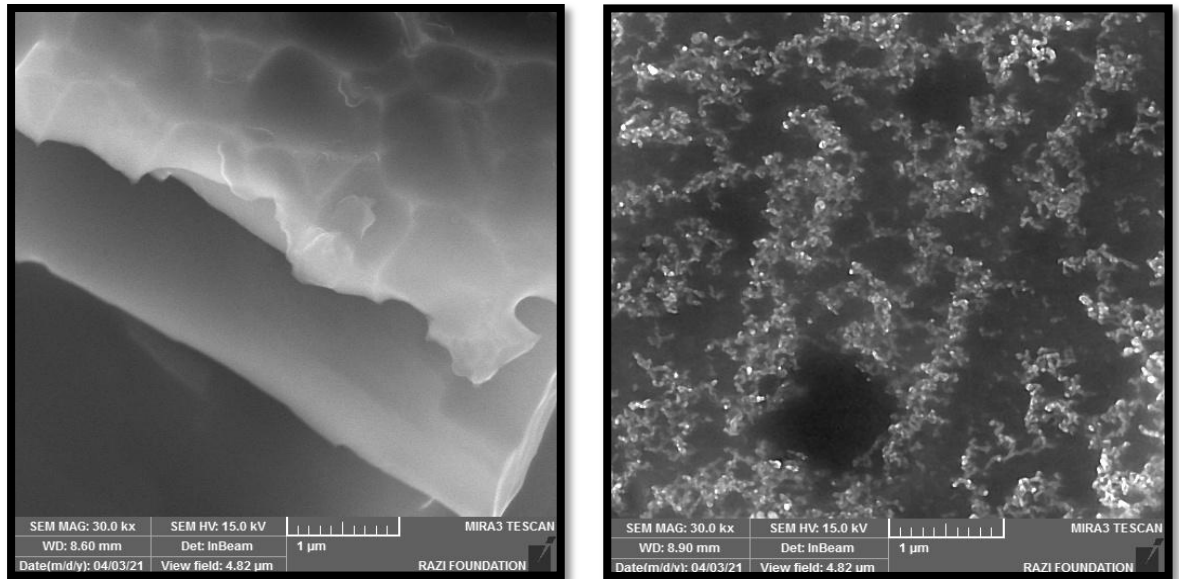
**A****B**

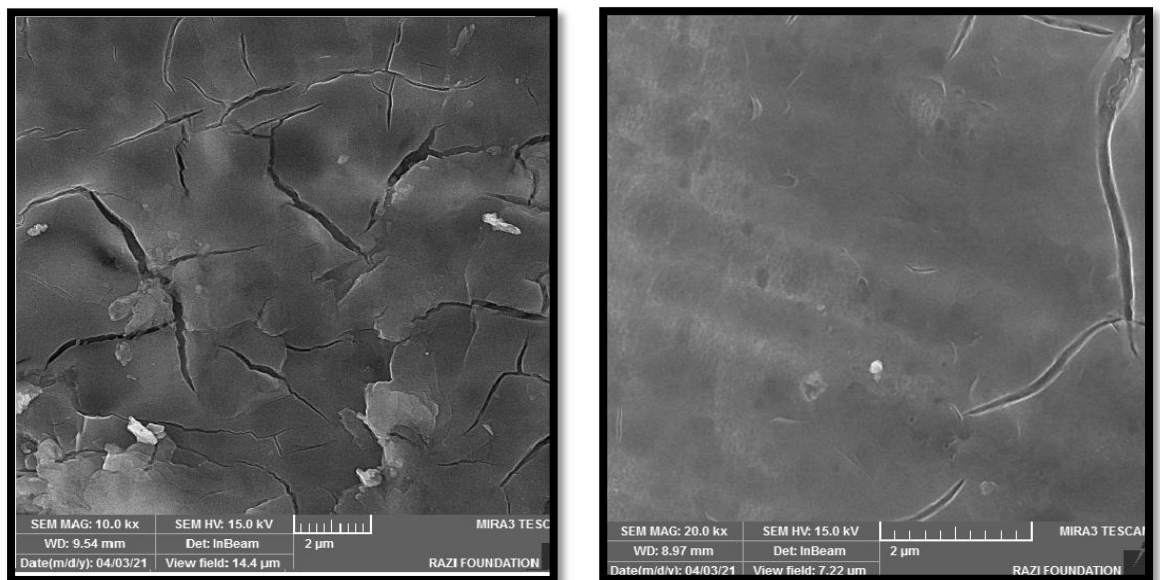
Fig.(4.57):SEM images of (a) Aluminum and (b) Aluminum alloy(AA2024-T3) surface before immersion in corrosion solution in order.



A

B

Fig.(4.58):SEM images of (a) Aluminum and(b) Aluminum alloy(AA2024-T3) surface after immersion in a corrosion solution(0.5M H₂SO₄) for (3h)at(313.15K).



A

B

Fig.(4.59): SEM images of (a) aluminum and (b) aluminum alloy(AA2024-T3) surface after immersion in presence of inhibitor (Aspirin) in order.

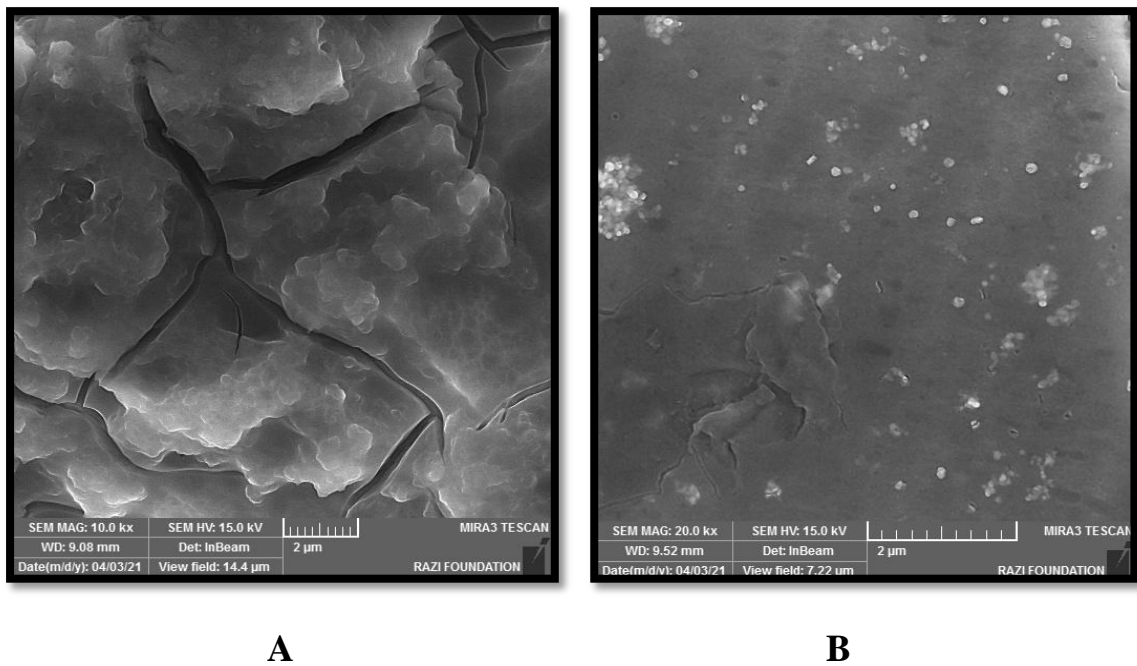


Fig.(4.60): SEM images (a) of aluminum and (b) aluminum alloy(AA2024-T3) surface after immersion in presence of inhibitor(Deoxycyclin).

4.7 Conclusions

1. Increasing the temperature lead the rate of corrosion aluminum and its alloy (AA2024-T3) in solution (0.5M H₂SO₄) increase Also.
2. Expired drugs (Aspirin and Deoxycyclin) with six concentrations (50,100,150,200,250 and 300ppm) were good inhibitors to protect aluminum and its alloy(AA2024-T3) from corrosion in (0.5MH₂SO₄) at (293.15,303.15 and 313.15 K).
3. With increasing concentrations of drug extracts and rising temperature, extract inhibition efficiency improves.
4. The adsorption of inhibitor molecules on the surface of aluminum and its alloys involves physical adsorption.
- 5.The adsorption of medicinal extract components on the surface of aluminum and its alloys, as well as the adsorption on the active sites, limit corrosion.
- 6.The Langmuir adsorption isotherm was used to test the adsorption isotherm as a way of better understanding the adsorption model.
- 7.The present thermodynamic parameters, together with the negative standard free energy values, it is the imply that the adsorption process is spontaneous and endothermic with a decrease in the entropy of the system.
8. The highest inhibition efficiency was obtained at (96.98%) at (40°C) and the inhibitory concentration of Aspirin (300ppm), and (93.25%) at (40°C) at the inhibitory concentration of Deoxycyclin (300ppm).
9. Image SEM confirm the corrosion of aluminum and its alloy (AA2024-T3) in(0.5MH₂SO₄) and its inhibition by the extract of expired Aspirin and Deoxycyclin, via adsorption of inhibitors on the surface of aluminum and its alloy (0.5MH₂SO₄) in acidic solution.

4.8 Future Studies

1. Using other drugs under the same conditions for example using medicines that are anti-bacterial.
2. Achieving the inhibition in other media (hydrochloric ac, nitric acidic and alkaline environments).
3. Study the inhibition by other techniques, such as polarization and hydrogen evolution method.
4. Repetition work on other metals such as low carbon steel, copper and zinc.

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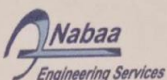
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Appendix

Appendix

Below is a picture of the results of the mineral sample examination of aluminum and its alloy (AA2024-T3).

ALNABAA CO.ENGINEERING SERVICES
Sample Testing of different Qualities



Chemical Results

Probe Nr. / sample ID : A1	Grundwerkstoff / material :	Al Pure Alloy
Kunde / customer : Miss Eman Saad	Abmessung / dimension :	Squre 30 x30 mm
Kom.-Nr. / commision : NA	Zusatzwerkstoff / filler metals :	NA
Labor Nr. / lab-no. : AL-NABAA LAB FOR ANALYSIS	Wärmebehandlung / heat treatment :	NA
PTQ-Nr. / PTQ-no. : NA	Schmelze-Nr. / heat-no. :	NA

Spektralanalyse Foundry-MASTER Werkstoff / grade :

	Al	Si	Fe	Cu	Mn	Mg	Zn	Cr
1	99,7	0,0469	0,181	0,0107	0,0069	0,0148	< 0,0150	< 0,0010
2	99,7	0,0335	0,135	0,0037	0,0079	0,0031	< 0,0150	< 0,0010
3	99,7	0,0367	0,162	0,0058	0,0062	0,0037	< 0,0150	< 0,0010
Ave	99,7	0,0390	0,159	0,0067	0,0070	0,0072	< 0,0150	< 0,0010

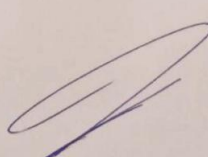
	Ni	Ti	Be	Ca	Pb	Sn	Sr	V
1	< 0,0050	< 0,0010	< 0,0010	0,0029	< 0,0050	< 0,0050	< 0,0010	0,0046
2	< 0,0050	< 0,0010	< 0,0010	0,0044	< 0,0050	< 0,0050	< 0,0010	0,0065
3	< 0,0050	< 0,0010	< 0,0010	0,0030	< 0,0050	< 0,0050	< 0,0010	0,0086
Ave	< 0,0050	< 0,0010	< 0,0010	0,0034	< 0,0050	< 0,0050	< 0,0010	0,0066

	Bi	Zr	B	Ga	Cd	Co	Ag	In
1	< 0,0100	< 0,0020	0,0016	0,0079	< 0,0030	< 0,0020	< 0,0010	< 0,0050
2	< 0,0100	< 0,0020	0,0043	0,0062	< 0,0030	< 0,0020	< 0,0010	< 0,0050
3	0,0236	< 0,0020	0,0048	0,0107	< 0,0030	< 0,0020	0,0020	< 0,0050
Ave	0,0111	< 0,0020	0,0036	0,0082	< 0,0030	< 0,0020	< 0,0010	< 0,0050


	Ce	Hf	La
1	< 0,0050	< 0,0050	< 0,0050
2	< 0,0050	< 0,0050	< 0,0050
3	< 0,0050	< 0,0050	< 0,0050
Ave	< 0,0050	< 0,0050	< 0,0050

Ort / town
Baghdad

Datum / date
25.10.2020



Prüfer / tester
Inspector:Jafar Abd



Sachverständiger / engineer
Eng. Khaldoon Ali

Appendix

ALNABAA CO. ENGINEERING SERVICES Sample Testing of different Qualities



Chemical Results

Probe Nr. / sample ID : A2 Grundwerkstoff / material : Al 20-24 Alloy
 Kunde / customer : Miss Eman Saad Abmessung / dimension : Rectangular 23x36 mm
 Kom.-Nr. / commission : NA Zusatzwerkstoff / filler metals : NA
 Labor Nr. / lab-no. : AL-NABAA LAB FOR ANALYSIS Wärmebehandlung / heat treatment : NA
 PTQ-Nr. / PTQ-no. : NA Schmelze-Nr. / heat-no. : NA

Spektralanalyse Foundry-MASTER Werkstoff / grade :

	Al	Si	Fe	Cu	Mn	Mg	Zn	Cr
1	93,7	0,0534	0,161	4,05	0,615	1,33	0,0578	0,0039
2	93,7	0,0484	0,132	3,84	0,673	1,46	0,0763	< 0,0010
3	93,7	0,0308	0,129	3,86	0,679	1,52	0,0807	< 0,0010
Ave	93,7	0,0442	0,140	3,92	0,655	1,44	0,0716	0,0013

	Ni	Ti	Be	Ca	Pb	Sn	Sr	V
1	< 0,0050	0,0168	< 0,0010	0,0016	< 0,0050	< 0,0050	< 0,0010	0,0067
2	< 0,0050	0,0176	< 0,0010	0,0019	< 0,0050	< 0,0050	< 0,0010	0,0045
3	< 0,0050	0,0190	< 0,0010	0,0026	< 0,0050	0,0089	< 0,0010	0,0032
Ave	< 0,0050	0,0178	< 0,0010	0,0020	< 0,0050	< 0,0050	< 0,0010	0,0048

	Bi	Zr	B	Ga	Cd	Co	Ag	In
1	< 0,0100	< 0,0020	0,0032	< 0,0010	< 0,0030	< 0,0020	< 0,0010	< 0,0050
2	< 0,0100	< 0,0020	0,0033	< 0,0010	< 0,0030	< 0,0020	0,0010	< 0,0050
3	< 0,0100	< 0,0020	0,0030	< 0,0010	< 0,0030	< 0,0020	< 0,0010	< 0,0050
Ave	< 0,0100	< 0,0020	0,0032	< 0,0010	< 0,0030	< 0,0020	< 0,0010	< 0,0050

	Ce	Hg	La
1	< 0,0050	< 0,0050	< 0,0050
2	< 0,0050	< 0,0050	< 0,0050
3	< 0,0050	< 0,0050	< 0,0050
Ave	< 0,0050	< 0,0050	< 0,0050



Ort / town Datum / date Prüfer / tester Sachverständiger / engineer
 Baghdad 25.10.2020 Inspector: Jafar Abd Eng. Khaldoon Ali

الخلاصة

التثبيت طريقة مهمة لتقليل من عملية التآكل في الألمنيوم وسبيكته (AA2024-T3) واختيار المثبط يكون مهم للغاية دون أي آثار جانبية.

في هذه الدراسة تم استخدام عقارين منتهين الصلاحية (Aspirin and Deoxycyclin) لاستخدامها كمثبطات لحماية الألمنيوم وسبيكته من التآكل في محلول $0.5M H_2SO_4$ عند درجات حرارية مختلفة ($20, 30, \text{and } 40^\circ C$)، ($293.15, 303.15 \text{ and } 313.15 K$)، وتم استخدام ستة تراكيز هي ($50, 100, 150, 200, 250, 300 \text{ ppm}$) من كل عقار.

تم التأكد من عملية التثبيت عن طريق اختبار التآكل (فقدان الوزن) وتم فحص الأسطح المثبطة وإجراء ديناميكية حرارية. وقد تم إجراء عملية استخلاص لاستعادة المادة الفعالة من الأدوية منتهية الصلاحية وتم إجراء بعض الفحوصات للمادة المستخلصة مثل اختبار التحليل الوصفي الطيفي بالأشعة تحت الحمراء (FTIR) للتأكد من وجود مجاميع فعالة في المستخلص وكذلك فحص كوموتوغرافيا السائل عالي الأداء (HPLC) لمعرفة نسبة المادة الفعالة في المستخلص.

أظهرت كفاءة التثبيت IE % نتائج جيدة للغاية في محلول $0.5M H_2SO_4$ حيث كانت القدرة التثبيطية بوجود (Aspirin) للألمنيوم النقي وسبيكته (AA2024-T3) هي ($96.98 \% \text{ and } 95.04\%$) على التوالي عند أعلى تركيز (300ppm) وأعلى درجة حرارة ($313.15 K$). اما بالنسبة لعقار (Deoxycyclin) فكانت نتائج التثبيت للألمنيوم النقي وسبيكته (AA2024-T3) هي ($93.25\% \text{ and } 87.95\%$) على التوالي عند نفس الظروف. وقد تم تطبيق ثلاثة ميكانيكيات لتفسير عملية أمتزاز مثبطات التآكل على سطح المعدن وقد وجد ان المواد المثبطة تتبع تفسير لانكماير Langmuir Adsorption Isotherm في ميكانيكية عملها أكثر من تفسير فريندلش Freundlich Adsorption Isotherm وتمكن Timken Adsorption Isotherm. وتم استخدام قيم ثابت الاتزان الناتجة من معادلة لانكماير لغرض حساب قيم الطاقة الحرة القياسية للأمتزاز (ΔG_{ads}° , Heat of Adsorption) لتحديد نوع الأمتزاز (فيزيائي أو كيميائي أو مشترك)، وفي هذه الدراسة كان الأمتزاز ينطوي على الأمتزاز الفيزيائي بالاعتماد على قيم طاقة التنشيط. وأكد فحص الأسطح المثبطة بواسطة فحص (SEM) أمتزاز جزيئات الدواء على السطح الألمنيوم وسبيكته (AA2024-T3) وكذلك بينت صور فحص AFM التي أظهرت الأسطح المثبطة اقل خشونة عن طريق تشكيل طبقة واقية جيدة من أمتزاز جزيئات المثبط على سطح المعدن لكونها المسؤولة عن تثبيت التآكل.



وزارة التعليم العالي والبحث العلمي

جامعة ديالى

كلية العلوم

قسم الكيمياء

**تشبيط تآكل الألمنيوم وسببته (AA2024-T3) في وسط حامضي باستخدام الأدوية
منتهية الصلاحية (الأسبرين والديوكسي سايكلين)**

رسالة مقدمة إلى

مجلس كلية العلوم / جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

إيمان سعد نصيف

بكالوريوس في علوم الكيمياء 2012

كلية العلوم – الجامعة المستنصرية

بإشراف

أ.د. أحمد نجم عبد