Corrosion behavior of steel (St 37-2) by using natural products as Inhibitors In Petroleum Medium

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Corrosion behavior of steel (St 37-2) by using natural products as Inhibitors In Petroleum Medium

A thesis Submitted

To

The Department of Materials engineering, University of Technology in a Partial Fulfillment of the Requirements for the Degree of Master in Science in Materials Engineering

By

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Abstract

The toxicity of number of organic and synthetic compounds have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. Therefore, an attempt is made to use natural products as plant extracts to investigate the corrosion inhibition of Steel (St 37-2) in petroleum medium (obtained from Iraqi refinery) using electrochemical studies. The inhibition was performed by four plant extracts including *Cinnamon* stems, *Ficuscarica*, *Sweet clover* and *Tobacco* leaves depending on presence of coumarins in these plants. Ethanolic extracts were characterized by UV-Visible, FTIR, and HPLC, these techniques confirm the presence of coumarins through the band of absorption at λ_{max}=274nm in UV-Visible spectrum. FTIR spectra of plant extracts confirm appear the stretching of C=O group near 1699.34cm^{-1}. Retention time of coumarins near 2.342 min confirms the presence of coumarins through HPLC analysis.

Galvanostatic test was conducted on steel 37-2 in petroleum medium in absence and presence of four plant extracts at four temperatures (323, 333, 343 and 353 K) by adding four concentrations of coumarin including 10, 40, 70 and 100 ppm and four concentrations of each extract including 1, 3, 5 and 7 mL/L. Generally, the presence of plant extracts shifts the corrosion potentials toward either active or noble direction suggesting that the selected extracts are mixed-type inhibitors. Corrosion current densities were decreased confirming the inhibitive action of natural products under inhibitors at experimental conditions. Inhibition efficiencies IE% confirm that the four extracts act as anticorrosion agents. 1 mL/L is the best concentrations of *cinnamon* extract, 3 mL/L is the best concentrations of *ficuscarica* and *sweet clover* extracts, while7 mL/L is the best concentration of *tobacco* extract, the best efficiencies ranged between 71 to 87%.

FTIR of film formed on steel surface in petroleum medium in the presence of natural inhibitors indicated the decreasing in the intensity of the important peaks in plants because of formation of Fe^{2+}—plant extract complexes due to adsorption of the inhibitor on steel surface. Adsorption isotherms are usually used to describe the adsorption process, and the straight lines of plotting C_{inh}/θ against C_{inh} indicate that the plant extracts obey Langmuir adsorption isotherm with regression coefficient close to unity and in the range $0.996 \geq R^2 \geq 0.917$ for four plant extracts. The values of equilibrium constant of the adsorption-desorption process K_{ads} are relatively small indicating that the interaction between the adsorbed extract molecules and steel surface is physically adsorbed, which has been confirmed through the small values of free energy (ΔG^o_{ads})indicating the electrostatic interactions between the charged molecules and the charged metal surface as physical adsorption. Other thermodynamic function are also calculated such as the

enthalpy of adsorption (ΔH^o_{ads})using Gibbs–Helmholtz equation and the entropy of adsorption (ΔS^o_{ads}), the values of these two functions were negative indicating the exothermic adsorption process and the reduction in disordering which takes place on going from reactants to the activated complex. The apparent activation energies (E_a^*) for the corrosion process in absence and presence of plant extracts were evaluated from Arrhenius equation, and the increasing of activation energies in the presence of plant extracts refers to the adsorption of the organic molecules which occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface. Since, we get activation energies equal to 46.41, 13.14, 24.01 and 14.65 kJ.mol^{-1} corresponding to 1mL/L *cinnamon*, 3mL/L *ficuscarica*, 3mL/L *sweet clover* and 7mL/L *tobacco* extract respectively compared with activation energy of uninhibited medium 10.57 kJ.mol^{-1}, the highest activation energy was in a petroleum medium containing *cinnamon* extract.

Optical microscopies show a noticeable reduction in corrosion sites and corrosion products on the corroded surface after adding the inhibitors as compared with the case of corrosion in the petroleum medium without inhibitor especially in the presence of the best concentration of each inhibitor.

Finally, Atomic Force Microscopy displays the surface topography of un-corroded metal surface (polished steel surface as reference sample) which is8.39 nm. The slight roughness observed on the polished steel surface is due to atmospheric corrosion. AFM of corroded metal surface displays few pits in the absence of the inhibitor immersed in petroleum medium equal to 44.7 nm. These data suggest that steel surface immersed in petroleum medium has a greater surface roughness than the polished metal surface, which shows that the unprotected steel surface is rougher. This is due to the corrosion of the steel in the petroleum medium. AFM of steel surface after immersion in petroleum medium containing 1mL/L of *Cinnamon* extract, 3mL/L *Ficuscarica* extract, 3mL/L *Sweet clover* extract and 7mL/L *Tobacco* extract, gave roughness values Ra of 0.631, 4.13, 1.1 and 5.89 nm respectively. These parameters confirm that the surface is smoother especially with *cinnamon*. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} − plant extract complex thereby inhibiting the corrosion of steel.

Chapter One

1-1 Corrosion of Steel

Corrosion has a major economic impact on the oil refining industry. The replacement cost of damaged equipment is a substantial capital expense. More importantly, due to the extremely hazardous nature of the fluids and gases processed in refineries, the safety and well being of both plant employees and the public are put at risk by corrosion. Catastrophic failures could result in severe damage to entire process units, neighboring communities, and the environment[1].

Of course, corrosion of metals used in construction of refining equipment is an expected phenomenon. Metals and alloys, unhindered by external influences, seek to return to their disordered, but natural, state. Outside influences, such as inhibitors, can effectively slow the rate at which this process occurs; even to the extent that rate is practically immeasurable. Mechanisms of refinery corrosion and methods of prevention have been studied by metallurgists, engineers, and chemists for many years and significant improvements have been accomplished. However, refining processes are complex, and corrosion problems require thorough analysis and systematic solutions.

Carbon steel has been widely employed as a construction material for pipe work in the oil and gas production such as down hole tubular, flow lines and transmission pipelines[2]. Steel, when exposed to an industrial atmosphere, reacts to form the reaction product of rust, of approximate composition $Fe_2O_3.H_2O$, which being loosely adherent does not form a protective barrier that isolates the metal from the environment; the reaction thus proceed sat an approximately linear rate until the metal is completely consumed [3].

Rust is nota determinate chemical substance but a complex material that changes continuously as it develops through the precipitation, evolution, and transformation of chemical species in the iron-oxygen-water system[4].

1-2 Corrosion Inhibition in Petroleum Industry

Corrosion phenomena are well-known in the petroleum industry and cause a maximum damage to oilfield equipment. Significant corrosion protection efforts have been made by petrochemical industries to prevent corrosion damage. The practice of corrosion prevention by adding substances which can significantly retard corrosion when added in small amounts is called inhibition. Inhibition is used internally with carbon steel pipes and vessels as an economic control alternative to stainless steels and alloys, and to coatings on non-metallic components. One unique advantage is that adding inhibitor can be implemented without disruption of a process.

The addition of an inhibitor (any reagent capable of converting an active corrosion process into a passive process) results in significant suppression of corrosion. Corrosion inhibitors are selected on the basis of solubility or dispersibility in the fluids which are to be inhibited. For instance, in a hydrocarbon system, a corrosion inhibitor soluble in hydrocarbon is used. Two phase systems composed of both hydrocarbons and water; utilize oil soluble water-dispersible inhibitors. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive industries [5].

1-3 Inhibitor Mechanisms

Neutralizers lessen the corrosivity of the environment by decreasing hydrogen ion (H^+) concentration, which reduces the concentration of the corrosive reactant. Neutralizers function by controlling the corrosion caused by acidic materials, such as hydrogen chloride, carbon dioxide (CO_2), sulfur dioxide (SO_2), carboxylic acids, and related compounds. These materials are found in small quantities in many process streams. However, because of such separation processes as distillation, one or more of these acidic species can concentrate in specific areas and cause severe corrosion. The area most susceptible to corrosion in the refinery is the heat exchanger, where the first drops of water condense (the initial condensate). An effective neutralizer will exhibit the same distillation/condensation properties as the acid it is designed to control.

Filming inhibitors function by strong adsorption, or chemisorption, and decrease attack by forming a barrier on the metal surface that resists penetration by corrosive. A filming inhibitor must possess a hydrocarbon portion attached to a strong polar group. The molecules are oriented on the metal surface, with the polar group adsorbed onto the metal surface and the hydrocarbon part extending away from the surface. The hydrocarbon end will attract the molecules of the process stream to provide an additional barrier to a potentially corrosive aqueous solution.

Scavengers perhaps the most widely used scavenger system is employed in boilers to remove oxygen from the feed water. Techniques such as steam stripping can be used to remove most of the dissolved oxygen from water; however, such methods become increasingly costly when the last traces of oxygen must be removed from the boiler feed water. Hydrazine and sodium sulfite are the two most widely used scavengers in boiler systems [6].

Miscellaneous inhibitors include such materials as scale inhibitors, which minimize deposition of scale on the metal surface, and biocides, which kill living organisms that can foul equipment.

1-4 Natural Products as Corrosion Inhibitor

A number of organic and synthetic compounds show a good anticorrosive activity, most of which are highly toxic to both human and environment. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In 1930, plant extracts dried stems, leaves, seeds and other plants were used in H_2SO_4 acid pickling baths. Animal proteins found in products of meat and milk industries were also used for retarding acid corrosion. The additives [7]used in acid, included *flour*, *bran*, *yeast*, *a mixture molasses* and vegetable oil, *starch* and hydrocarbons (tars and oils) are used as corrosion inhibitors.

1-5 Literature Survey

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of different metals and alloys which are present in contact with aggressive environments. Many studies have been carried out to find suitable compounds to use as corrosion inhibitors. Most of these compounds are synthetic chemicals which may be very expensive and hazardous to living creatures and environments. It is very important to choose cheap and safely handled compounds to be used as corrosion inhibitors. Some of translations and images of the most common plants are listed in the index of plants page (186).

Mumtaz in 2004 focused on development of naturally occurring substances as corrosion inhibitors. The available literature on corrosion inhibitors obtained from naturally occurring substances has been reviewed. The characteristic features of the investigations have been highlighted [8]. Shaheen et al. in 2007 described the investigations using aqueous extracts of leaves of medicinal plants as environmentally friendly corrosion inhibitors of mild steel in synthetic ocean water by weight loss method. These natural products were designed for application in Indian oil and gas industry and other environmentally sensitive platforms; exploiting their low toxicity-as medicinal plants and ease of biodegradation-as water soluble extracts. All the extracts exhibited low bioaccumulation and good corrosion protection [9].

Pandian et al. in 2008 used inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment and are an accepted practice. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency[10].

Buchweishaija and Mhinzi in 2008 investigated the inhibitive effect of the gum exudates from *Acacia seyal* on the corrosion of mild steel in drinking water using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results obtained show that gum exudates could serve as effective inhibitors for the corrosion of steel in drinking water network. The percentage inhibition increases with increasing the concentration of the gum at 30 ^{o}C. The percentage inhibitor efficiency above 95 % was attained at gum concentration of 400 ppm. The corrosion rates of steel and inhibition efficiencies of the gum exudates obtained from impedance and polarization measurements were in good agreement. Potentiodynamic polarization studies clearly reveal that the gum behaves predominantly as an anodic inhibitor. The study also shows that the inhibition efficiency is insignificantly affected by the temperature rise of the medium [11].

Boris et al. in 2009 evaluated several types of corrosion inhibitors. Active ingredients of those inhibitors included long chain amines, fatty amides, imidazolines, fatty acids and their salts. Inhibitors were tested at the concentration range of 50-200 ppm in the electrolyte andelectrolyte/hydrocarbon mixture in the presence of CO_2 and H_2S in static and dynamic conditions. Several evaluations were performed when corrosion inhibitors were added into electrolyte containing flow modifiers. The results, which include the corrosion and electrochemical testing data, show that generally tested corrosion inhibitors are effective in studied range of flow rates and compatible with flow modifiers [12].

Buchweishaija in 2009 investigated the inhibitive performance of gum exudates from *Acacia drepanolobium* and *Acacia senegal* from Tanzania, towards the corrosion of mild steel in fresh water. The experimental methods included potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies. The results indicate that gum exudates (Acacia drepanolobium and Acacia senegal) exhibit good inhibition characteristics to corrosion on mild steel under freshwater medium and the inhibition efficiency of up to 90.7% and 99.7% respectively was attainedat 30^{o}C. Furthermore, the studies have shown that the inhibition performance remained above90% on both Acacia exudates independent of the raise in temperature. Polarization measurements revealed that the investigated inhibitors are mixed type for mild steel corrosion in fresh water with significant reduction of anodic current densities. The results obtained in this work show that these gum exudates of Acacia senegal and Acacia drepanolobium can serve as effective green inhibitors for the corrosion of mild steel in fresh water systems [13].

Ambrish et al. in 2010 studied the inhibition of the corrosion of mild steel in hydrochloric acid solution by the fruits extract of Shahjan (*Moringaoleifera*), *Pipali* (*Piper longum*) and *Orange* (*Citrus aurantium*) using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization and linear polarization techniques. Inhibition was found to increase with increasing concentration of the extract. The effect of temperature, immersion time and acid concentration on the corrosion behavior of mild steel in 1 M HCl with addition of extract was also studied. The adsorption of the extract on the mild steel surface obeyed the Langmuir adsorption isotherm. Values of inhibition efficiency calculated from weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) are in good agreement. Polarization curves show that fruits extract behaves as a mixed-type inhibitor in hydrochloric acid. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated. The adsorbed film on mild steel surface containing fruits extract was also measured by Fourier transform infrared spectroscopy (FTIR). The results obtained show that the fruits extract could serve as effective inhibitor of the corrosion of mildsteel in hydrochloric acid media [14].

Loto et al. in 2011 investigated corrosion and plants extracts inhibitive protection of mild steel specimens immersed in 0.5 M hydrochloric acid at ambient temperature by gravimetric and metallographic methods. Extracts of *kola* plant and *tobacco* in different concentrations were used as ‘green’ inhibitors. The results obtained from the weight loss method, calculated corrosion rates, inhibitor efficiencies and the metallographic observations from metallurgical microscopy. Addition of different concentrations of the plants extracts gave considerable reduction in the weight loss and in the corrosion rate of the test samples. This apparent corrosion inhibition was associated with the protective film provided on the steel’s surface by the complex chemical constituents of the plants extracts. Effective protection of the mild steel was achieved more from the tobacco extract and also from the extract of kola leaf [15].

I.B. Obot et al.in 2011 studiedthe corrosion inhibitive effects of *Aningeriarobusta* extract onaluminium in 2 M HCl solution and the influence of potassium iodide additives on the inhibition efficiency using hydrogen evolution method at 30 and 60 ^{o}C .Inhibition efficiency was determined by comparing the corrosion rates in the absence and presence of additives. The trend of inhibition efficiency with temperature was used to propose the mechanism of inhibition. It was found that the Aningeriarobusta extract acts as an inhibitor for acid-induced corrosion of aluminium. Inhibition efficiency (%IE) of the extract increased with an increase in concentration of the *Aningeriarobusta* extract and with increase intemperature. On the other hand, inhibition efficiency (%IE) synergistically increased on addition of potassium iodide but decreased with increase in temperature. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the concentrations and temperatures[16].

Ameer and Fekry in 2011 studied corrosion inhibition of mild steel in H_3PO_4 containing chloride or sulphate ions using different electrochemical techniques. The corrosion and hydrogen evolution of mild steel alloy in 2M H_3PO_4 acid containing 0.5M NaCl can be effectively inhibited by addition of natural product compound of different concentrations. However, in 2M H_3PO_4 containing 0.5M Na_2SO_4 corrosion cannot be effectively inhibited. The results of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements confirm the synergistic effects which describe the increase in the effectiveness of a corrosion inhibitor in the presence of Cl^- ions in the corrosive medium. Polarization and EIS results are in good agreement with each other. The obtained results were confirmed by surface examination using scanning electron microscope[17].

Abu-Dalo et al. in 2012 studied the inhibition effect of exudates gum from *Acacia trees* (*Gum Acacia, GA*) on the corrosion of mild steel in acidic media by weight loss, hydrogen evolution, and electrochemical polarization methods; also, surface morphology was analyzed by Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) techniques. The results indicate that inhibitor efficiency (IE%) increases with increasing inhibitor concentration. The inhibitor efficiency (IE%) in hydrochloric acid is much more than those in sulfuric acid due to the synergistic effect. Electrochemical polarization studies showed that Gum Acacia acts as mixed type inhibitors. The results reveal that Gum Acacia provides a very good protection to mild steel against corrosion in acidic media. FTIR, SEM and XPS confirmed the existence of an absorbed protective film on the mild steel surface [18].

Shivakumar et al. in 2012 tested the leaf extracts of *centellaasiatica* (CE) as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4 by using gravimetric, polarization and electrochemical impedance spectroscopy (EIS) measurements. The data obtained from all the three methods are in good agreement with each other. Results indicate that leaf extracts of CE is a good green corrosion inhibitor for mild steel corrosion in 0.5 M H_2SO_4 solution. The inhibition efficiency was found to increase with increase in CE extracts concentration. A maximum inhibition efficiency of 95.08% was observed for 1200 ppm at 303K. Polarization measurements showed that the CE extracts act as mixed type of inhibitor. Temperature studies revealed a decrease in inhibition efficiency with increase in temperature which suggests physicsorption mechanism. The adsorption characteristics of CE extracts of on mild steel surface obey Langmuir isotherm.

Both kinetic and thermodynamics adsorption parameters were calculated and discussed, and SEM was used to analyze the surface adsorbed film [19].

Sangeetha et al. in 2012 used an aqueous extract of *asafoetida* as a corrosion inhibitor in controlling corrosion of carbon steel. The main constituent of this extract is umbelliferone. It has excellent inhibition efficiency (%IE) of 98% at Zn^{2+} (25 ppm) by the weight loss method. The protective film has been analyzed using Atomic Force Microscopic (AFM) and FTIR spectroscopic techniques. Protective film formed on the metal surface is confirmed by using electrochemical studies such as potentiodynamic polarization technique. Polarization study reveals that this system functions as mixed type of inhibitor [20].

M. Ramananda Singh and Gurmeet Singh in 2012 studied the inhibitory effect of extract of *Hibiscus cannabinus* on corrosion of mild steel in aqueous 0.5 M H_2SO_4 by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency increases on increasing in concentration of the extract and decreases with rise in temperature. Potentiodynamic Polarization measurement indicates that Hibiscus cannabinus acts as a mixed-type inhibitor. The increase in activation energy of corrosion process in the presence of the extract indicates that the extract retards the rate of corrosion of mild steel in 0.5 M H_2SO_4 solution. The nature of adsorption of the extract on mild steel surface is found to obey Langmuir adsorption isotherm. EIS measurement result is also correlated with the result of polarization. SEM study confirmed the adsorption of inhibitor molecules on mild steel surface [21].

Benali et al. in 2013 studied the corrosion and inhibition behavior of mild steel in sulfuric acid + 5% EtOH in the presence of tannin extract of *Chamaeropshumilis* plant and potassium iodide (KI) using the electrochemical methods. They found that the inhibition efficiency increases with Chamaeropshumilis extract concentration. The addition of potassium iodide to LF-Ch extract in solution increased the inhibition efficiency of this latter. A synergistic effect was observed between KI and extract with optimum of concentration of 100 mg/L Chamaeropshumilis extract + 0.025% potassium iodide. Adsorption of extract alone or in combination with potassium iodide on the metal surface obeyed the Langmuir adsorption isotherm and thermodynamic calculations reveal that the adsorption of inhibitor is of chemical nature. The adsorption of Chamaeropshumilis extract on the mild steel in aggressive medium leads to the formation of a protective film which grows in thickness and effectiveness with increasing exposure time [22].

Fouda et al. in 2013 studied the inhibiting effect of some quinazoline derivatives on the corrosion of carbon steel in 2M HCl by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) techniques. The results show that the inhibition efficiency increases with increasing the inhibitor concentration, while it decreases with increasing the temperature. The adsorption of quinazoline derivatives on the carbon steel surface obeys Temkin adsorption isotherm. Some thermodynamic parameters were calculated and discussed. Polarization curves show that quinazoline derivatives are mixed-type inhibitors but the cathode is more polarized than the anode. The results obtained from chemical and electrochemical techniques are in good agreement [23].

Rajam et al. in 2013 evaluated the inhibition efficiency (%IE) of an aqueous extract of *garlic* in controlling corrosion of carbon steel in well water in the absence and presence of Zn^{2+} by weight loss method. The formulation consisting of 2 mL of garlic extract and 25 ppm Zn^{2+} offers 70% inhibition efficiency to carbon steel immersed in well water. Polarization study reveals that this formulation controls the anodic reaction predominantly. FTIR spectra reveal that the protective film consists of Fe^{2+}–allicin complex and $Zn(OH)_2$ [24].

Iloamaeka et al. in 2013 studied the use of leaves extract of *Emilia sonchifolia* and *Vitexdoniana* as corrosion inhibitors of mild steel in 2.5M HCl medium using gasometric method at 30°C and 60°C. The result obtained show that inhibition efficiency of Emilia sonchifolia leaves extract on the surface of the mild steel was 60.38% at 30°C and 53.13% at 60°C while that of Vitexdoniana leave extract was 68.22% at 30°C and 54.98% at 60°C. Adsorption of Emilia sonchifolia leaves extract on the surface of the mild steel follows Langmuir, Tempkin and Freunlich adsorption isotherm while adsorption of Vitexdonania leaves extract on the surface of the mild steel obeyed Langmuir and Tempkin adsorption isotherm. Physical adsorption is proposed from the E_a, ΔH and ΔG calculated [25].

1-6 Aim of The Work

The object of the work is to direct attention to inhibitive properties of some natural compounds as the extracts of some common plants through:

1- Select Cinnamon stems and Ficuscarica, Sweet clover and Tobacco leaves to be used as corrosion inhibitors for steel(St 37-2) in petroleum medium with four concentrations of each extract include 1, 3, 5 and 7 mL/L.

2- Characterize ethanolic extracts with different techniques.

3- The study is extended to investigate the effect of temperature on the inhibition efficiency at 323, 333, 343 and 353K.

4- Calculate adsorption parameters to identify the adsorption type.

5- Evaluate some thermodynamic parameters and activation energies.

Chapter Two

2-1 Introduction

This chapter includes overview about corrosion in refinery and the methods will be used to corrosion control especially using inhibitors. Also it is contains the types and mechanism of common inhibitors and why it should be use natural inhibitors instead of chemical compounds inhibitors.

2-2 Corrosion in the Refinery

Refineries comprise a number of individual technology based processing facilities with varying objectives, and integrated as necessary to meet product targets. The types, size, number and flow sequence of a specific refinery(i.e., refinery configuration) will vary depending on crude oil quality, required product mix and quality, and environmental, safety, economic or other constraints [26].

The major refinery processing steps or technologies can be categorized into six functional areas:

1- Separation,

2- Conversion or cracking,

3- Combination,

4- Reformulation,

5- Treating and other specialty or support operations.

Table (2-1) lists various refinery units and process streams that are often susceptible to corrosion and effectively treated with process additives. Discussion of a few of the processes helps in the understanding of corrosion inhibitors that are used in a typical refinery environment. Corrosion inhibitors are also applied in numerous water treatment processes within a refinery, such as in cooling water and steam generation systems [27].

The refining of crude oil into useful fuels and other products produces a number of corrosive environments. The most common is an aqueous environment containing inorganic and organic acids. However, other aqueous corrosion processes in the refinery can also be due to the presence of oxygen, bisulfide, cyanide, microbiological growth, or other corrosion-inducing species. Nonaqueous corrosive environments also exist in refining processes. Foremost corrosion is caused by organic acids at high temperatures, commonly termed *naphthenic acid corrosion.* Sulfide and other sulfur species contained in the hydrocarbon stream can also be corrosive at high concentrations and at high temperatures.

Corrosion most commonly occurs as the water condenses in the distillation process and the corrosive species dissolves into the condensed water. This is often termed initial condensate corrosion [27].

Table (2-1): Typical applications for refinery corrosion inhibitors [27].

Unit	Process stream	Type of corrosion	Filming inhibitor	Neutralizer
Crude distillation	Crude tower overhead	Pitting	X	X
	Vacuum tower overhead		X	X
	Steam-jet vacuum system		X	…
Fluid catalytic cracking, coker	Fractionator overhead	Erosion Corrosion	X	…
	Compressed wet gas		X	…
	Absorber lean oil		X	…
	Debutanizer overhead		X	…
	Depropanizer overhead		X	X
Hydroprocessing	Stabilizer overheads	stress corrosion cracking (SCC)	X	X
	Effluent		X	…
Alkylation (H_2SO_4)	Deisobutanizer tower overhead	Pitting	X	X
	Debutanizer overhead		X	X
	Depropanizer overhead		X	X
Alkylation (HF)	Debutanizer overhead	Pitting	X	…
	Depropanizer overhead		X	…
Catalytic reformer	Light ends stripper overhead	crevice corrosion	X	X
	Pre-fractionator overhead		X	X
	Effluent		X	X
	Debutanizer overhead		X	X
	Depropanizer overhead		X	X
	Hydrogen stripper feed		X	…
	Hydrogen scrubber water		…	X

Generally, water distills along with the naphtha fraction into the condensing section of the system, commonly referred to as the “overhead.” In a few process units, a portion of the water may condense inthe column and be removed along with a heavier hydrocarbon fraction.

Water washing of the overhead piping and exchangers is a common practice in many refineries. Water washing is intended to reduce corrosion primarily by dilution of the corrosive species and removal of deposits [28].

Catalytic and thermal cracking units such as fluid catalytic cracking units (FCCU) and delayed coking units typically require corrosion- inhibition applications. In these units, considerable amounts of hydrocarbon andinorganic gases are produced. Ammonia, hydrogen sulfide, hydrogen cyanide, and other gases formed in the cracking process are removed overhead in fractionation columns along with significant quantities of water.

Typically, this leads to a corrosive environment of sulfide-type corrosion in an alkaline aqueous environment [29].

Nonaqueous corrosion is also a concern in many areas of a refinery. High temperatures encountered in processing units have led to corrosion by naphthenic acids and sulfur-containing species [30].

Hydroprocessing (hydrodesulfurization, hydrocracking, hydrofining) units operate under high pressures and temperatures and are susceptible to various corrosion mechanisms [31,32].

2-3 Corrosion Prevention Measures

Corrosion prevention aims at removing or reducing the effect of one or more of the conditions leading to corrosion using the following measures:

1- Selecting a material that does not corrode in the actual environment.

2- Changing the environment, e.g. removing the oxygen or adding anticorrosion chemicals (inhibitors).

3- Using a design that will avoid corrosion, e.g. preventing the collection of water so that the metal surface can be kept dry.

4- Changing the potential, most often by making the metal more negative and thus counteracting the natural tendency of the positive metal ions to be transferred from the metal to the environment.

5- Applying coatings to the metal surface, usually in order to make a barrier between the metal and the corrosive environment [32].

2-4 Corrosion Inhibitors

Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [33-36]. In acid media, nitrogen-based materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors. In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors. Inhibitors decrease or prevent the reaction of the metal with the media [36].

Theses inhibitors reduce the corrosion rate by(i)adsorption of ions/molecules onto metal surface,(ii)increasing or decreasing the anodic and/or cathodic reaction,(iii)decreasing the diffusion rate for reactants to the surface of the metal,(iv)decreasing the electrical resistance of the metal surface, and (v)inhibitors that are often easy to apply and have in situ application advantage.

Several factors including cost and amount, easy availability and most important safety to environment and its species need to be considered when choosing an inhibitor [36].

Adsorption depends mainly on the charge and nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent and other ionic species, temperature of corrosion reaction and on the electrochemical potential at solution – interface. Adsorption of inhibitor involves the formation of two types of interaction responsible for bonding of inhibitor to a metal surface. The first one (physical adsorption) is weak undirected interaction and is due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of metal. The potential of zero charge plays an important role in the electrostatic adsorption process.

The second type of interaction (adsorption) occurs when directed forces govern the interaction between the adsorbate and adsorbent. Chemical adsorption involves charge sharing or charge transfer from adsorbates to the metal surface atoms in order to form a coordinate type of bond. Chemical adsorption has a free energy of adsorption and activation energy higher than physical adsorption and, hence, usually it is irreversible[36].

2-5 Examples of Corrosion Inhibitors

Inhibitors used in practice are seldom pure substances, but are usually mixtures that may be byproducts, for example, of some industrial chemical processes for which the active constituent isnot known. Commercial inhibitor packages may contain, in addition to the active ingredients forinhibition, other chemicals, including surfactants, deemulsifiers, carriers (e.g., solvents) and biocides [36].

The active ingredients of organic inhibitors invariably contain one or more functional groups containing one or more hetero atoms, N, O, S, P, or Se (selenium), through which the inhibitors anchor onto the metal surface. These groups are attached to a parent chain (backbone), which increases the ability of the inhibitor molecule to cover a large surface area. Common repeating units of the parent chain are methyl and phenylgroups. The backbone may contain additional molecules, or substituent groups, to enhance the electronic bonding strength of the anchoring group on the metal and/or to enhance the surface coverage [36].

2-5-1 Inhibitors Containing the Oxygen Atom

Benzoic acid and substituted benzoic acids are widely used as corrosion inhibitors. Adsorption and inhibitor efficiencies of benzoic acids depend on the nature of the substituents. Electrondonating substituents increase inhibition by increasing the electron density of the anchoring group(-COOH group); on the other hand, electron-withdrawing, substituents decrease inhibitionby decreasing the electron density [37].

2-5-2 Inhibitors Containing the Nitrogen Atom

Benzotriazole (BTA) and its derivatives are effective inhibitors for many metals, especially copper, in a variety of conditions. At low concentrations, BTA is adsorbed slightly on the surface. Atsufficiently high solution concentrations, bulk precipitation of the complex on the surface occurs, inhibiting corrosion. Formation of this complex is a slow process and, as a result, the inhibitor efficiency of BTA increases with time [38].

2-5-3 Inhibitors Containing the Sulfur Atom

Thioureaand its derivatives are used as corrosion inhibitors for a variety of metals. They are nontoxic and are not an environmental hazard. The variation in the inhibitor efficiencies of various derivatives of thiourea depends on the molecular weight. By using lower concentrations of large molecules, higher inhibitor efficiencies can be obtained [39].

2-5-4 Electronically Conducting Polymers

In situ polymerisation of heterocyclic compounds, such as pyrrole and thiophene and aniline, produces homogeneous, adhesive films on the metal surface. These films are electronically conducting and have the advantage of tolerance to microdefects and minor scratches.

Conductivity can be up to 100 S/cm and can be varied depending on the extent of oxidation, from semiconductor to metal. Because of these properties, the films repassivate any exposed areas of metal where there are defects in the passive film. Conducting polymers are now used as inhibitors for metal corrosion [40].

2-5-5 Coordination Complexes

A variety of chelants provide either corrosion inhibition or corrosion acceleration, depending on the structure and functional groups. The chelants displaying high surface activity and low solubility in solution are effective corrosion inhibitors. If they do not have these characteristics, they stimulate corrosion. The 8-hydroxyquinoline molecule satisfies the structural requirements for surface chelation, but formation of a nonadherent film is a distinct disadvantage (Fig. 2-1). On the other hand, pyrocatechols (Fig. 2-2), forming adherent chelants on the metal surface, are effective inhibitors. Inhibition efficiency can be increased by decreasing the solubility through alkylation (increase in chain length) [41].

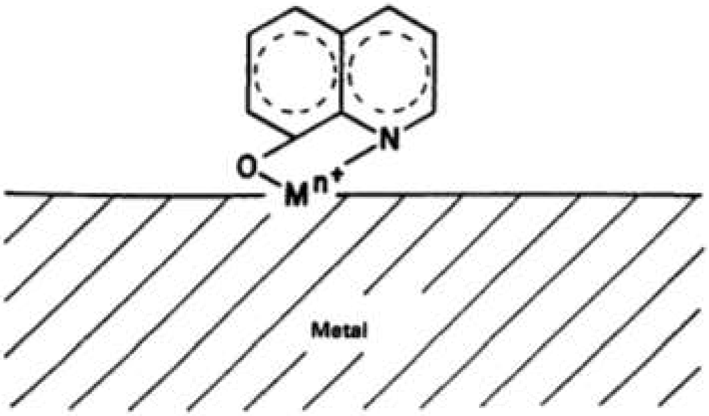


Fig.(2-1): 8-Hydroxyquinoline surface chelation (Stable chelate complex is formed,but is solu orrosion inhibition)[41].

Fig. (2-2): Pyrocatecholsforms insoluble chelate complex with the metal,efficient corrosion inhibitor [41].

2-6 Organic Inhibitors

Organic inhibitors generally have heteroatoms. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence O < N < S < P.

A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group. When an H atom attached to the C in the ring is replaced by a substituent group ($–NH_2$, $–NO_2$, –CHO, or –COOH) it improves inhibition [11]. The electron density in the metal at the point of attachment changes resulting in the retardation of the cathodic or anodic reactions. Electrons are consumed at the cathode and are furnished at the anode. Some factors that contribute to the action of inhibitors are:

(i)Chain length,
(ii)Size of the molecule,
(iii)Bonding, aromatic/conjugate,
(iv)Strength of bonding to the substrate,
(v)Cross-linking ability,
(vi)Solubility in the environment.

The role of inhibitors is to form a barrier of one or several molecular layers against acid attack. This protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. Sulphur and/or nitrogen-containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors [11].

Thiophene, hydrazine derivatives offer special affinity to inhibit corrosion of metals in acid solutions. Inorganic substances such as phosphates, chromates, dichromates, silicates, borates, tungstates, molybdates, and arsenates have been found effective as inhibitors of metal corrosion. Pyrrole and derivatives are believed to exhibit good protection against corrosion in acidic media. These inhibitors have also found useful application in the formulation of primers and anticorrosive coatings, but a major disadvantage is their toxicity and as such their use has come under severe criticism [11].

Inhibitors are often added in industrial processes to secure metal dissolution from acid solutions. Standard anti corrosion coatings developed till date passively prevent the interaction of corrosion species and the metal.

The known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, nontoxic and ecofriendly processes have now urged researchers to focus on the use of natural products. Increasingly, there is a need to develop sophisticated new generation coatings for improved performance, especially in view of Cr VI being banned and labeled as a carcinogen. The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having heteroatoms in their aromatic or long-chain carbon system. However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors [11].

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment.

Recently, studies on the use of some drugs as corrosion inhibitors have been reported by some researchers [42,43]. Most of these drugs are heterocyclic compounds and were found to be environmentally friendly, hence, they have great potentials of competing with plant extracts.

Efforts to find naturally organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified. Several reports are available on the various natural products used as green inhibitors as shown in Tables (2-2) and (2-3). Low-grade gram *flour*,*natural honey*, *onion*, *potato*, *gelatin*, plant roots, leaves, seeds, and flowers gums have been reported as good inhibitors. However, most of them have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (millimolar solutions) [43].

Table (2-2): Green inhibitors used for corrosion inhibition of steel [43].

Sl. no.	Metal	Inhibitor source	Active ingredient
(1)	Steel	Tamarind	
(2)	Steel	Tea leaves	
(3)	Steel	Pomegranate juice and peels	
(4)	Steel	Emblicaofficinalis	
(5)	Steel	Terminaliabellerica	
(6)	Steel	Eucalyptus oil	Monomtrene 1,8-cineole
(7)		Rosemary	
(8)	C-steel, Ni, Zn	Lawsonia extract (Henna)	Lawsone (2-hydroxy-1, 4-napthoquinone resin and tannin, coumarine, Gallic, acid, and sterols)
(9)	Mild steel	Gum exudates	Hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and nonreducing sugars
(10)	Mild steel	Musa sapientum peels (Banana peels)	
(11)	Carbon steel	Natural amino acids—alanine, glycine, and leucine	
(12)	Steel	Natural amino acids	
(13)	Mild steel	Garcinia kola seed	Primary and secondary amines Unsaturated fatty acids and biflavnone
(14)	Steel	Auforpioturkiale	Protein hydrolysis
(15)	Steel	Azydractaindica	Protein hydrolysis
(16)	Steel	Aloe leaves	
(17)	Steel	Mango/orange peels	
(18)	Steel	Hibiscus sabdariffa (Calyx extract) in 1 M H_2SO_4 and 2 M HCl solutions, Stock 10–50%	Molecular protonated organic species in the extract. Ascorbic acid, amino acids, flavonoids, Pigments and carotene

Table (2-3): Green Inhibitors used for corrosion inhibition of aluminum, aluminum alloys, and other metals and alloys [43].

Sl. no.	Metal	Inhibitor source	Active ingredient
(1)	Al	$CeCl_3$ and mercaptobenzothiazole (MBT)	
(2)	Al, steel	Aqueous extract of tobacco plant and its parts	
(3)	Al	Vanillin	
(4)	Al-Mg alloy	Aqueous extract of Rosmarin usofficinalis—Neutral phenol subfraction of the aqueous extract	Catechin
(5)	Al	Sulphates/molybdates and dichromates as passivators	
(6)	Al	Amino and polyamino acids—aspartic acid	
(7)	Al	Pyridine and its selected derivatives (symmetric collidine and 2,5-dibrompyridine)	
(8)	Al	Citric acid	
(9)	Fe, Al	Benzoic acid	
(10)	Al	Rutin and quercetin	
(11)	Al		
(12)	Al	Polybutadieonic acid	
(13)	Al and Zn	Saccharides—mannose and fructose	
(14)	Al, Al-6061 and Al-Cu	Neutral solutions using sulphates, molybdates, and dichromates	
(15)	Al	Vernoniaamygdalina (Bitter leaf)	
(16)	Al	Prosopis—cineraria (khejari)	
(17)	Al	Tannin beetroot	
(18)	Al	Saponin	
(19)	Al	Acacia concianna	
(20)	Al and Zn	Saccharides	
(21)	Al	Opuntia (modified stems cladodes)	
(22)	Al-Mg alloy	Rosmarinusofficinalis	
(23)	Zn	Metal chelates of citric acid	
(24)	Zn	Onion juice	S-containing acids (glutamyl peptides) S-(1-propenyl) L-cysteine sulfoxide, and S-2-carboxypropyl glutathione
(25)	Sn	Natural honey (acacia chestnut)	

2-7 Renewable Resources in Corrosion Resistance

Corrosion generally occurs when mild steel comes in contact with oxygen and water. The presence of anodic and cathodic sites on steel surface and their reaction with water and oxygen transforms metal (iron) atom to ions, finally through a series of chemical reactions, hydrated ferric oxide forms (iron) rust. Another anaerobic (without oxygen) corrosion, micro-biological corrosion may occur if conditions favor the growth and multiplication of microbes, i.e., bacteria and fungi [44]. The steps to reduce, combator completely eradicate corrosion require the elimination or suppression of such chemical reactions by the use of corrosion inhibitors, pigments, cathodic protection, coatings and others, providing barrier properties, adhesion between substrate and coatings, corrosion reducing activity and overall an active anticorrosion effect. The effectiveness of coatings as potential anticorrosion agents depends upon their type, the type of substrate, corrodents to which these are exposed and others. For efficient service, coatings should bear very good adhesion to the substrate resulting in low permeability (to oxygen, water) and good “wet” adhesion [44].

The renewable resources or natural biopolymers such as *lignin*, *starch*, cellulose, *cashewnut shell liquid*, *rice husk*, sucrose, caffeic acid, lactic acid, tannic acid, furan, proteins, glycerol, and vegetable oils contain hydroxyls, aldehydes, ketones, carboxyls, double bonds, ester, ether and other functional groups. These functional groups impart good adhesion and corrosion resistance performance to the substrate. Also, the performance an be further improved by chemical transformations, use of modifiers (inorganic reinforcements, nanomaterials) and other methods[44].

2-8 Plant Extracts

Plants naturally synthesize chemical compounds in defence against fungi, insects and herbivorous mammals. Some of these compounds or phytochemicals such as alkaloids, terpenoids, flavonoids, polyphenols and glycosides prove beneficial to humans in uniquemanner for the treatment of several diseases. These compounds are identical in structure and function to conventional drugs. Extracts from parts of plants such as roots, stems, and leaves also contain such extraordinary phytochemicals that are used as pesticides, antimicrobials, drugs and herbal medicines. Plant extracts are excessively used as corrosion inhibitors[45]. An interesting review in this context is compiled by Raja and Sethuraman, 2008[46]. Plant extracts serve as anticorrosion agents to various metals such as mild steel, copper, zinc, tin, nickel, aluminium and its alloys[47-49].

2-9 Extraction Methods

Medicinal plants have been the mainstay of traditional herbal medicine amongst ruraldwellers worldwide since antiquity to date. The therapeutic use of plants certainly goes back to the Sumerian and the Akkadian civilizations in about the third millenium BC. Over the years they have assumed a very central stage in modern civilization as natural source of chemotherapy as well as amongst scientist in search for alternative sources of drugs. About3.4 billion people in the developing world depend on plant-based traditional medicines [50].

The study of natural products on the other hand is called phytochemistry. Phytochemicals have been isolated and characterized from fruits such as grapes and apples, vegetables such as broccoli and onion, spices such as turmeric, beverages such as green tea and red wine, as well as many other sources. Some extraction methods for phytochemicals are listed below:

1- Solvent extraction

Various solvents have been used to extract different phytoconstituents. The plant parts are dried immediately either in an artificial environment at low temperature (50-60°C) or dried preferably in shade so as to bring down the initial large moisture content to enable its prolonged storage life. The dried berries are pulverised by mechanical grinders and the oil is removed by solvent extraction. The defatted material is then extracted in a soxhlet apparatus or by soaking in water or alcohol (95% v/v). The resulting alcoholic extract is filtered, concentrated in vacuum or by evaporation, treated with HCl (12N) and refluxed for at least six hours. This can then be concentrated and used to determine the presence of phytoconstituents. Generally, the saponins do have high molecular weight and hence their isolation in the purest form poses some practical difficulties. The plant parts (tubers, roots, stems, leave etc)are washed sliced and extracted with hot water or ethanol (95% v/v) for several hours. The resulting extract is filtered, concentrated *in vacuum* and the desired constituent is precipitated with ether. Exhaustive extraction is usually carried out with different solvents of increasing polarity in order to extract as much as possible the most active components with highest biological activity [50].

2- Supercritical fluid extraction (SFE)

This is the most technologically advanced extraction system. Super Critical Fluid Extraction (SFE) involves use of gases, usually CO_2, and compressing the min to a dense liquid. This liquid is then pumped through a cylinder containing the material to be extracted. From there, the extract-laden liquid is pumped into a separation chamber where the extract is separated from the gas and the gas is recovered for re-use [50].

3- Microwave-Assisted extraction

Microwave-Assisted extraction applications include the extraction of high-value compounds from natural sources including phytonutrients, nutraceutical and functional food ingredients and pharmaceutical actives from biomass. Compared to conventional solvent extraction methods, Microwave-Assisted extraction technology offers some combination of the following advantages: **1.** Improved products, increased purity of crude extracts, improved stability of marker compounds, possibility to use less toxic solvents; **2.**Reduced processing costs, increased recovery and purity of marker compounds, very fast extraction rates, reduced energy and solvent usage. With microwave-derived extraction as opposed to diffusion, very fast extraction rates and greater solvent flexibility can be achieved [50].

4- Solid phase extraction

This involves sorption of solutes from a liquid medium onto a solid adsorbent by the same mechanisms by which molecules are retained on chromatographic stationary phases. These adsorbents, like chromatographic media, come in the form of beads or resins that can be used in column or in batch form [50].

5- Chromatographic fingerprinting and marker compound analysis

Chromatographic fingerprint of an Herbal Medicine (HM) is a chromatographic pattern of the extract of some common chemical components of pharmacologically active and or chemical characteristics. This chromatographic profile should be featured by the fundamental attributions of “integrity” and “fuzziness” or “sameness” and “differences” so as to chemically represent the HM investigated [50].

6- Advances in chromatographic techniques

These techniques include:

a- Liquid chromatography

1- Preparative high performance liquid chromatography

2- Liquid Chromatography- Mass Spectroscopy (LC-MS)

3- Liquid Chromatography- Nuclear Magnetic Resonance (LC-NMR)

b- Gas chromatography

1- Gas Chromatography Fourier Transform Infrared spectrometry

2- Gas Chromatography-Mass Spectroscopy

C- Supercritical Fluid Chromatography (SFC) [50]

2-10 Coumarin

Coumarin is widely distributed in the plant kingdom, but for commercial use has been mostly produced synthetically for many years. It is used as an odour-enhancer to achieve a long-lasting effect when combined with natural essential oils such as *lavender*, *citrus*, *rosemary* and *oak moss*. Coumarin is used in tobacco to enhance its natural aroma. It is also applied in large quantities to give pleasant aromas to household materials and industrial products or to mask unpleasant odours. Coumarins act as antioxidants, enzyme inhibitors, and precursors of toxic substances. Coumarins have long been recognized to possess anti-inflammatory, anti-oxidant, anti-allergic, hepatoprotective, anti-thrombotic, anti-viral and anti-carcinogenic activities [11].

In industry, coumarin is used in rubber and plastic materials and in paints and sprays to neutralize unpleasant odours. In other fields, coumarin has a significant use in the electroplating industry, mostly in the automotive area, to provide high polished quality to chrome-plated steel, but this use is declining [11].

Coumarin was subsequently identified in a large number of plants belonging to many different families. Its better known occurrences are in *sweet clover*, *sweet* *woodruff (Asperulaodorata)*, *vanilla leaf (Trilisaodoratissima)*, *vanilla beans (Vanilla planifolia),cassia (Cinnamorumcassia)*, *lavender (Lavendulaofficinalis)* and *balsam of Peru (Myroxylonpereirae)*. Coumarin has been isolated from legumes, orchids, grasses and citrus fruits. It is found at particularly high levels in some essential oils, such as cinnamon leaf and bark oil, cassia leaf oil and lavender oil [11]. Coumarin has the chemical structure which is contained in some products as shown in Fig. (2-3).

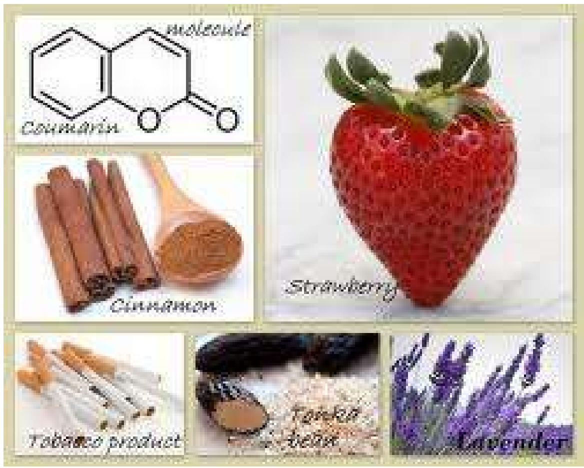


Fig. (2-3): Chemical structure of coumarin and some products containing it.

In addition to biological activities it is used as additives to food and cosmetics and optical brightening agents. Fig. (2-4) illustrates the applications of coumarins [51].

2-11 Cinnamon

Cinnamon is a spice obtained from the inner bark of several trees from the genus Cinnamomum that is used in both sweet and savoury foods. Cinnamon is the name for perhaps a dozen species of trees and the commercial spice products that some of them produce. All are members of the genus Cinnamomum in the family Lauraceae. Only a few of them are grown commercially for spice.

The flavour of cinnamon is due to an aromatic essential oil that makes up 0.5% to 1% of its composition. This essential oil is prepared by roughly pounding the bark, macerating it in sea water, and then quickly distilling the whole. It is of a golden-yellow colour, with the characteristic odour of cinnamon and a very hot aromatic taste. The pungent taste and scent come from cinnamic aldehyde or cinnamaldehyde (about 90% of the essential oil from the bark) and, by reaction with oxygen as it ages, it darkens in colour and forms resinous compounds. Other chemical components of the essential oil include ethyl cinnamate, eugenol (found mostly in the leaves), beta-caryophyllene, linalool, and methyl chavicol.

Cinnamon is used in traditional medicine, and several studies have tested chemicals extracted from cinnamon for various possible medicinal effects.In an experiment testing the effects of various plants used in traditional Indian medicine, an extract of Cinnamomum cassia had an effect on HIV-1. Another study found that eugenol, a chemical found in cinnamon essential oils, and in other plants, inhibited the replication of the virus causing herpes in vitro.

Two studies [52,53] have shown that including cinnamon and cinnamon extract in the diet may help type 2 diabetics to control blood glucose levels. One study used C. cassia, while the other study used an extract (made from “Chinese Cinnamomum aromaticum”, an older name for C. cassia).

Pharmacological experiments suggest that dietary cinnamon-derived cinnamic aldehyde (cinnamaldehyde) activates the Nrf2- (nuclear factor “erthroid-derived2”,like 2 also known NFE2L2) dependent antioxidant response in human epithelial colon cells and may therefore represent an experimental chemopreventive dietary factor targeting colorectal carcinogenesis.

Recent research documents antimelanoma activity of cinnamic aldehyde observed in cell culture and a mouse model of human melanoma.

A 2011 study isolated a substance cinnamon extract in the cinnamon plant that inhibits development of Alzheimer's disease in mice. cinnamon extract, an extract of cinnamon bark, seems to treat a mouse model of Alzheimer's disease[54].Fig. (2-4) shows the cinnamon sticks and bark.

Cinnamon sticks *Cinnamon bark*

Fig. (2-4): Cinnamon

2-12 FicusCarica

The common fig (Ficuscarica) is a species of plant in the genus Ficus. It is the source of the fruit also called the fig, and as such is an important crop in those areas where it is grown commercially. Native to the Middle East and western Asia, it has been sought out and cultivated by man since ancient times, and is now widely grown throughout the temperate world, both for its fruit and as an ornamental plant. Figs are among the richest plant sources of calcium and fiber. They have smaller amounts of many other nutrients. Figs have a laxative effect and contain many antioxidants.

They are a good source of flavonoids and polyphenols including gallic acid, chlorogenic acid, syringic acid, and rutin. In one study, a 40-gram portion of dried figs (two medium size figs) produced a significant increase in plasma antioxidant capacity [55].Fig. (2-5) shows the ficuscarica tree.

Fig. (2-5): The ficuscarica tree.

2-13 Sweet Clovers

Melilotusalbus (Bokhara clover, honey clover, tree clover, sweet clover, white-flowered sweet clover, white sweet clover, white melilot), is a legume sometimes grown for forage. White sweet clover is a major source of nectar for an apiary. Its characteristic sweet odour, intensified by drying, is derived from coumarin. It has been used in herbal medicine. It contains dicoumarol, which is an anticoagulant. It also has high sugar content. White sweet clover can grow up to 2 meters in height and can produce abundant amounts of seeds that readily float and disperse in water. Figure (2-6) shows the white sweet clover[56].

Fig. (2-6): White sweet clover.

2-14 Tobacco

Tobacco is a plant within the genus Nicotiana of the Solanaceae (nightshade) family. There are more than 70 species of tobacco. Products manufactured from dried tobacco leaves include cigars, cigarettes, snuff, pipe tobacco, chewing tobacco and flavored shisha tobacco.

Further uses of tobacco are in plant bioengineering and as ornamentals, and chemical components of tobacco are used in some pesticides and medications.

The addictive alkaloid nicotine is popularly considered the most characteristic constituent of tobacco but the harmful effects of tobacco consumption can also derive from the thousands of different compounds generated in the smoke, including polycyclic aromatic hydrocarbons (such as benzopyrene),formaldehyde, cadmium, nickel, arsenic, tobacco-specific nitrosamines (TSNAs), phenols, and many others. Tobacco also contains beta-carboline alkaloids which inhibit monoamine oxidase.

Many plants contain nicotine, a powerful neurotoxin to insects. However, tobaccos contain a higher concentration of nicotine than most other plants, which are often poisonous to humans and other animals. Fig. (2-7) shows the tobacco and nicotine[57].

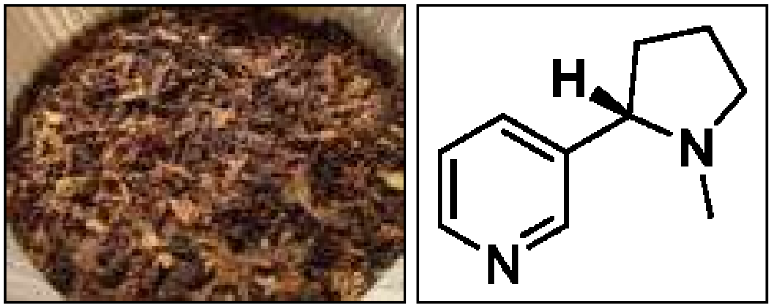


Fig. (2-7): Tobacco leaves and Nicotine.

Chapter Three

3-1 Introduction

The experimental section of this research can be divided to the following steps:

1- Selection of natural materials to extract the green inhibitors from depending on the presence of coumarin in these materials. These materials include *cinnamon*, *ficus carica*, *sweet clover* and *tobacco*.

2-Characterization of the plant extracts by UV-Visible, FTIR and HPLC techniques.

3-Steel (St 37-2) was prepared for corrosion test in petroleum medium which was obtained from Light Naptha Unit in Al-Durra Refinery.

4- Four different concentrations of each natural inhibitor were selected to study inhibition including 1, 3, 5 and 7 mL/L at four temperatures (323, 333, 343 and 353) K.

5- Corrosion inhibition was studied using electrochemical measurements supported by FTIR, optical microscopy and AFM.

3-2 Materials and Chemicals

3-2-1 Carbon Steel

Steel(St 37-2)obtained from Iraqi refinery was used in this work to test the corrosion and inhibition in petroleum medium. The chemical composition of steel alloy is shown in Table (3-1) obtained by SPECTRO MAX$_X$in State Company for

Inspection and Engineering Rehabilitation(SIER)–Ministry of Industry and Minerals, as shown in Fig.(3-1).

Table (3-1): Chemical composition of steel.

Element	*C*	*Si*	*Mn*	*P*	*S*	*Cr*	*Mo*	*Ni*	*Cu*	*Al*	*Co*	*Fe*
Wt%	0.121	0.22	0.44	0.014	0.016	0.041	0.002	0.022	0.055	0.02	0.002	Bal.

Fig.(3-1): SPECTRO MAX$_X$.

3-2-2 Petroleum Medium

Petroleum medium which was used in this work was obtained from Al-Durra Refinery at Light Naphtha Unit. Some inspections were achieved to analyze this medium include Total Dissolved Salts (TDS) and electrical conductivity of Petroleum medium were measured using TDS & EC Meter technique and Type of device WTW SERIES Lab cond 720,(Fig. 3-2),at Materials Eng. Department-Corrosion Lab and were equal to 296 mg/L, 300 µS/cm respectively. pH was equal 5.25 measured by using pH Meter, type WTW SERIES, as shown in Fig. (3-3), while Total weight percent of Carbon, Hydrogen, Nitrogen and Sulfur equal to 48.67%, 8.73%, 0.13% and 0.71% respectively by using CHNS/O Elements

Analyzer (Type of device PERKIN ELEMAR, Series II 2400) at Ministry of Science and Technology-Materials Researches Directory as shown in Fig. (3-4).

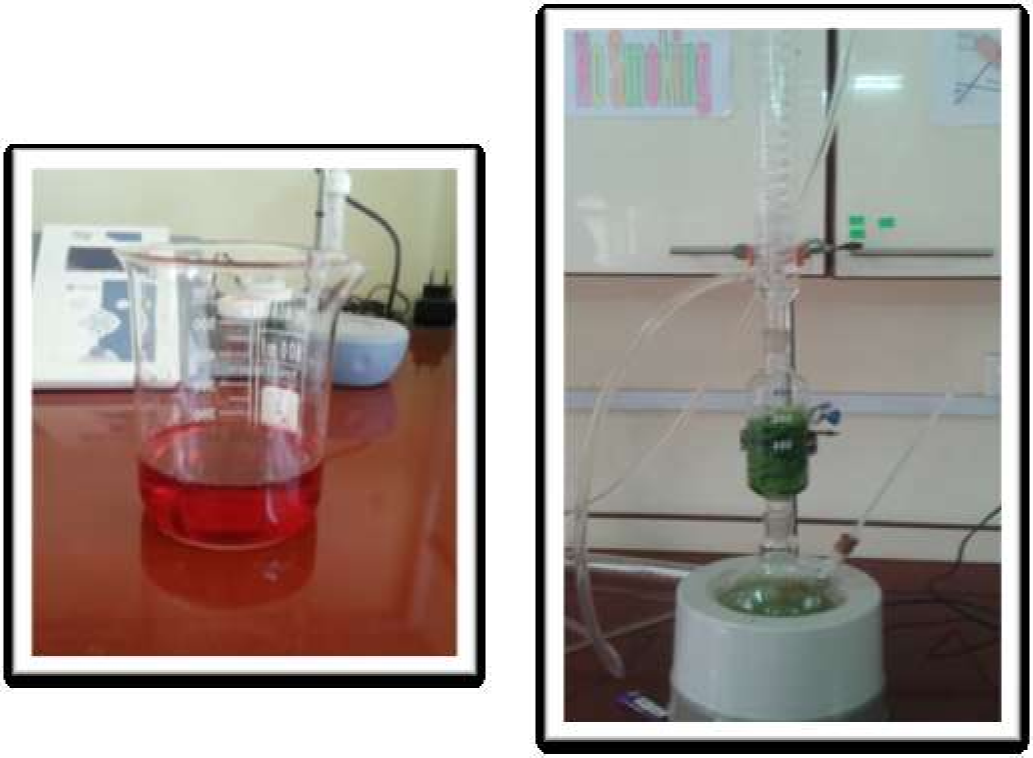
Fig.(3-2):TDS& EC Meter.

Fig.(3-3): pH meter.

Fig.(3-4):CHNS\O Elements Analyzer.

3-3 Extraction of Natural Products

Four plants were selected to extract the green inhibitors they include *cinnamon* stems, *ficuscarica*, *sweet clover* and *tobacco* leaves. These plants were washed with distilled water and draied. Stems and leaves of plants were ground and then soaked in one liter of bidistilled water and left overnight. An ethanolic extract of plants was prepared by grinding 5gand dissolving in200 mL ethanol (99.9%)[20], the suspending impurities were filtered, making up to 100 mL by evaporation, Fig.(3-5a), while hot extraction by system shown in Fig. (3-5b) produced oil extract. Four concentrations of each extract were used as inhibitor in present work they include 1, 3, 5 and 7 mL/L. FTIR spectra were recorded to ground stems and leaves using FTIR-8400s Shimadzu as shown in Fig. (3-6).



(a) (b)

Fig.(3-5): Equipments of extraction.

Many techniques were used to identify the presence of coumarins in plant extracts such as UV-Visible obtained from Japan Shimadzu 8400 S as shown in Fig. (3-7). High performance liquid chromatography HPLC also used to identify the extracts obtained from Japan, model RESERVOR TRAY, column dimension 25x4.6 cm, 75methanol/25water as solvent, wavelength (λ) =280 nm and flow rate = 1.8 m/min as shown in Fig. (3-8).

Fig.(3-6): Fourier Transform Infrared Spectrophotometer.

Fig.(3-7):UV- Visible spectroscopy.

Fig.(3-8):HPLC instrument.

3-4 Specimen Preparation

To study electrochemicaltest, steel(St 37-2) specimens were prepared according to the following steps**:**

1. Cutting

Surface condition of specimen is considered as an important factor in corrosion resistance; hence, it is necessary to prepare uniform surface. Square specimens in size (1.5cm×1.5cm×4mm) were obtained as a final specimen shape.

2. Mounting

The cut up specimen was mounted by cold mounting using pyrax polymars to isolate all sides but one and a hole was made on one side for electrical connection as shown in Fig.(3-9), theobtained conductive surface area equals to(2.25cm^2).

3. Grinding and Polishing

The mounted specimens were then ground with SiC emery papers in sequence of300, 400, 600, 800, 1200 and 2000grit to get flat and scratch-free surface by Grinder and Polisher MoPao 160E shown in Fig.(3-10).

The specimens were polished using polish cloth and alpha alumina 0.5µm and 1µm,and then washed with distilled water. The polished specimens were degreased with acetone, dried and kept in a desiccators over a silica gel pad and used for electrochemical investigation.

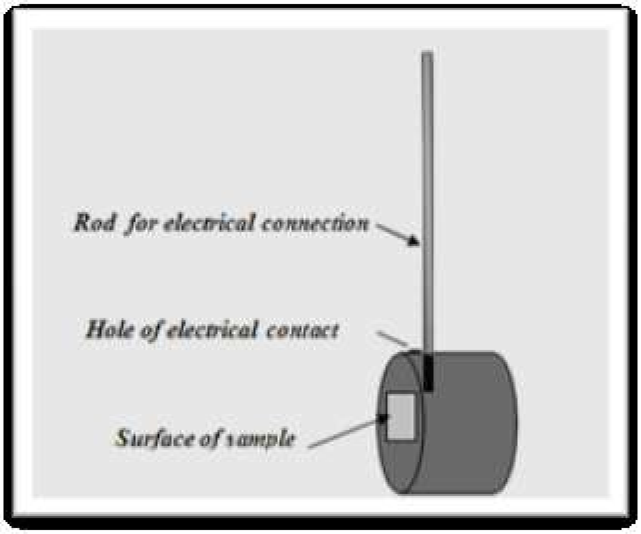


Fig.(3-9): A schematic diagram of working electrode.

Fig.(3-10): Grinder and Polisher apparatus.

3-5 Corrosion Tests

3-5-1 Open Circuit Potential

The samples were immersed in the electrolyte and the potential was monitored as a function of time with respect to SCE, until the potential reached a stable value. WINKING M Lab potentiostat (Fig. 3-11) was used to carry out OCP test which was recorded during immersion working electrode in electrolyte (petroleum medium with and without inhibitors) for 600sec. versus saturated calomel electrode (SCE).

3-5-2 Polarization Test

Measurements were carried out by changing the electrode current automatically from -15 to +15 mA at scan rate of 1 mA.sec^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion parameters [58,59] with special software as shown in Fig. (3-12).

Fig. (3-11): Potentiostat/ Galvanostat instrument.

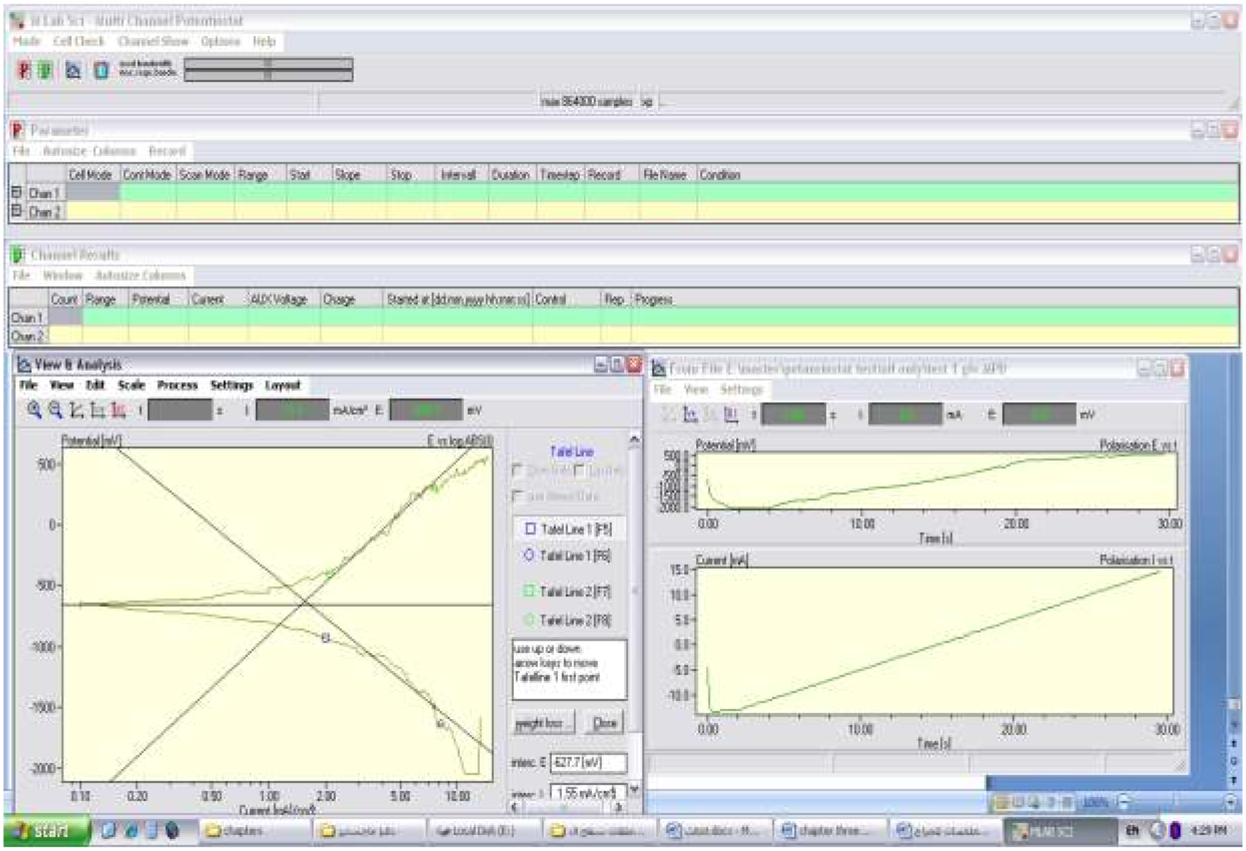


Fig.(3-12): Processing for entered data to estimate corrosion parameter.

3-5-3 Corrosion Cell and Electrodes

A corrosion cell consists of the following:

1- Working Electrode

Mounted steel (St 37-2) specimens were used as working electrode with surface area equal to 2.25 cm^2. The potential scan started after the specimen were immersed in the test medium after 600 sec.

2- Reference Electrode

The reference electrode used in this study was saturated calomel electrode (SCE); by using a Luggin capillary with salt-bridge connection to the reference electrode, the bridge probe tip was fixed about (1 mm) from the surface of the working electrode that was exposed to the solution to minimize the experimental error. The auxiliary electrodes, the Luggin bridge and other components were placed in the test cell in the usual procedures, the tip of the Luggin capillary was placed as close as physically possible to the surface of the working electrode in the corrosion cell, all system can be seen in Fig. (3-13).

3- Auxiliary Electrode

The auxiliary electrode used in the electrochemical cell was platinum type seated directly opposite to the working electrode.

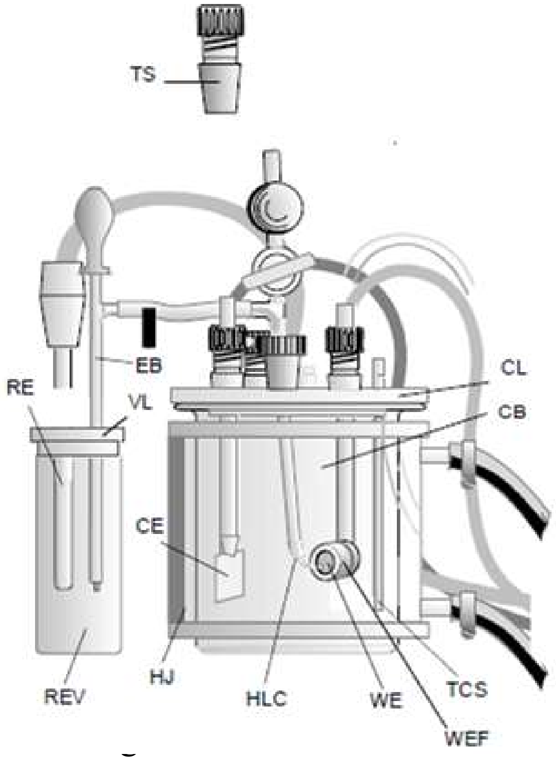


Fig.(3-13):A sc osion testing.

Standard corrosion cell: cell beaker 0.5 liter or 1 liter (CB), PTFE cell lid (CL), separate reference electrode vessel (REV) with PTFE lid (VL), four pipe- and electrode sockets (TS), Haber-Luggin capillary (HLC), platinum counter electrode (CE), working electrode fixtures (WEF) electrolyte bridge with frit (EB), heating jacket (HJ), reference electrode (RE).

3-6 FTIR Spectra

The film formed on the metal surface (after immersion in the petroleum medium for 15 days) was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded by FTIR-8400SShimadzuFourier Transform Infrared Spectrophotometer. The result was discussed to confirm the inhibitive action of natural products.

3-7 Optical Microscopy Examination

Steel(St 37-2) specimens were examined before and after corrosion and inhibition experiments at a magnification of200x and 500xby NIKON, ECLIPSE-ME600 Optical Microscope shown in Fig. (3-14).

Fig.(3-14): Optical Microscopy.

3-8 Atomic Force Microscopy (AFM)

The AFM imaging of insulated surface structure at atomic resolution consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface [60]. Atomic force microscopy was carried out to display the topography of surface and measure the roughness. The origin of AFM instrument is Angstrom Advanced Inc.USA, model AA3000 220V as shown in Fig. (3-15).

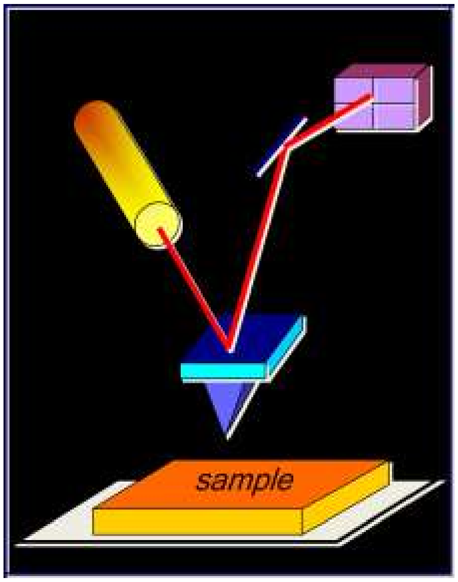


Fig.(3-15): Block diagram of atomic force microscope [60].

Chapter Four

4-1 Introduction

This chapter involves review to characterize the extracted materials by UV-visible and FTIR spectroscopy in addition to HPLC test. This chapter also includes review of corrosion behavior of steel (St 37-2), which is used as tanks and drums in Iraqi refinery, in petroleum medium in the absence and presence of some extracted natural materials at four temperatures (323, 333, 343, and 353) K through potential – time measurements and Tafel plots. FTIR, Optical microscopy and AFM supported the results of electrochemical studies.

4-2 Coumarin and Natural Products

Fig. (4-1) illustrates the UV-visible spectrum of pure coumarin in ethanol in addition to spectra of plant extracts which include Cinnamon, Ficuscarica, Sweet clover and Tobacco, this figure confirms the presence of coumarins in selected plants. Table (4-1) shows the wave lengths of the important peaks in coumarin and extracts.

Coumarins exhibit two types of absorption bands which result from overlapping of benzene and pyrone rings with some molecular orbitals and then give significant spectra in the range of 250 – 330 nm[61-63]. The first band is medium intensity and occurs between 300 and 330 nm at a maximum wave length λ_{max}=311nm corresponding to C =C−C=O group, while the second band has high intensity and occurs in the range 250 – 300 nm at λ_{max}=274nm corresponding to absorption of benzene ring. Another spectrum may appear in the wave number range of 200 – 240 nm due to unsaturated lactone spectra. Appendix A includes the UV-Visible spectrum of each extract with its details.

Fig. (4-2) shows the FTIR spectrum of coumarin with the most important peaks. It can be seen from this figure the stretching of CH—aromatic at 3059.20 and 2999.41 cm^{-1}, stretching of C=O group appearsat1699.34 cm^{-1}. Weak band of C—C stretch occurs at 1558.54 cm^{-1} in addition to stretching of C—O at 1103.32 cm^{-1}. Many peaks appear in the range of 600 to 1000 cm^{-1} due to =CH vinyl and =CH aromatic bending out of plane[64,65].

Figs. (4-3) to (4-6) illustrate the FTIR spectra of selected plants which confirm the presence of coumarin in these materials, also the FTIR spectra can be seen in Appendix B.

High-performance liquid chromatography (HPLC)has become a mainstay of natural product isolation and purification. The various modes available (e.g., normal-phase, reversed-phase, size exclusion, and ion-exchange) to date can be used to purify most classes of natural products.

Fig. (4-7) shows the HPLC test for pure coumarin under tested conditions in ethanol, this figure shows that coumarin appears at retention time of 2.342 min. Fig. (4-8) indicates the HPLC of plant extracts which confirms the presence of coumarin or its derivatives in these extracts. In HPLC test of cinnamon extract can show the peak of retention time of coumarin appears at 2.433 min, while in Ficus carica, Sweet clover and Tobacco extracts the retention time was 2.672, 2.331 and 2.439 min respectively. In addition to presence other components in these extracts[66,67].

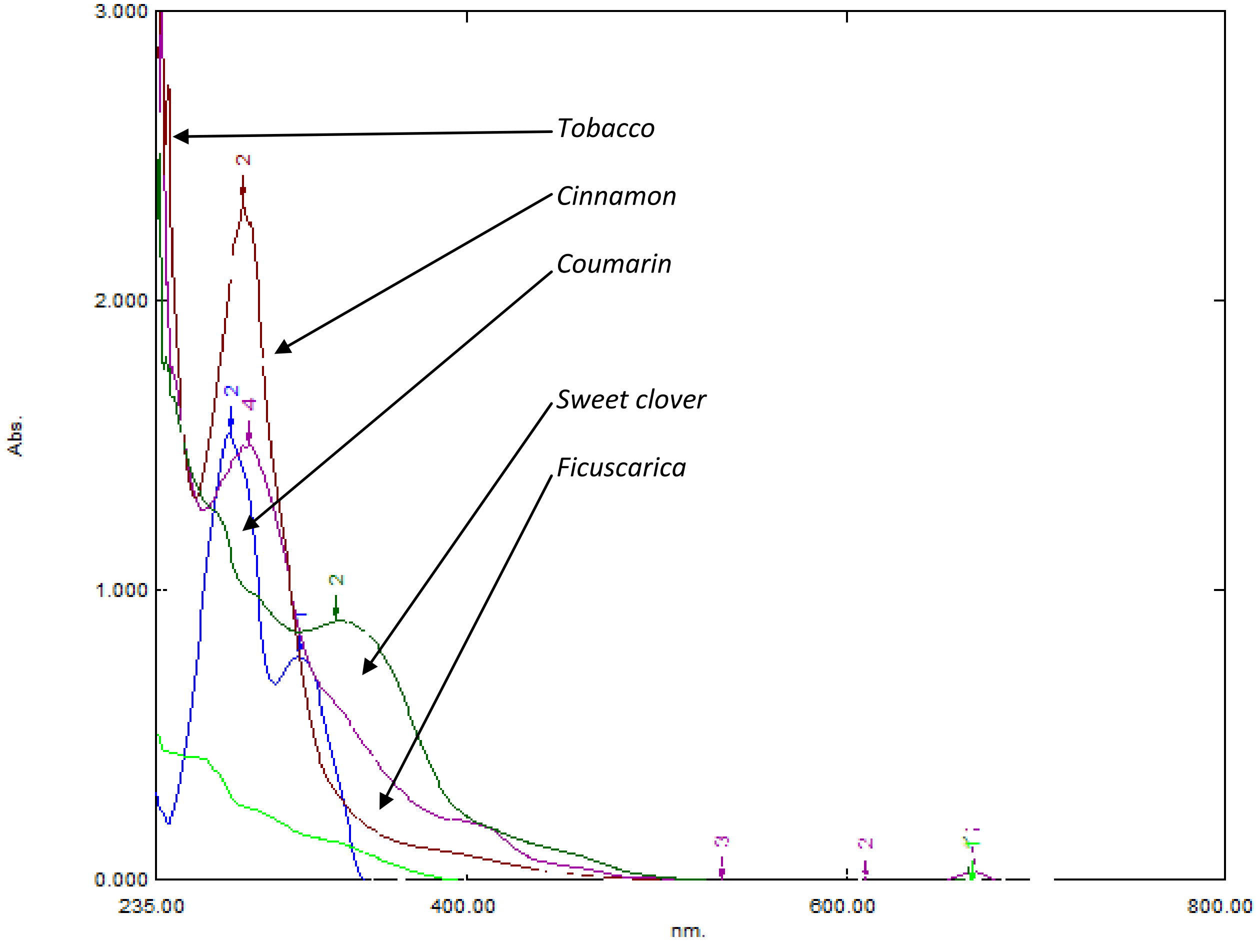


Fig. (4-1): UV-Visible spectrum for coumarin and plant extracts.

Table (4-1): Wave lengths and absorbance in UV-Visible spectra for coumarin and extracts.

Material	Peak	Wave length/ nm	Abs.	Color
Coumarin	1	311	0.769	Blue
	2	274	1.546	
Cinnamon	2	281	2.350	Brown
Ficuscarica	4	284	1.500	Violet
Sweet clover	2	330	0.895	Green
Tobacco	3	216	3.860	Pink

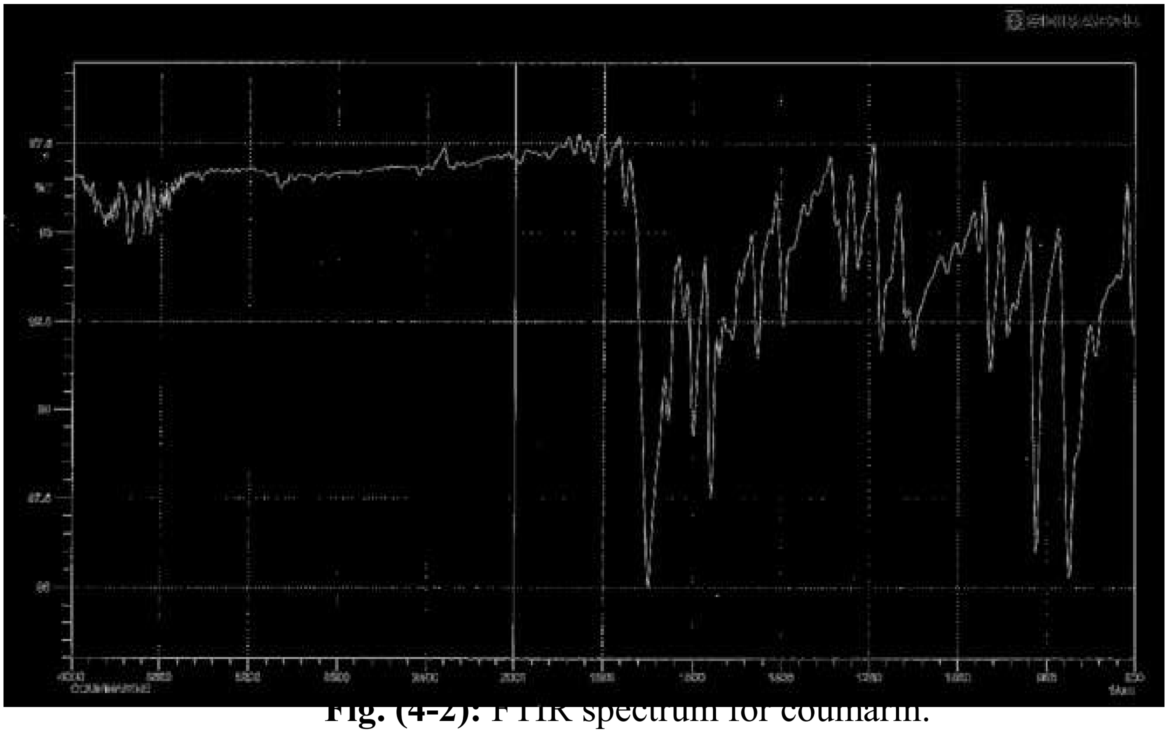


Fig. (4-2): FTIR spectrum for coumarin.

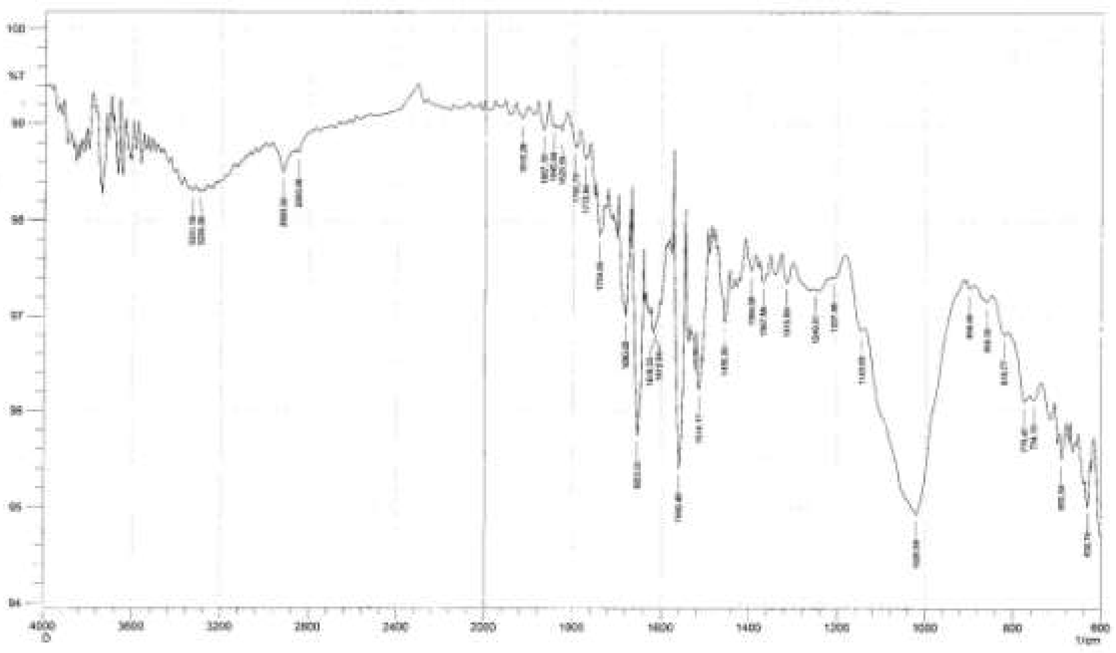


Fig. (4-3): FTIR spectrum for cinnamon stems.

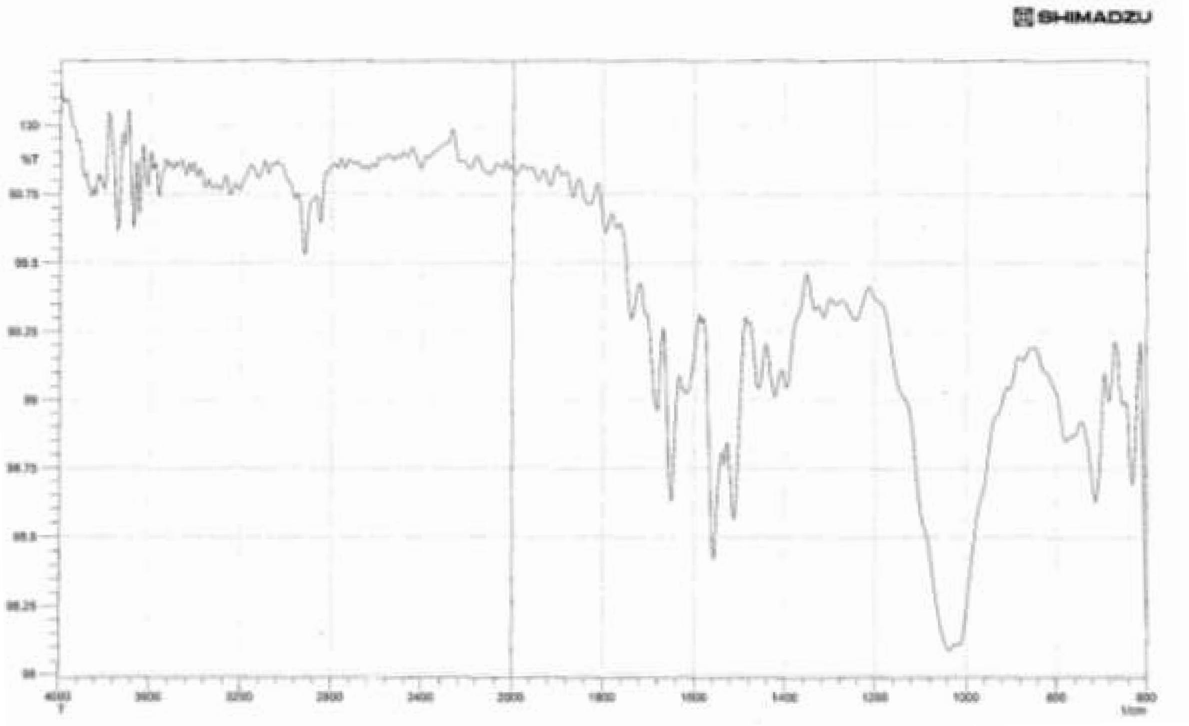


Fig. (4-4): FTIR spectrum for Ficuscarica leaves.

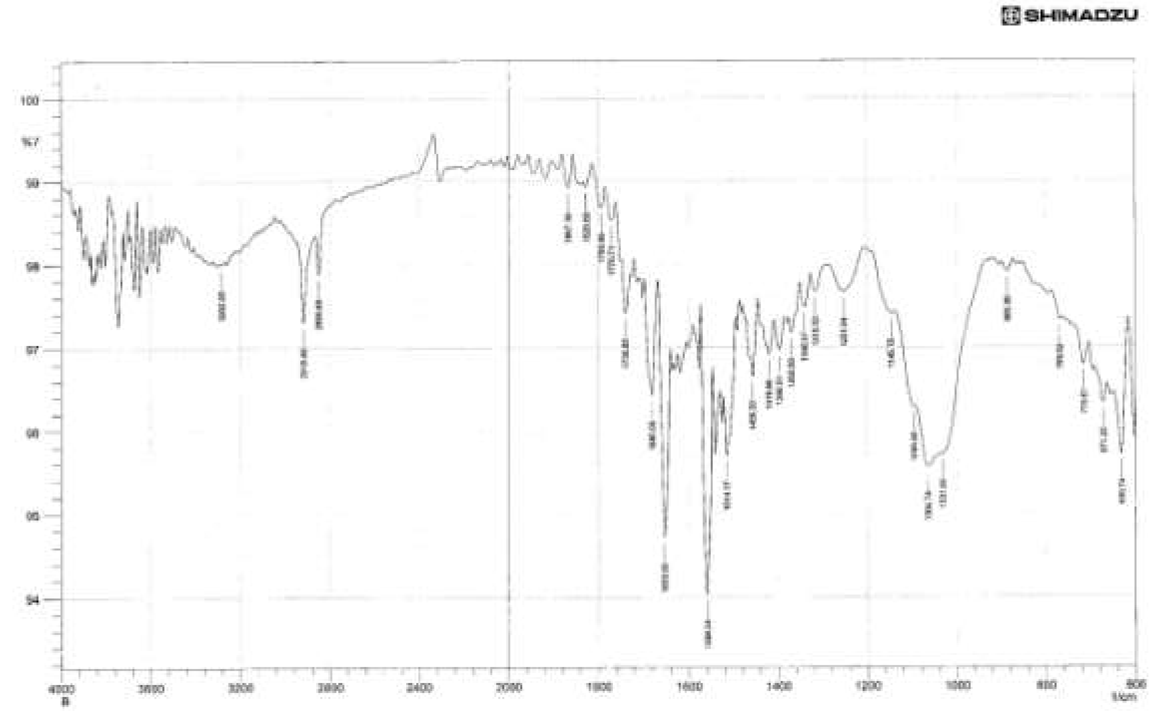


Fig. (4-5): FTIR spectrum for Sweet clover leaves.

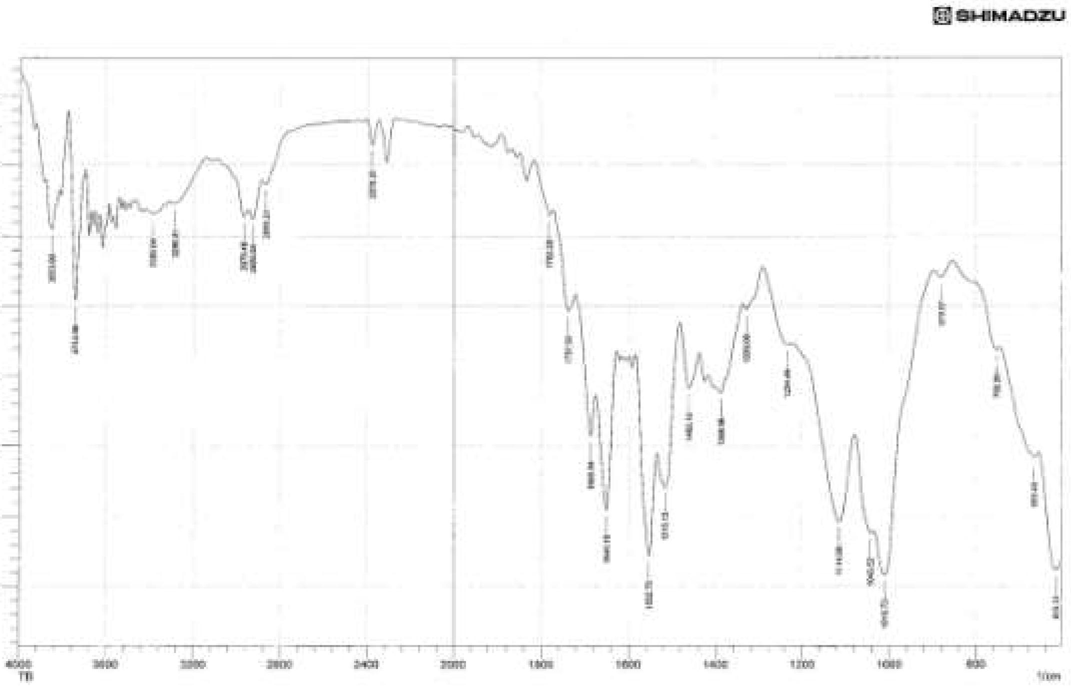


Fig. (4-6): FTIR spectrum for Tobacco leaves.

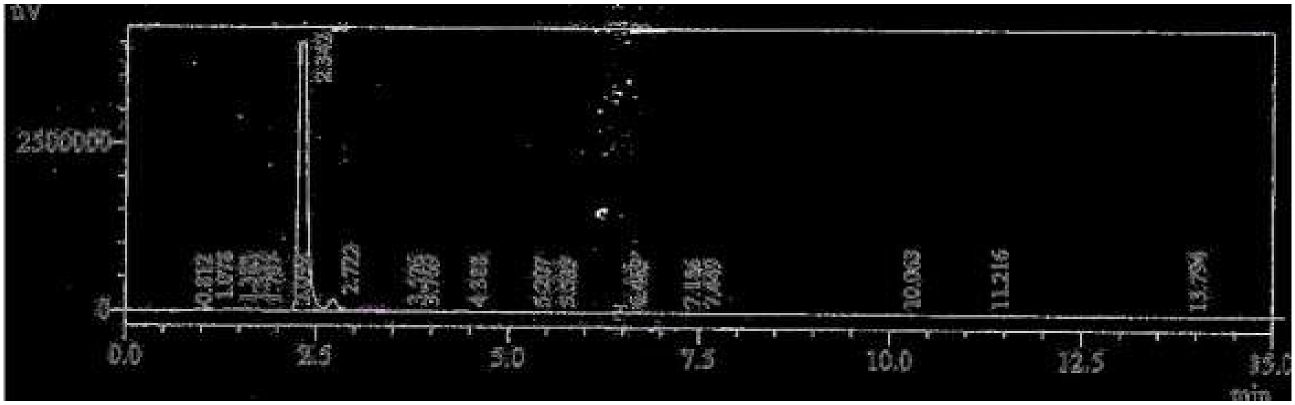


Fig.(4-7): HPLC for pure coumarin in ethanol.

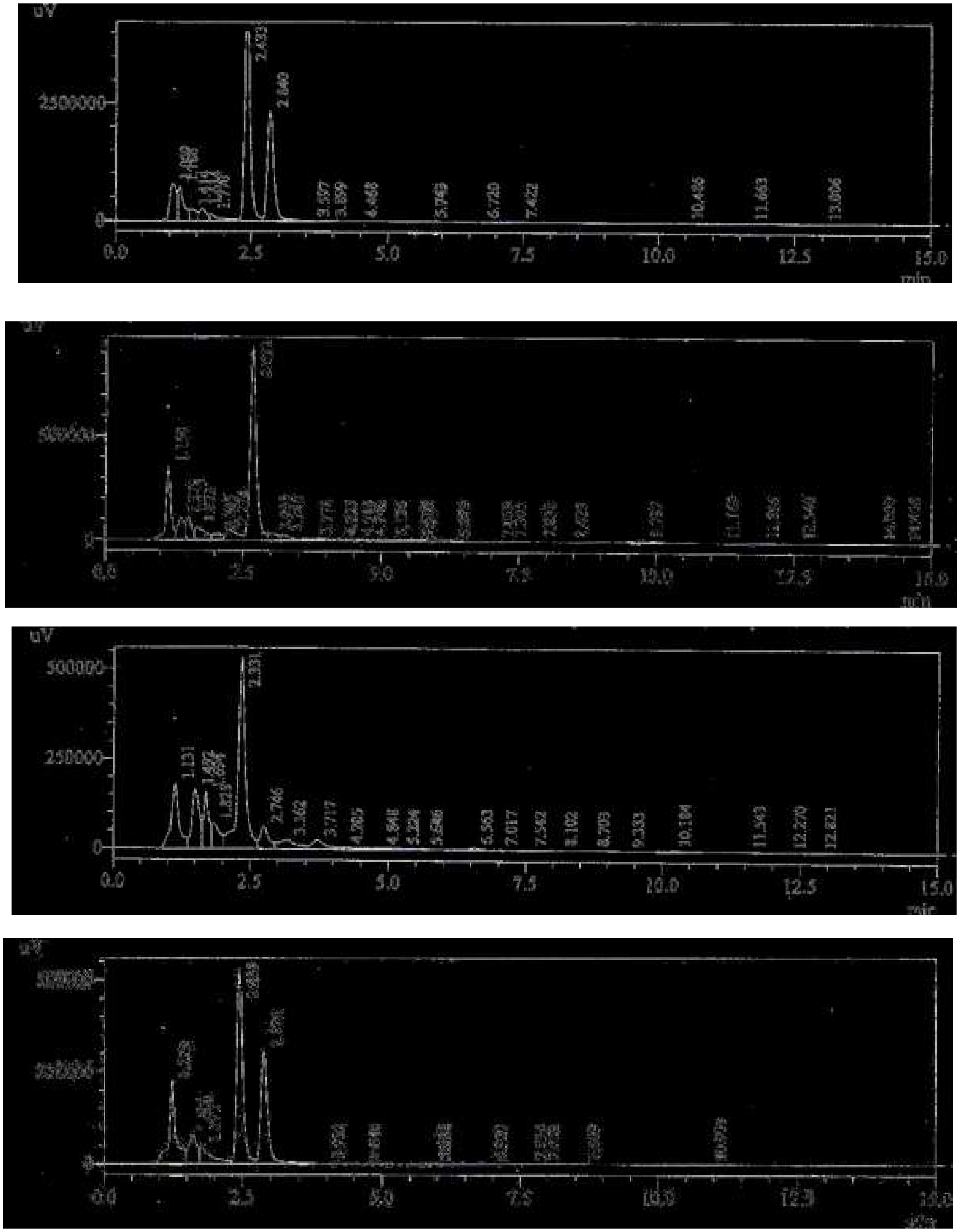


Fig.(4-8): HPLC for plant extracts.

4-3 Corrosion Behavior in Petroleum Medium

Fig. (4-9) shows the potential – time measurements for carbon steel in petroleum medium at four temperatures (323, 333, 343and 353) K (50, 60, 70 and 80^{o}C). The potential of the sample was followed as a function of time in order to study the evolution of the film chemistry as it came to equilibrium with solution [68].

The galvanostatic curves for steel(St 37-2)in petroleum medium at four temperatures are shown in Fig. (4-10),these curves indicate the cathodic and anodic regions. At anodic sites, oxidation of metals can occur according to the following equation:

$$Fe \rightarrow Fe^{2+} + 2e \quad …….(4\text{-}1)$$

While at cathodic sites, many reactions can occur. The main cathodic reduction in acidic medium is evolution of hydrogen as follows:

$$2H^{+} + 2e \rightarrow H_2 \quad …..(4\text{-}2)$$

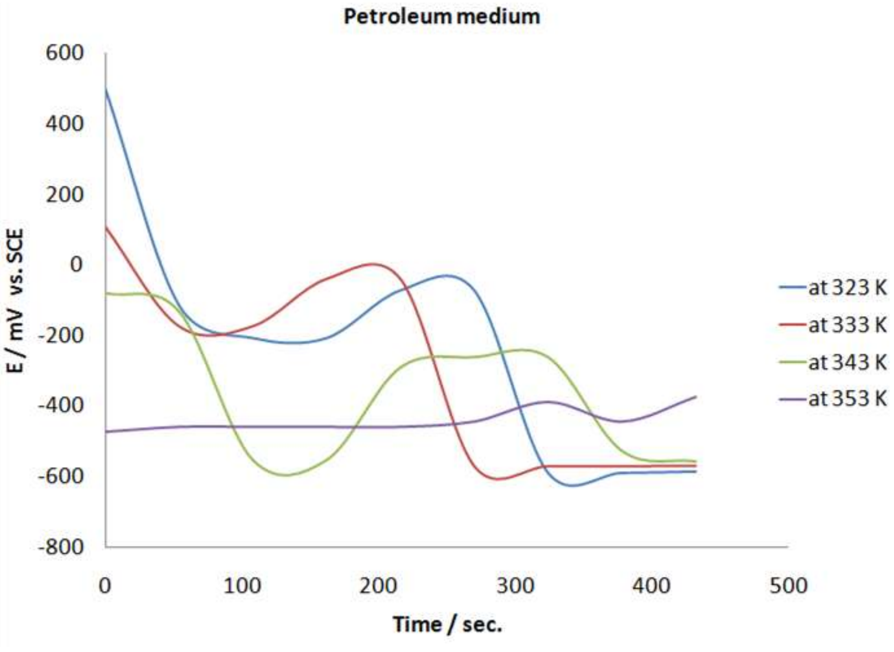


Fig. (4-9): Potential – time measurements of steel in petroleum medium only at four temperatures.

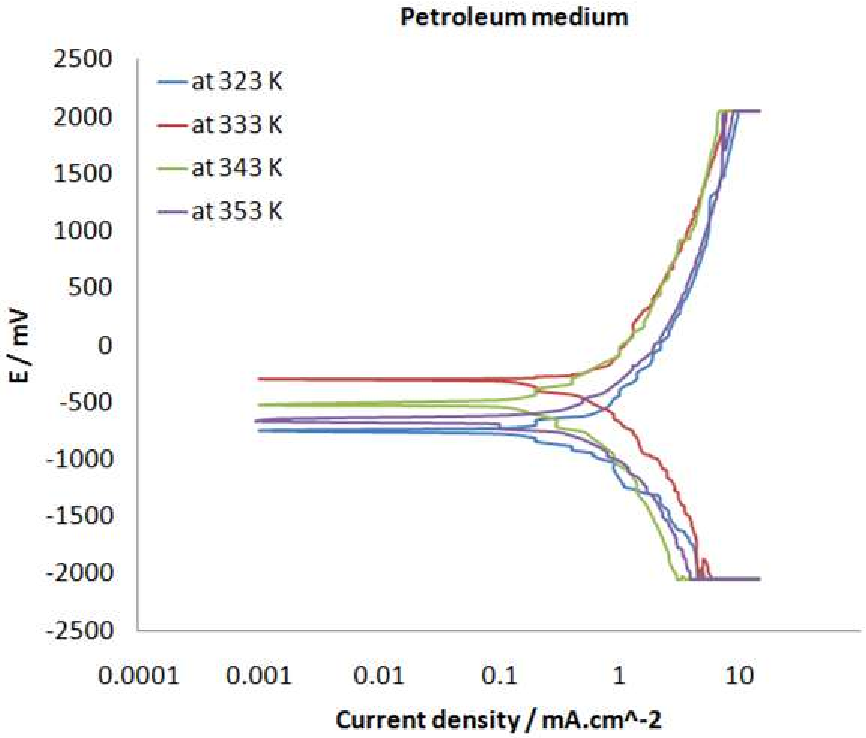


Fig. (4-10): Tafel plot of steel in petroleum medium at four temperatures.

4-4 Corrosion Inhibition By Coumarin

Coumarin selected to attempt for inhibition of steel(St 37-2) in petroleum medium, and then some plants containing coumarins were selected for extraction process.

Fig. (4-11) shows the variation of potential with time for steel in petroleum medium in the presence of four concentrations of coumarin including 10, 40, 70 and 100 ppm at four temperatures. This figure indicates the more stable of variation in potentials with time which may be attributed to coverage the steel surface by coumarin molecules, i.e., they behave as organic inhibitor. The open circuit potential values E_{oc} in the presence of coumarin with four concentrations more noble than that in the absence of coumarin are shown in Table (4-2).

Fig. (4-12) shows the Tafel plots of steel in petroleum medium in the presence of four concentrations of coumarin at four temperatures. The values of associated electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves as shown in Appendix D.

The data of Table (4-2) shows the corrosion parameters for steel in petroleum medium in the absence and presence of coumarin, they indicate that corrosion potentials E_{corr} shifts either to noble or active direction, i.e. coumarin behaves as a mixed type inhibitor. Corrosion current densities i_{corr} become lower in values, in addition, cathodic and anodic Tafel slopes b_c&b_a shift to lower values. The later result enhances the behavior of coumarin as amixed inhibitor.

The inhibition efficiency IE (%) can be calculated using the equation given below[69]:

$$IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \ldots\ldots (4\text{-}1)$$

where $(i_{corr})_a$ and $(i_{corr})_p$ are the corrosion current density ($\mu A.cm^{-2}$) in the absence and the presence of the inhibitor, respectively.

The values of IE% in Table (4-2) are acceptable due to presence of carbonyl group (C=O) in the lactone ring of coumarin. The little efficiency is due to benzene ring which shares its electrons with carbonyl group by resonance effect. This phenomenon reduces the electronic density on oxygen atom of carbonyl group.

At constant concentration, the increasing of temperature led to increasing of corrosion current density, while the variation in corrosion potential was noticed.

Corrosion rates C_R were calculated using the formula $C_R = 0.13 \times i_{corr} \times \left(\frac{e}{\rho}\right)$ in mil per year, where e and ρ are equivalent weight and density of carbon steel respectively as listed in Table (4-2).

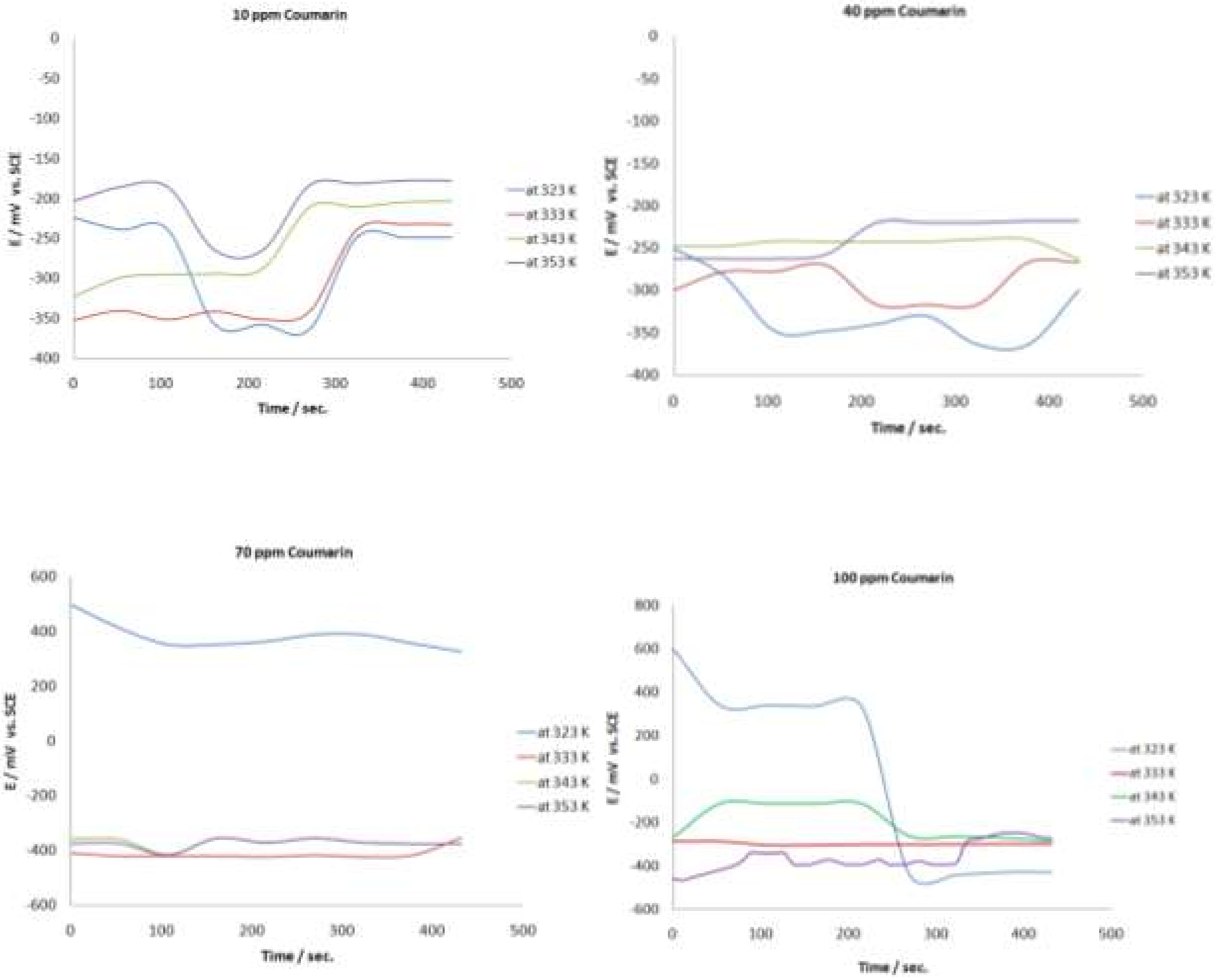


Fig. (4-11): Potential – time measurements of steel in petroleum medium in the presence of four concentrations of pure coumarin at four temperatures.

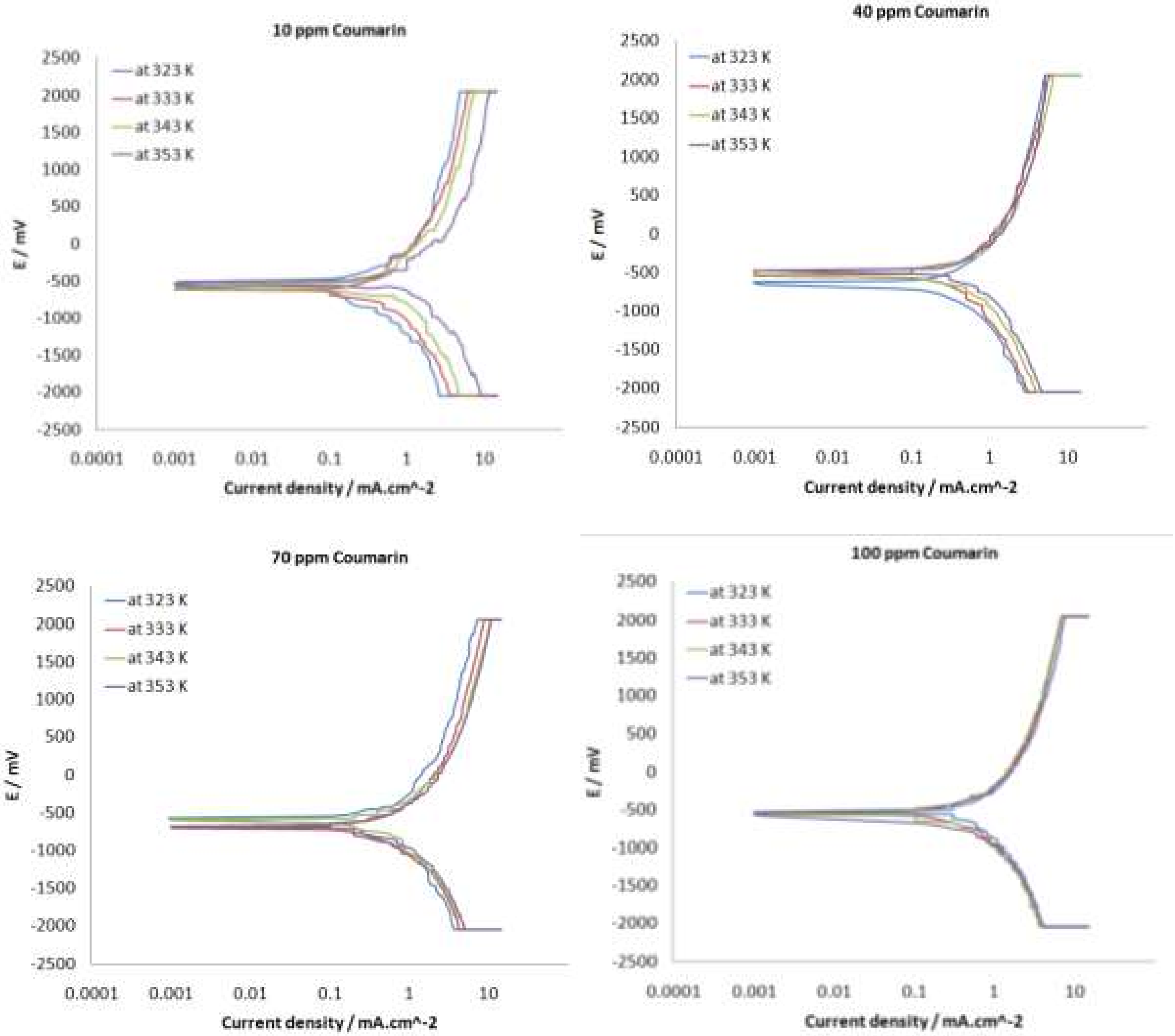


Fig. (4-12): Tafel plots of carbon steel in petroleum medium in the presence of four concentrations of pure coumarin at four temperatures.

Table (4-2): Corrosion parameters for polarization of steel in petroleum medium in the absence and presence of pure coumarin at four temperatures.

Conc. of coumarin	***Temp. K***	***E_{oc} mV***	***E_{corr} mV***	***i_{corr} $\mu A.cm^{-2}$***	***C_R mpy***	***IE%***
0	323	-585	-759.8	497.68	232.4166	-
	333	-570	-322.0	682.72	318.8302	-
	343	-558	-496.2	694.09	324.14	-
	353	-375	-665.1	719.78	336.1373	-
10 ppm	323	-249	-560.5	76.82	35.87494	**84.56438**
	333	-232	-636.8	256.42	119.7481	62.44141
	343	-204	-554.7	387.02	180.7383	44.24066
	353	-178	-514.3	476.53	222.5395	33.79505
40 ppm	323	-300	-643.8	208.19	97.22473	58.1679
	333	-267	-547.9	218.52	102.0488	67.99273
	343	-264	-501.3	227.72	106.3452	67.19157
	353	-218	-478.9	331.18	154.6611	53.98872
70 ppm	323	325	-567.8	102.51	47.87217	79.40243
	333	-356	-701.1	182.36	85.16212	73.2892
	343	-377	-599.4	222.40	103.8608	67.95805
	353	-366	-679.3	240.01	112.0847	66.65509
100 ppm	323	-430	-343.9	199.13	92.99371	59.98835
	333	-300	-358.1	289.25	135.0798	57.6327
	343	-288	-547.3	177.48	82.88316	74.42983
	353	-272	-552.1	224.57	104.8742	68.80019

4-5 Corrosion Inhibition By Cinnamon

Cinnamon extract was used in four different concentrations including1, 3, 5 and 7 mL/L. Fig. (4-13)shows the variation of potentials with time for steel in petroleum medium in the presence of four concentrations of cinnamon at four different temperatures, generally, the E_{oc} values in the presence of cinnamon are more noble than that in the absence of it as listed in Table (4-2) it this result may be attributed to coverage of the steel surface with cinnamon extract. Fig. (4-14) illustrates the Tafel plots for effect of cinnamon as inhibitor and from the corrosion data which are listed in Table (4-3) can be seen that the corrosion potentials E_{corr} shift either to negative or to positive direction due to the behavior of the cinnamon as a mixed inhibitor, while corrosion current densities i_{corr} are lower compared with the case of absence the cinnamon. From the values of inhibition efficiencies, it can be said that the cinnamon extract is a good inhibitor for steel in petroleum medium in the experimental temperatures range.

The best efficiency was noticed in the presence of 1 mL/L of cinnamon extract. The inhibitive action of cinnamon extract may be due to active ingredients especially eugenol [70,71]. Also, cinnamon contains some active components such as Cinnamldehyde, Cinnamylalcohol ,Cinnamic acid and 4-methoxycinnamaldehyde which are used for corrosion inhibition [72].

The increasing of temperature gave various behavior with corrosion parameters.

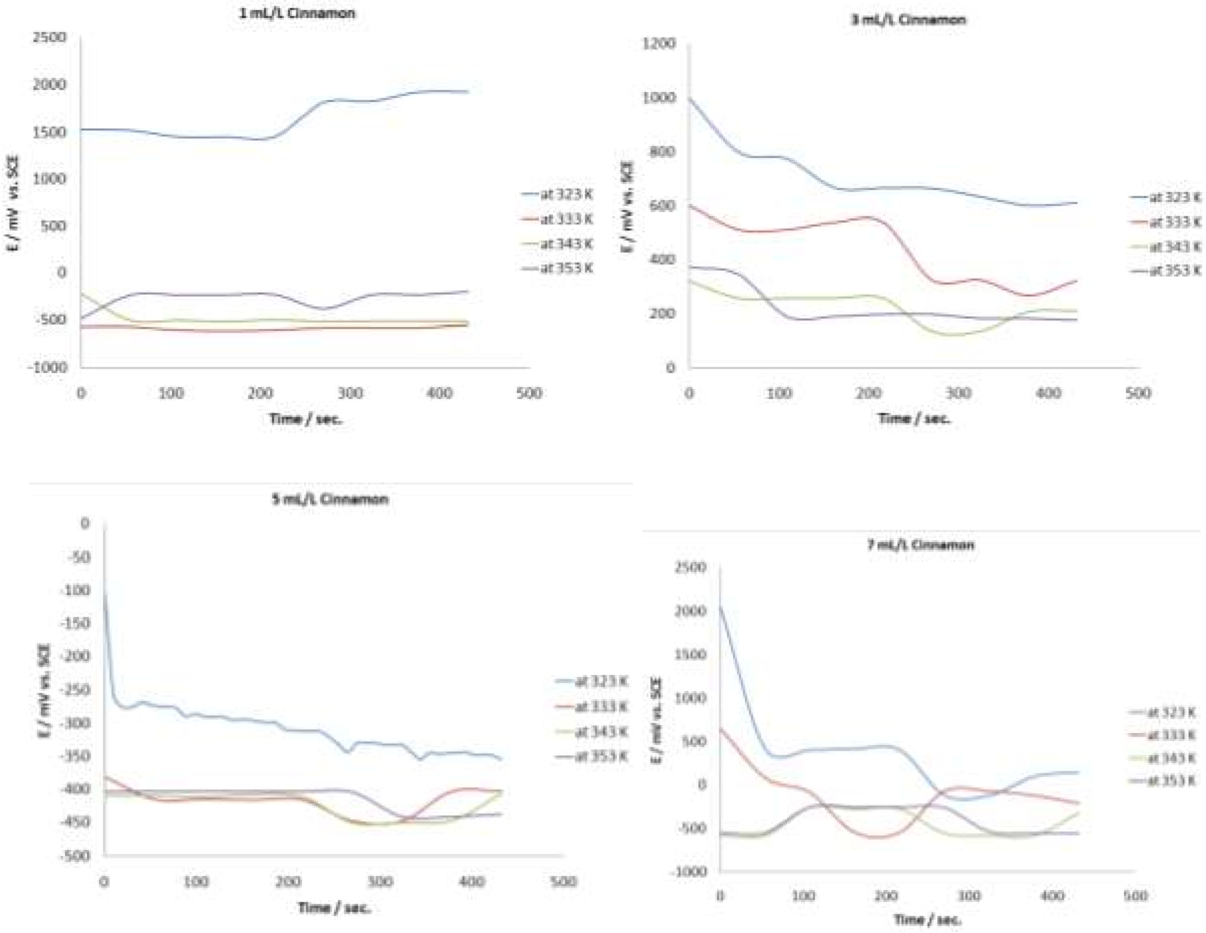


Fig. (4-13): Potential – time measurements of steel in petroleum medium in the presence of four concentrations of cinnamon extract at four temperatures.

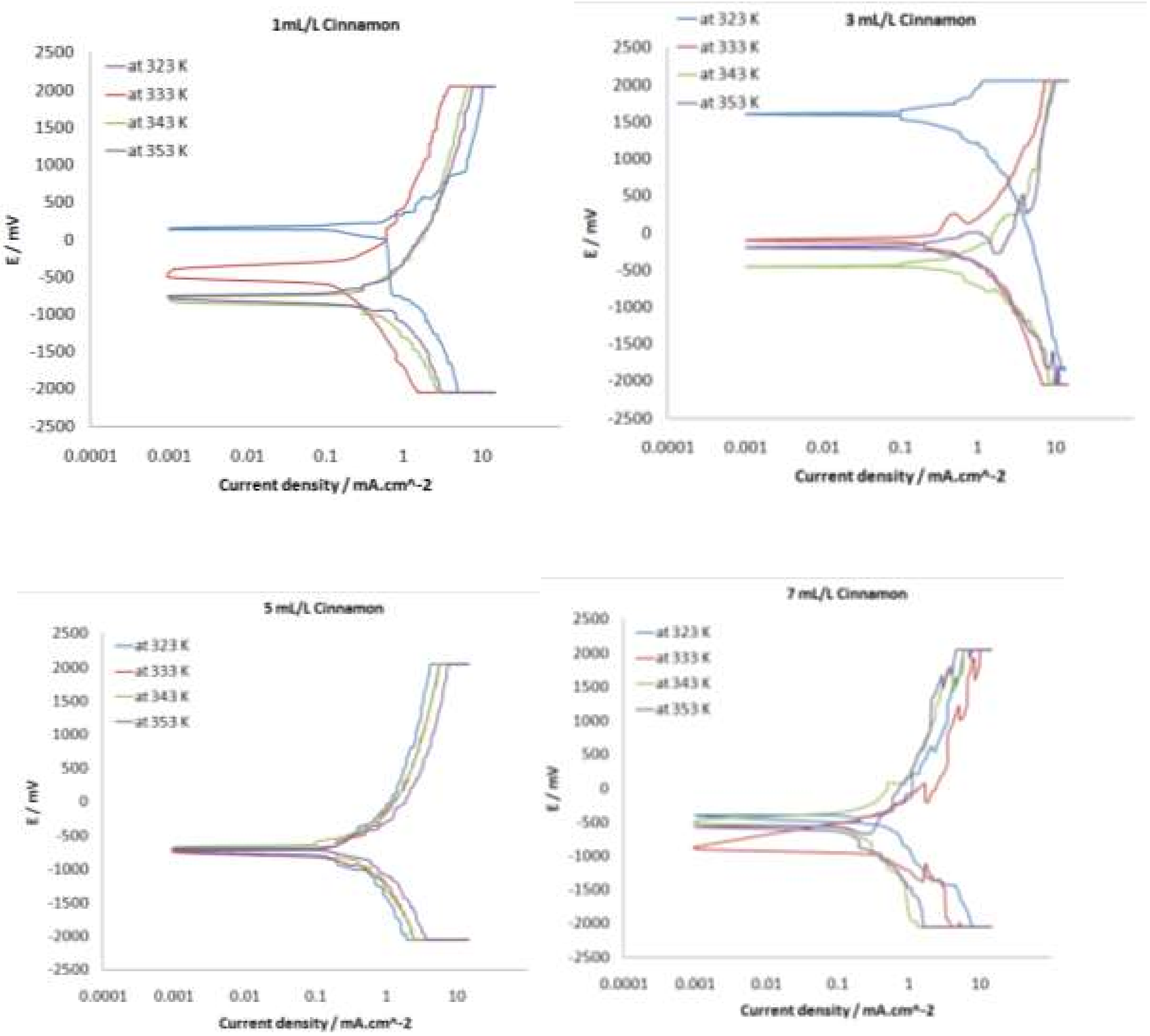


Fig. (4-14): Tafel plots of steel in petroleum medium in the presence of four concentrations of cinnamon extract at four temperatures.

Table (4-3): Corrosion parameters for polarization of steel in petroleum medium in the absence and presence of alcoholic extracted cinnamon at four temperatures.

Conc. of extracted	***Temp. K***	E_{oc} ***mV***	E_{corr} ***mV***	i_{corr} ***μA.cm^{-2}***	C_R ***mpy***	***IE%***
0	323	-585	-759.8	497.68	232.4166	-
	333	-570	-322.0	682.72	318.8302	-
	343	-558	-496.2	694.09	324.14	-
	353	-375	-665.1	719.78	336.1373	-
1 mL/L	323	1920	158.0	77.41	36.15047	**84.44583**
	333	-548	-440.0	105.99	49.49733	**84.47533**
	343	-514	-815.4	184.53	86.17551	**73.41411**
	353	-198	-759.6	343.49	160.4098	52.27847
3 mL/L	323	610	1609.7	69.42	32.41914	**86.05128**
	333	322	-113.5	187.32	87.47844	**72.56269**
	343	210	-433.3	260.30	121.5601	62.49766
	353	177	-184.7	275.26	128.5464	61.75776
5 mL/L	323	-355	-766.6	147.06	68.67702	**70.45089**
	333	-403	-756.0	203.23	94.90841	**70.23231**
	343	-407	-650.0	215.43	100.6058	68.96224
	353	-437	-673.1	316.21	147.6701	56.06852
7 mL/L	323	150	-468.8	173.05	80.81435	65.22866
	333	-206	-813.9	197.64	92.29788	**71.05109**
	343	-317	-481.8	144.42	67.44414	**79.1929**
	353	-553	-687.1	289.43	135.1638	59.7891

4-6 Corrosion Inhibition By FicusCarica

Ethanolic extract of Ficuscarica was used as inhibitor to inhibit the corrosion of steel (St 37-2)in petroleum medium with four different concentrations. The data of plots of the potentials against time as shown in Fig. (4-15) illustrate the more stable film formation at material/medium interface in addition to obtain more noble values of E_{oc}. The data of Tafel plots as shown in Fig. (4-16) show ficuscarica extract enhances the effect of inhibition. The values of E_{corr} indicate the role of ficuscarica extract as mixed inhibitor, corrosion current densities i_{corr} become lower and Tafel slopes also decrease confirming that the type of inhibitor is mixed.

The inhibition of corrosion gave good efficiencies especially at 3mL/L of ficuscarica extract. The main role of inhibition in ficuscarica ingredients is due to presence Indol which contains −NH− group and is used as good inhibitor by Quartarone and co-workers [73], in addition to other components such as Cinnamldehyde, Benzyl alcohol ,Cinnamic acid and Coumarin[74].

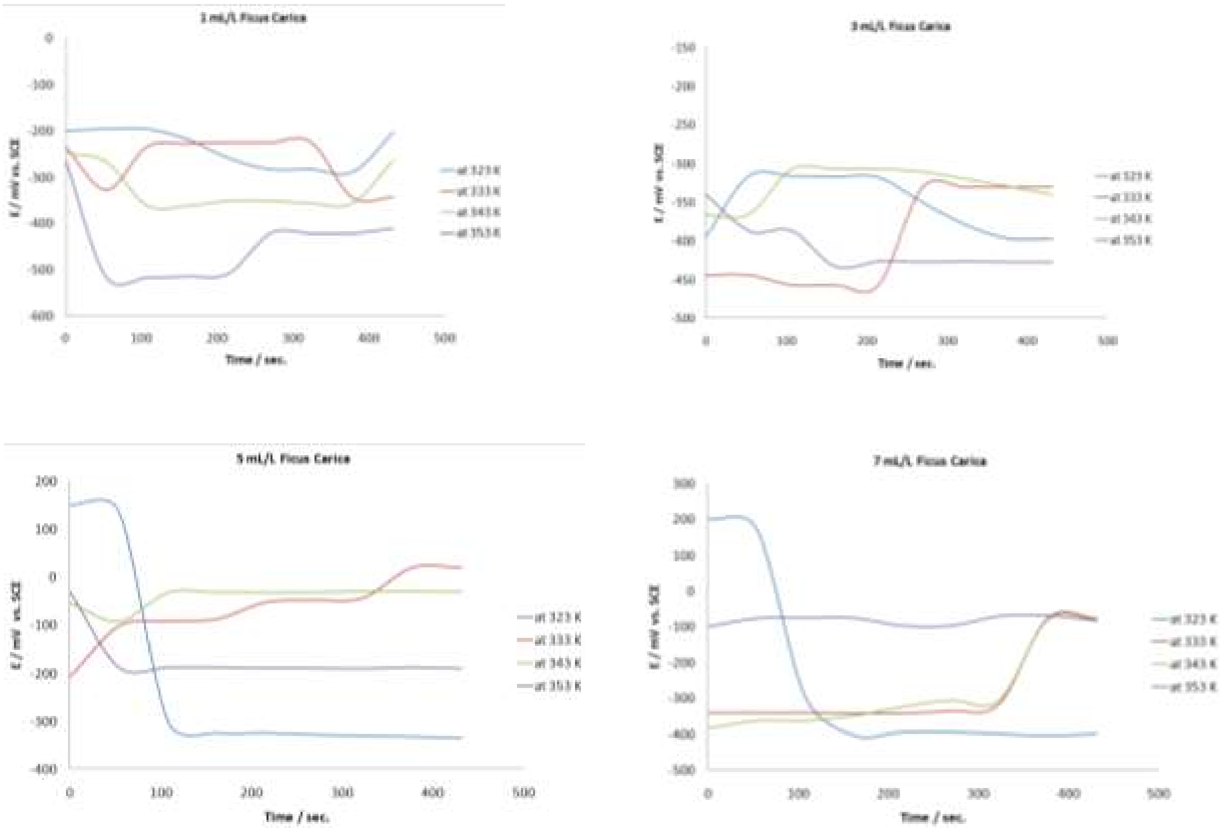


Fig. (4-15): Potential – time measurements of steel in petroleum medium in the presence of four concentrations of ficuscarica extract at four temperatures.

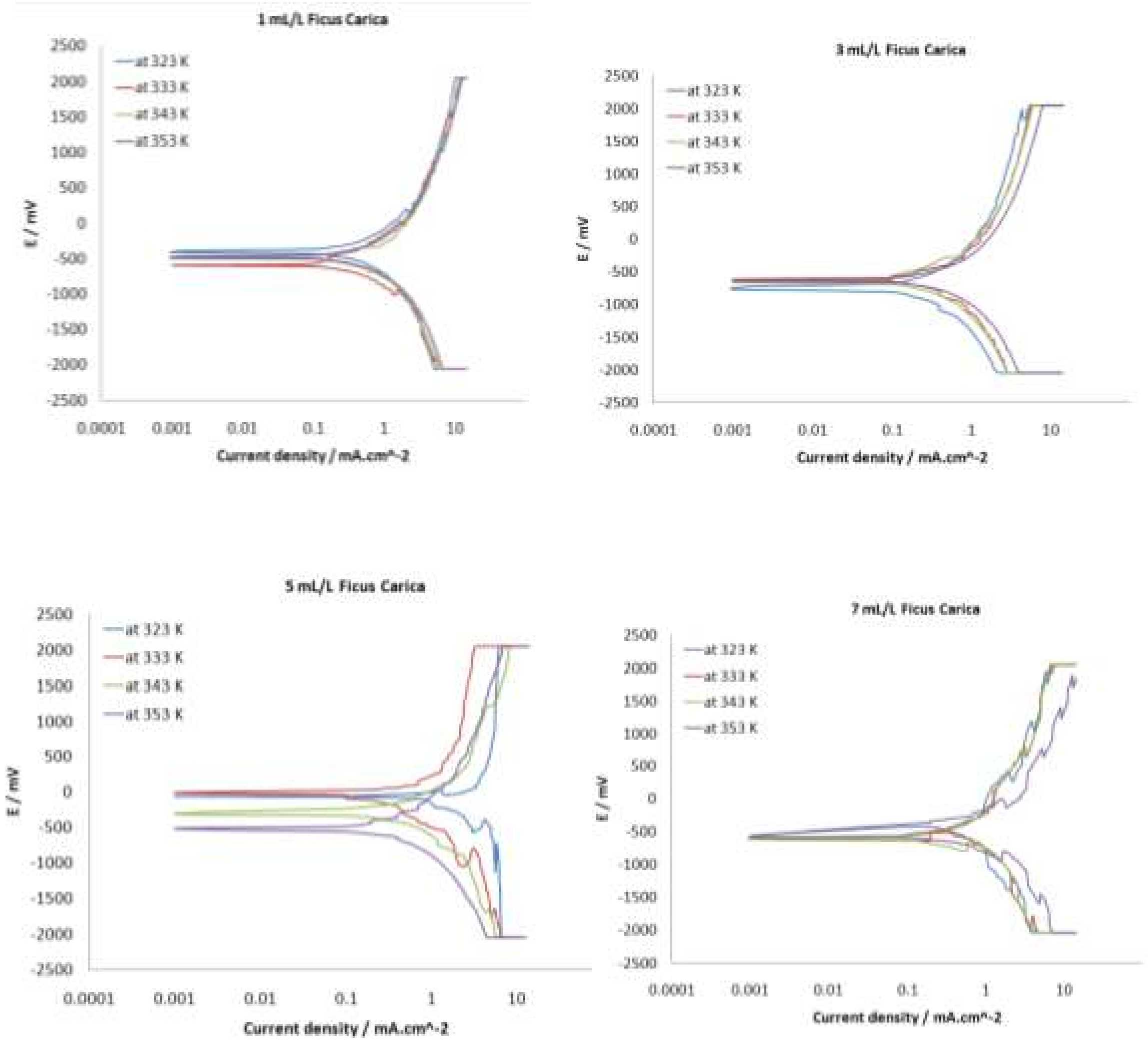


Fig. (4-16): Tafel plots of steel in petroleum medium in the presence of four concentrations of ficuscarica extract at four temperatures.

Table (4-4): Corrosion parameters for polarization of steel in petroleum medium in the absence and presence of alcoholic extracted ficuscarica at four temperatures.

Conc. of extracted	***Temp. K***	E_{oc} ***mV***	E_{corr} ***mV***	i_{corr} $\mu A.cm^{-2}$	C_R ***mpy***	***IE%***
0	323	-585	-759.8	497.68	232.4166	-
	333	-570	-322.0	682.72	318.8302	-
	343	-558	-496.2	694.09	324.14	-
	353	-375	-665.1	719.78	336.1373	-
1 mL/L	323	-203	-390.6	217.40	101.5258	56.31731
	333	-343	-572.0	221.63	103.5012	67.53720
	343	-263	-493.2	266.68	124.5396	61.57847
	353	-411	-467.6	295.78	138.1293	58.90689
3 mL/L	323	-397	-733.0	129.27	60.36909	**74.02548**
	333	-331	-600.3	145.31	67.85977	**78.71602**
	343	-340	-479.3	166.63	77.81621	**75.99303**
	353	-427	-639.3	198.32	92.61544	**72.44714**
5 mL/L	323	-335	-148.2	142.34	66.47278	**71.39929**
	333	+19	-7.1	153.12	71.50704	**77.57206**
	343	-31	-293.8	169.68	79.24056	**75.5536**
	353	-191	-517.9	143.70	67.1079	**80.03557**
7 mL/L	323	-400	-546.8	257.44	120.2245	48.27198
	333	-76	-533.9	265.60	124.0352	61.09679
	343	-81	-601.2	252.49	117.9128	63.62287
	353	-83	-531.9	224.99	105.0703	68.74184

4-7 Corrosion Inhibition By Sweet Clover

The same behavior of previous inhibitors can be noticed when sweet clover extract was added as inhibitor. Fig. (4-17) shows the variation of potential with time for the corrosion of steel in petroleum medium containing four concentrations of sweet clover extract at four temperatures. The data of open circuit potentials indicate that this potential becomes more noble. Fig. (4-18) illustrates the Tafel plots of steel in petroleum medium in the presence of four concentrations of sweet clover extract at four temperatures, and by extrapolation method, the data of corrosion were estimated. These data refer to that sweet clover extract behavior as mixed inhibitor enhanced by the values of Tafel slopes.

The inhibition efficiencies indicate that 3 mL/L of sweet clover extract give the best inhibition, where sweet clover contain dicoumarol (4- hydroxycoumarin) [75].The big molecule of dicoumarol with its chemical functionality groups may adsorb on cathodic and anodic sites and blocking these sites to form barrier reducing of corrosion rate.

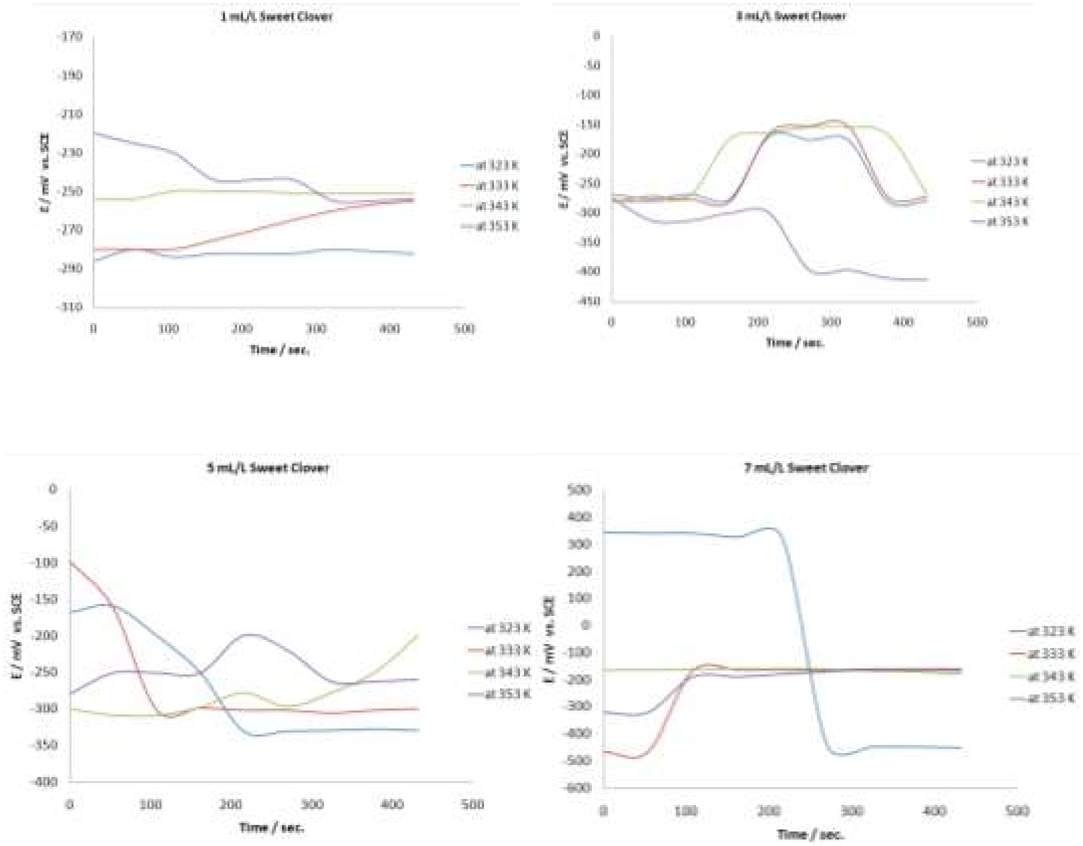


Fig. (4-17): Potential – time measurements of steel in petroleum medium in the presence of four concentrations of sweet clover extract at four temperatures.

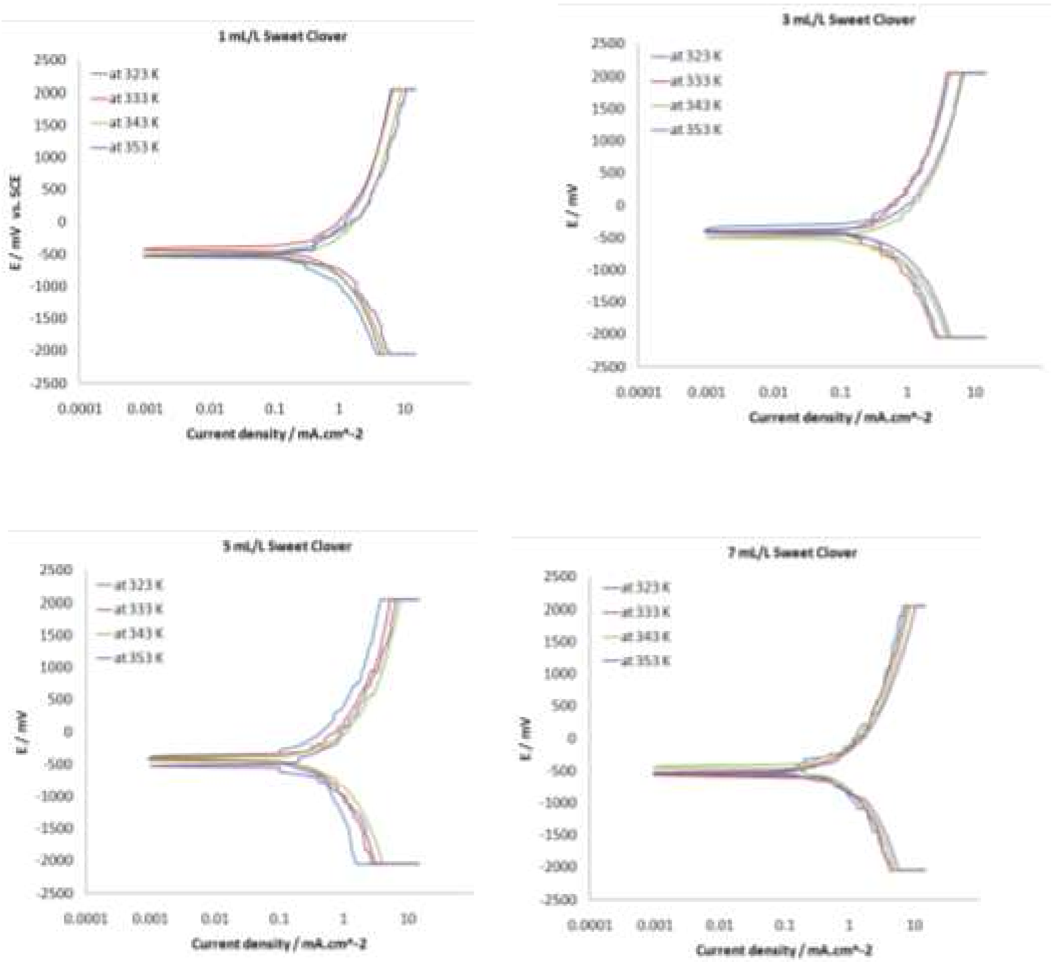


Fig. (4-18): Tafel plots of steel in petroleum medium in the presence of four concentrations of sweet clover extract at four temperatures.

Table (4-5): Corrosion parameters for polarization of steel in petroleum medium in the absence and presence of alcoholic extracted sweet clover at four temperatures.

Conc. of extracted	***Temp. K***	***E_{oc} mV***	***E_{corr} mV***	***i_{corr} $\mu A.cm^{-2}$***	***C_R mpy***	***IE%***
0	323	-585	-759.8	497.68	232.4166	-
	333	-570	-322.0	682.72	318.8302	-
	343	-558	-496.2	694.09	324.14	-
	353	-375	-665.1	719.78	336.1373	-
1 mL/L	323	-282	-523.4	150.46	70.26482	69.76772
	333	-255	-426.4	217.65	101.6426	68.12017
	343	-251	-510.9	228.89	106.8916	67.02301
	353	-254	-522.6	230.85	107.807	67.92770
3 mL/L	323	-281	-360.6	79.95	37.33665	**83.93546**
	333	-273	-431.6	128.30	59.9161	**81.20752**
	343	-268	-498.8	143.88	67.19196	**79.27070**
	353	-415	-410.2	181.60	84.8072	**74.77007**
5 mL/L	323	-330	-376.5	125.51	58.61317	**74.78098**
	333	-300	-415.9	171.11	79.90837	**74.93702**
	343	-200	-417.7	155.95	72.82865	**77.53173**
	353	-260	-535.0	193.18	90.21506	**73.16124**
7 mL/L	323	-450	-496.7	168.26	78.57742	66.19113
	333	-162	-511.2	232.19	108.4327	65.99045
	343	-180	-428.4	231.49	108.1058	66.64842
	353	-167	-543.6	227.08	106.0464	68.45147

4-8 Corrosion Inhibition By Tobacco

The inhibiting activity of tobacco extract was studied to inhibit steel (St 37-2)in petroleum medium in the presence of four concentrations of extracted tobacco leaves. The relationship between potential and time can be seen in Fig. (4-19) and the data of E_{oc} indicate shifting the potential toward noble or active direction which means there is a protective layer which may form and breakdown on the metallic surface. Corrosion parameters which are estimated from Tafel plots, as shown in Fig. (4-20), indicate that the tobacco extract is a mixed inhibitor supported by Tafel slopes values. Corrosion current densities decreased leading to occurring of the corrosion inhibition. 7 mL/L of inhibitor gave the best efficiencies.

The alkaloid nicotine (containing N atoms) is the most characteristic constituent of tobacco in addition to polycyclic aromatic hydrocarbons such as coumarin, formaldehyde, nitrosamines and phenol [76,77], which may be contributed the inhibitive action in tobacco extract.

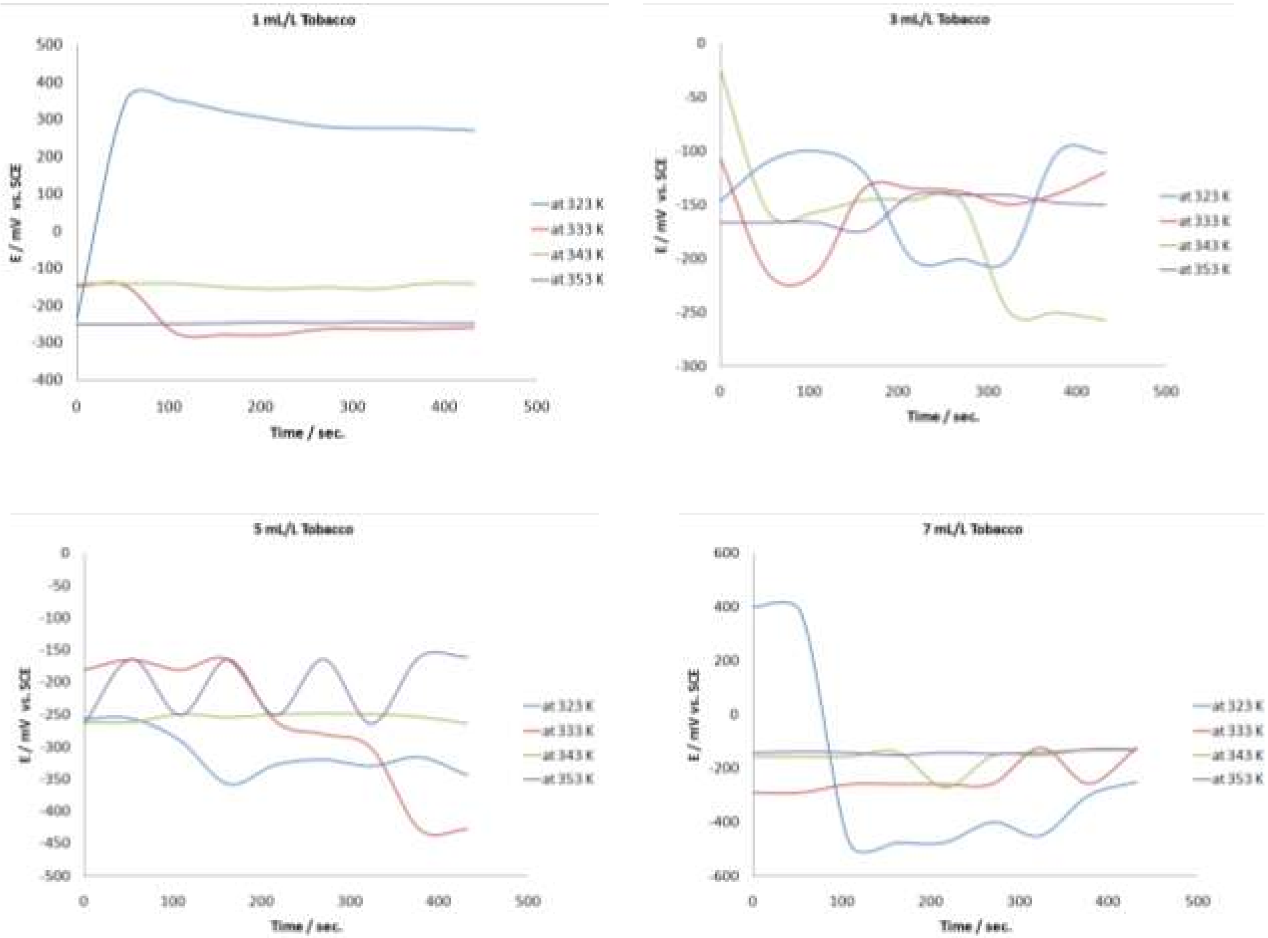


Fig. (4-19): Potential – time measurements of steel in petroleum medium in the presence of four concentrations of tobacco extract at four temperatures.

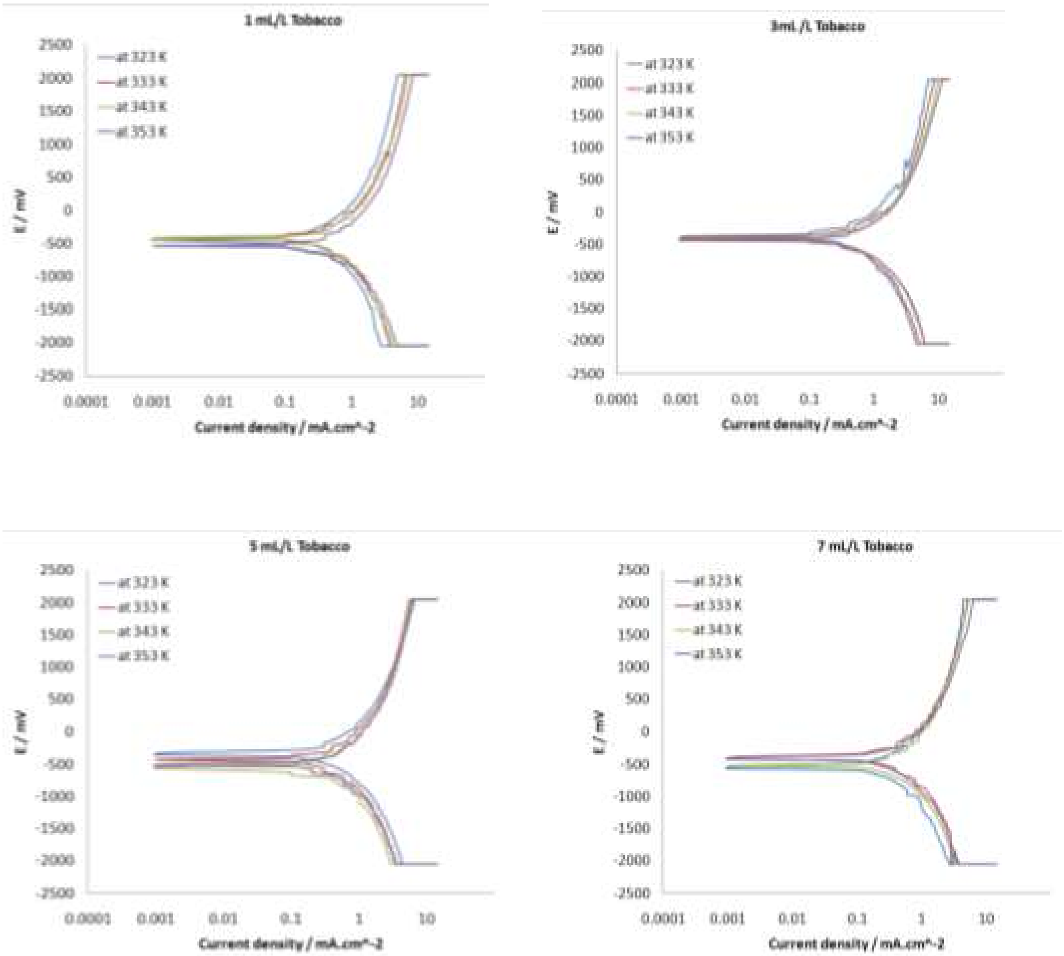


Fig. (4-20): Tafel plots of steel in petroleum medium in the presence of four concentrations of tobacco extract at four temperatures.

Table (4-6): Corrosion parameters for polarization of steel in petroleum medium in the absence and presence of alcoholic extracted tobacco at four temperatures.

Conc. of extracted	***Temp. K***	***E_{oc} mV***	***E_{corr} mV***	***i_{corr} μA.cm^{-2}***	***C_R mpy***	***IE%***
0	323	-585	-759.8	497.68	232.4166	-
	333	-570	-322.0	682.72	318.8302	-
	343	-558	-496.2	694.09	324.14	-
	353	-375	-665.1	719.78	336.1373	-
1 mL/L	323	270	-428.6	205.70	96.0619	58.66822
	333	-260	-435.5	236.26	110.3334	65.39431
	343	-141	-425.1	211.54	98.78918	69.52268
	353	-248	-549.3	247.87	115.7553	65.56309
3 mL/La	323	-102	-375.3	205.89	96.15063	58.63004
	333	-120	-389.7	222.95	104.1177	67.34386
	343	-257	-414.8	226.82	105.9249	67.32124
	353	-150	-428.3	260.09	121.462	63.86535
5 mL/L	323	-344	-354.1	165.91	77.47997	66.66332
	333	-428	-437.2	166.58	77.79286	**75.60054**
	343	-264	-539.4	199.66	93.24122	**71.23428**
	353	-161	-509.5	261.68	122.2046	63.64445
7 mL/L	323	-250	-540.3	120.15	56.11005	**75.85798**
	333	-124	-388.9	158.54	74.03818	**76.77818**
	343	-127	-506.3	174.05	81.28135	**74.92400**
	353	-130	-407.5	196.58	91.80286	**72.68888**

4-9 FTIR Spectra

Infrared reflection – absorption spectroscopy integrate into electrochemical measurements, it becomes possible to obtain atomic and molecular information about adsorbents or films of reaction products on electrode surfaces in electrochemical environments [78,79].

These tests were measured after immersion of the steel(St 37-2) specimens for 15 days in petroleum medium in absence and presence of inhibitors with four different concentrations of each inhibitor at room temperature. All FTIR spectra results for all concentrations are shown in Appendix (B).

Fig. (4-21) shows the FTIR of film formed on steel surface in petroleum medium in the absence of natural inhibitors.

The FTIR spectrum indicates many peaks, the most important of which may be due to adsorption of compounds contained in petroleum medium. The peaks at left of 3600 cm^{-1} may be attributed to Free OH and H—bond. The broad peak of O—H stretch for carboxylic acids, alcohols or phenols appear at 2980.12 and 2885.6 cm^{-1}.

The peaks at 2360.93 and 2332.02 $cm^{-1}$are attributed to C—H aromatic and C—H aliphatic stretch. The peak at 1651.12and 1558.54 $cm^{-1}$are due to C=C aromatic stretching because disubstituted or symmetrically substituted, triple bond gives no absorption or weak absorption. The most prominent band is that due to C—O stretch at 1020.38 cm^{-1} in alcohols, ethers or ester. These peaks confirm that the petroleum medium is a mixture of many hydrocarbons.

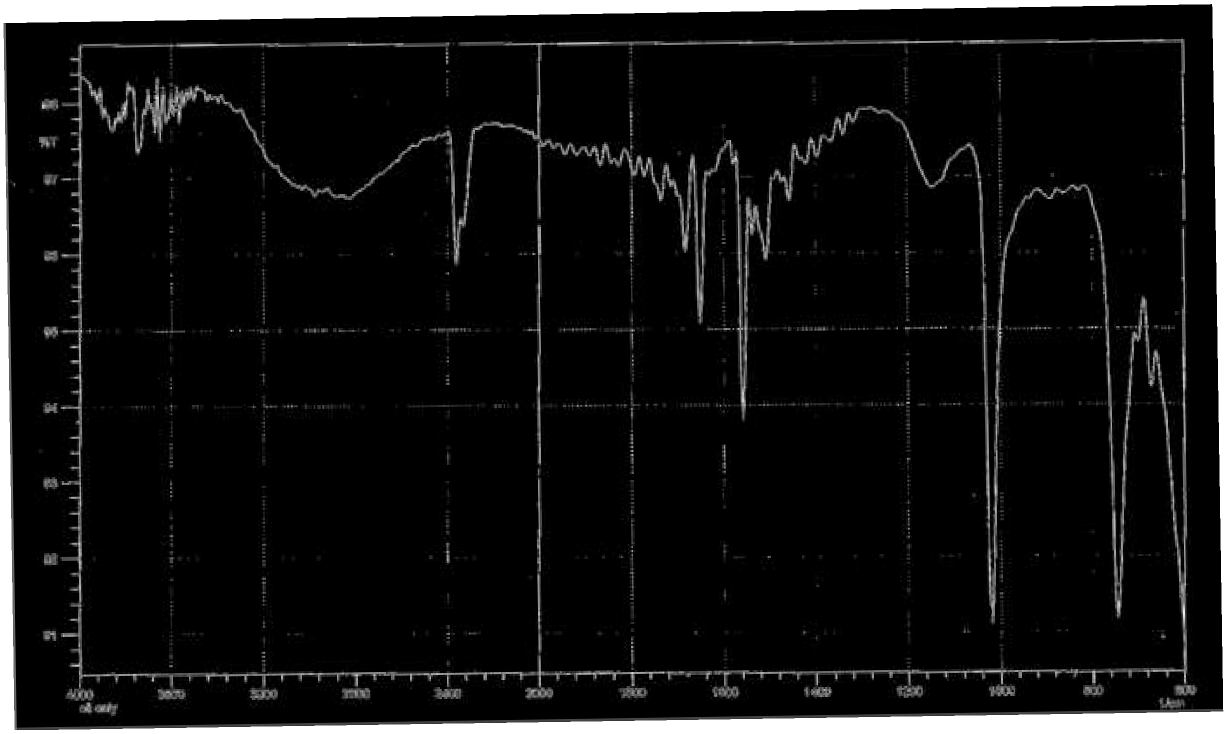


Fig. (4-21): FTIR spectrum of film formed on the steel surface after immersion in petroleum medium in the absence of inhibitor for 15 days.

The results of FTIR spectroscopy are in good agreement with the electrochemical measurements (polarization behavior) where it can be observed that the best concentration of each inhibitor gave the good analysis by FTIR through decreasing the stretching of most important bands and the broad band of H—bonded disappears due to the solvation of Fe^{2+} in petroleum medium. The Comparison among different concentrations for each inhibitor can be seen in Appendix B. As a result, FTIR spectrum for film formed with the best concentration of plant extracts show the decrease in the intensity of the important peaks because of formation of Fe^{2+}—plant extracts complexes.

4-10 Adsorption Isotherms

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Frumkin, Temkin, Flory-Huggins, Dhar-Flory- Huggins, Bockris-Swinkels and the recently formulated thermodynamic/kinetic model of El-Awady et al. [80-82]. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clues to the nature of the metal- inhibitor interaction.

In order to obtain the adsorption isotherm, the degree of surface coverage (θ) for various concentrations of the inhibitor has been calculated according to following equation [83]:

$$\theta = \left[1 - \frac{i_{inh.}}{i_{unin\ .}}\right] \text{.....(4-2)}$$

Langmuir isotherm was tested for its fit to the experimental data. The plots of C_{inh}/θ against C_{inh} for the four plant extracts at four temperatures in the range 323 – 353 K were straight lines (Fig. 4-22) indicating that the plant extracts obey Langmuir adsorption isotherm which isgiven by the following equation [23]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \text{......(4-3)}$$

where, K_{ads} is the equilibrium constant of the adsorption-desorption process, θ is the degree of surface coverage and C_{inh} is concentration of inhibitor in the bulk solution. The linear regression coefficient is close to unity, hence, adsorption of inhibitor follows Langmuir adsorption isotherm. R^2 values are in the range $0.996 \geq R^2 \geq 0.917$ as listed in Table (4-7).

The Langmuir isotherm is based on the assumption that each site of metal surface holds one adsorbed specie. Therefore, one adsorbed H_2O molecule is replaced by one molecule of the inhibitor adsorbate (plant extracts) on the steel surface.

The apparent free energy of adsorption (ΔG^{o}_{ads}) is calculated from the relation [83]:

$$\Delta G^{o}_{ads} \quad = -2.303RTlog55.5\, K_{ads}, \quad whereK_{ads} = \frac{\theta}{C(1-\theta)} \ldots\ldots (4\text{-}4)$$

The values of K_{ads} and ΔG^{o}_{ads} are shown in Tables (4-7) to (4-10) for plant extracts as inhibitors.

The negative values of ΔG^{o}_{ads} indicat the spontaneous adsorption of the plant extracts and reveal strong interaction between inhibitor molecules and metal surface[82-84].The values of K_{ads} are relatively small indicating that the interaction between the adsorbed extract molecules and steel surface is physically adsorbed. This is also supported by lower negative (ΔG^{o}_{ads}) values for plant extracts. Generally, values of (ΔG^{o}_{ads})up to –20 kJ/mol are consistent with electrostatic interactions between the charged molecules and the charged metal surface, which indicates physical adsorption [85].

The enthalpy of adsorption (ΔH^{o}_{ads}) can be calculated from the Gibbs–Helmholtz equation:

$$\left[\frac{\partial\left(\Delta G^{o}_{ads}/T\right)}{\partial T}\right]_{P} = -\frac{\Delta H^{o}_{ads}}{T^{o}} \ldots\ldots (4\text{-}5)$$

This equation can be arranged to following equation:

$$\frac{\Delta G^{o}_{ads}}{T} = \frac{\Delta H^{o}_{ads}}{T} + K_{ads} \ldots\ldots (4\text{-}6)$$

The negative sign of ΔH^{o}_{ads} in petroleum medium indicates that the adsorption of inhibitor molecule is exothermic process. Generally, an exothermic adsorption process signifies either physic- or chemisorption while endothermic process is attributable unequivocally to chemisorptions[86], i.e., this result is in good agreement with the results of K_{ads} and ΔG^{o}_{ads}.

The entropy of adsorption ΔS^{o}_{ads} can be calculated by using following equation:

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T\Delta S^{o}_{ads} \quad .....(4\text{-}7)$$

The value of ΔS^{o}_{ads} is negative indicating that plant extracts retain the metal ions and reduce the dissolution of steel in petroleum medium in presence of corrosion inhibitors as shown in Tables (4-8) to (4-11). Also the negative values of ΔS^{o}_{ads} imply that the activated complex in the rate determining step denotes an association rather than a dissociation step, meaning that a reduction in disordering takes place on going from reactants to the activated complex.

Generally, the inhibitive characteristics of such compounds are derived from the adsorption ability of their molecules, with the polar group acting as the reaction center for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent, and efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the adsorption layers formed under particular conditions.

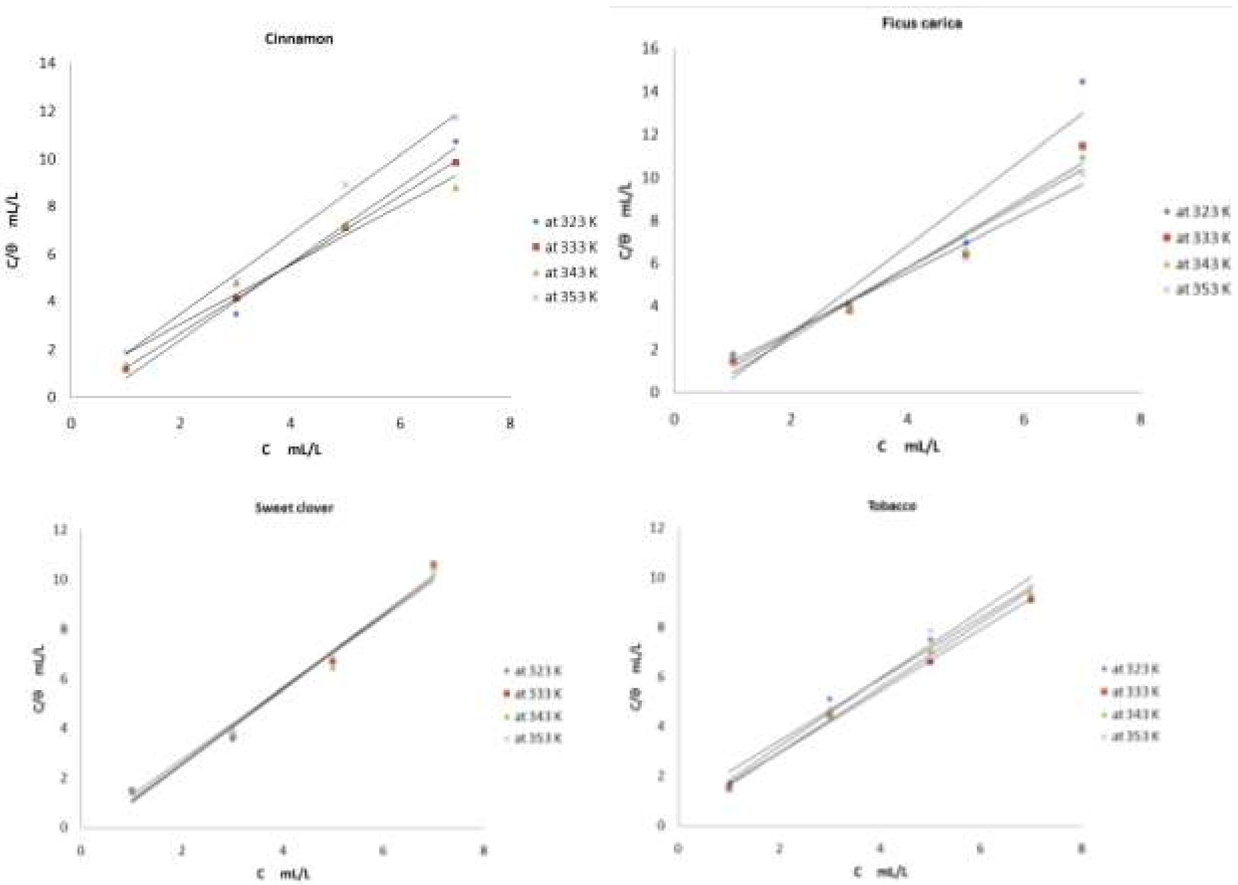


Fig.(4-22): Langmuir adsorption plots for steel in petroleum medium with different concentrations of plant extracts at four temperatures.

Table (4-7): The linear regression coefficient for adsorption of plant extracts on steel surface in petroleum medium at different temperature.

Extract	*Temp. /K*	*R^2*	*Extract*	*Temp. /K*	*R^2*
Cinnamon	323	0.957	Sweet clover	323	0.983
	333	0.954		333	0.984
	343	0.973		343	0.981
	353	0.994		353	0.995
Ficuscarica	323	0.917	Tobacco	323	0.977
	333	0.963		333	0.996
	343	0.976		343	0.996
	353	0.979		353	0.984

Table (4-8): Thermodynamic function for adsorption of cinnamon extract in petroleum medium at four temperatures.

Conc. of extracted	*Temp. K*	K_{ads}	ΔG^o_{ads} $kJ.mol^{-1}$	ΔH^o_{ads} $kJ.mol^{-1}$	ΔS^o_{ads} $kJ.mol^{-1}K^{-1}$
1 mL/L	323	5.429	-14.99	-1768.56	-5.429
	333	5.441	-15.46	-1827.31	-5.441
	343	2.761	-14.04	-961.063	-2.761
	353	1.095	-11.79	-398.325	-1.095
3 mL/L	323	2.056	-12.44	-676.528	-2.056
	333	0.882	-10.53	-304.236	-0.882
	343	0.556	-9.56	-200.268	-0.556
	353	0.538	-9.75	-199.664	-0.538
5 mL/L	323	0.477	-8.62	-162.691	-0.477
	333	0.472	-8.84	-166.016	-0.472
	343	0.444	-8.94	-161.232	-0.444
	353	0.255	-7.61	-97.625	-0.255
7 mL/L	323	0.268	-7.09	-93.654	-0.268
	333	0.351	-8.04	-124.923	-0.351
	343	0.544	-9.50	-196.092	-0.544
	353	0.212	-7.08	-81.916	-0.212

Table (4-9): Thermodynamic function for adsorption of ficuscarica extract in petroleum medium at four temperatures.

Conc. of extracted	*Temp. K*	K_{ads}	ΔG^o_{ads} $kJ.mol^{-1}$	ΔH^o_{ads} $kJ.mol^{-1}$	ΔS^o_{ads} $kJ.mol^{-1}K^{-1}$
1 mL/L	323	1.28922	-11.2161	-427.634	-1.28922
	333	2.08043	-12.8591	-705.642	-2.08043
	343	1.602676	-12.5176	-562.235	-1.60268
	353	1.433504	-12.5624	-518.589	-1.4335
3 mL/L	323	0.949952	-10.414	-317.248	-0.94995
	333	1.232788	-11.4422	-421.961	-1.23279
	343	1.055151	-11.3518	-373.269	-1.05515
	353	0.876456	-11.1501	-320.539	-0.87646
5 mL/L	323	0.499276	-8.72455	-169.991	-0.49928
	333	0.691742	-9.87754	-240.228	-0.69174
	343	0.61813	-9.86035	-221.879	-0.61813
	353	0.801803	-10.8946	-293.931	-0.8018
7 mL/L	323	0.133313	-5.25641	-48.3165	-0.13331
	333	0.224357	-6.82865	-81.5395	-0.22436
	343	0.249856	-7.33395	-93.0346	-0.24986
	353	0.314169	-8.20522	-119.107	-0.31417

Table (4-10): Thermodynamic function for adsorption of sweet clover extract in petroleum medium at four temperatures.

Conc. of extracted	*Temp. K*	K_{ads}	ΔG^{o}_{ads} $kJ.mol^{-1}$	ΔH^{o}_{ads} $kJ.mol^{-1}$	ΔS^{o}_{ads} $kJ.mol^{-1}K^{-1}$
1 mL/L	323	2.307753	-12.7453	-758.15	-2.30775
	333	2.136763	-12.9315	-724.474	-2.13676
	343	2.032417	-13.1802	-710.299	-2.03242
	353	2.117985	-13.6828	-761.332	-2.11799
3 mL/L	323	1.741571	-12.006	-574.533	-1.74157
	333	1.440471	-11.8637	-491.541	-1.44047
	343	1.27472	-11.8791	-449.108	-1.27472
	353	0.987845	-11.4936	-360.203	-0.98785
5 mL/L	323	0.593053	-9.17663	-200.733	-0.59305
	333	0.597989	-9.48318	-208.614	-0.59799
	343	0.690155	-10.1678	-246.891	-0.69016
	353	0.545184	-9.78738	-202.237	-0.54518
7 mL/L	323	0.279685	-7.20252	-97.5408	-0.27969
	333	0.277187	-7.40123	-99.7045	-0.27719
	343	0.285474	-7.70565	-105.623	-0.28547
	353	0.309953	-8.16645	-117.58	-0.30995

Table (4-11): Thermodynamic function for adsorption of tobacco extract in petroleum medium at four temperatures.

Conc. of extracted	***Temp. K***	K_{ads}	ΔG^{o}_{ads} $kJ.mol^{-1}$	ΔH^{o}_{ads} $kJ.mol^{-1}$	ΔS^{o}_{ads} $kJ.mol^{-1}K^{-1}$
1 mL/L	323	1.419433	-11.4688	-469.946	-1.41943
	333	1.889672	-12.5987	-641.859	-1.88967
	343	2.281163	-13.5022	-795.941	-2.28116
	353	1.903853	-13.3769	-685.437	-1.90385
3 mL/L	323	0.472404	-8.57924	-161.166	-0.4724
	333	0.687408	-9.86052	-238.767	-0.68741
	343	0.68669	-10.1537	-245.688	-0.68669
	353	0.589133	-10.0099	-217.974	-0.58913
5 mL/L	323	0.399934	-8.14184	-137.321	-0.39993
	333	0.619672	-9.57963	-215.93	-0.61967
	343	0.495265	-9.24227	-179.118	-0.49527
	353	0.350116	-8.51618	-132.107	-0.35012
7 mL/L	323	0.44888	-8.44509	-153.433	-0.44888
	333	0.472323	-8.84439	-166.128	-0.47232
	343	0.426749	-8.82698	-155.202	-0.42675
	353	0.380218	-8.75294	-142.97	-0.38022

To elucidate the mechanism of inhibitor adsorption, it is necessary to establish the adsorption modes of the inhibiting species, whether molecular or ionic. The predominant adsorption mode will be dependent on factors such as the extract composition, type of anion as well as chemical changes to the extract. The physical adsorption mechanism, obtained from electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal is due to the electric field existing at the metal/solution interface. A negative surface charge will favour the adsorption of cations whereas; anion adsorption is favoured by positive surface charge. The apparent activation energies (E_a^*) for the corrosion process in absence and presence of plant extracts are evaluated from Arrhenius equation [87]:

$$\log C_R = \log A - \left[\frac{E_a^*}{2.303\ RT}\right] \ldots\ldots (4\text{-}8)$$

where C_R is the corrosion rate (g/cm^2.min), A is the constant frequency factor and E_a^* is the apparent activation energy, R is the gas constant (8.314 J.mol^{-1}K^{-1}) and T is the absolute temperature. By plotting of logarithm of the corrosion rate of steel in petroleum medium in absence and presence of plant extracts versus the reciprocal absolute temperature range (323 – 353 K), give straight lines with slope equal to ($-E_a^*/2.303R$) represented in Fig. (4-23). The data of activation energy are listed in Table (4-12) which demonstrates that the presence of plant extracts in petroleum medium increases the values of E_a^*compared to its unhibited form.

Adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface [84]. The best concentration of each extract has the highest activation energy for certain inhibitor.

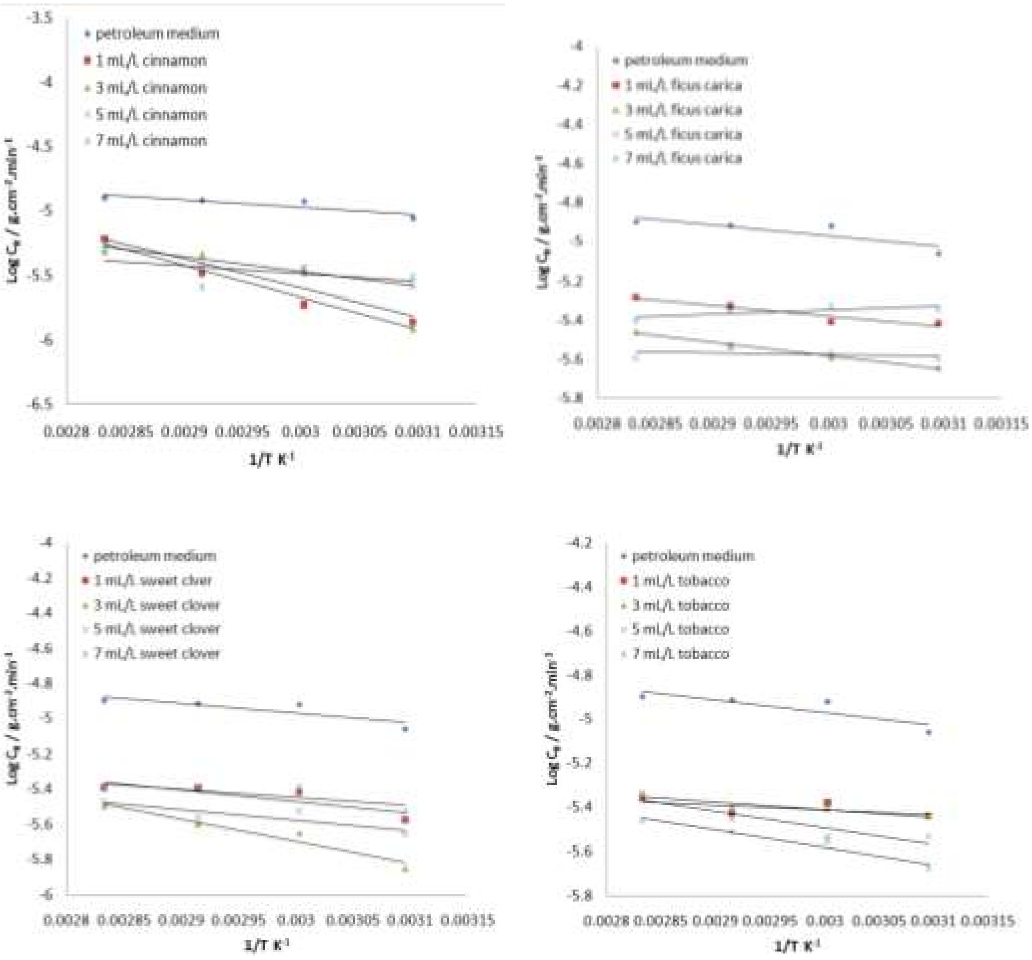


Fig. (4-23): Arrhenius plots of the corrosion rate for steel in petroleum medium in absence and presence of plant extracts.

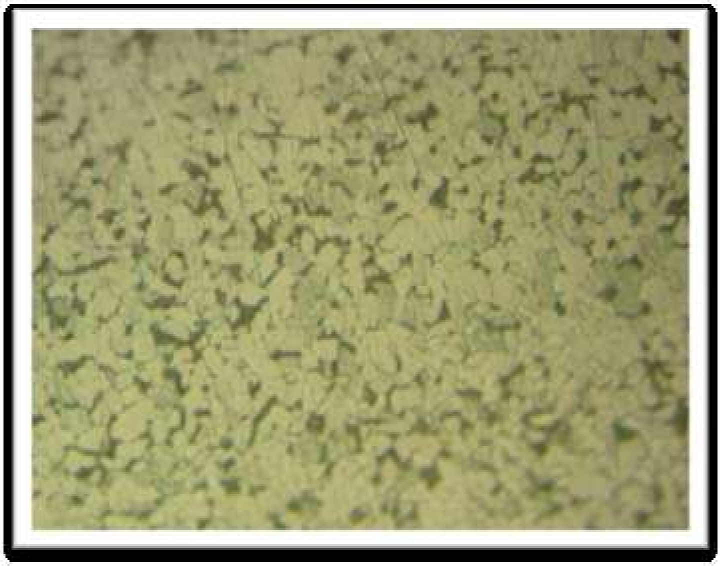
Table (4-12): Activation energies for adsorption of plant extracts on steel in petroleum medium.

Extract	***Conc./ mL/L***	$E_a^* / kJ.mol^{-1}$
Petroleum medium	-	10.57
Cinnamon	1	**46.41**
	3	41.88
	5	21.80
	7	11.10
Ficuscarica	1	10.23
	3	**13.14**
	5	1.35
	7	-4.14
Sweet clover	1	12.57
	3	**24.01**
	5	11.19
	7	8.50
Tobacco	1	4.15
	3	6.63
	5	14.21
	7	**14.65**

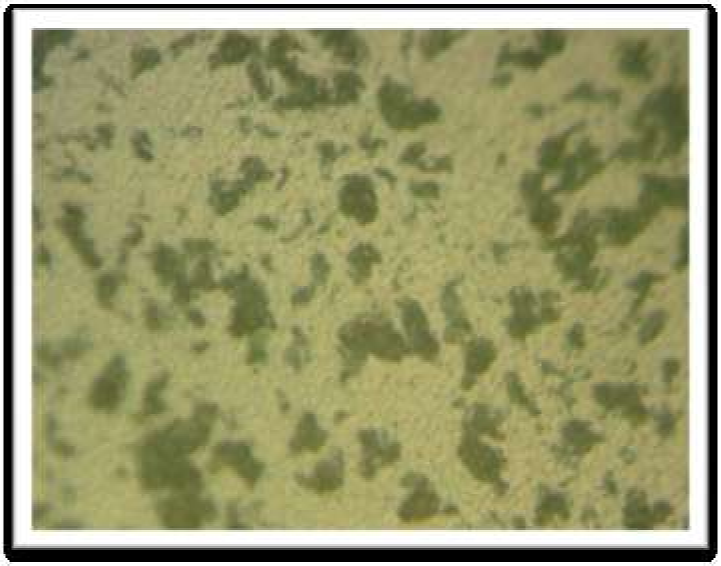
4-11 Optical Microscopy

Optical microscope test shows the surface of steel before and after adding plant extracts in four concentrations of each inhibitor as shown in Figs. (4-24) to (4-30).It is concluded that corrosion has added some undesirable features to the material specimen. These figures show a noticeable reduction in corrosion sites and corrosion products on the corroded surface after adding the inhibitors as compared with the case of corrosion in the petroleum medium without inhibitor especially in the presence of the best concentration of each inhibitor

The optical microscopy of surface of corroded specimen in petroleum medium without inhibitor shows flakes with dark color which refer to corrosion products due to exposure to aggressive corrosion which results from direct exposure to petroleum medium, but in the presence of the inhibitors there is a much smaller damage on the surface and a rather clear color. This is attributed to the formation of a good protective film on the steel surface which prevents direct contact between metal and petroleum medium.

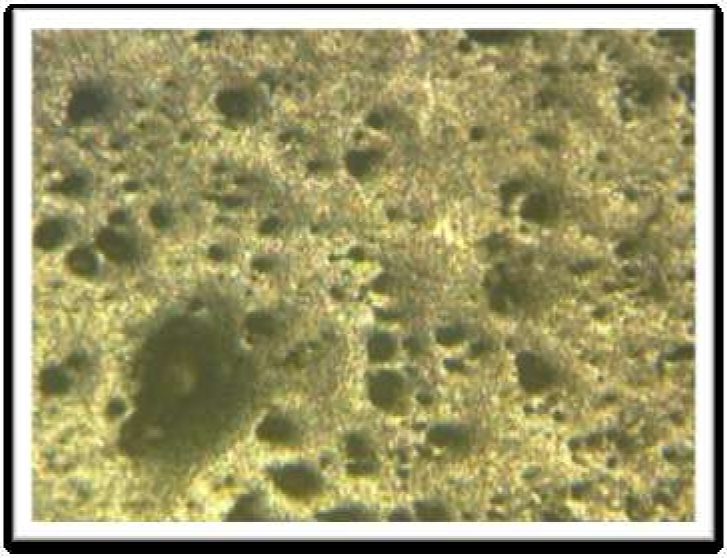


200X

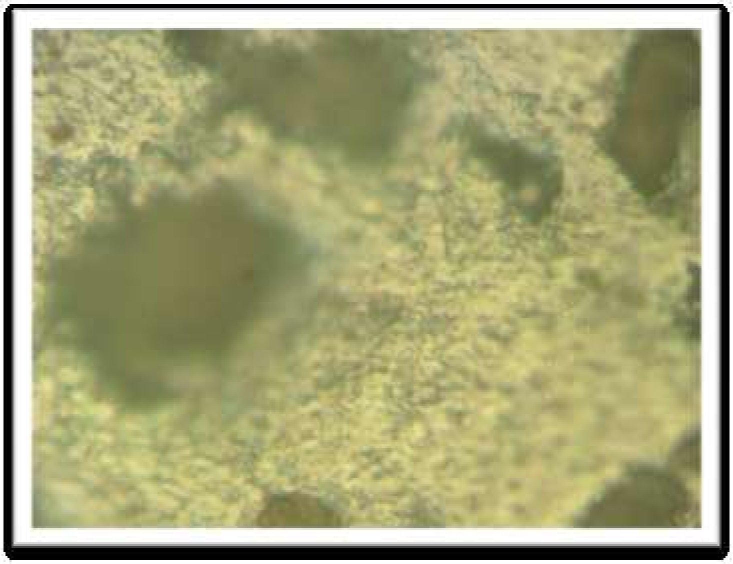


500X

Fig. (4-24): Optical microscopy image for polished steel at two magnitudes.

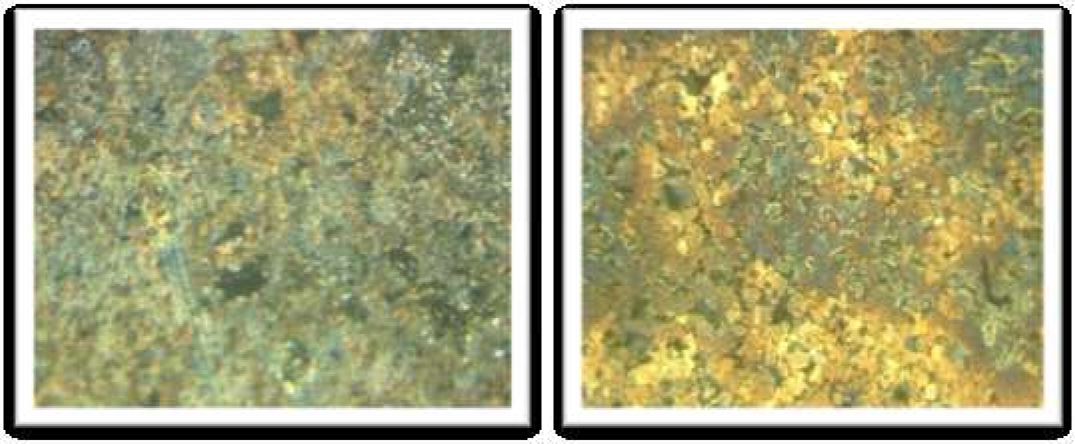


200X



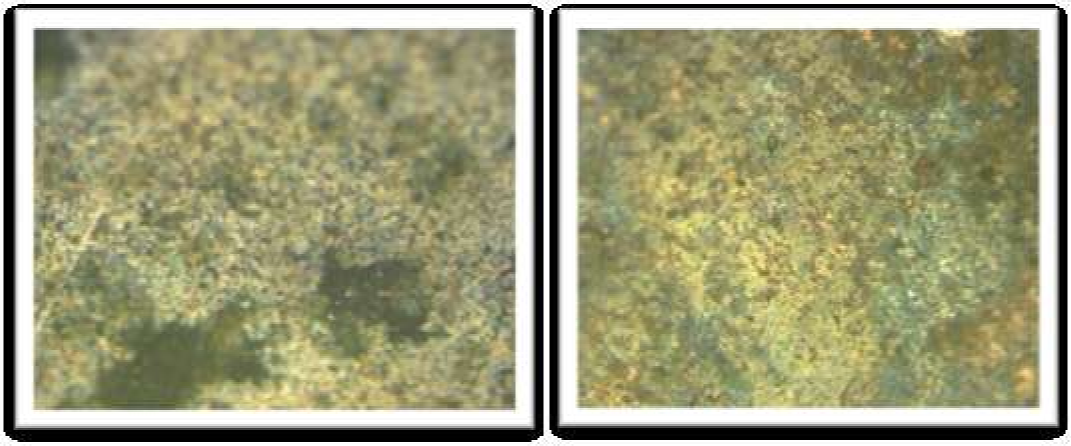
500X

Fig. (4-25): Optical microscopy image for steel after corrosion in petroleum medium at two magnitudes.



10 ppm

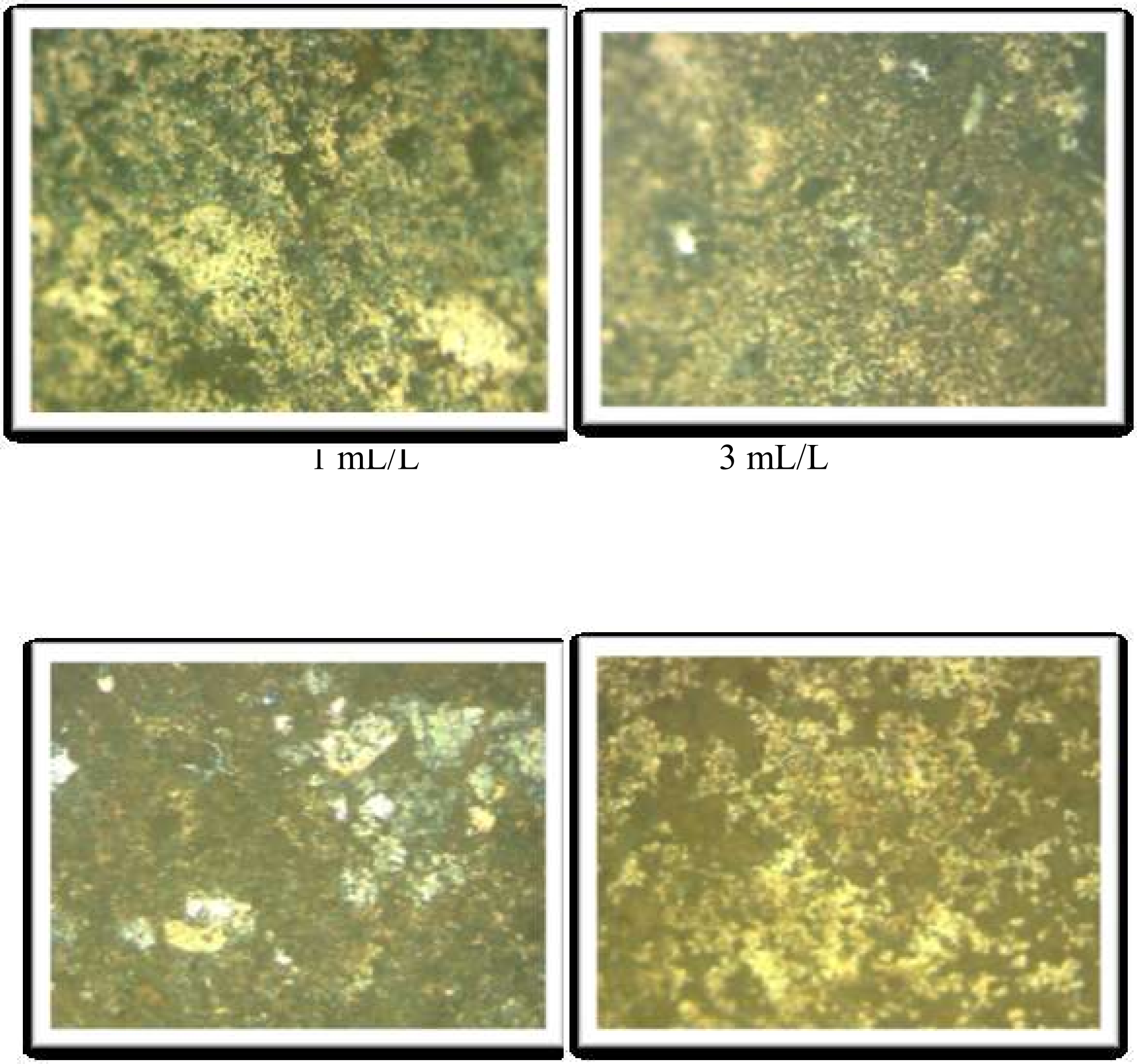
40 ppm



70 ppm

100 ppm

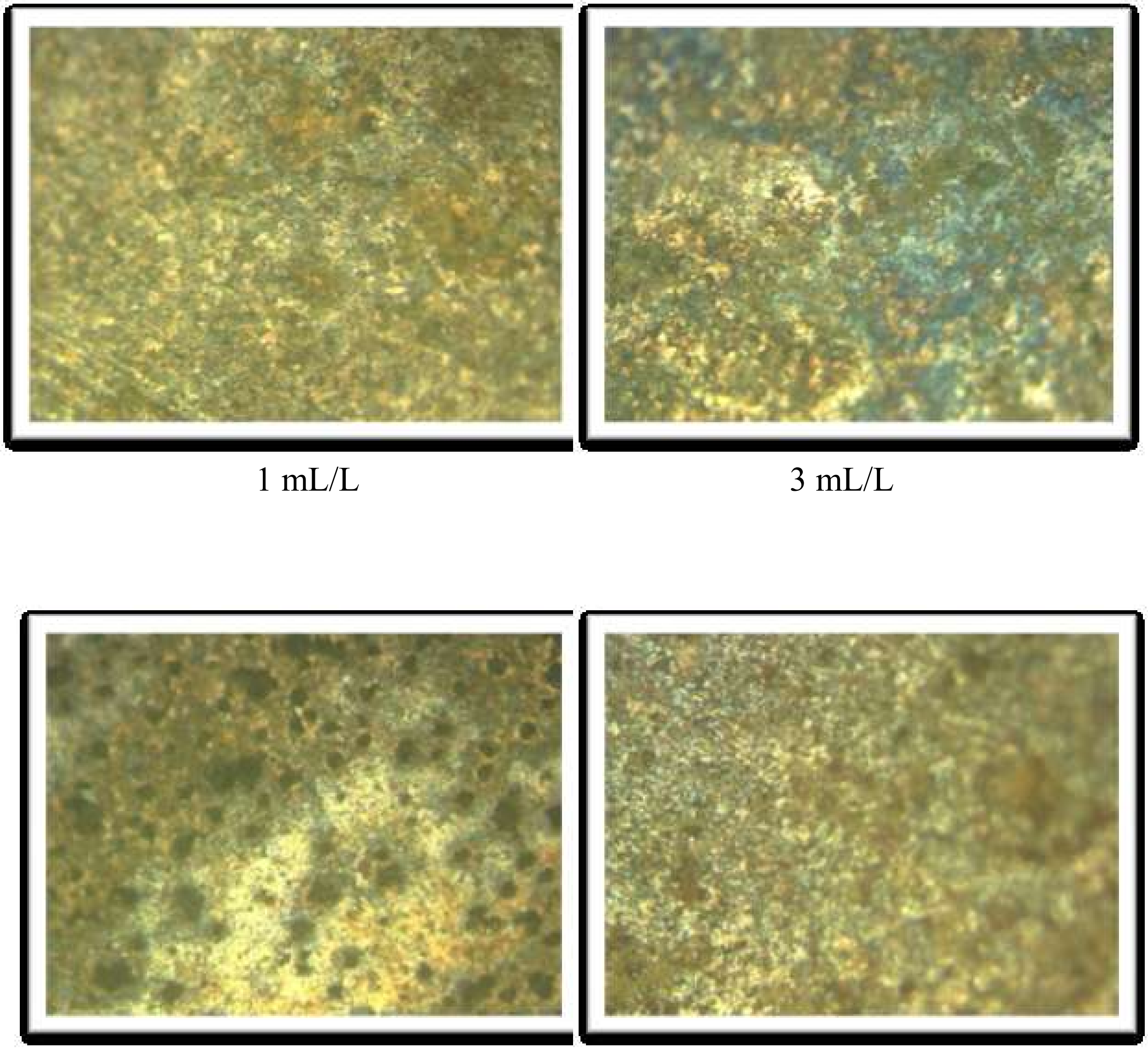
Fig. (4-26): Optical microscopy image for steel after corrosion in petroleum medium in presence of coumarin with four concentrations at 200X.



1 mL/L 3 mL/L

5 mL/L 7 mL/L

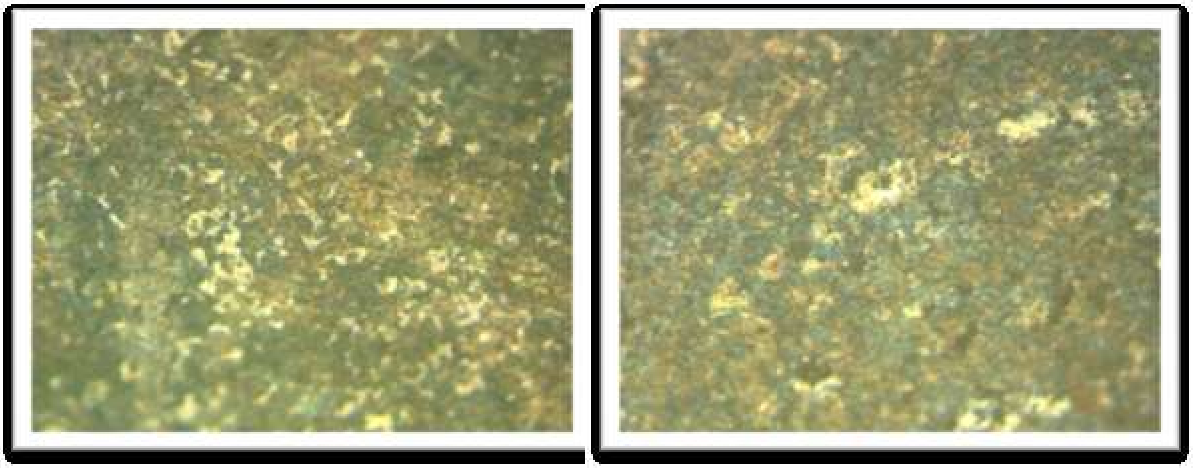
Fig. (4-27): Optical microscopy image for steel after corrosion in petroleum medium in presence of extracted cinnamon with four concentrations at 200X.



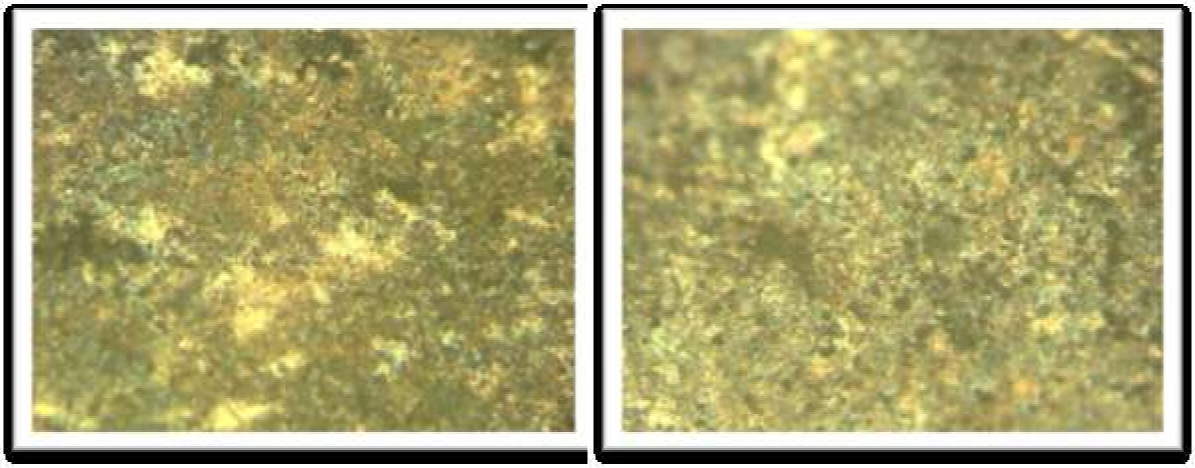
1 mL/L 3 mL/L

5 mL/L 7 mL/L

Fig. (4-28): Optical microscopy image for steel after corrosion in petroleum medium in presence of extracted ficuscarica with four concentrations at 200X.

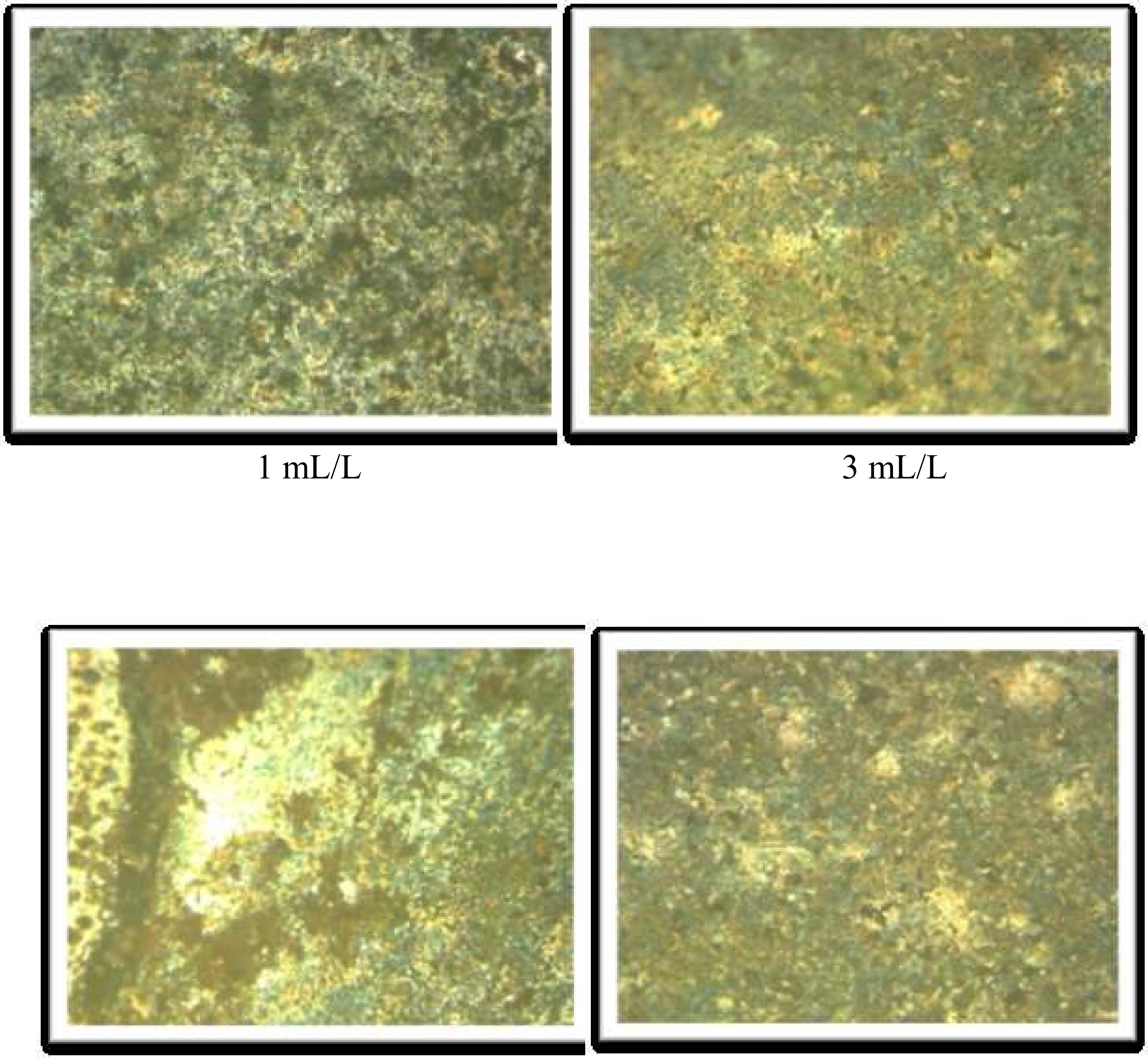


1 mL/L 3 mL/L



5 mL/L 7 mL/L

Fig. (4-29): Optical microscopy image for steel after corrosion in petroleum medium in presence of extracted sweet clover with four concentrations at 200X.



1 mL/L 3 mL/L

5 mL/L 7 ml/L

Fig. (4-30): Optical microscopy image for steel after corrosion in petroleum medium in presence of extracted tobacco with four concentrations at 200X.

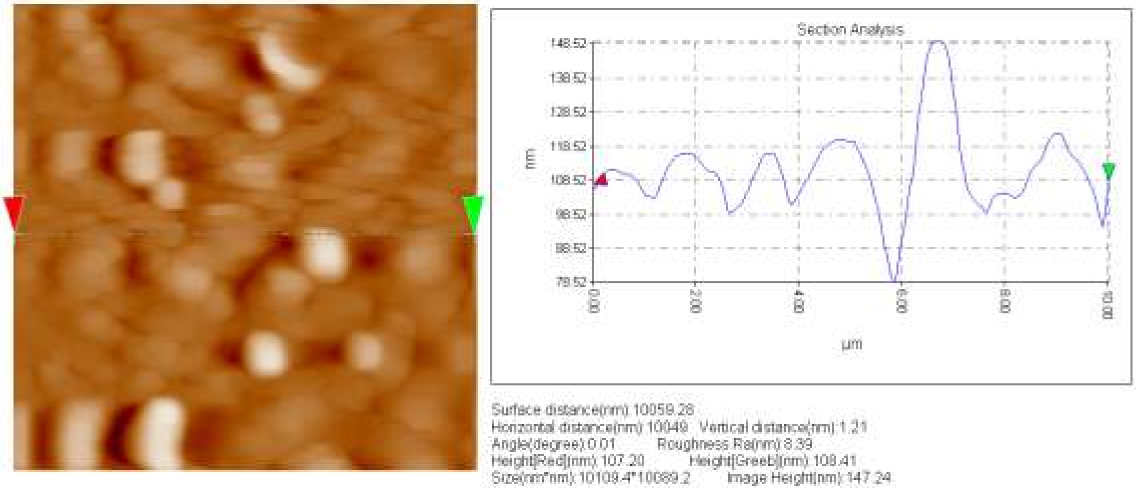
4-12 Atomic Force Microscopy Characterization

AFM is a powerful technique to investigate the surface morphology at nano- to micro-scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface[87-

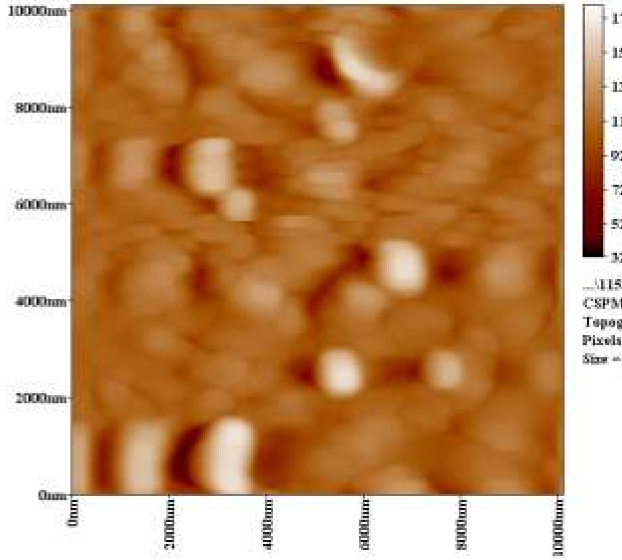
91]. The three dimensional (3D) AFM morphologies and the AFM cross sectional profile for polished steel surface (reference specimen), steel surface immersed in petroleum medium (blank specimen) and steel surface immersed in petroleum medium containing the formulation of the best concentration of each plant extract are shown in Figs.(4-31) to (4-36).

Fig. (4-31)displays the surface topography of un-corroded metal surface. The value of Ra for the polished carbon steel surface (reference sample) is8.39 nm. The slight roughness observed on the polished steel surface is due to atmospheric corrosion. Fig.(4-32) displays the corroded metal surface with few pits in the absence of the inhibitor immersed in petroleum medium. The Ra for the carbon steel surface is 44.7 nm. These data suggests that steel surface immersed in petroleum medium has a greater surface roughness than the polished metal surface, which shows that the unprotected steel surface is rougher and this is due to the corrosion of the steel in petroleum medium. Figs.(4-33) to (4-36)display the steel surface after immersion in petroleum medium containing 1mL/L of Cinnamon extract, 3mL/L Ficuscarica extract, 3mL/L Sweet clover extract and 7mL/L Tobacco extract, the Ra values for the steel surface are 0.631, 4.13, 1.1 and 5.89 nm respectively. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} − plant extract complex thereby inhibiting the corrosion of steel [89].Granularity Cumulation Distribution Reports of all specimens are shown in Appendix E. The above results are in agreement with the results of Khaled and Ebenso[92] and Sangeetha et al. [20] when they used the AFM technique for corrosion inhibition measurements.

The results of surface roughness show that the order of inhibition efficiency takes the following sequence: 1mL/L cinnamon extract > 3mL/L Sweet clover >3mL/L Ficuscarica> 7mL/L Tobacco extract.



Cross-sectional image



3D

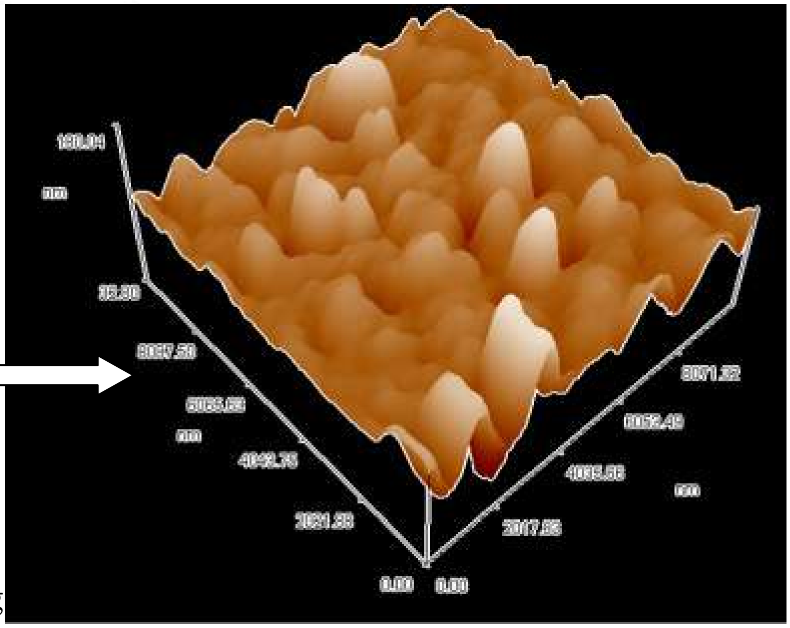


Fig. (4-31):AFM imag

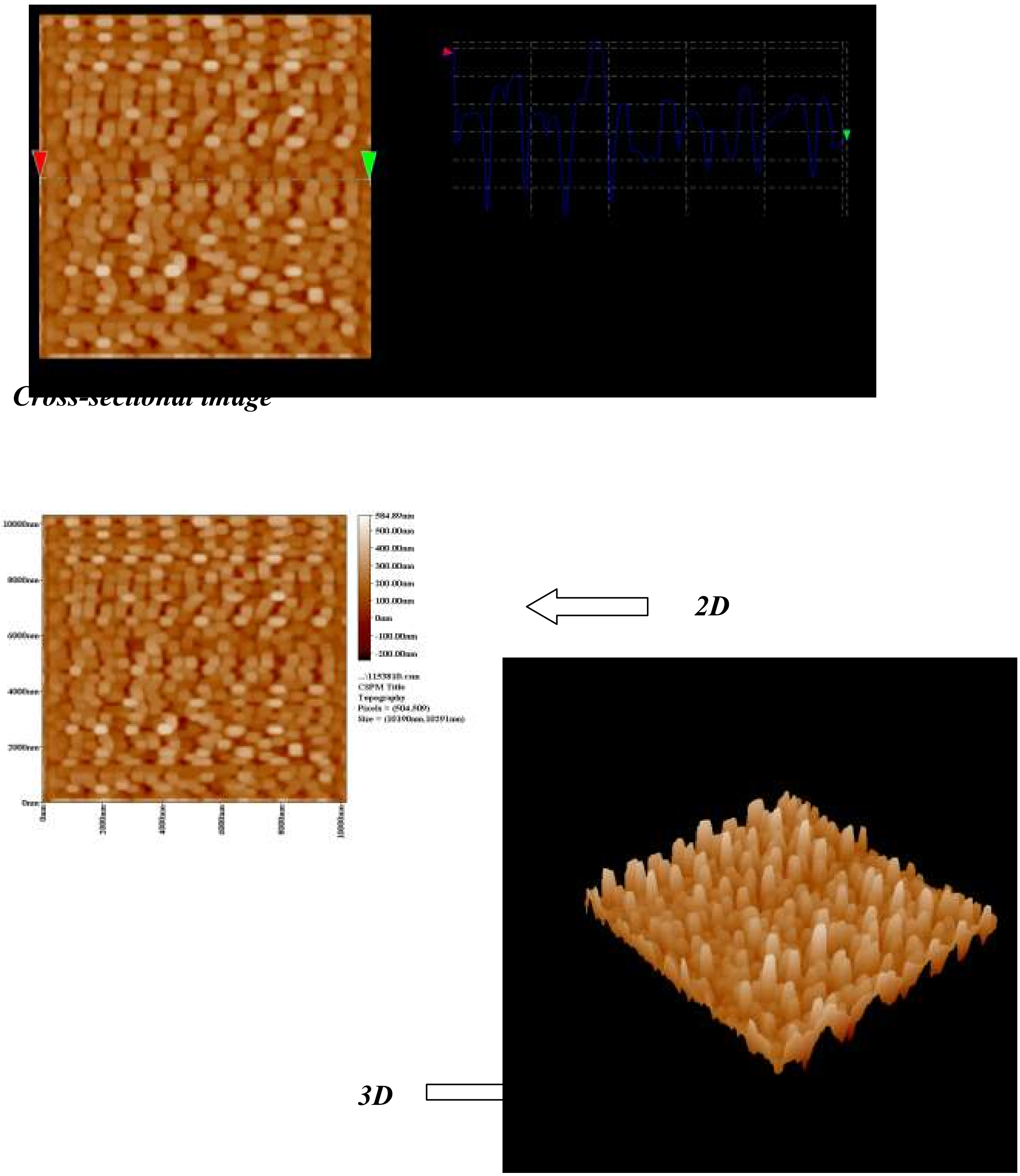


Fig. (4-32): AFM images of the surface of steel immersed in petroleum medium (blank).

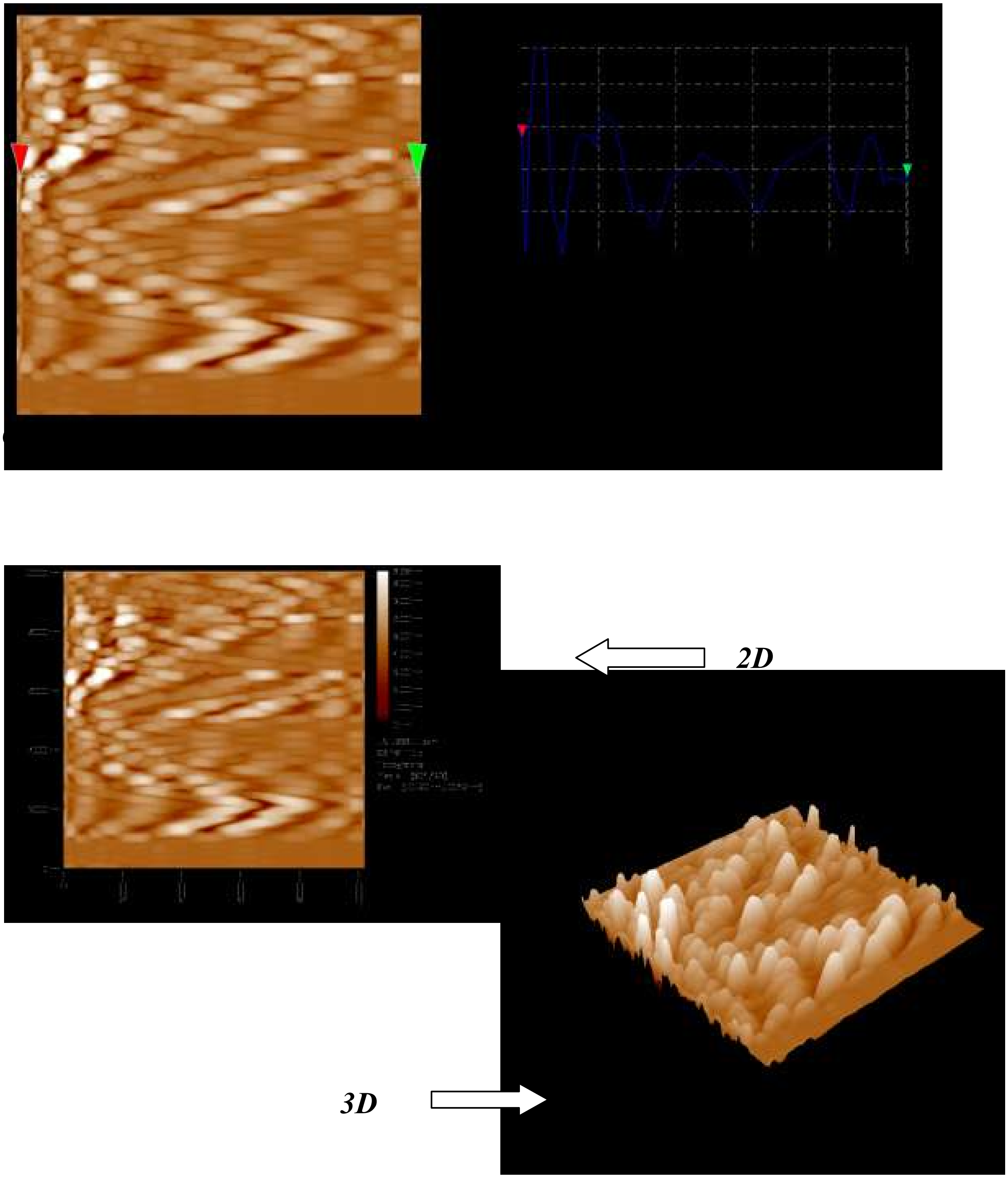
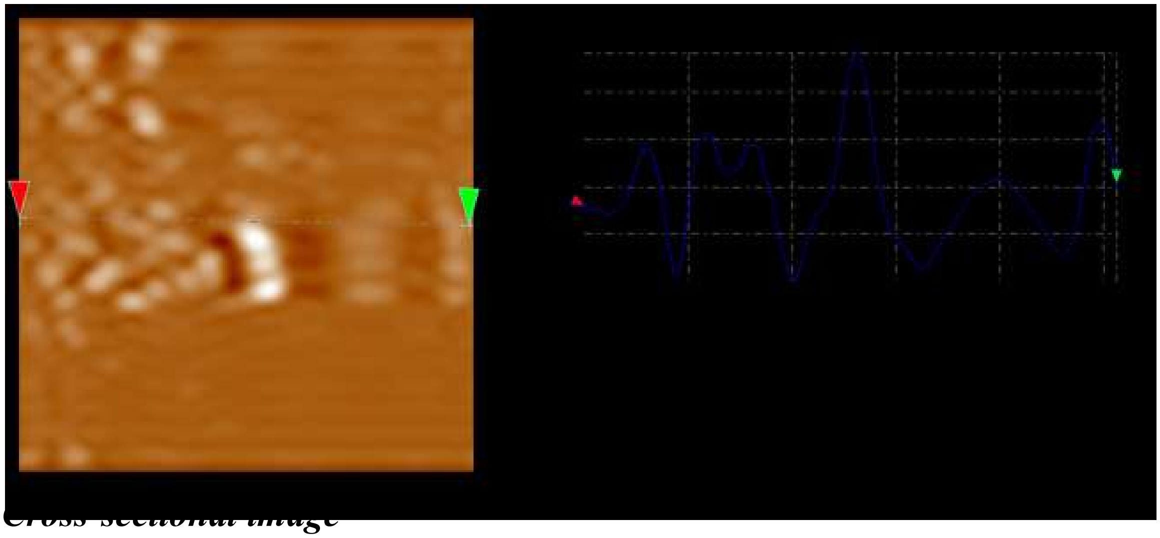


Fig. (4-33): AFM images of the surface of steel immersed in petroleum medium containing 1mL/L Cinnamon extract.



Cross-sectional image

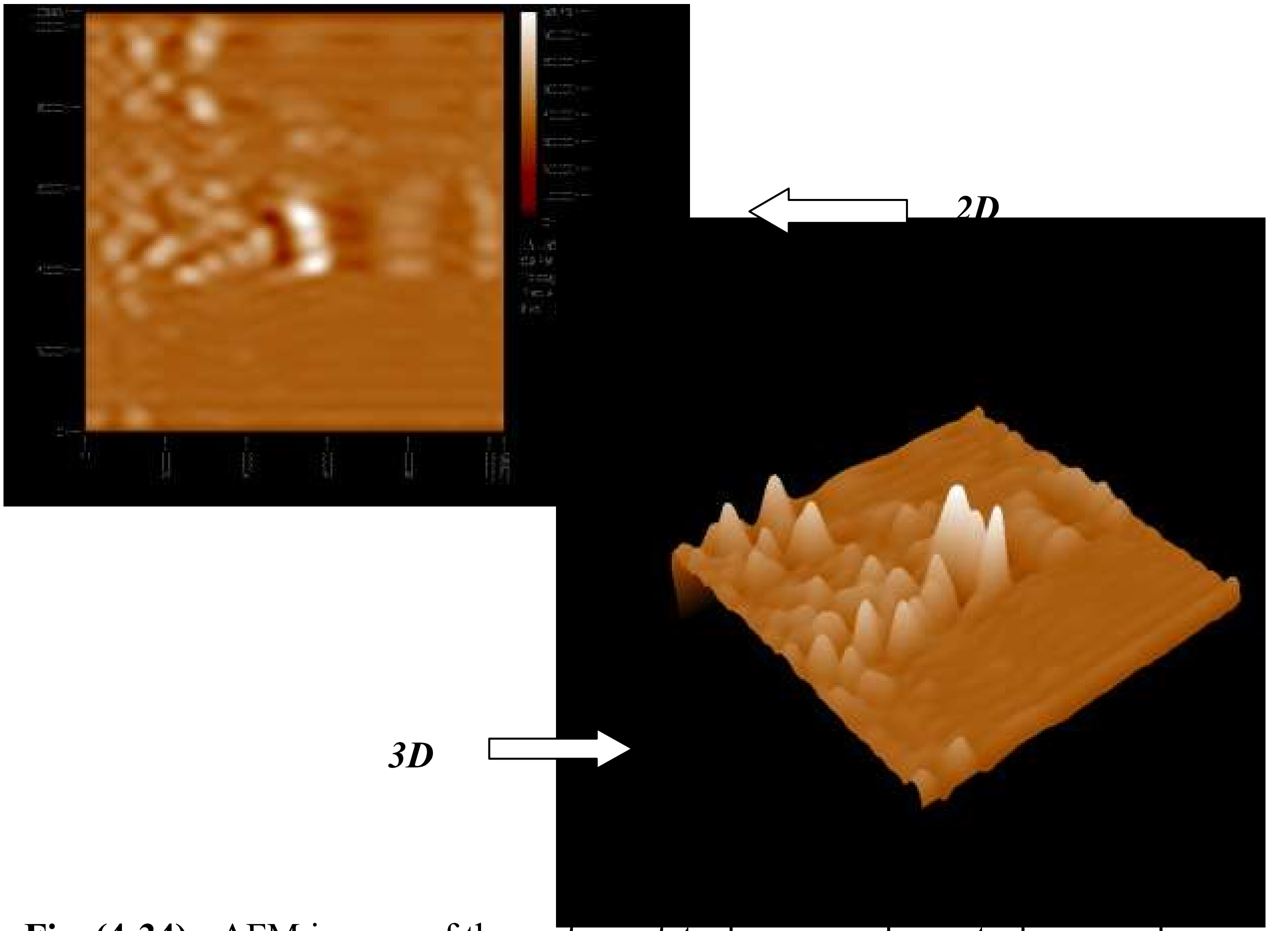


Fig. (4-34): AFM images of the surface ofsteel immersed in petroleum medium containing 3mL/L Ficuscarica extract.

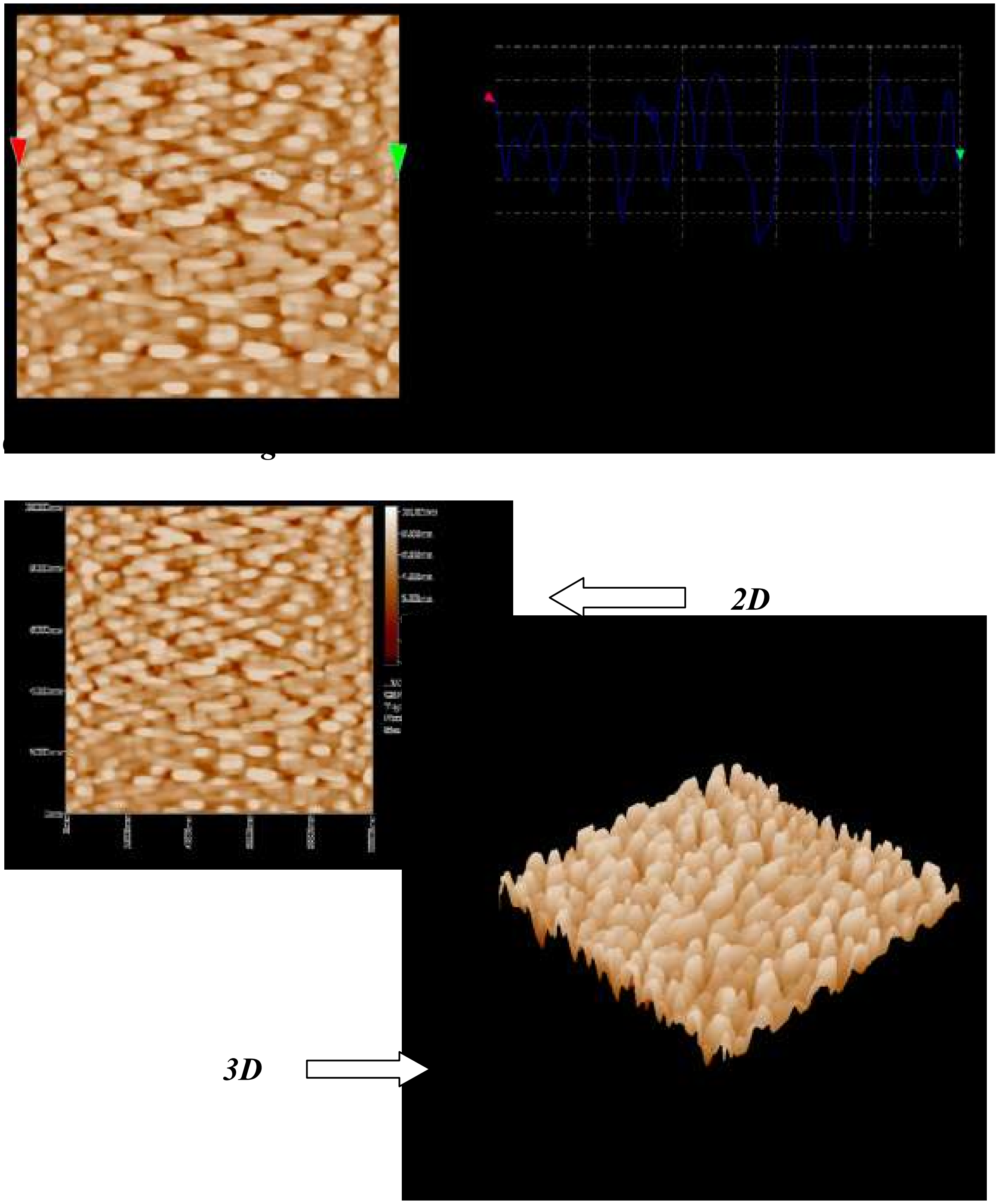


Fig. (4-35): AFM images of the surface of steel immersed in petroleum medium containing 3mL/L Sweet clover extract.

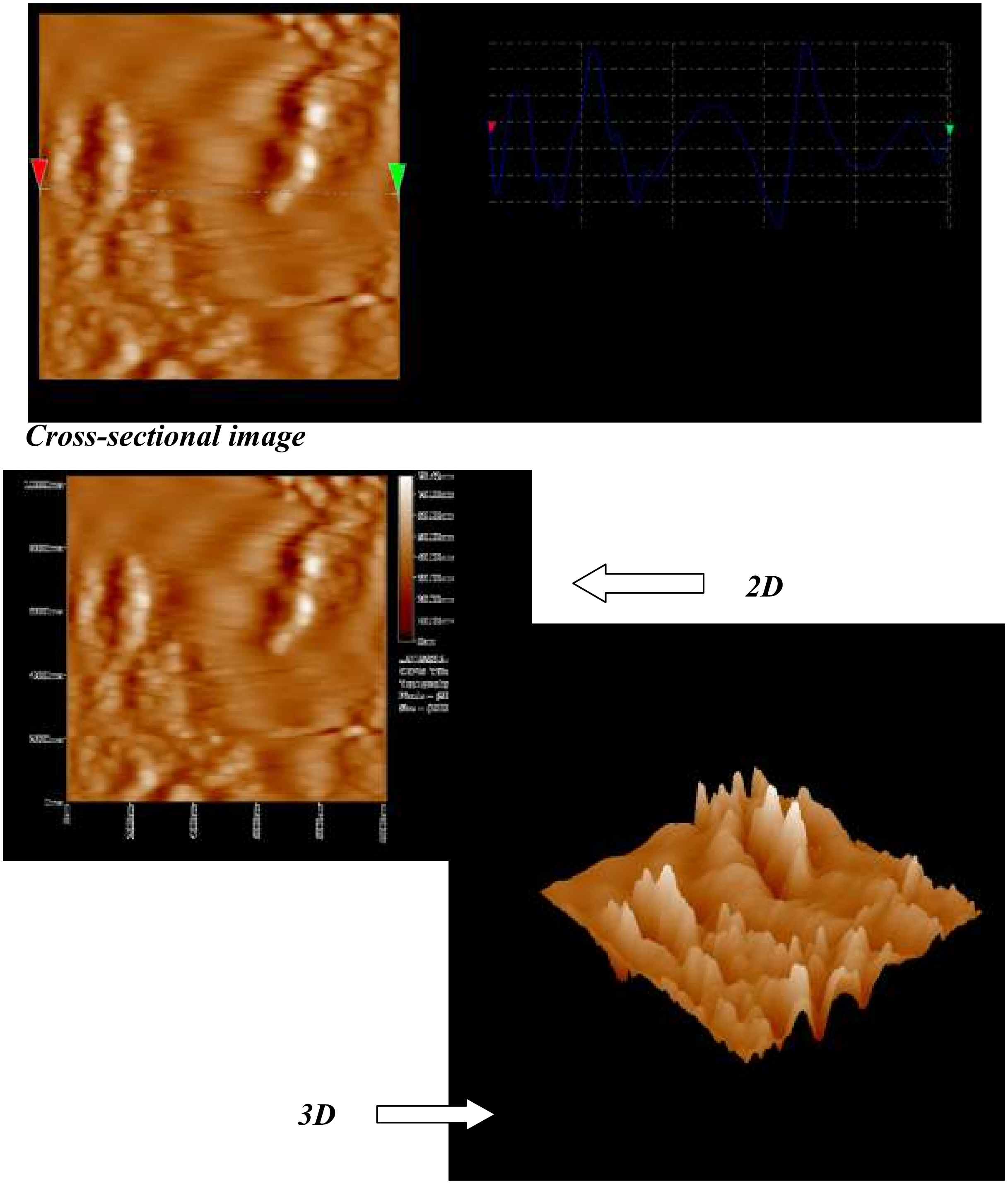


Fig. (4-36): AFM images of the surface ofsteel immersed in petroleum medium containing 3mL/L Tobacco extract.

4-13 Economical Feasibility

Although the costs attributed to corrosion damages of all kinds have been estimated to be of the order of 3 to 5 percent of industrialized countries' gross national product, the responsibilities associated with these problems are sometimes quite diffuse. Corrosion of metals cost the U.S. economy almost $300 billion per year at 1995 prices. Broader application of corrosion-resistant materials and the application of the best corrosion-related technical practices could reduce approximately one-third of these costs.

More than 130 economic sectors had revealed that metallic corrosion cost the United States $82 billion in 1975, or 4.9 percent of its gross national product. It was also found that 60 percent of that cost was unavoidable.

The remaining $33 billion (40 percent) was said to be "avoidable" and incurred by failure to use the best practices then known.

In present work, the best inhibitor is cinnamon extract with concentration 1mL/L which gave IE% up to ~80% in temperature ranges 323-353K. The cost of preparation 30 mL of cinnamon extract is 372 ID. In Iraqi refinery, they injects 25-30 mL in 35000000 L through inhibition process. Therefore, the cost one injection of cinnamon extract equal to 372 ID and the number of injections depend on size of tanks, volume of fluid, type of environment and experimental conditions.

This cost is too low compared with the cost of buying chemical and synthetic inhibitor.

Chapter Five

5-1 Conclusions

From the electrochemical studies a corrosion inhibition for steel (St 37-2) in petroleum medium in presence of plant extracts supported by other analysis techniques and calculations, the following conclusions can be drawn:

1-Ethanolic extracts of *Cinnamon* stems, *Ficuscarica* leaves, *Sweet clover* leaves and *Tobacco* leaves are acceptable inhibitors for steel in petroleum medium at four temperatures (323, 333, 343 and 353) K.

2- The plant extracts are mixed-type inhibitor as shown by the values of corrosion potentials and Tafel slopes, and they give acceptable efficiencies. The best concentration of each extract is 1mL/L for *Cinnamon*, 3mL/L for *Ficuscarica*, 3mL/L *Sweet clover* and 7mL/L *Tobacco*. The efficiencies vary with increasing temperature due to a variety of cathodic and anodic sites on inhibited steel surface.

3- The straight lines of plotting C_{inh}/θ against C_{inh} for the four plant extracts at four temperatures (323, 333, 343 and 353)K indicate that the plant extracts obey Langmuir adsorption isotherm with the linear regression coefficient R^2close to unity, and range of $0.996 \geq R^2 \geq 0.917$.

4- The relatively small values of the equilibrium constant of the adsorption-desorption process K_{ads} and the negative values of ΔG^o_{ads} indicate the spontaneously physical adsorption process of extracted inhibitors. When comparision is made among the four inhibitors, it can be seen that the cinnamon is the best.

5-The negative sign of ΔH^o_{ads} values indicates that the adsorption of inhibitor molecule is an exothermic process and either physic- or chemisorption. The increase in concentration leads to decrease of negativity of ΔH^o_{ads} values.

6- The negative sign of ΔS^o_{ads} values indicates that plant extracts retain the metal ions and reduce the dissolution of steel and the activated complex at the rate determining step denotes an association rather than a dissociation step. The most negative values of ΔS^o_{ads} were for cinnamon extract.

7- The increase in activation energies E_a^* confirms the inhibitive action of plant extracts, where adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface. The highest activation energy is in presence of *cinnamon* extract compared with other extracts.

8- Optical microscopy test shows a noticeable reduction in corrosion sites and corrosion products on the corroded surface after adding the inhibitors as compared with the case of corrosion in the petroleum medium without inhibitor especially in the presence of the *cinnamon* extract.

9-AFM studies confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+}–plant extract complex on the metal surface thereby inhibiting the corrosion of steel (St 37-2) in petroleum medium. The decrease in roughness is arranged as follows:

1mL/L cinnamon extract – 3mL/L sweet clover extract – 3mL/L ficuscarica extract – 7mL/L tobacco extract

5-2 Suggestions for Further Studies

From the present work, can be recommended for further studies as follows:

1- Attempt to use oil extract of natural products as inhibitors in petroleum medium and other media.

2- Carry out the experiments at a wide range of temperatures using the same plant extracts to inhibit corrosion in many metals and alloys in different media.

3- Study the inhibition with other techniques such as electronic impedance spectroscopy EIS, scanning electron microscopy SEM and energy dispersive spectroscopy EDS.

4- Study the effect of mixed natural plants to corrosion inhibition.

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