Enhance protection of Carbon Steel from Rust by using Cypress Essential Oil as Anti-Corrosion in Acidic Media

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Abstract

Carbon steel corrosion prevention is a process of great deal that has always drown a great attention. This research includes the using of volatile oil extract from the Mediterranean cypress plant in preventing carbon steel corrosion by adding it to the corrosion solutions in different quantities. Acidic media at a concentration of 1M was used as corrosive media. Two methods were used for the effect of cypress oil on corrosion protection: Firstly, the metal was coated with a thin layer of volatile oil found in the plant along with sodium silicate, and secondly, different amounts were added to the corroding medium at a certain temperature. Corrosion inhibition was examined by Atomic Force Microscopy (AFM), High-Performance Liquid Chromatography (HPLC), and FT-IR spectra. Up to 96% protection was achieved in acidic medium.

Keywords: Carbon Steel, Corrosion, Inhibition

Introduction

As a definition, corrosion is an electro-chemical reaction that appear between the environment and the metal, which ends up in destruction parts of the metal. Corrosion is classified as wet and dry [1, 2]. The factors that affect the surface of metal according to the state, nature, and conditions of the corrosive environments. Corrosion is divided into several forms: galvanic corrosion, uniform (general) corrosion, crevice corrosion, pitting corrosion, selective corrosion, intergranular corrosion erosion corrosion, and stress cracking corrosion[3, 4.[

Iron is a vital metal, it is utilised in wide fields, however, properties of the metal can change and deform due to corrosion. In addition to the huge economic damage due maintenance protection processes, there is also the pollution caused by metal corrosion, which constitutes a pollution problem in the industrial system [5.[

Coating with organic materials can be used to enhance the ability and effectiveness of protection of metals from corrosion [6-8]. Organic compounds that have heterogeneous atoms in their structure can be used to protect iron from corrosion. Atoms including oxygen, nitrogen, and sulfur, can facilitate the adsorption of the compound on the metal surface which forms a layer that insulate and protects metal from the effects of the outer environments. For example; Veedu and his group used leaf extract of tropical Mangifera indica L[9] to keep iron from corrosion in the saline medium (sodium chloride salt 3.5%) , Spiral ginger extraction was utilized by Costus afer to protect iron from corrosion in the acidic medium (hydrochloric acid 0.5 M) using the gravimetric method, as well as using

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of henna leaves aqueous extract (Lawsonia) as an inhibitor of carbon steel corrosion in acidic solutions. Furthermore it was found that increasing the concentration of the extract resulted in elevation in protection efficiency[8. [

Material and Methods

Preparation and extraction of volatile oils for the studied plant

Hydro-distillation (Clevenging) method was applied to extract Oil. Water evaporates in a closed container, then in another closed container, vapor passes through plant samples with a hole that allows the steam to escape and passes through the condenser after it passes through the plant samples for 3 hours at 4 ºC [10, 11]Then the oil was separated from condensed liquid using separating funnel and kept, at a specific temperature, in special bottles [9, 12-14.[

2.2Preparation of a Metal Samples

By immersing the metal in concentrated HCl, the oxide layer and impurities were removed from metal surface then washed with distilled water [15]. Using silicon carbide sheets of different smoothness the metal surface was smoothed. To prevent grains of smoothing paper from adhesion on the surface of the metal, wet smoothing method was applied. Lastly, ethanol was used as washing solution for metal sample prior to preserve it in the dryer away from any moisture[16.[

Preparation of Solutions

.1Blank solution: HCl was diluted with distilled water (DW) to prepare 1M, and transferred into a 1-liter volumetric flask, then completing it to the mark with DW

.2Sample solutions: Different concentrations of sample solution (0.05,0.1 and 0.5ppm) were prepared by dissolving sample in a little DW, then it is transferred to a volumetric flask, after adding the previously prepared blank solution, the appropriate amount of DW was added[17, 18.[

Carbon steel contains many elements; some of them are responsible for its hardness, such as manganese and silicon. Other elements are found in in small quantities such phosphorus and sulfur. Table (1) shows the composition of carbon steel [6, 9.[

Table 1. Chemical composition of carbon steel.

Metal	C%	S%	Mn%	Si%	Cu%	P%	Ni%	Cr%	Fe%
Carbon Steel 45	0.36-0.42	0.05	1.00-1.40	0.15-0.30	0.50	0.05	0.20	0.20	96.88-97.49

To protect the metal from corrosion, cypress oil was used in two ways:

.1Addition different concentrations of oil to the corrosive medium at specific temperatures.

.2Mixing of sodium silicate with cypress oil to make a paste of thin layer that covers the metal and applying Tafel curves to study it[4, 19.[

An inhibition efficiency of (95-96) % was obtained from oil extract, and as the concentration of used oil increased (0.05, 0.1, 0.5) ppm, the corrosion current density decreased. The concentration of 0.5 ppm. gave the highest value of corrosion protection, as shown in Table (2). Highest inhibition efficiency of 99% was observed when using oil as coating for metal as shown in Table (3

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Table 2. Corrosion parameters for blank and inhibitor in NaCl solutions at different concentration

Comp.	*Temp (k)*	*$-E_{corr}$ (mV)*	*I_{corr} $(A/cm^2)*10^{-6}$*	*-Bc (mV/Dec)*	*Ba (mV/Dec)*	*WL $(g/m^2.d)$*	*PL (mm/y)*	*IE%*
Blank	**298**	-691.9	868.05	-200.2	94.6	217	10.1	-
	318	-711.0	1050	-105.3	96.9	263	12.2	-
0.05	**298**	-447.4	45.36	-153.3	87.0	11.3	0.526	95
	318	-460.3	57.52	-160.1	114.6	14.4	0.668	95
0.1	**298**	-460.1	38.30	-113.4	76.1	9.57	0.445	96
	318	-469.7	43.17	-122.0	94.4	10.8	0.501	96
0.5	**298**	-429.0	32.13	-95.5	70.3	8.03	0.373	96
	318	-453.4	37.36	-117.4	73.1	9.34	0.434	96

Table 3. Shows the corrosion parameter of oil extract in the saline medium as a direct coating.

Comp.	*Temp (K)*	*$-E_{corr}$ (mV)*	*I_{corr} $(A/cm^2)*10^{-6}$*	*-Bc (mV/Dec)*	*Ba (mV/Dec)*	*WL $(g/m^2.d)$*	*PL (mm/y)*	*IE%*
Blank	**298**	-691.9	868.05	-200.2	94.6	217	10.1	-
sample	**298**	185.1	3.55	-252.6	149.2	0.887	0.0412	99

Ecorr.: corrosion potential,Icorr.: corrosion current density , bc: cathodic Tafel slope, ba: anodic Tafel slope, WL: weight loss, PL: penetration loss, %IE inhibition efficiency

Results and Discussion

Through the cathodic and anodic Tafel curves, corrosion current density and corrosion voltage were measured in both the absence and presence of oil in the acidic solution. From Figures 1, 2, and 3, anodic (ba) and cathodic (bc) Tafel slopes were also determined .The Tafel diagram revealed that presence of oil shifts (Ecorr) to a high value compared to the blank solution, indicating that the protection is anodic[5, 20]. Tafel plot data also proposes the same results as to consider an anodic protection functions because Ecorr of carbon steel has shifted to a higher position in the presence of the oil in comparison to blank solution. The percentage of inhibition is calculated from the equation [1].

$$\% \ IE=(I\ corr.-Icorr.(inh))/(Icorr.) \times 100 \quad (1)$$

Where %IE; is a percentage of inhibition efficiency; Icorr.; is a Corrosion Current Absence of inhibitor; Icorr.(inh) a corrosion current in the presence of the inhibitor.

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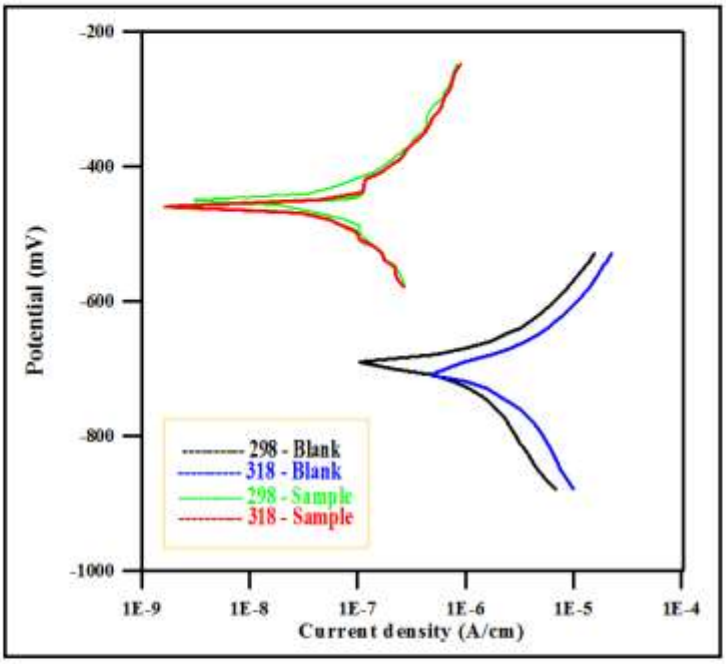

Figure 1. Polarization curves of blank solution and sample in 0.05 ppm concentration.

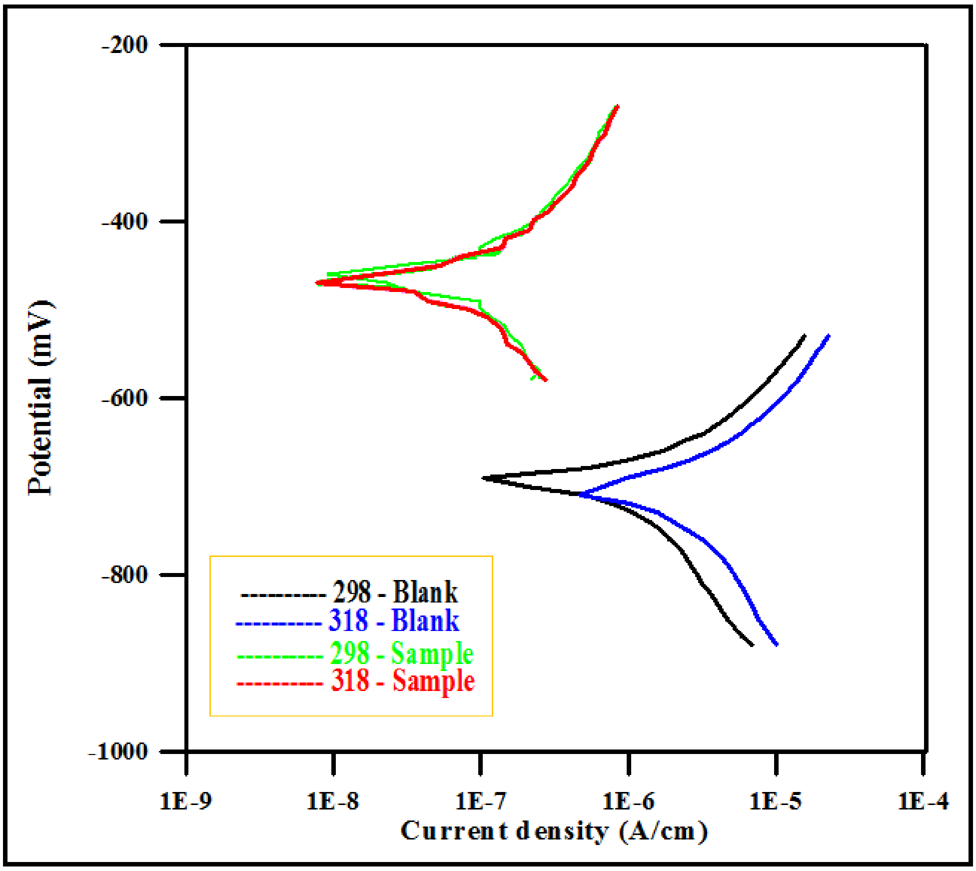

Figure 2. Polarization curves of blank solution and sample in 0.1 ppm concentration

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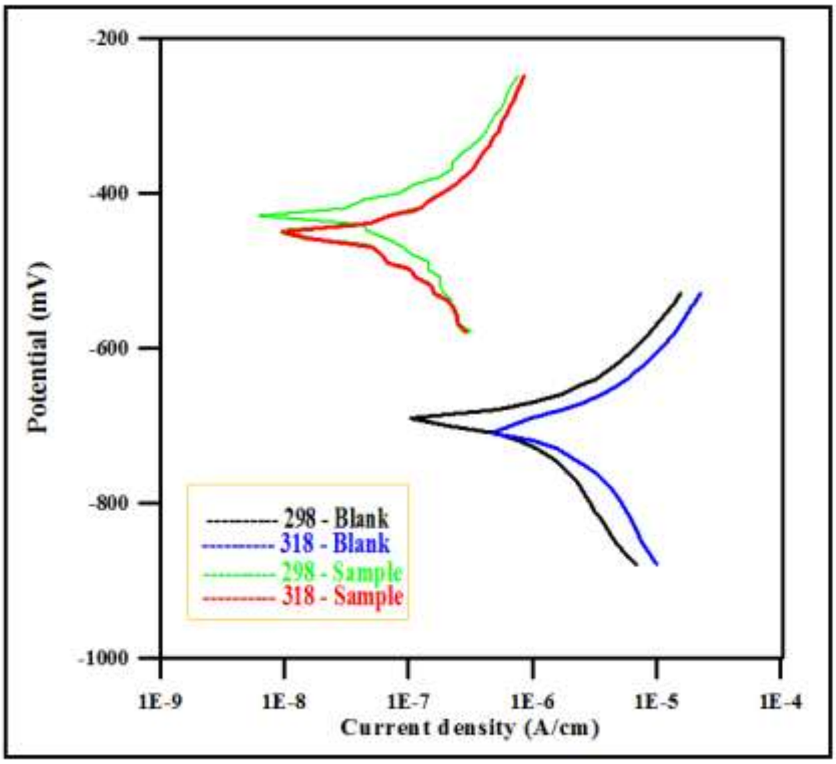

Figure 3. Polarization curves of blank solution and sample in 0. 5 ppm concentration

Atomic Force Microscope

AFM method is used to study the properties of grains, and surface layers in materials such as organic and inorganic composites, metallic and polymer. Several imaging modes give information about the surface of the sample, and provide detailed 3D images [21]. Atomic for both approaches presence and absence of inhibitor are beneficial.

To examine the extracted cypress oil AFM was used, the Figures (4) and (5) show that small surface areas provide good protection for the metal from corrosion and the distribution of its particles is good [22].

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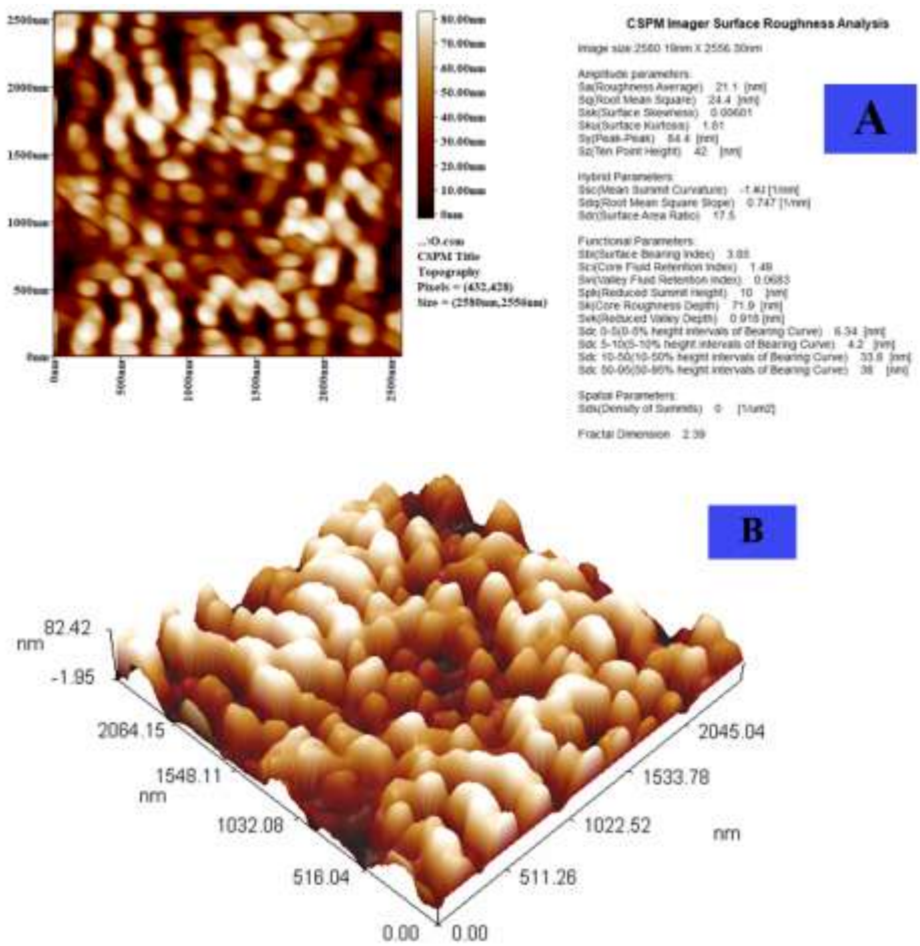

Figure 4. (A) Two-dimensional image, (B) Three-dimensional image of the metal surface before using the inhibitor in atomic force device.

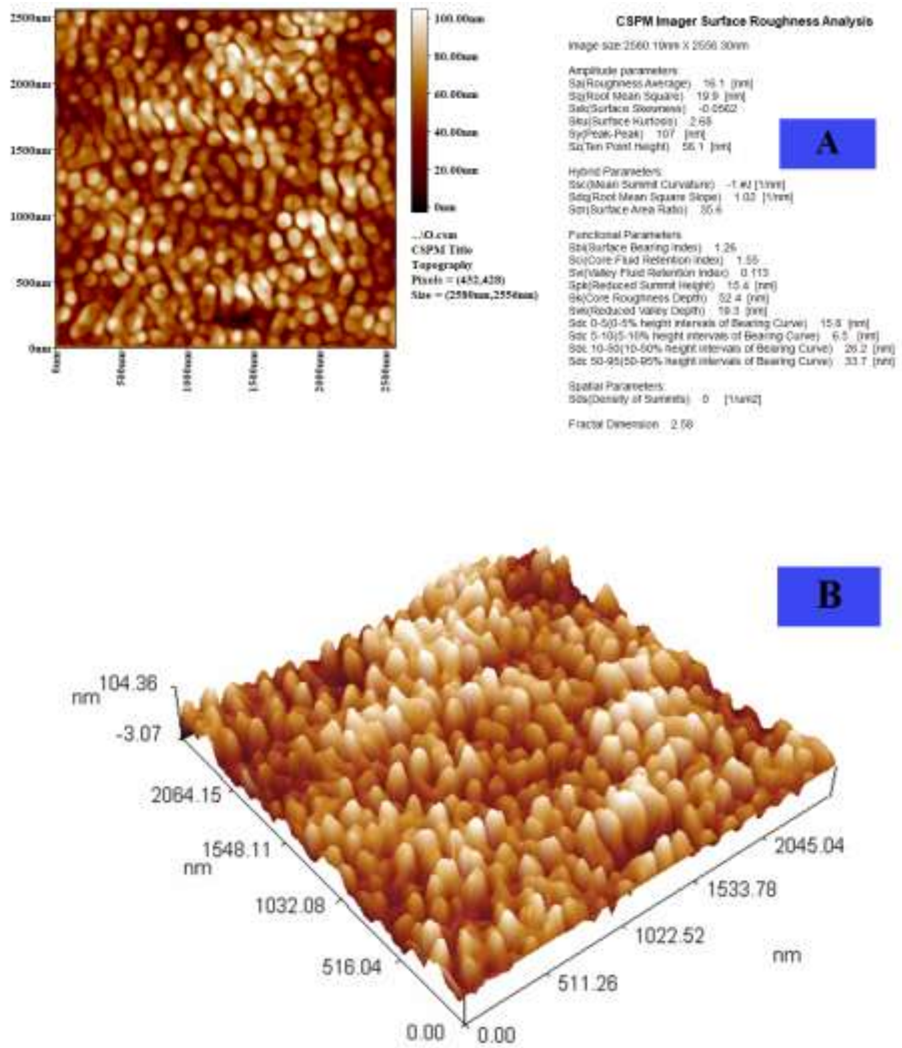

Figure 5. (A) Two-dimensional image, (B) Three-dimensional image of the metal surface after using the inhibitor in atomic force device.

Infrared Spectroscopy:

The infrared spectrum of the extracted oil was examined, where the spectrum showed the presence of a group of main beams of functional groups found in the compounds that make up the extract, and the important of these groups are stretching vibrations of hydroxyl groups (O-H), whether phenolic or those belonging to alcohol supplements and carboxylic acids, which appeared at 3409 cm-1, these peak appear wide due to the overlap between these groups. C-H Aromatic stretching vibration for C-H bonds appeared at 3010 cm-1 and aliphatic C-H groups appeared in the range 2871 cm-1 to 2929 cm-1. The other groups are considered important groups which is (C = O) stretching vibration, it appeared at 1652-1724 cm-1, and they belong to the carbonyl and carboxyl groups. The other absorption packages, which appeared at 1446 cm-1 and 1371 cm-1, are due to C=C stretching aromatic bonds and the C-N stretching bond respectively, from this spectrum we conclude the presence of groups, which have a significant impact on the effectiveness of these compounds, both in protection against corrosion [23, 24]

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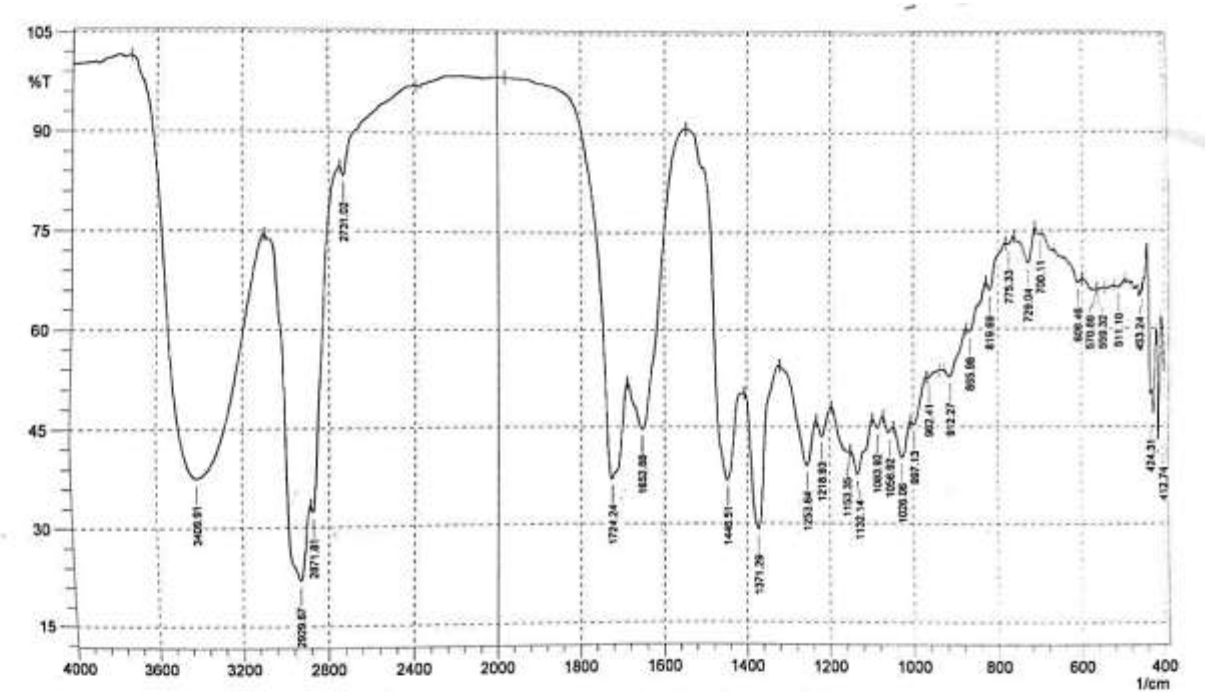

Figure 6. The (FTIR) Spectrum of the extracted cypress oil.

Quantitative and Qualitative estimation for active compounds

A high-performance liquid chromatography device used to estimate active compounds by injecting. The sample beam height, detention time, flow rate, stationary phase[2, 31] and temperature were determined for some of the following compounds: chlorogenic, rutin, 4-hydroxy benzoic, qurctin cinnamaldehyde and catechol, it was found to be present in in cypress oil extract oil at different concentrations, as the highest concentration was observed in Rutin compound, which contains a large amount of phenols[11, 25.[

Table 4. Shows the materials and their concentration (M) measured according to the high-performance liquid chromatography technique (HPLC).

Concentration	Material
0.196054	rutin
14.77422	catechol
143.2383	4-hydroxy benzoic
33.56301	qurctin
101.5749	cinnamaldehyde
3.372609	chlorogenic

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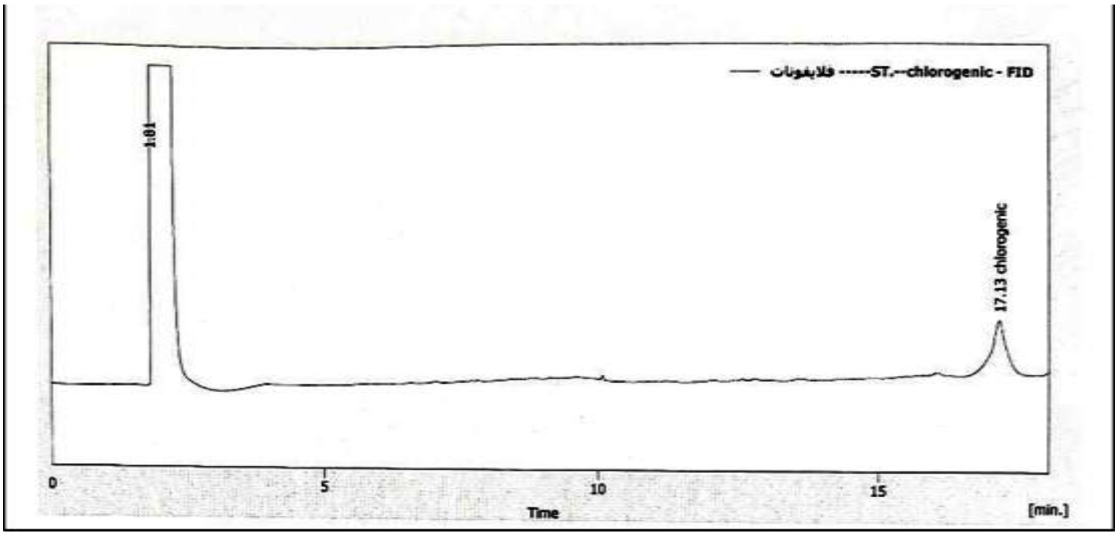
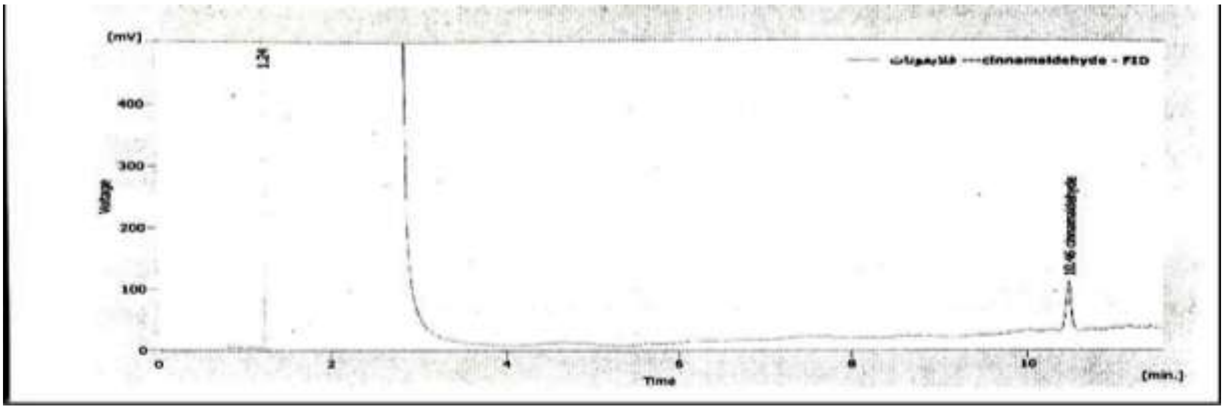


Result Table (Uncal-فلايفونات-----ST.—chlorogenic-FID)

	Reten.Time (min)	Area (mV.s)	Height (mV)	Area (%)	Height (%)	W05 (min)	Compound Name
1	0.097	3.533	0.294	0.0	0.0	0.15	
2	1.807	27866.816	991.322	96.8	90.8	0.44	
3	17.130	922.277	100.378	3.2	9.2	0.15	chlorogenic
	Total	28792.626	1091.994	100.0	100.0		

Figure 7. The standard curve of the chlorogenic compound in the oil extract.



Result Table (Uncal-فلايفونات----cinnamladehyde -FID)

	Reten.Time (min)	Area (mV.s)	Height (mV)	Area (%)	Height (%)	W05 (min)	Compound Name
1	1.243	96329.931	984.935	99.5	92.6	1.61	
2	10.457	500.398	79.154	0.5	7.4	0.07	cinnamladehyde
	Total	96830.329	1064.089	100.0	100.0		

Figure 8.The standard curve of cinnamaldehyde in the oil extract.

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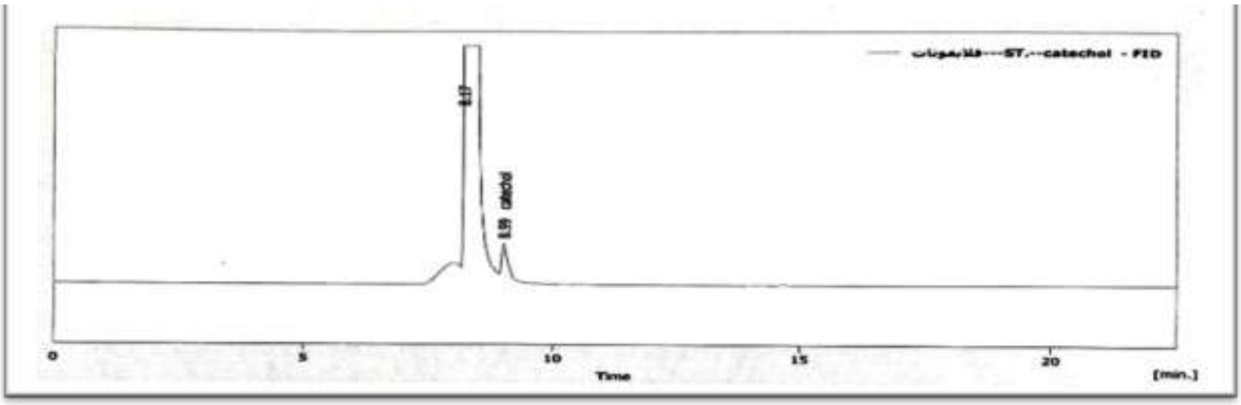
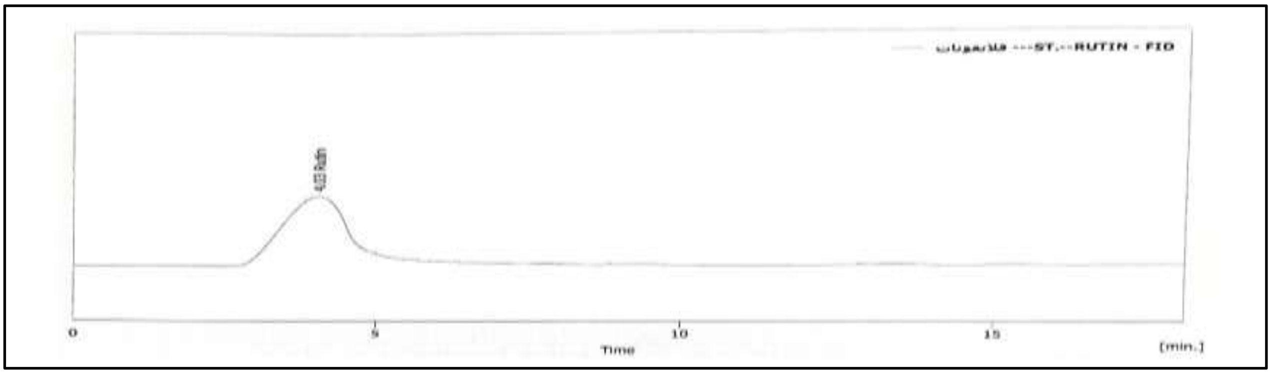


Result Table (Uncal-فلايفونات-----ST.— catechol -FID)

	Reten.Time (min)	Area (mV.s)	Height (mV)	Area (%)	Height (%)	W05 (min)	Compound Name
1	8.170	20173.728	919.352	95.1	87.5	0.34	
2	8.993	1031.104	131.016	4.9	12.5	0.11	catechol
	Total	21204.832	1051.168	100.0	100.0		

Figure 9. The standard curve of catechol in the oil extract.



Result Table (Uncal-فلايفونات-----ST.— Rutin -FID)

	Reten.Time (min)	Area (mV.s)	Height (mV)	Area (%)	Height (%)	W05 (min)	Compound Name
1	4.030	16954.340	264.740	100.0	100.0	1.05	Rutin
	Total	16954.340	264.740	100.0	100.0		

Figure 10. The standard curve of Rutin compound in the oil extract

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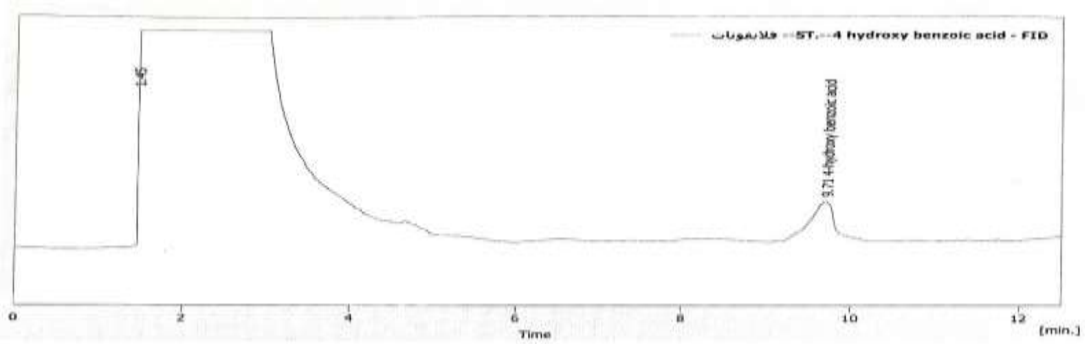
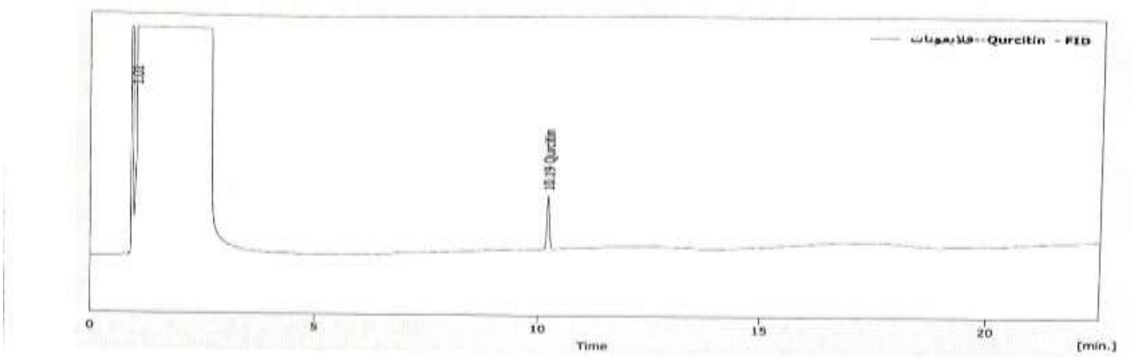


Result Table (Uncal-فلايفونات-----ST.— 4-hyroxy benzoic acid-FID)

	Reten.Time (min)	Area (mV.s)	Height (mV)	Area (%)	Height (%)	W05 (min)	Compound Name
1	1.453	123101.069	984.042	99.9	97.6	1.85	
2	9.707	146.979	23.908	0.1	2.4	0.10	4-hyroxy benzoic acid
	Total	123248.048	1007.949	100.0	100.0		

Figure 11. The standard curve of 4-hydroxy benzoic acid in the oil extract.



Result Table (Uncal-فلايفونات--- Qurctin -FID)

	Reten.Time (min)	Area (mV.s)	Height (mV)	Area (%)	Height (%)	W05 (min)	Compound Name
1	1.010	88659.211	825.783	98.9	78.0	1.67	
2	10.193	945.576	232.704	1.1	22.0	0.06	Qurctin
	Total	89604.786	1058.487	100.0	100.0		

Figure 12.The standard curve of Qurctin in the oil extract

Conclusion

Using The volatile oil of the cypress plant as protector from corrosion for carbon steel, where it gave protection percentage up to (99%) as coating for carbon steel medium as well as results of up to (96%) as additive in solution, where different concentrations and different temperatures were applied to mimic the external environment. these results are excellent compared to synthetic organic compounds that are used as anti-corrosion compounds because of their undesirable environmental impact as well as their high cost. For all that, Mediterranean cypress oil, which is one of the available and eco-friendly materials that can be grown in abundance and

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used safely as anti-corrosive material without harming the environment
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