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Wild Clary Plant Extract as Corrosion Inhibitor for Carbon Steel in Seawater Medium

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HIGHLIGHTS

- Wild clary extract is considered a good inhibitor of carbon steel
- The research methodology is a method for the principle of sustainability and recycling of waste
- It is an easy and inexpensive extraction method.

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ABSTRACT

Aqueous extract of wild clary has been used in place of a corrosion inhibitor in the corrosion control of carbon steel. The major components of this extract are Ethan amine, Amino-octadic, and 4H-Pyran-4-one. It has an excellent inhibition efficiency (IE) of 83.078% at a concentration of 20 (mL/L) and a temperature of 298 (K). The extract was characterized by FTIR and GC MS, where the antibacterial was tested and the protective film was analyzed on the samples using FTIR spectra. The protective film formed on the metal surface is confirmed using an electrochemical study by Potentiostat, which revealed that this extract was a mixed-type inhibitor.

1. Introduction

Plant extracts have become important because of the environmentally friendly and renewable source and the wide range of inhibitors needed. The plant extracts are considered a very rich source of naturally manufactured chemicals that can be extracted in a simple process at a low cost. Most natural products were previously used as corrosion inhibitors for various metals in different environments [1-2], an aqueous extract from the wild clary powder is taken because it has a perfect corrosion inhibitor for carbon steel in seawater. Many authors paid attention to protecting carbon steel by natural extracts, including leaves and stem extracts of dilleniid dicot genus acuta [3], Andrographis paniculate extract [4], extract of asafetida [5], allium sativum extract [6], chamaerops humilis [7], chenopodium ambrosioides extract [8], tobacco plant extract [9], hyptis aqueous extract [10], extracts of cinnamon stems [11], ficus carica [12], sweet clover [13] and tobacco leaves [14], pumpkin peels [15], Sumac (Rhus) extract [16], olive leaf [17], extract of allium cepa seeds [18], and alcoholic extract of coffee [19]. The extract was used from wild clary powder because it is a good corrosion inhibitor for carbon steel in seawater. The extract was characterized by FTIR and GC MS, where the antibacterial was tested and the inhibition efficiency (IE) of the corrosion control system for ground carbon steel, which was submerged in seawater in the absence and presence of the inhibitor and at different temperatures, was evaluated by studying the polarization and analyzing the protective film on the samples using FTIR spectra.

2. Experimental work

2.1 Material

2.1.1 Preparation of the plant extract

A wild clary plant was selected as a green extract inhibitor, where this plant was washed with distilled water and it was dried. Then, it was ground and prepared by adding 5 grams of the ground plant in 200 mL of ethanol (99.9%)[20], and the suspended impurities were filtered, making up to 100 mL by evaporation. Five concentrations of the extract have been used, including 5, 10, 15, 20, and 25 mL/L.

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2.1.2 Preparation of the Specimen

Carbon steel was used in this work with the chemical composition of steel alloys, which is shown in Table1, obtained by Foundry – Master XPERT in the Centralized Device for Standardization and Quality Control –Ministry of Planning. Specimens of the dimensions (2cm x 2cm x 4 mm) were polished to a mirror finish, degreased with ethanol, and then dried and stored in a plastic container used for electrochemical examination.

Table 1: Chemical composition of carbon steel

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al	Co	Fe
Wt.%	0.161	0.271	0.425	0.0073	0.0049	0.0771	0.004	0.0142	0.0506	0.001	0.001	Bal

2.1.3 Preparation of the medium

Seawater was prepared in this study by adding 35 grams of salt (NaCl) to one liter of water, which was used as a corrosive medium.

2.2 Electrochemical measurements

Measurements were performed with Potentiostat (WINKINK MLab 200) from Bank Company with three electrodes, where the working electrode is steel samples, the reference electrode is Ag/AgCl electrode and the counter electrode is Pt electrode which is arranged in cells under temperature-controlled to (298, 318 and 338 K). First, the potential of the open circuit (OCP) was present, and then the polarization curves were recorded by automatically changing the electrode voltage of +200 mV around the OCP. All measurements were performed in 3.5% NaCl as a corrosive medium. The linear Tafel sections of the region of the anodic and cathode curves were extrapolated for corrosion potential to obtain corrosion data.

2.3 Fourier-transform infrared spectroscopy (FTIR)

The film that was formed on the surface of the carbon steel (the active substance) was carefully removed and mixed well with KBr. FTIR spectra were recorded by (IRPrestige-21), in the Environment and Water Department / Ministry of Science and Technology.

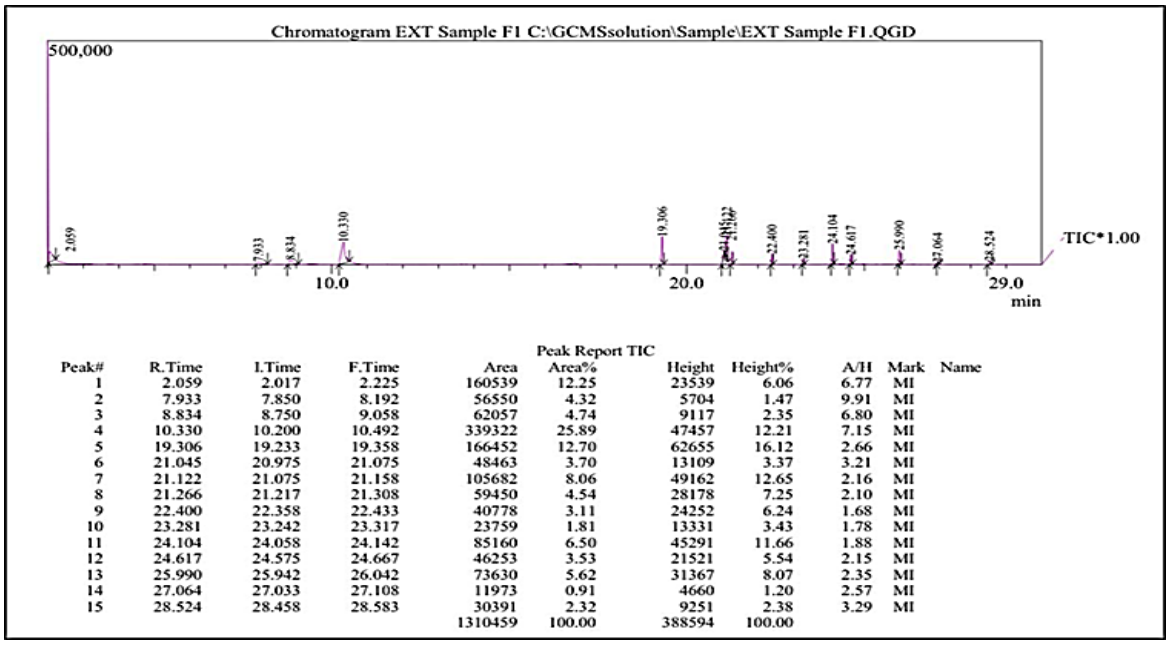
3. Experimental results

3.1 Characterization of the Extracted Material

In order to prepare the corrosion inhibitor, we need to obtain the active ingredients in the extracted plant, where many steps were performed as shown in the experimental part to obtain the active substances from the wild clary plant, and some tests were done to characterize these materials.

3.1.1 Gas Chromatography-Mass Spectrometry (GC-MS)

The GC MS technique was used to analyze the active compounds in the extract. Figure 1 shows GC MS data for the active substances, including Ethan amine, Amino-octadic, and 4H-Pyran-4-one. These figures indicate the presence of active substances in a large curve compared to the standard substances in small shapes, as shown in Figure 2.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	2.059	2.017	2.225	160539	12.25	23539	6.06	6.77	MI	
2	7.933	7.850	8.192	56550	4.32	5704	1.47	9.91	MI	
3	8.834	8.750	9.058	62057	4.74	9117	2.35	6.80	MI	
4	10.330	10.200	10.492	339322	25.89	47457	12.21	7.15	MI	
5	19.306	19.233	19.358	166452	12.70	62655	16.12	2.66	MI	
6	21.045	20.975	21.075	48463	3.70	13109	3.37	3.21	MI	
7	21.122	21.075	21.158	105682	8.06	49162	12.65	2.16	MI	
8	21.266	21.217	21.308	59450	4.54	28178	7.25	2.10	MI	
9	22.400	22.358	22.433	40778	3.11	24252	6.24	1.68	MI	
10	23.281	23.242	23.317	23759	1.81	13331	3.43	1.78	MI	
11	24.104	24.058	24.142	85160	6.50	45291	11.66	1.88	MI	
12	24.617	24.575	24.667	46253	3.53	21521	5.54	2.15	MI	
13	25.990	25.942	26.042	73630	5.62	31367	8.07	2.35	MI	
14	27.064	27.033	27.108	11973	0.91	4660	1.20	2.57	MI	
15	28.524	28.458	28.583	30391	2.32	9251	2.38	3.29	MI	
				1310459	100.00	388594	100.00			

Figure 1: GC- MS analysis for the extracted active material from wild clary plant compared with the standard material

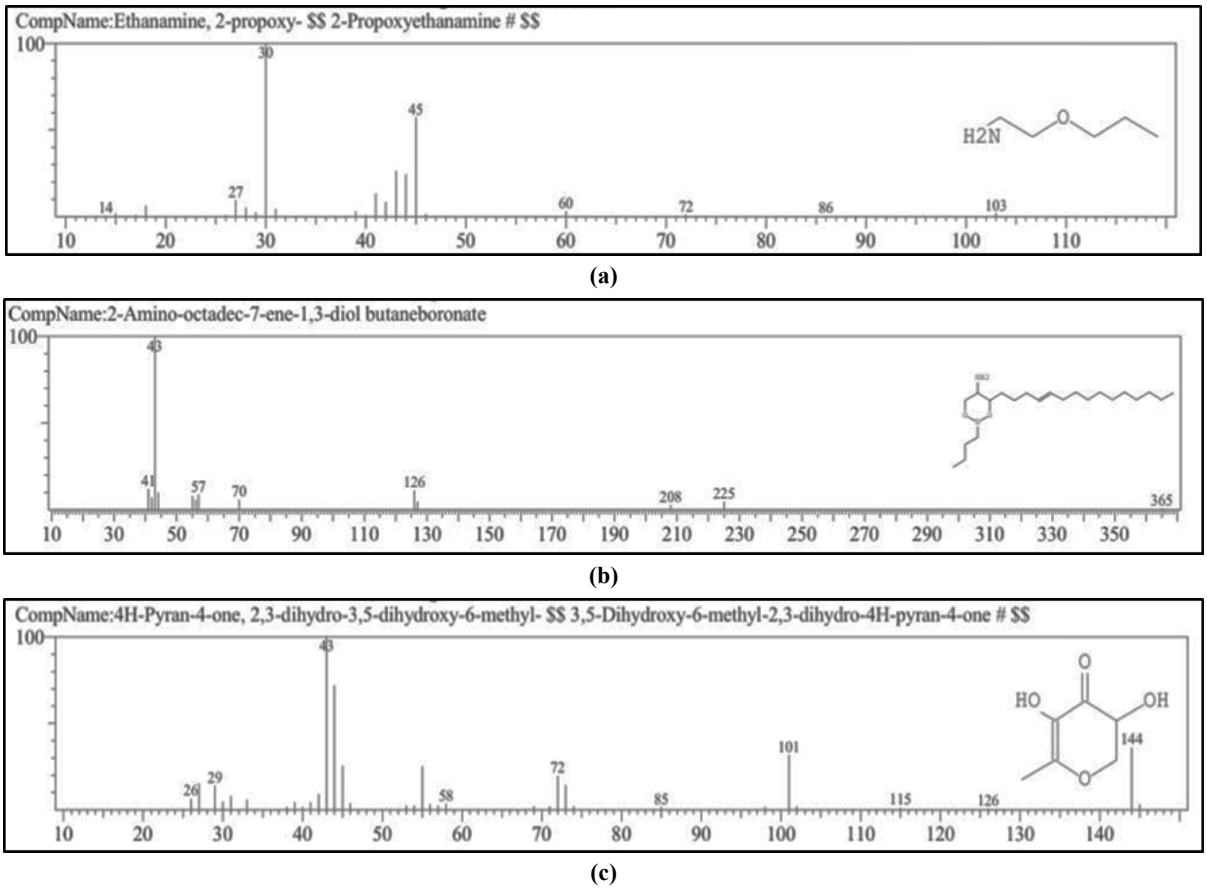


Figure 2: The extracted active material from wild clary plant (a) Ethan amine (b) Amino-octadic (c) 4H-Pyran-4-one

3.1.2 FTIR spectrum

FTIR spectrum is an excellent method for characterizing organic materials. Figure 3 shows the FTIR spectrum of the active substances in the extract, showing the peaks properties of aliphatic and aromatic C—H expansion at 3322 cm -1, which were incorporated with broadband at the same wavenumber attributed to the O—H group and H—bonded, in addition to the appearance of N—H extension in amine at 2920 cm-1. C=O group appears at ≈1710 cm-1 and the aromatic C=C vibration occurs as two bands at about 1654 cm-1 and ≈1475 cm-1, which also contributed to C—N expansion. The C-O expansion in the ether appeared at 1066 cm-1.

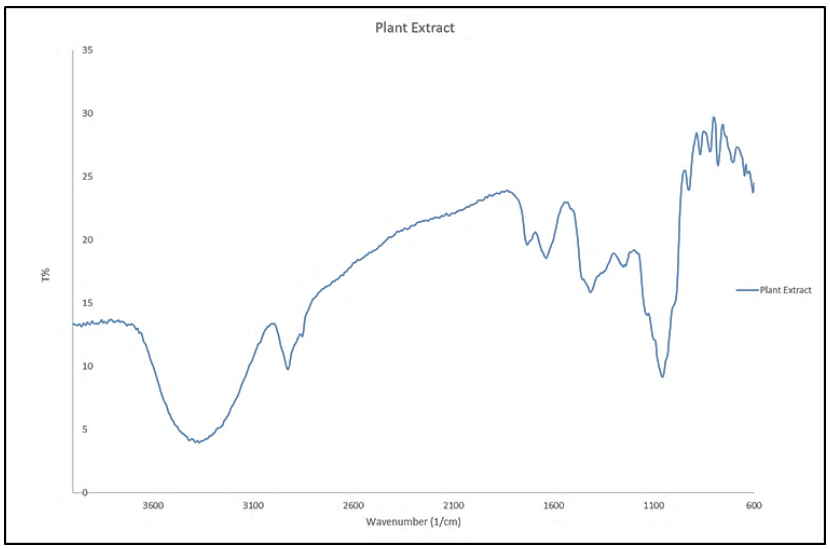


Figure 3: FTIR spectra of the extracted wild clary

3.1.3 Antibacterial action

The antibacterial activity test, as shown in Figure 4, showed the inhibitor's ability to kill some types of bacteria that have the ability to grow in the middle of seawater. Aliphatic and aromatic hydrocarbons can be degraded by Gram-positive bacteria such as Staphylococcus aureus and Streptococcus spp, and Gram-negative bacteria such as Pseudomonas aeruginosa, Klebsiella, and Candida albicans. The disk diffusion approach was used to show the region of inhibition activity at all

concentrations tested for each compound. The results, as listed in Table 2, showed that the concentrations of the wild clary compound in (50 mL and 100 mL) have different activities against bacteria. The biological activity results obtained from these compounds have made them a good inhibitor of some bacteria that contribute to increased corrosion in carbon steel used in the seawater medium.

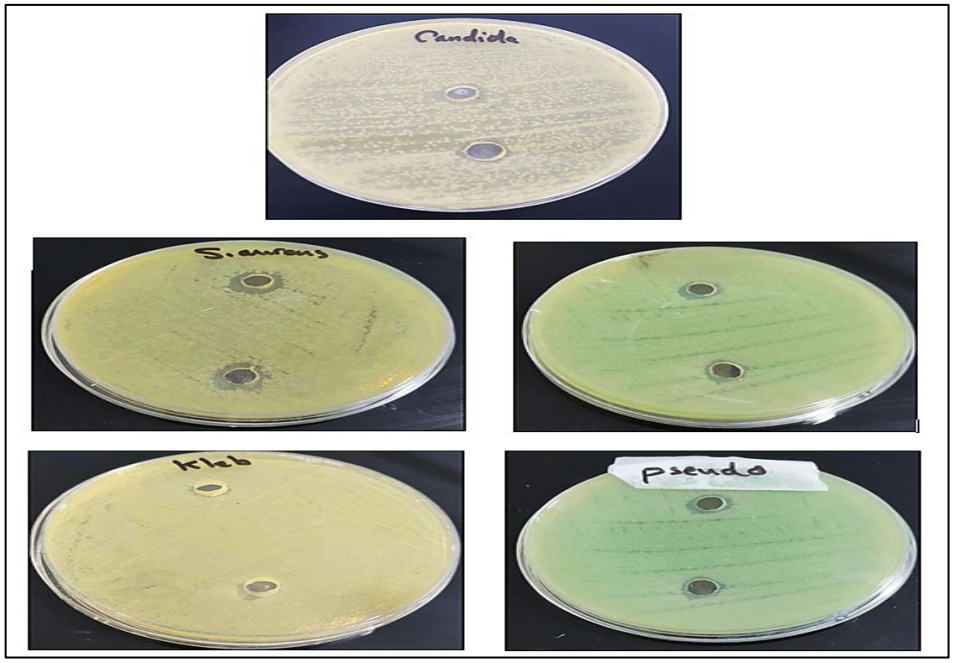


Figure 4: Final fracture pattern of the proposed specimens in splitting tensile test

Table 2: Data of antibacterial test

Conc. (mL/L)	Type of bacteria				
	Klebsiella	***Pseudomonas aeruginosa***	***Staphylococcus aureus***	***Streptococcus***	***Candida albicans***
50	0	5mm	10mm	6mm	0
100	0	8mm	8mm	5mm	10mm

3.2 Potentiodynamic Polarization measurement

Figure 5 shows the polarization curves of a sample of carbon steel in a medium of seawater without the presence of an inhibitor and at three temperatures of (298, 318, and 338 K). The wild clary extract was selected to try to inhibit the steels (AISI l015) in a medium of seawater. The values of the open-circuit voltage Eoc in the presence of wild clary extract at five concentrations were nobler than that in the absence of wild clary, as shown in Table 3. Figure 6 shows Tafel plots in seawater at five concentrations of the wild clary extract and at three temperatures. Valuable associated electrochemical parameters such as corrosion potential (Ecorr) and corrosion current density (icorr) were calculated from the anodic junction and Teal catholic slopes for polarization curves. The data in Table 3 show the corrosion coefficients of carbon steels in seawater in the absence and presence of the wild clary extract, and they indicate that Ector shifts either into a noble or active direction, i.e., the wild clary extract acts as an inhibitor of the mixed type. The density of the icorr corrosion current becomes lower, and the cathodic and anodic slopes shifted to lower values. The subsequent result reinforces the behavior of the wild clary extract as a good inhibitor. Other data can be calculated as listed in Table 4 including corrosion rate (CR), which is calculated by Eq. (1) [21]:

$$C_R(mpy) = 0.13 \times i_{corr}(\frac{e}{\rho}) \quad (1)$$

Where e and ρ are the equivalent weight and density of the substrate.

While inhibition efficiency (IE %) was calculated as given in Eq. (2) [22] :

$$IE\% = \left[1 - \frac{i_{corr,inhibited\ medium}}{i_{corr,un\ inhibited\ medium}}\right] \times 100 \quad (2)$$

Where icorr, inhibited medium and icorr, the uninhibited medium is the corrosion current density in the presence and absence of the inhibitor, respectively.

Then, the polarization resistance (Rp) was calculated according to Eq. (3):

$$R_p = \frac{b_c \times b_a}{2.303 \times i_{corr}(b_c + b_a)} \quad (3)$$

Where bc and ba are the catholic and anodic Tafel slopes.

Finally, the porosity percentage (PP %) was calculated as follows (4) :

$$PP\% = \frac{R_{p,uninhibited}}{R_{p,inhibited}} 10^{\frac{-\Delta E}{b_a}} \times 100 \quad (4)$$

Where Rp, uncoated, and Rp, coated are the polarization resistances in the absence and presence of the inhibitor, respectively, ΔE is the difference in corrosion potentials and ba is the anodic Tafel slop of the steel in the absence of the inhibitor.The data in Table 4 indicate that in the presence of 20 mL/L we get the lowest corrosion rate, the highest efficiency, more resistance and the lowest porosity.

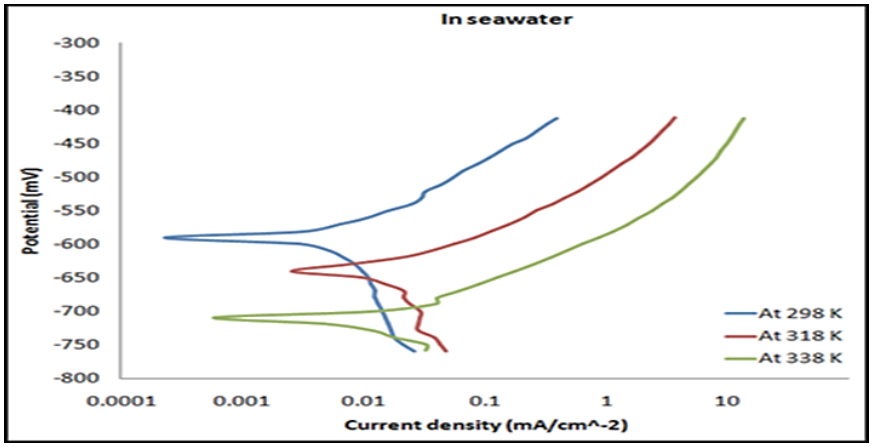


Figure 5: The polarization curves of a sample of carbon steel in a medium of seawater without the presence of an inhibitor

Table 3: Test results of deep beam specimens

Conc.(mL/L)	$Temp.(K)$	$-Ecorr(mV)$	Icorr (µA.cm2)	-bc	+ba
				mV.dec-1	
0	298	590.1	9.81	225.7	88.4
	318	639.5	11.36	173.7	63.8
	338	709.2	12.98	29.2	38.5
5	298	604.1	4.54	213.5	77.6
	318	645.2	5.55	290.4	63.3
	338	684.0	6.42	113.6	44.6
10	298	650.8	2.04	107.4	64.9
	318	650.6	3.16	162.5	50.0
	338	680.2	4.87	85.2	47.4
15	298	520.1	1.82	146.5	87.5
	318	606.8	3.38	126.9	61.5
	338	630.5	3.95	113.8	52.8
20	298	624.8	1.66	310.5	68.4
	318	653.4	2.15	272.9	58.5
	338	693.5	3.56	117.6	49.4
25	298	562.9	2.33	192.3	81.3
	318	622.9	3.03	158.7	59.1
	338	673.1	5.27	100.9	54.2

Table 4: Corrosion parameters for polarization of carbon steel in the seawater medium in the absence and presence of the wild clary extract at three temperatures

Conc.(mL/L)	Temp.(K)	CR(mpy)	IE (%)	Rp×103(Ω.cm2)	PP(%)
0	298	4.578	-	2.812	-
	318	5.301	-	1.784	-
	338	6.057	-	0.556	-
5	298	2.118	53.720	5.443	74.396
	318	2.59	51.144	4.066	53.898
	338	2.996	50.539	2.166	5.687
10	298	0.952	79.204	8.611	158.71
	318	1.474	72.183	5.254	50.686
	338	2.272	62.480	2.716	3.613
15	298	0.849	81.447	13.070	3.474
	318	1.577	70.246	5.322	10.299
	338	1.843	69.568	3.965	0.127
20	298	0.774	83.078	14.662	47.354
	318	1.003	81.073	9.729	30.283
	338	1.661	72.573	4.2430	5.124
25	298	1.087	76.248	10.649	13.002
	318	1.414	73.327	6.171	15.880
	338	2.459	59.399	2.905	2.209

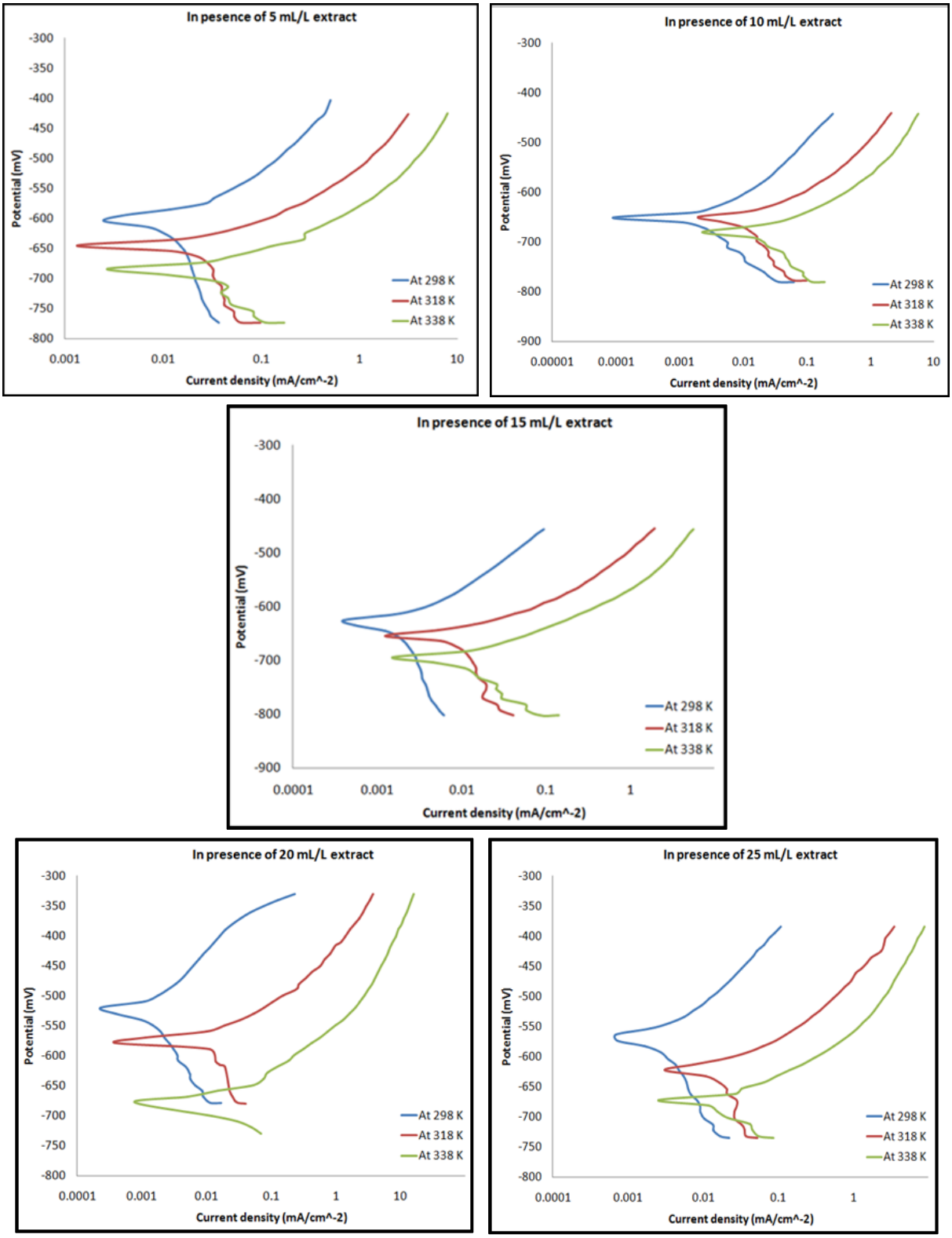


Figure 6: The polarization curves in seawater at five concentrations of the wild clary extract and at three temperatures

3.3 FTIR

The functional centers in the inhibitor attract the positively charged surface to absorb as a barrier to isolate the steel surface from the corrosive solution due to the formation of the protective film. The FTIR analysis was performed after the immersion of steel samples (AISI l015) for 15 days in seawater in the presence of an inhibitor with five different concentrations at room temperature, as shown in Figure 7, which indicates that the films were formed on the steel surface with the most important peaks that might be due to the adsorption centers in the extract. The FTIR analysis of the film that was formed after inhibition gives an indication of a decrease in the intensity of the groups interacting with the metal surface in the tested inhibitor that refers to attraction with amine groups and the oxygen in ether groups to form Fe2+—wild clary complexes.

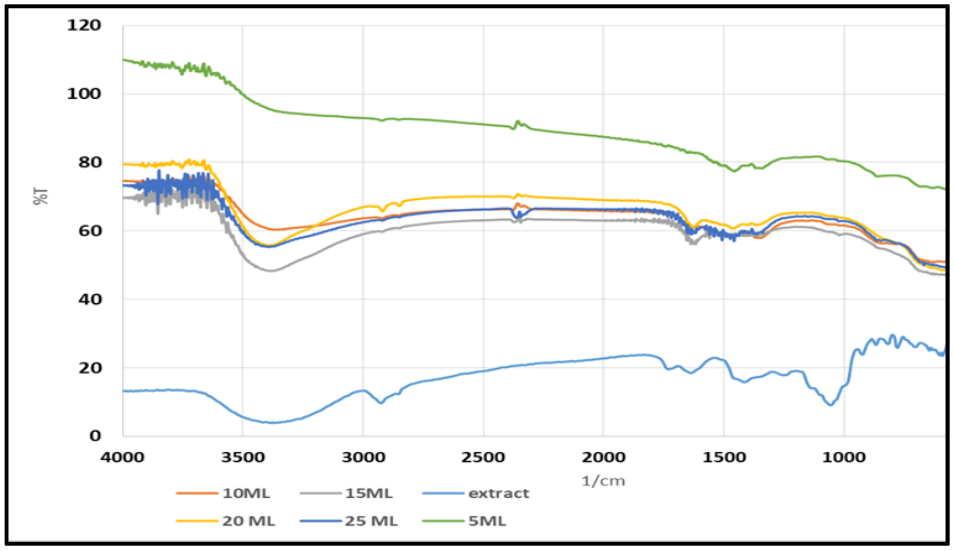


Figure 7: The films formed on the steel surface with the most important peaks that may be due to the adsorption centers in the extract in the FTIR analysis

4. Conclusions

1) The biological activity results obtained from compounds in the extract make the inhibitor good against bacteria that contribute to increased corrosion in carbon steel used in the seawater medium.
2) The corrosion potential Ecorr shifts either in the noble or active direction, i.e., the wild clary extract acts as an inhibitor of the mixed type.
3) There was a decrease in the intensity of the groups interacting with the metal surface in the tested inhibitor, which refers to attraction with amine groups and the oxygen in ether groups to form Fe2+—wild clary complexes.
4) The FTIR spectrum also showed an absorption ray in the bounded region between (2850 – 2750) cm-1 which is due to the carbonyl group (C≡O) that significantly emerged within a concentration of 20 mL/L.

Author contribution

All authors contributed equally to this work.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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