



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

Zainab S. Aziz *, Rana A. Majed, Majid H. Abd

Materials Engineering Dept., University of Technology-Iraq, Alsina'a street, 10066 Baghdad, Iraq.

*Corresponding author Email: mae.19.15@grad.uotechnology.edu.iq

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.

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.

ARTICLE INFO

Handling editor: Jawad K. Olewi

Keywords:

Wild clary
GC MS
Corrosion inhibitor
Antibacterial

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.

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 Table 1, 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.

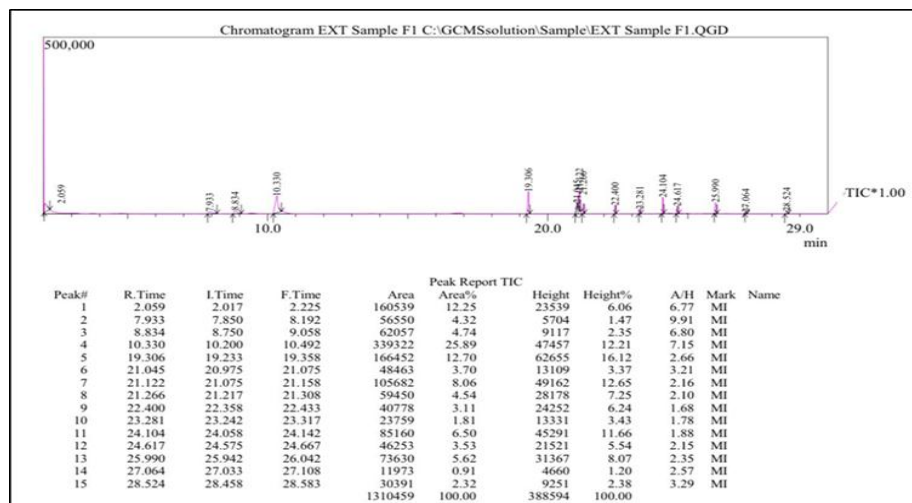
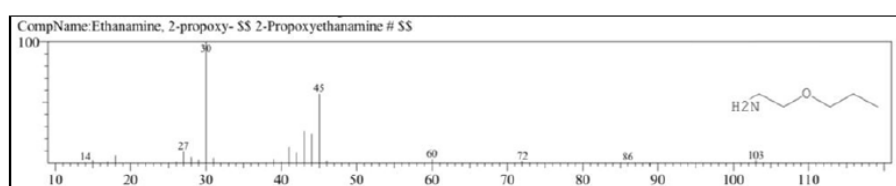
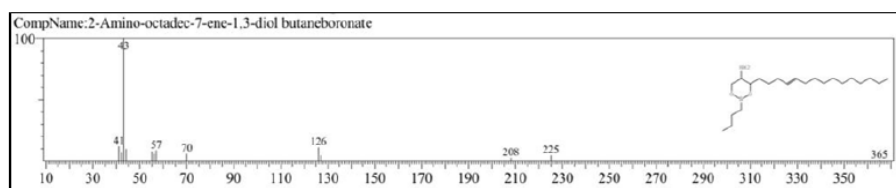


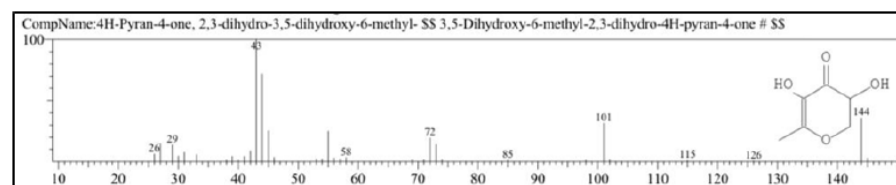
Figure 1: GC- MS analysis for the extracted active material from wild clary plant compared with the standard material



(a)



(b)



(c)

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 $\approx 1710 \text{ cm}^{-1}$ and the aromatic C=C vibration occurs as two bands at about 1654 cm^{-1} and $\approx 1475 \text{ cm}^{-1}$, which also contributed to C—N expansion. The C-O expansion in the ether appeared at 1066 cm^{-1} .

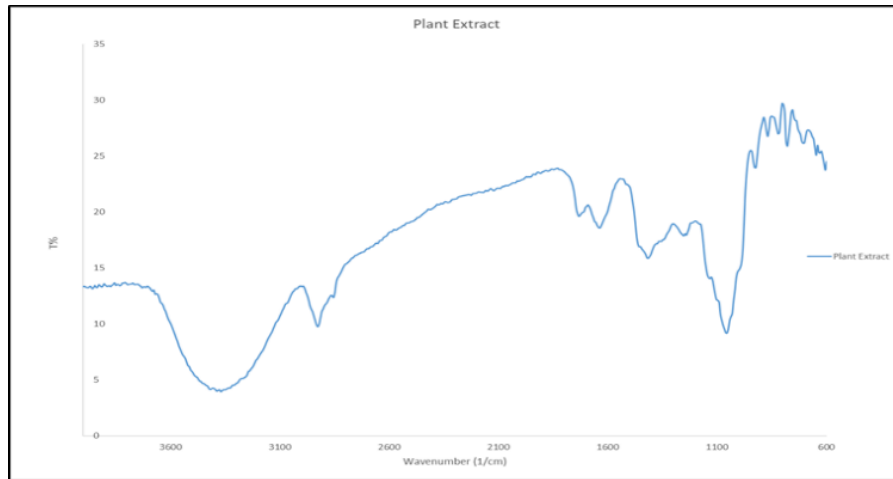


Figure 3: FTIR spectra of the extracted wild clary

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.

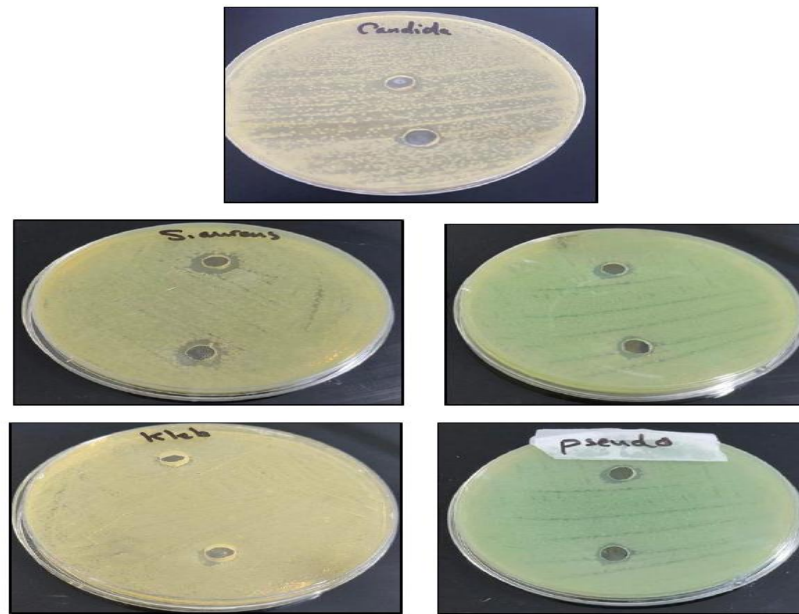


Figure 4: Final fracture pattern of the proposed specimens in splitting tensile test

Table 2: Data of antibacterial test

Conc. (mL/L)	Type of bacteria				
	<i>Klebsiella</i>	<i>Pseudomonas aeruginosa</i>	<i>Staphylococcus aureus</i>	<i>Streptococcus</i>	<i>Candida albicans</i>
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 1015) in a medium of seawater. The values of the open-circuit voltage E_{oc} 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 (E_{corr}) and corrosion current density (i_{corr}) were calculated from the anodic junction and Teal cathodic 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 i_{corr} 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]:

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

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]:

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

Where $i_{corr, inhibited\ medium}$ and $i_{corr, the\ uninhibited\ medium}$ is the corrosion current density in the presence and absence of the inhibitor, respectively.

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

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

Where b_c and b_a are the cathodic and anodic Tafel slopes.

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

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

Where $R_{p,uncoated}$, and $R_{p,coated}$ are the polarization resistances in the absence and presence of the inhibitor, respectively, ΔE is the difference in corrosion potentials and b_a 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.

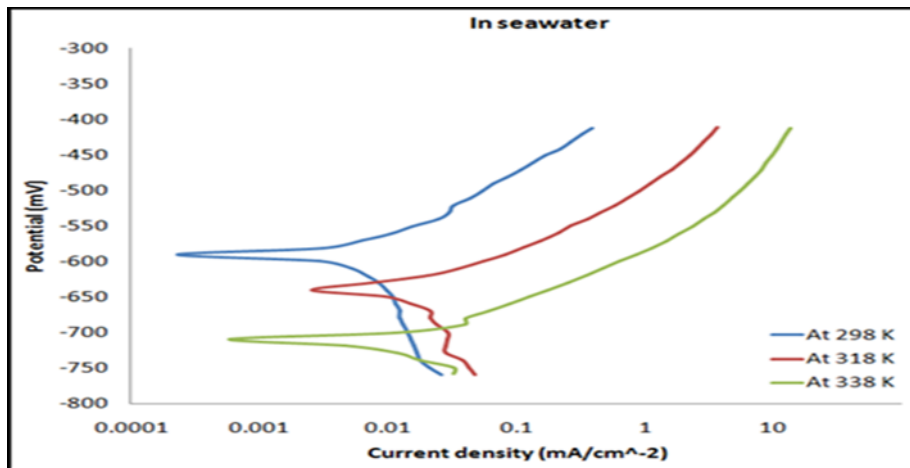


Figure 5: The polarization curves of a sample of carbon steel in a medium of seawater without the presence of an inhibitor

Table 3: Test results of deep beam specimens

Conc.(mL/L)	Temp. (K)	-E _{corr} (mV)	I _{corr} (µA.cm ²)	mV.dec-1	
				-bc	+ba
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

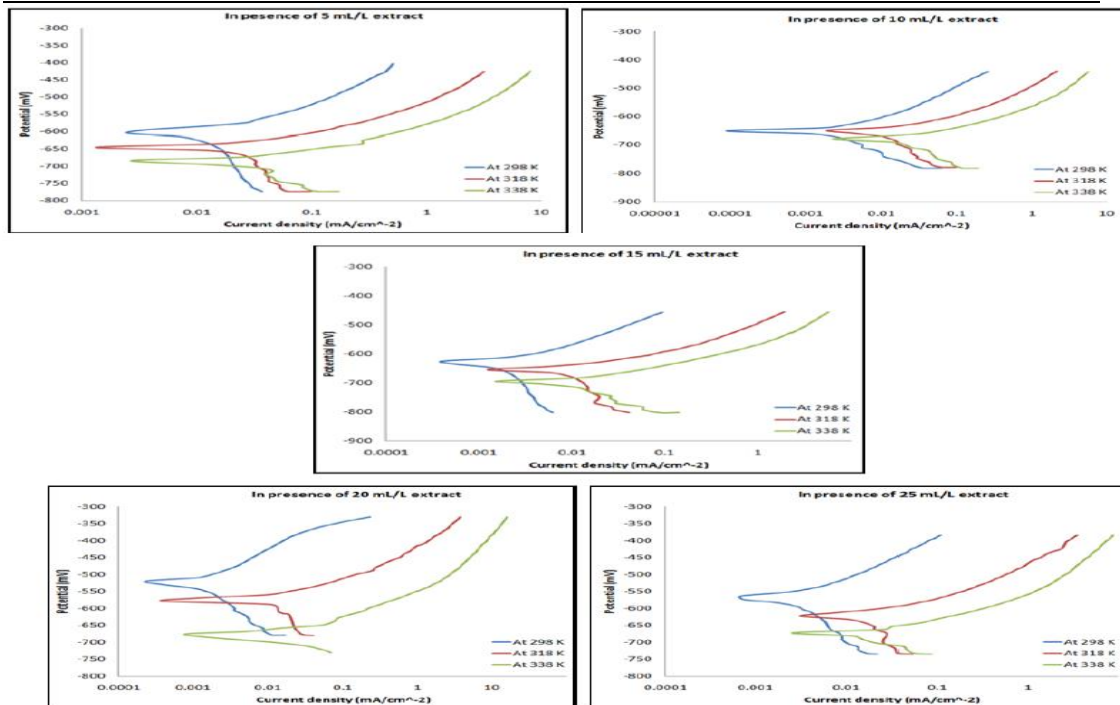


Figure 6: The polarization curves in seawater at five concentrations of the wild clary extract and at three temperatures

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

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 1015) 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 Fe^{2+} —wild clary complexes.

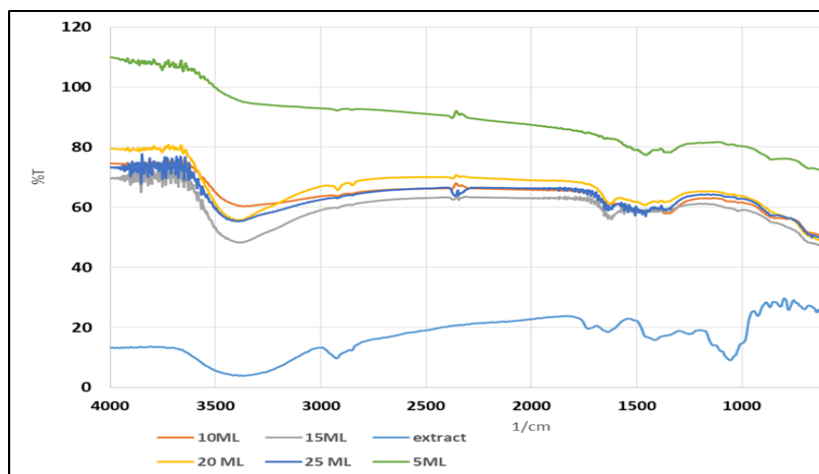


Figure 7: The films formed on the steel surface with the most important peaks that may be due to the adsorption centers in the extract in the FTIR analysis

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 E_{corr} 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 Fe^{2+} —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.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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.

References

- [1] S. S. Zhang and T. R. Jow, Aluminum corrosion in electrolyte of Li-ion battery, *Journal of Power Sources*, 109, (2002), 458–464.
- [2] E. E. Oguzie, Corrosion inhibition of aluminium in acidic and alkaline media by sansevieria trifasciata extract, *Corrosion Science*, 49, (2007), 1527–1539.

- [3] S.A. Umoren, U.M. Eduok, M.M. Solomon and A.P. Udoh, Corrosion inhibition by leaves and stem extracts of *Sida acuta* for mild steel in 1 M H₂SO₄ solutions investigated by chemical and spectroscopic techniques, *Arabian Journal of Chemistry*, 9, (2016), 209-S224.
- [4] F. Bouhlal, N. Labjar, F. Abdoun, A. Mazkour, M. Serghini-Idrissi, M. El Mahi, El M. Lotfi, and S. El Hajjaji, Electrochemical and thermodynamic investigation on corrosion inhibition of C38 steel in 1M hydrochloric acid using the hydro-alcoholic extract of used coffee grounds, *International Journal of Corrosion*, (2020), 1- 14.
- [5] M. Aiboudi, F. Yousfi, G. Fekkar, L. Bouyazza, M. Ramdani, M. El Azzouzi and I. Abdel-Rahman, Eco-friendly allium cepa L. seeds extracts as corrosion inhibitor for mild steel in 1 M HCl solutions *J. Mater. Environ. Sci.*, 10, (2019), 339-346.
- [6] H. M. Elabbasy & A. S. Fouda, Olive leaf as green corrosion inhibitor for C-steel in Sulfamic acid solution, *Green Chemistry Letters and Reviews*, 12, (2019), 332–342.
- [7] R. A. Majed, Sumac (*Rhus*) extract as green inhibitor for steel in seawater, *International Journal of Scientific Research in Science, Engineering and Technology (IJSRSET)*, 2, (2016), 353-358.
- [8] R.A. Majed, Corrosion inhibition by pumpkin peels extract in petroleum environment, *American Chemical Science Journal*, 5, (2015), 32-40.
- [9] R. A. Majed, M. H. Alzuhairi, and H. A. Abdullah, Evaluation the inhibition of steel in petroleum medium by tobacco leaves extract, *International Journal of Innovative Research in Science & Engineering*, 2, (2014), 484-492.
- [10] R. A. Majed, M. H. Alzuhairi, and H. A. Abdullah, Sweet clover leaves as green inhibitor in petroleum medium, *Journal of King of Abdulaziz University – Science*, 25, (2013), 33-51.
- [11] R. A. Majed, M. H. Alzuhairi, and H. A. Abdullah, Corrosion inhibition of steel in petroleum medium by ficus carica extract, *Asian Journal of Engineering and Technology*, 2, (2014), 235-243.
- [12] R. A. Majed, M. H. Alzuhairi, and H. A. Abdullah, Corrosion inhibition by natural extracts at 50°C, *International Journal of Engineering Sciences & Research Technology*, 3, (2014), 642-652.
- [13] P. Muthukrishnan, B. Jeyaprabha, and P. Prakash, Mild steel corrosion inhibition by aqueous extract of *Hyptis suaveolens* leaves, *Int J Ind Chem*, 5, (2014), 1-11.
- [14] A. S. Fouda, G. Y. Elewady, K. Shalabi and S. Habouba, Tobacco plant extracts as save corrosion inhibitor for carbon steel in hydrochloric acid solutions, *International Journal of Advanced Research*, 2, (2014), 817-832.
- [15] L. Bammou, M. Belkhaoud, R. Salghi, O. Benali, A. Zarrouk, H. Zarrok, and B. Hammouti, Corrosion inhibition of steel in sulfuric acidic solution by the chenopodium ambrosioides extracts, *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 16, (2014), 83–90.
- [16] O. Benali, H. Benmehdi, O. Hasnaoui, C. Selles, and R. Salghi, Green corrosion inhibitor: inhibitive action of tannin extract of *Chamaerops humilis* plant for the corrosion of mild steel in 0.5M H₂SO₄ *J. Mater. Environ. Sci.*, 4, (2013), 127-138.
- [17] K. Rajam, S. Rajendran, and R. Saranya, Allium sativum (Garlic) extract as nontoxic corrosion inhibitor, *Journal of Chemistry*, (2013), 1- 4.
- [18] M. Sangeetha, S. Rajendran, J. Sathiyabama and P. Prabhakar, Asafoetida extract (ASF) as green corrosion inhibitor for mild steel in sea water, *International Research Journal of Environment Sciences*, 1, (2012), 14-21.
- [19] A. Singh, E. E. Ebenso and M. A. Quraishi, Corrosion inhibition of carbon steel in HCl solution by some plant extracts, *International Journal of Corrosion*, (2012), 1-20.
- [20] C. G. Dariva and A. F. Galio, Corrosion Inhibitors – Principles, Mechanisms and Applications, *Developments in corrosion protection journal*, 16, (2014), 365-378.
- [21] A. S. Fouda, H. Ibrahim, S. Rashwaan, A. El-Hossiany and R. M. Ahmed, Expired drug (pantoprazole sodium) as a corrosion inhibitor for high carbon steel in hydrochloric acid solution, *International Journal of Electrochemical Science*, 13, (2018), 6327 – 6346.
- [22] B. M. El-Gendy, S. T. Atwa, A. A. Ahmed and A. Y. EL-Etre Corrosion inhibition of carbon steel X52 by new schiff base in HCl solution, *Journal of Basic and Environmental Sciences, Journal of Basic and Environmental Sciences*, 3, (2016), 47- 54.