Journal of the Taiwan Institute of Chemical Engineers 165 (2024) 105771

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.journals.elsevier.com/journal-of-the-taiwan-institute-of-chemical-engineers

Trifolium repens extracts as a green corrosion inhibitor for carbon steel in a 3.5% NaCl solution

Sobhi Nour El Houda [a,b,*], Boukhouiete Amel [c], Foudia Malika [b]

[a] *Departement of chemistry, Water and Environment Science and Technology Laboratory, Mohamed Cherif Messaadia University, Souk-Ahras, Algeria*
[b] *Laboratory of energy and electrochemistry of solid (LEES), University Ferhat Abbas Setif 1, Setif, Algeria*
[c] *Departement of chemistry, University Badji-Mokhtar, Annaba, Algeria*

ARTICLE INFO

Keywords:
Trifolium repens
Carbon steel
Corrosion
Inhibitor
Chloride media

ABSTRACT

Background: Material degradation is a major issue that has been the subject of intense research and investigation by the scientific community. It has harmful consequences that require serious and careful intervention. However, restrictions on the use of inhibitors containing toxic compounds pose a significant challenge to the implementation of effective corrosion treatments. This has necessitated a continuous search for new and innovative ways to protect against material damage. Plant-derived natural inhibitors offer several advantages, including potent inhibitory effects, lack of toxicity, biodegradability, and environmentally sustainable origins. The purpose of this research was to evaluate the corrosion resistance of API5LX60 carbon steel in a 3.5 % NaCl environment using Trifolium repens as an environmentally friendly inhibitor.
Methods: The inhibitor extract was analysed using Fourier Transform Infrared (FTIR) spectroscopy. However, gravimetry and electrochemical methods (potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)) were used to investigate the corrosion behaviour. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the surface morphology.
Significant findings: After testing a range of concentrations in a 3.5 % NaCl medium, the highest level of inhibition (98 %) was obtained at 20 ppm, confirming the mixed action of the inhibitor with predominantly cathodic action. The inhibition mechanism involved physical adsorption on metal surfaces according to the Langmuir model, which enhances the corrosion-inhibiting ability; the extract forms a protective layer that successfully inhibits corrosion, as confirmed through electrochemical and surface analysis. These results demonstrate that the extract acts as a potent anticorrosive agent.

1. Introduction

The use of API5LX60 steel pipes plays a crucial role in several infrastructure projects in Algeria, notably in the water, oil, and gas sectors. However, the constant attack of corrosive conditions represents a significant obstacle to the durability and lifespan of these pipes. Corrosion is an unavoidable problem in metallurgy, although its harmful effects can be reduced by careful intervention [1].

It is difficult to stop corrosion completely. However, inhibitors can effectively control the rate of corrosion. These chemicals can prevent or slow down the corrosive processes that affect metals in their working environment. The search for corrosion inhibitors has shifted towards sustainable solutions that contain various organic compounds containing heteroatoms such as nitrogen (N), sulphur (S), oxygen (O) and phosphorus (P), as well as other beneficial functional groups. Plant extracts, such as those derived from leaves, seeds, flowers and peels, have shown great potential as effective steel protection agents [2-13]. These organic molecules enhance the process of attaching to steel surfaces by using their atoms and groups as adsorption sites. Research into the efficiency of green inhibitors has increased significantly in recent years. In many environmental conditions, this research has shown that green inhibitors are effective [14-29].

The widespread presence of Trifolium repens in Algerian pastures has sparked interest in its potential as a rust inhibitor. The plant grows well in areas with abundant rainfall and diverse landscapes, making it ideal for improving pasture growth. Known for its nutrient-rich, easily

* Corresponding author at: Departement of chemistry, Water and Environment Science and Technology Laboratory, Mohamed Cherif Messaadia University, Souk-Ahras, Algeria; Laboratory of Energy and Electrochemistry of Solid (LEES), University Ferhat Abbas 1, Setif, Algeria.
E-mail address: n.sobhi@univ-soukahras.dz (S. Nour El Houda).

https://doi.org/10.1016/j.jtice.2024.105771
Received 24 June 2024; Received in revised form 2 September 2024; Accepted 11 September 2024
Available online 18 September 2024
1876-1070/

digestible green fodder with a high protein content, Trifolium repens shows great promise as a rust inhibitor [30-35].

As shown in Fig. 1, Trifolium repens belongs to the Leguminosae, which is well known for its importance in agriculture and its exceptionally diverse species composition. Trifolium repens is an excellent nitrogen fixer, capable of producing high quality animal feed. In addition, Trifolium species have been used in the formulation of traditional herbal treatments by civilisations around the world [34]. More and more people are becoming aware of the medicinal potential of Trifolium plants. Extensive scientific investigations into the biological activities of a large number of Trifolium species have revealed a substantial reservoir of flavonoids, isoflavonoids and other potent antioxidant compounds [36].

A number of Trifolium species have emerged as an important therapeutic agent by exploiting these major bioactive compounds. These effects range from antiseptic and analgesic to anti-inflammatory and anti-cancer. They even promote angiogenesis [37].

An analysis of Trifolium repens identified various flavonoid compounds, particularly flavones such as acacetin, luteolin, and several others with hydroxy and methoxy groups. Another study used spectrophotometric and chromatographic methods to detect and separate flavonoids in Trifolium repens. The identified flavones include 5,6,7,8-tetrahydroxy-4′-methoxy flavone, 4′,5,6,7,8-pentahydroxy-3-methoxyflavone, and 3,5,6,7,8-pentahydroxy-4′-methoxyflavone, among others, as shown in Fig.2 [38] .

Around of 61 volatiles compounds have been identified, including prominent molecules are illustrated in Fig. 3 [39].

This study investigates the effect of Trifolium repens on the corrosion of carbon steel API5LX60 in a 3.5 % NaCl solution. Inhibitor doses ranging from 5 to 30 ppm are used. A comprehensive approach is used to investigate the physical interactions between the chemical components of the inhibitor molecules and the steel surface. The methods of weight loss, polarisation analysis, electrochemical impedance spectroscopy (EIS), Scanning electron microscopy (S.E.M) and atomic force microscopy (A.F.M), characterisation and Fourier transform infrared spectroscopy (F.T.I.R) will be used systematically to understand this mechanism. These methods will provide valuable insights into the potential of Trifolium repens as a sustainable solution in corrosion mitigation strategies.

2. Experimental

2.1. Inhibitor extraction

The Trifolium repens plant was air-dried, then ground to a fine powder. One liter of dichloromethane was used to dissolve 100 g of the powdered plant material. The mixture was stirred at room temperature for 24 h, followed by filtration and evaporation on a rotary evaporator at 50 °C for four hours. The solid extract was collected, weighed, and stored for further use. Standard solutions were prepared by dissolving the extract in appropriate solvents to obtain concentrations of 5, 10, 20, and 30 ppm. Fig. 4

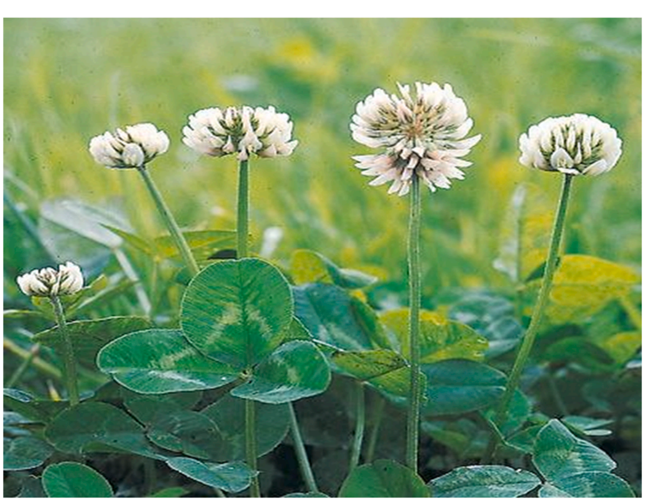

Fig. 1. Trifolium repens.

2.2. Solution and material

To obtain the NaCl 3.5 % solution, 1000 mL of distilled water was utilized to dilute 35 g of NaCl, to which various concentrations of inhibitor were added until the final concentration ranged from 5 to 30 ppm.

The electrochemical experiments employed an API5LX60 cube with a surface area of 1.0 cm^2 as the working electrode (WE). The cube is coated with epoxy resin, leaving a well-prepared uncovered surface area of 1.0 cm^2. Prior to the start of any experimental procedures, each sample was subjected to an intensive polishing procedure using sandpaper of various grits ranging from 100 to 2000 grade. The API5LX60 samples were subjected to additional cleaning protocols: an acetone-based ultrasonic bath treatment, ethanol rinsing and air drying.

2.3. Weight loss method

The test coupons that were prepared as described above were submerged in 100 mL of the aggressive solution, containing 3.5 % NaCl and 20 ppm Trifolium repens. This was done to quantify the weight loss analysis.

The samples were removed from the solution after an identical period (24–168 h), washed with distilled water, dried with filter paper and weighed again. To reduce the error rate, each test was performed three times. The weight reduction (W1 - W2) can be obtained by measuring the weights of the samples before (W1) and after (W2) each experiment.

W1 represents the weight loss of API5LX60 when exposed to inhibited NaCl 3.5 % solution, while W2 represents the weight loss of API5LX60 when exposed to uninhibited solution. Calculations were made to determine the corrosion rates employing the given equation:

$$\boldsymbol{CR} = \frac{\Delta \boldsymbol{w}}{\boldsymbol{S.t}} \tag{1}$$

The weight loss is denoted by ΔW (g), S represents the surface of the specimen in (cm^2), and t represents the period of immersion in (h). The corrosion rate is quantified in CR ($g.cm^{-2}.h$).

The inhibition efficiency IE% was calculated using the Eq. (2):

$$\boldsymbol{IE}(\%) = \left(\frac{\boldsymbol{CR_{corr}} - \mathrm{CR_{inh}}}{\boldsymbol{CR}_{\mathrm{corr}}}\right) \mathrm{x}\ 100 \tag{2}$$

CR_{corr} and CR_{inh} are the corrosion rate with and without the addition of the inhibitor, respectively.

2.4. Electrochemical tests

Electrochemical measurements were performed using a PGZ301 potentiostat equipped with Volta Master 4 software. The test setup used a standard three-electrode configuration: API5LX60 served as the working electrode, a saturated Ag/AgCl electrode as the reference and a platinum sheet as the counter electrode. Electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 100 kHz to 0.01 Hz using a 10 mV sinusoidal voltage as the excitation signal.

The corrosion inhibition efficiency can be determined by using the following formula:

$$\boldsymbol{IE}\% = \frac{\boldsymbol{R_{ct\ inh}} - \boldsymbol{R_{ct\ blank}}}{\boldsymbol{R_{ct\ inh}}} \times 100 \tag{3}$$

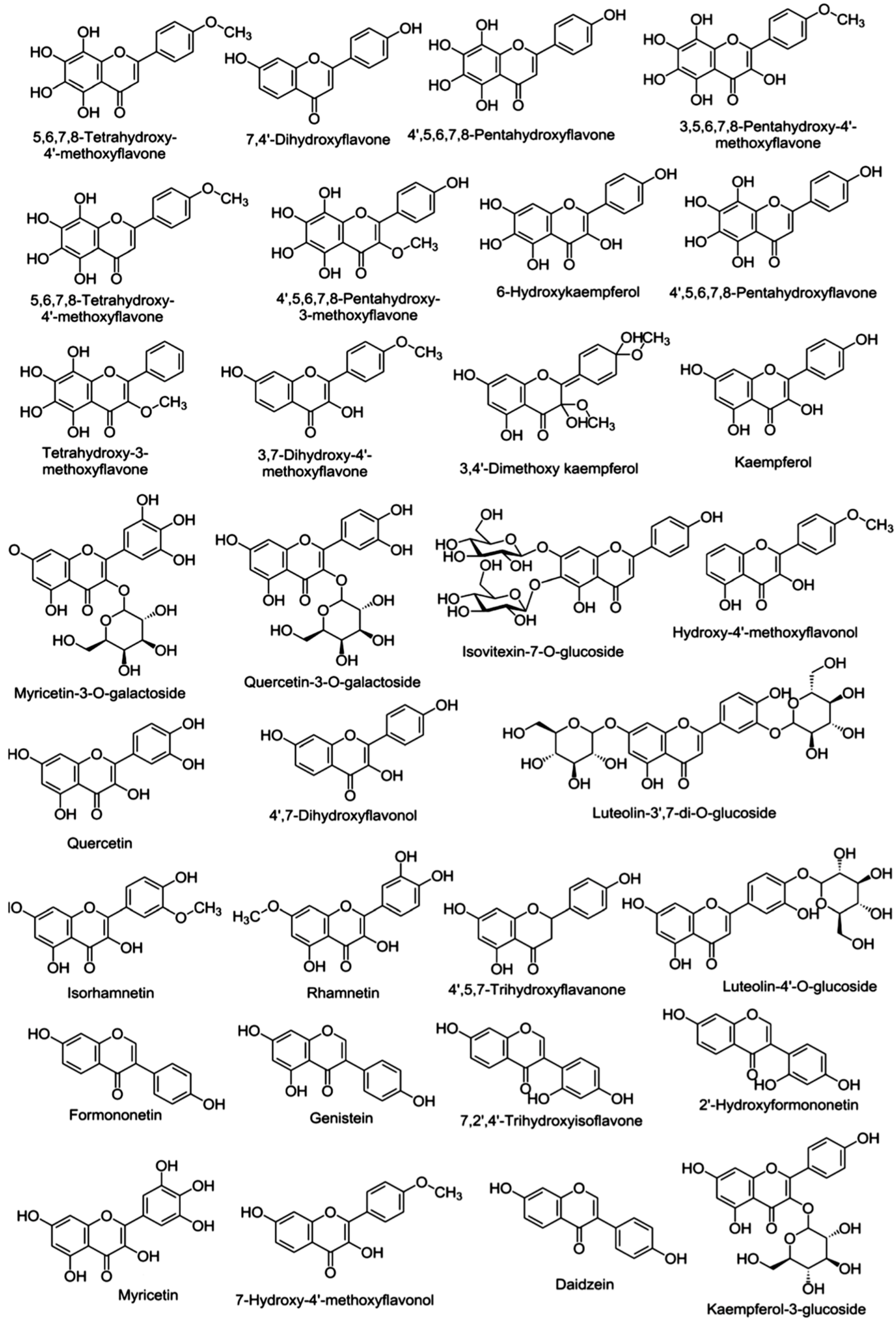

Fig. 2. Principal phenolic chemicals of Trifolium repens Structure[39].

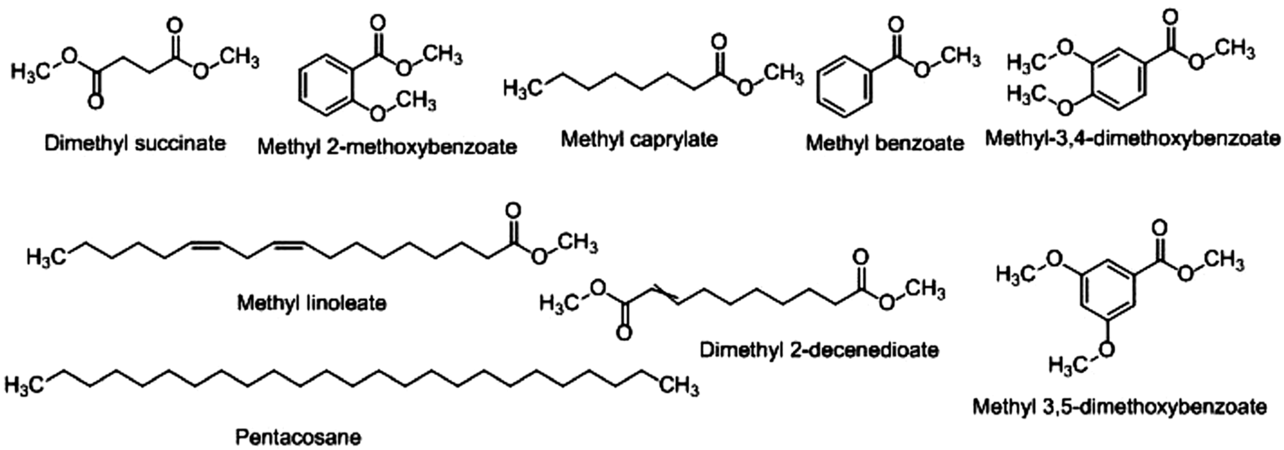

Fig. 3. Structure of major volatile compounds in Trifolium repens[39].

Fig. 4. The process of plant extraction using solvent extraction.

$R_{ct\ blank}$ and $R_{ct\ inh}$ denote the transfert charge resistance in the agressive media with and without the addition of the inhibitor.

Tafel tests were conducted at 0.5 mV/s, ranging from ±250 mV (vs. OCP). The calculation of inhibition efficiency (IE%) is like the following equation:

$$IE\% = \frac{i_{corr\ Blank} - i_{corr\ inh}}{i_{corr\ Blank}} \times 100 \tag{4}$$

In the test solution, the symbols $i_{corrblank}$ and $i_{corrinh}$ correspond to the corrosion current densities before and after the addition of the inhibitor, respectively.

2.5. Surface morphology study (S.E.M)

To investigate the impact of Trifolium repens film on API 5LX60 steel, scanning electron microscopy (SEM) was employed. Using a JEOL JSM-6510LV microscope equipped with an INCA Oxford attachment, metal coupons were analyzed after 48 h of corrosion exposure, both with and without the optimal inhibitor concentration. Prior to SEM analysis, the coupons were washed, dried and prepared for examination.

2.6. Atomic force microscopy (A.F.M) characterisation

The surface morphology of API5LX60 steel was studied using an Asylum Research Atomic Force Microscope (AFM), specifically the Classic MFP-3D model from Oxford Instruments. The study compared the surface conditions in the presence and absence of Trifolium repens. AFM micrographs were taken of specimens immerged in a 3.5 % NaCl solution, both with and without 20 ppm Trifolium repens, for a period of 48 h.

3. Result and discussions

3.1. Inhibitor characterization

3.1.1. Fourier transform infrared spectroscopy analysis (F.T.I.R)

The infrared spectrum of Trifolium repens is illustrated in Fig.5. The spectra obtained show large peaks characteristic of Trifolium repens. Phenol shows -OH stretching bands in the range of 3450 to 3300 cm^{-1}. The spectra show weak vibrational bands characteristic of the aliphatic C—H bond, specifically the $-CH_2$ and $-CH_3$ groups, in the range of 2965 to 2840 cm^{-1}.

The bands observed at 1450 and 1600 cm^{-1} indicate the stretching of C = C bonds in aromatic rings (indicating the presence of three or four rings) or amines. The peak at 1265 cm^{-1} indicates the stretching of the C—O bond, whereas the frequency of 895 cm^{-1} relates to the presence of disubstituted aromatic Ctri-H. The peak observed at 1373 in the spectra is attributed to the presence of δCH_3. There are multiple prominent peaks observed between 1010 and 1057cm^{-1}, which are likely attributed to the stretching of C—O bonds in the acid amine inhibitor. The infrared (FTIR) absorption band at 1722 cm^{-1} is typically associated with the stretching vibrations of the double carbon-oxygen bonds (C = O) in certain functional groups [22].

In addition, FTIR analyses were performed on both the pure inhibitor and the inhibitor adsorbed onto API5L X60 used to identify the active compounds of the inhibitor. These analyses were carried out over 24 h at a concentration of 20 ppm at 25 °C. Fig. 6 exhibits the FTIR spectra of the results obtained.

The infrared spectra of the adsorbed inhibitor on the steel surface exhibited a high degree of similarity to those of the pure inhibitor, with only slight variations. The spectral investigations provide clear evidence that Trifolium repnes contains molecules with polar groups, which are believed to be favourable for adsorption onto the API5LX60 surface.

3.2. Measurements of weight loss

As a result of immersing the API5LX60 for different time in 3.5 % NaCl with and without Trifolium repens inhibitor at a fixed concentration of 20 ppm, the mass loss of the steel was evaluated at 25 ± 1 °C after immersion. The findings indicate a significant stability of the Trifolium repens extract, despite a slight decrease in inhibition efficiency over time [40].Table 1 summarize the results that were obtained.

After a total of 168 h of complete immersion, the level of inhibition efficiency reaches 81 %. This phenomenon can be explained by the presence of a remarkably resilient inhibitory layer.

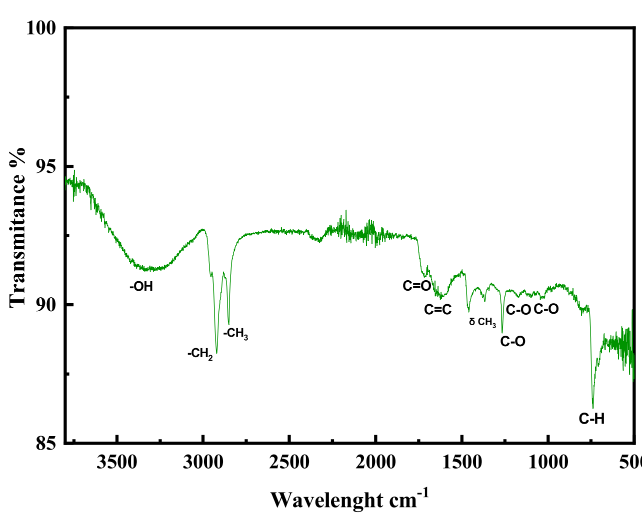

Fig. 5. The IR analyses of Trifolium repens.

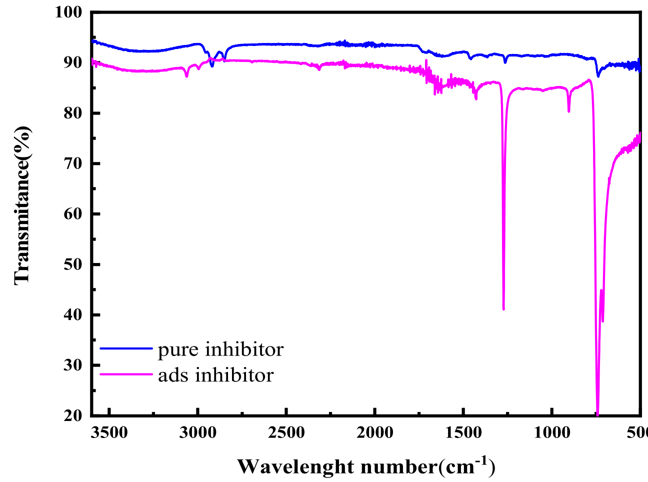

Fig. 6. FTIR spectra of pur and adsorbed inhibitor on API5LX60 surface.

Table 1
Parameters of the relationship between the IE% and immersion time.

Time(h)	*Δw(g)*	CR (g.cm^{-2}.h) × 10^{-6}	*IE(%)*
24	0.0003	8.333	98.10
72	0.0010	9.259	90.65
120	0.0019	1.055	83.76
168	0.0020	7.936	81.82

3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was used to validate the effectiveness of the protection provided by Trifolium repens.

Figs 7 and 8 present the Nyquist and Bode plots of API5LX60 immersed in a NaCl solution at 298 K. Fig. 7 demonstrates the influence of varying doses of the inhibitor in a 3.5 % NaCl solution. Trifolium repens did not modify the structure of the carbon steel's capacitance loop in comparison to the uninhibited solution, suggesting that Trifolium molecules adhered to the API5LX60 surface, creating a protective film [40].

In addition, Nyquist plot is characterised by a depressed semicircle, which represents the capacitance of the double layer and its polarisation resistance. This resistance process is critical in preventing corrosion.

Bode plots indicate that as the concentration of Trifolium repens rise,

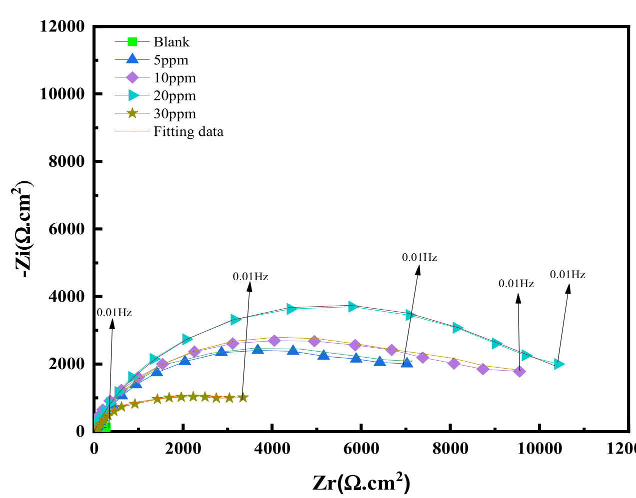

Fig. 7. EIS Diagrams for API5LX60 Pipe in 3.5 % NaCl solution, in the absence and presence of different doses of Trifolium repens at 298 K in Nyquist representation.

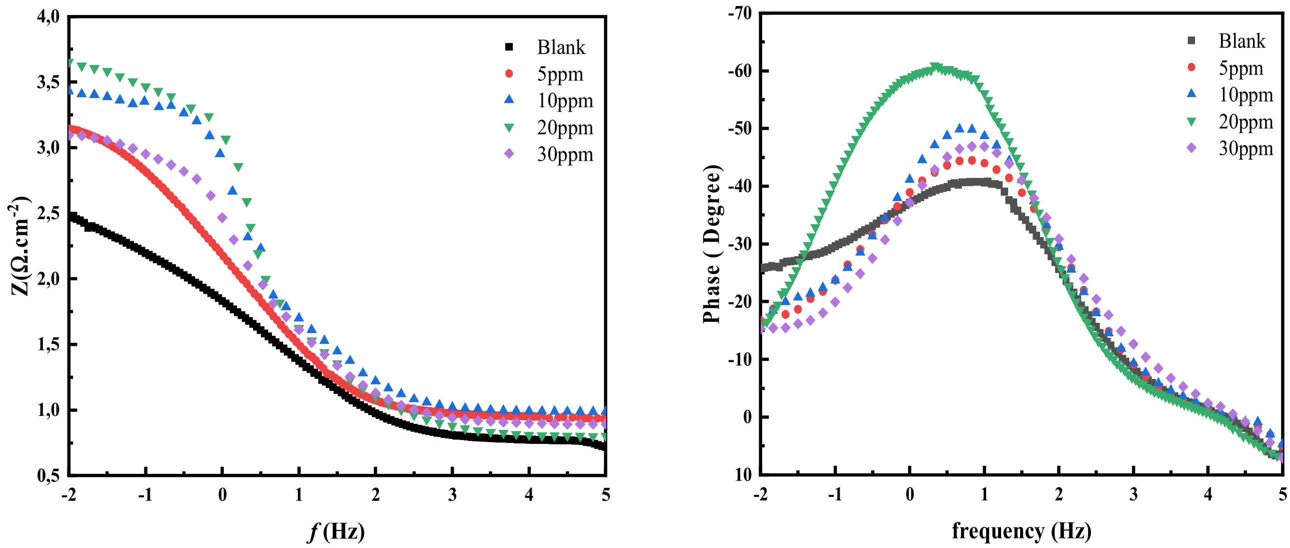

Fig. 8. EIS graphs for API5LX60 in 3,5 % NaCl solution in the presence and the absence of the Trifolium repens at 25C° in Bode modulus.

the peak size also increases, suggesting a decrease in the capacitive behavior of API5LX60 steel, indicative of Trifolium repens molecule adsorption on the metal surface [41].

The equivalent circuit model depicted in Fig. 9 was used to analyse the EIS spectra and the results obtained are presented in Table 2 below. The symbols Rs, Rct and Rf represent the resistances related to the solution at the interface of the working/reference electrodes, the charge transfer mechanism and the surface layer, respectively; in this case, all these resistances are replaced by the polarisation resistance (Rp= Rct + Rs +Rf) [42-45]. The constant phase elements corresponding to the double electrical layer and surface film are designated CPEdl and CPEf respectively. These elements indicate their capacitance properties, which are influenced by their non-ideal nature [46]. The n parameter quantifies the variation of the CPE from ideal capacitance,affected by the porous nature of the metal surface and the arrangement of pores.The chi-squared statistic (χ^2), which is <1 %, indicates an excellent fit among the experimental data and the model [47]. In addition, the *Rp* values showed a good correlation with the difference amount of Trifolium repens, indicating an increased protective capacity with increasing dosage. The inhibition efficiency values also rise with increasing concentrations of Trifolium repens, with the highest value recorded at 97.27 % at a concentration of 20 ppm, demonstrating its exceptional corrosion inhibition capability. Moreover, the *CPEdl* value progressively decreased with higher concentrations of Trifolium repens.This decrease occurs because the Trifolium repens molecules replace the water molecules that were previously adsorbed at the Metal/solution interface [48]. As a result, API5LX60 was successfully protected against corrosion in sodium chloride solution by the creation of a protective film of extract molecules.

The data presented in Table 2 below shows a correlation between the concentration of Trifolium repens extract and the increase in charge transfer resistance (Rct) values. This ultimately provides greater inhibition efficiency.

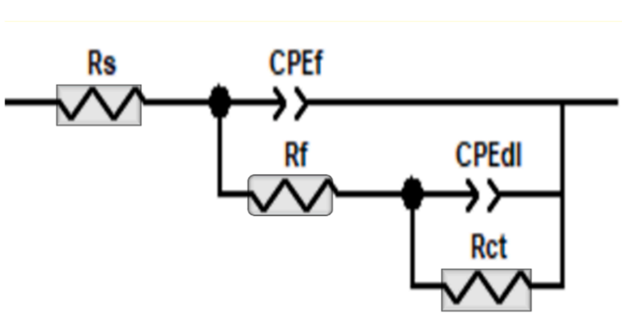

Fig. 9. Electrical equivalent circuit for simulating impedance spectra.

Subsequently, it was determined that an increase in the concentration of Trifolium repens could lead to a corresponding the rise in the thickness of the double layer, as predicted by Helmholtz's model [49]:

$$C\mathbf{dl} = \varepsilon^{0}.\varepsilon.\mathbf{S}/\mathbf{e} \tag{5}$$

$\boldsymbol{\varepsilon^0,\varepsilon}$ are describe the dielectric constant of the vacuum and the medium, respectively.

S: is specimen studied surface

e: is the surface film thickness

3.4. Potentiodynamic polarization

Fig.10 present the polarisation plots of API5LX60 steel in NaCl 3.5 % solutions at room temperature, with and without various doses of the green inhibitor (Trifolium repens).

The findings depict that the cathodic and anodic reactions shift towards more positive and negative potentials respectively. The important corrosion data derived from these curves are presented Table 3 presents the potentiodynamic polarisation parameters (*i*corr, *E*corr, *βa, βc*), which indicate that as the concentration of the extract increases, the corrosion current density (*icorr)* decreases. This observation indicates that the Trifolium repens effectively inhibits corrosion of API5LX60 steel in the tested environment. The inhibition efficiency (IE%) increase with higher doses of the extract, which led to the creation of a protective film on the steel surface, demonstrating the Trifolium repens extract's effectiveness as an inhibitor. Both anodic and cathodic reactions were suppressed with increasing inhibitor concentrations, with a more pronounced cathodic impact. The addition of the Trifolium repens slightly altered the Tafel slopes (*βc*, βa), indicating that the inhibitor similarly affects both reactions. Tafel slopes quantify the kinetic barriers associated for anodic and cathodic reactions. According to previous studies [50,51], an inhibitor can be classified as either cathodic or anodic if the change in Ecorr is greater than 85 mV . In this study, all displacement was < 85 mV, indicating that the Trifolium repens extract is a mixed-type inhibitor, affecting both cathodic and anodic processes by blocking active sites on the metal surface [11]. The values of icorr decreased the Trifolium repens concentration increased, demonstrating that the inhibition efficiency improved at higher inhibitor doses, this trend aligns with findings from other methods [52] .

Table 2
The obtained EIS values for API5LX60 Pipe in 3.5 % sodium chloride in the presence and the absence of diffrents concentrations of Trifolium repens.

C (ppm)	Rs ($\Omega.cm^2$)	Rf ($\Omega.cm^2$)	CPE_f ($S^{n1}.\Omega^{-1}\beta.cm^{-2}$) $\times 10^{-3}$	n_1	Rct ($K\Omega.cm^2$)	CPEdl ($S^{n1}\beta.\Omega^{-1}\beta.cm^{-2}$) $\times 10^{-3}$	n_2	$\chi^2 \times 10^{-3}$	IE%
0	4.657	11.25	0.353	0.95	0.35	1.074	0.59	6.78	–
5	6.831	276.1	0.253	0.89	7.87	0.817	0.88	2.86	**95.55**
10	2.351	281.5	0.119	0.88	9.94	0.659	0.75	2.98	**96.48**
20	5.844	398.9	0.115	1	12.92	0.118	0.78	4.81	**97.29**
30	6.488	145.5	0.122	0.99	4.65	0.132	0.82	2.75	**92.47**

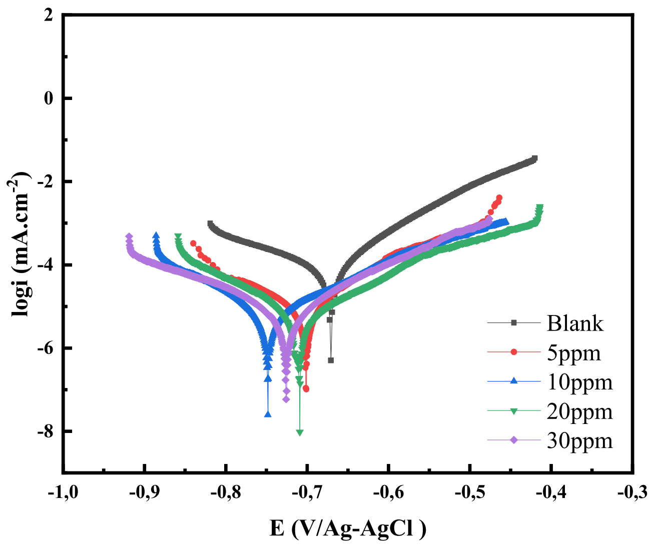

Fig. 10. Polarization curves for the corrosion of API5LX60 steel in NaCl 3.5 % in absence and presence of different concentrations of Trifolium repens.

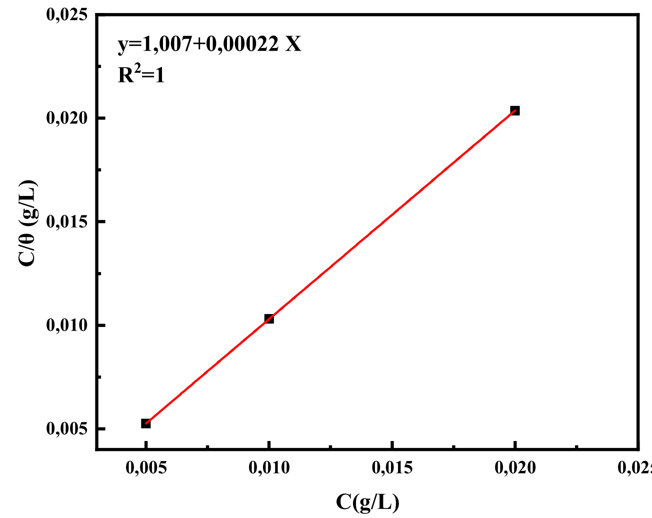

Fig. 11. Langmuir isotherm for the degree of surface coverage versus concentration of inhibitor in NaCl 3.5 %.

Table 3
Potentiodynamic polarisation characteristics for API5LX60 corrosion in NaCl 3.5 % solution without and with various Trifolium repens concentrations.

C (ppm)	Ecorr (mV/ Ag-AgCl)	I corr (mA.cm^{-2})	Rp (KΩ. cm^2)	βa (mV/ dec)	-βc (mV/ dec)	IE %
0	−668	0.167	0.42	94.0	201.6	/
5	−701	0.008	3.26	74.5	55.7	**95.21**
10	−748	0.005	4.93	118.7	97.4	**97.01**
20	−706	0.003	5.46	107.3	94.9	**98.20**
30	−723	0.007	3.29	111.6	139.8	**95.81**

3.5. Adsorption isotherm

Understanding the adsorption isotherm in its entirety provides important insights into the interaction with the inhibitor and the carbon steel surface. We have examined several adsorption isotherms to accurately represent the adsorption behaviour of the inhibitor under investigation. It is essential to establish a direct relationship between the degree of surface coverage (θ) and the inhibitor concentration (C). The Langmuir isotherm is evaluated and can be expressed by Eq. (6):

$$\frac{C}{\theta} = \frac{1}{Kads} \times C \tag{6}$$

For various inhibitor doses in a medium, the recovery rate (θ) is calculated from polarisation curves using Eq. (7):

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{7}$$

From the plot of **C/ θ** as a function of **C** (Fig. 11), we determine the value of $\mathbf{K_{ads}}$ (adsorptive equilibrium constant) from the intersection with the **C/ axis**.

This value correlates well with those reported in the literature [41, 53,54]. Eq. (3) is utilized to determine the free enthalpy value (**ΔG°ads**) for the inhibitor, as stated in reference [54] .

$$\Delta G^{\circ} ads = -RTln(Kads \times C_{H2O}) \tag{8}$$

The symbole **R** denote the universal constant of ideal gases, **T** is temperature, and the concentration of water in the solution is C_{H2O}, expressed as 1000 g.L^{-1} [43,55-57].

In addition, water molecules in the solvent can adhere to the interface between the metal and the solution. Therefore, adsorbing organic inhibitor molecules from aqueous solutions can be seen as a quasi-substitution process involving water molecules at the electrode surface and organic compounds in the aqueous phase. The presence of H_2O (ads) is evident [58].

$$\mathbf{Org_{(sol)}} + \mathbf{nH_2O_{(ads)}} \rightarrow \mathbf{Org_{(ads)}} + \mathbf{nH_2O_{(sol)}} \tag{9}$$

In this reaction, the organic compound in the solution reacts with water molecules on the surface, forming adsorbed organic molecules and solvated water molecules.

Organic species are present in the aqueous solution, while others are adsorbed onto the metallic surface. Water molecules adsorbed on a metallic surface are represented by H_2O (ads). At the same time, the size ratio, denoted as n, indicates the number of organic molecules that can replace a single water molecule. Adsorption isotherms provide fundamental data on the adsorption of inhibitors on metal surfaces.

Several tests were carried out to find the best fit and Fig. 11 shows that it was the Langmuir adsorption isotherm. The high linear regression value (R^2=1) supports this conclusion. We believe that the chemicals extracted from Trifolium repens adhere to specific sites on the metal, forming a uniform and consistent protective layer [56,59,60]. The slope of the plot is 1.007. This means that the molecules occupy 1.007 sites on the steel surface, rather than just one [56,61].

The molecules in the Trifolium repens extract have a remarkable ability to adsorb and adhere consistently to the metal surface. This is evidenced by the calculated adsorption constant (*K*ads = 4.55 $L.g^{-1}$) derived from Eq. (7) and shown in Fig. 9 [43,55]. Kads demonstrates the notable adsorption capacity of the isolated molecules to the API5LX60 surface. Since, it can be assumed that the adsorption of Trifolium repens molecules on the API5LX60 surface is more favourable than their desorption [29] .

The measured ΔG°ads value of −20.881 kJ/mol suggests that the particles from the Trifolium repense extract adhere to the outermost layer of the steel through self-adsorption. These results agree with previous research [43,61] indicating that the adsorption of Trifolium repense extract is influenced by physical interactions with the extract molecules and the surface. The spontaneity of the adsorption process is confirmed by the negative value of ΔG°ads and the stability of the adsorbed layer on the metal surface [57] .

3.6. SEM caracterisation

Scanning Electron Microscopy (SEM) was used to obtain images of the steel surface to evaluate the corrosion inhibition performance of the Trifolium repens molecule in a 3.5 % NaCl environment. Fig. 12(a) shows a polished metal coupon used as a reference. Fig. 12(b) shows the steel surface after exposure in the corrosive solution, revealing the effects of corrosion. In contrast, Fig. 12(c) and 12(d) show the steel surface after immersion for 2 days in a sodium chloride solution containing 20 ppm of the Trifolium repens extract inhibitor. These micrographs show the protective layer formed by the inhibitor, which effectively mitigates corrosion on the steel surface.

Fig.12(a) shows a smooth surface. After 2 days of immersion in 3.5 % NaCl (Fig. 12(b)), the steel surface was attacked by pitting, while the introduction of Trifolium repens extract, as depicted in Fig.12 (c, d), led to the elimination of pitting and the development of an adherent film on the steel's surface.

3.7. AFM analysis

The AFM technique was employed to investigate the surface microstructure of metals following corrosion testing [62,63]. Fig.13 illustrates the 2D and 3D AFM images of the metal surface with and without immersion in a 3.5 % NaCl corrosive environment for 48 h.

The results are presented as root mean square (RMS) roughness. The addition of the inhibitor (Fig. 13-c) has a significant effect on the surface morphology, with an average roughness of 51.030 nm. The sample's surface indicates a similar morphology with a homogeneous surface. However, in the absence of Trifolium (Fig. 13-b), the surface of the sample becomes rough and shows dense pits, probably caused by the corrosive environment. The surface roughness is 268.178 nm compared to the polished steel roughness of approximately 25.452 nm, indicating a much smoother surface (Fig. 13-a).

4. Conclusion

- Trifolium repens extract effectively inhibits the corrosion of API5LX60 steel in a 3.5 % sodium chloride medium.

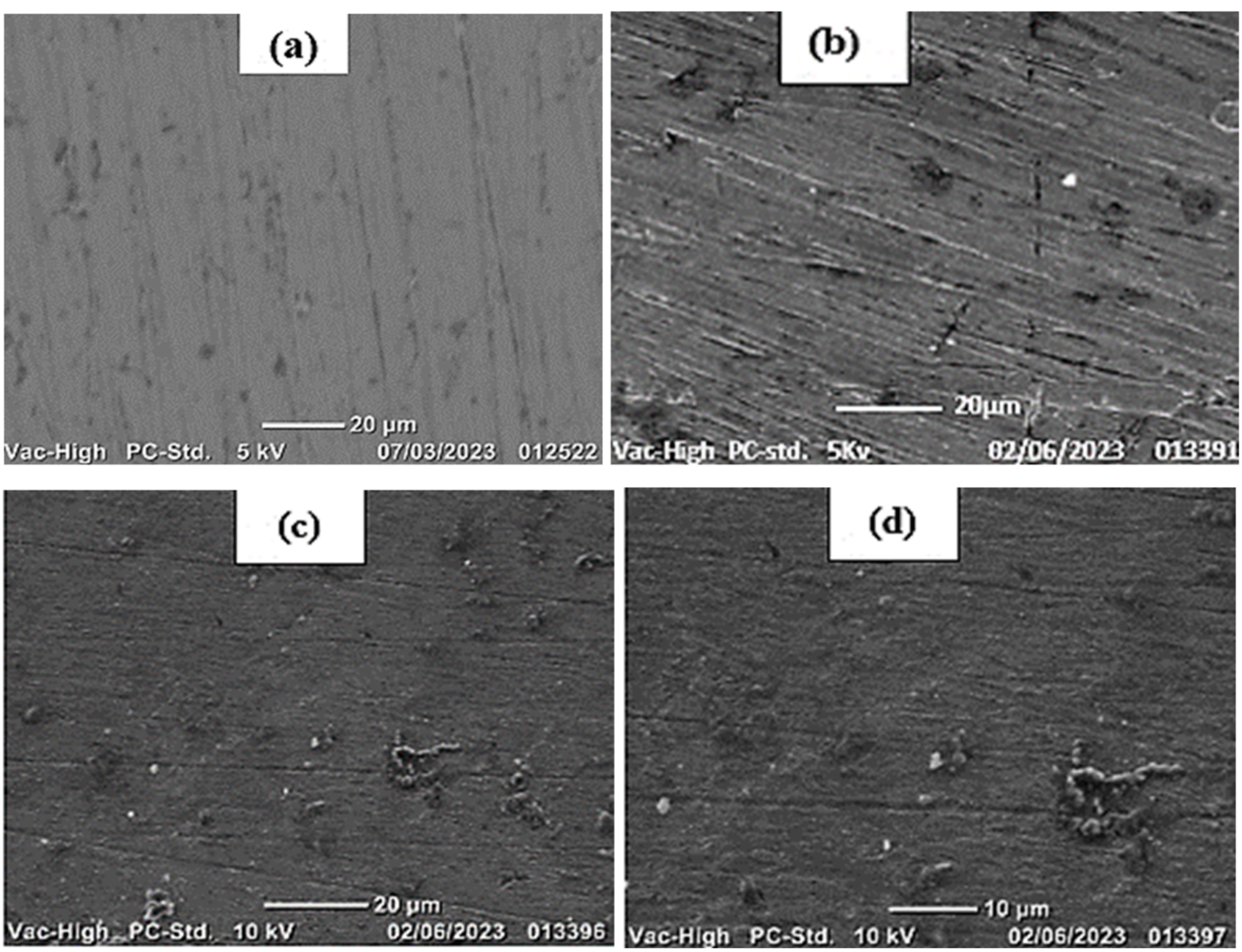

Fig. 12. SEM images of API5LX60 Pipe steel electrodes after 2 days, (a)steel before immersion;(b) steel after immersion in the corrosive solution;(c, d) immerged in NaCl 3.5 % solution with inhibitor at 20 ppm.

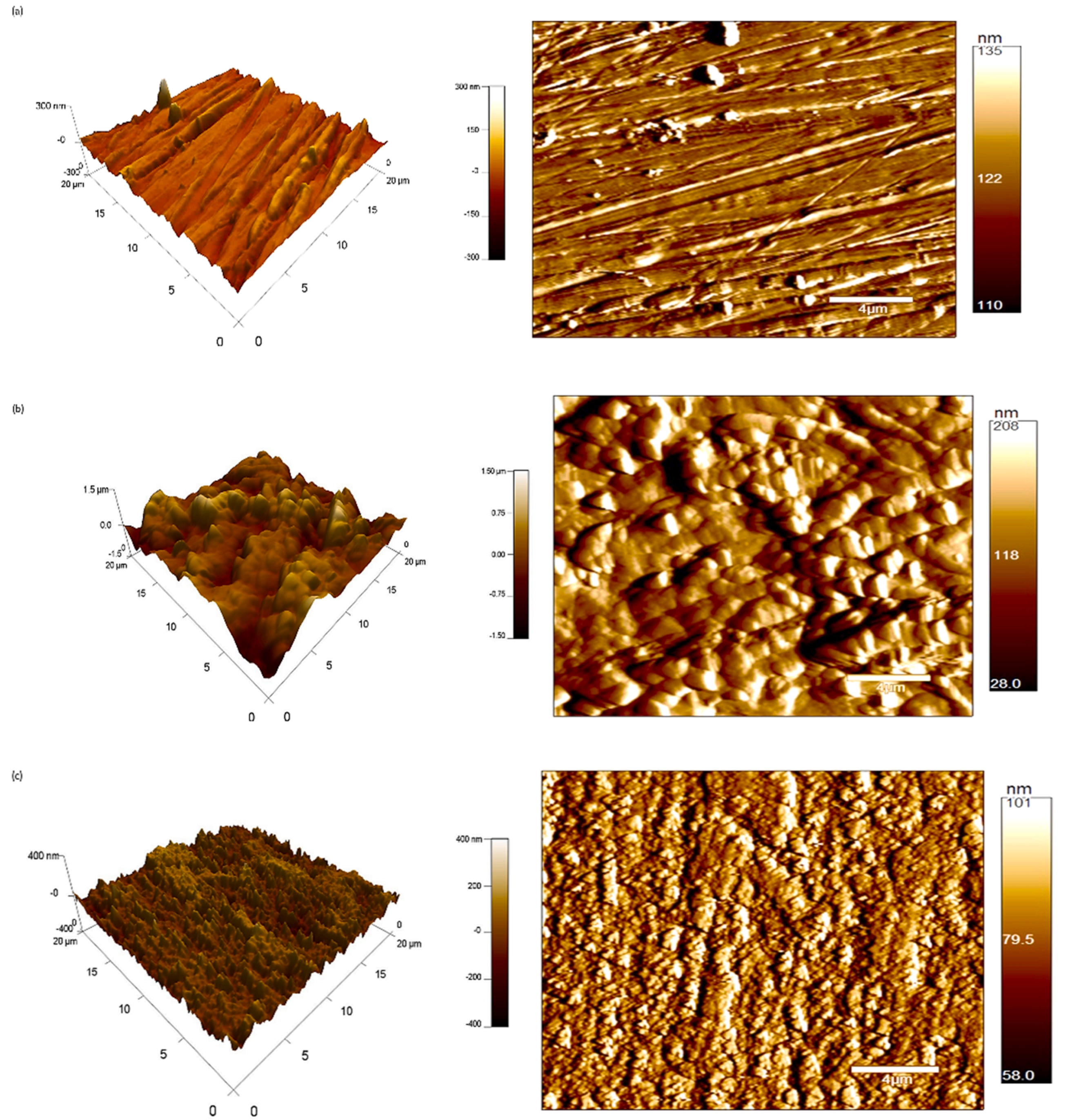

Fig. 13. AFM images of API5LX60 Pipe steel electrodes after 2 days, (a)steel without immersion;(b) in NaCl 3.5 % for 2 days;(c) immersed in NaCl 3.5 % solution with inhibitor at 20 ppm.

- The highest inhibition efficiency of 98 % was observed at a concentration of 20 ppm.
- The Langmuir isotherm model indicates that the Trifolium repens molecules adsorb onto the steel surface.
- Formation of a protective film by the inhibitor was corroborated through electrochemical studies and surface analysis techniques.
- The extract demonstrates significant promise as an environmentally friendly corrosion inhibitor for carbon steel.
- The findings provided from both the EIS and weight loss approaches exhibit strong agreement.

CRediT authorship contribution statement

Sobhi Nour El Houda: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation. **Boukhouiete Amel:** Writing – review & editing, Supervision, Project administration. **Foudia Malika:** Writing – review & editing, Supervision, Software, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could appear to have influenced the work reported in this paper.

Acknowledgments

We are very thankful to the Algerian Ministry of Higher Education and Scientific Research (MESRS) and the general direction of research (DGRSDT) for their help and support.

Statements and Declarations

The work presented in the paper is original and has not been previously published or submitted elsewhere.

References

[1] Muthukrishnan P, Jeyaprabha B, Prakash et P. Adsorption and corrosion inhibiting behavior of Lannea coromandelica leaf extract on mild steel corrosion. Arab J Chem 2017;10. p. S2343-S2354.
[2] Asadi N, Ramezanzadeh M, Bahlakeh G, Ramezanzadeh et B. Utilizing Lemon Balm extract as an effective green corrosion inhibitor for mild steel in 1M HCl solution: a detailed experimental, molecular dynamics, Monte Carlo and quantum mechanics study. J Taiwan Inst Chem Eng 2019;95:252-272.
[3] Chen J, Wu Y, Guo L, Li W, Tan B, Brahmia et A. Insight into the anti-corrosion mechanism of Pisum sativum L leaves extract as the degradable inhibitor for Q235 steel in sulfuric acid medium. J Taiwan Inst Chem Eng 2023;143:104664.
[4] El-Asri A, et al. Carissa macrocarpa extract (ECM) as a new efficient and ecologically friendly corrosion inhibitor for copper in nitric acid: experimental and theoretical approach. J Taiwan Inst Chem Eng 2023;142:104633.
[5] Li X, Deng S, Du G, Xie et X. Synergistic inhibition effect of walnut green husk extract and sodium lignosulfonate on the corrosion of cold rolled steel in phosphoric acid solution. J Taiwan Inst Chem Eng 2020;114:263-283.
[6] Mehta RK, Gupta SK, Yadav et M. Studies on pyrimidine derivative as green corrosion inhibitor in acidic environment: electrochemical and computational approach. J Environ Chem Eng 2022;10(5):108499. n.
[7] Tehrani MEHN, Ghahremani P, Ramezanzadeh M, Bahlakeh G, Ramezanzadeh et B. Theoretical and experimental assessment of a green corrosion inhibitor extracted from Malva sylvestris. J Environ Chem Eng 2021;9(3):105256. n.
[8] Wu Y, et al. Orange peel extracts as biodegradable corrosion inhibitor for magnesium alloy in NaCl solution: experimental and theoretical studies. J Taiwan Inst Chem Eng 2020;115:35-46.
[9] Xu Z, Tan B, Zhang S, Chen J, Li et W. Exploring of an ecological corrosion inhibitor of wood hibiscus leaf extract for the Cu/H2SO4 system based on experimental study and theoretical calculations. J Taiwan Inst Chem Eng 2023;143:104686.
[10] Zhang X, Yang L, Zhang Y, Tan B, Zheng X, Li et W. Combined electrochemical/ surface and theoretical assessments of Rosa laevigata extract as an eco-friendly corrosion inhibitor for copper in acidic medium. J Taiwan Inst Chem Eng 2022; 136:104408.
[11] SOBHI SNour-El-Houda. Amel BOUKHOUIETE, Corrosion inhibition of API5L X60 steel in sulfuric acid using gum arabic. Rev Roum Chim 2023. vol .68.1-2.02.
[12] Sobhi NEH, Boukhouiete A, Foudia M, Benidir et S. Study on the performance of green corrosion inhibitor in protection of API5LX60 in seawater environment. Rev Roum Chim 2023;68(n 7-8):383-389.
[13] Tan B, et al. Insight into anti-corrosion mechanism of Dalbergia odorifera leaves extract as a biodegradable inhibitor for X70 steel in sulfuric acid medium. Ind Crops Prod 2023;194:116106.
[14] Tan B, Gong Z, He W, Xiong J, Guo L, Marzouki et R. Insight into the anti-corrosion mechanism of crop waste Arachis hypogaea L. leaf extract for copper in sulfuric acid medium. Sustain Chem Pharm 2024;38:101449.
[15] Carmona-Hernandez A, Campechano-Lira C, Espinoza-Vázquez A, Ramírez-Cano JA, Orozco-Cruz R, Galván-Martínez et R. Electrochemical and DFT theoretical evaluation of the Randia monantha Benth extract as an eco-friendly corrosion inhibitor for mild steel in 1 M HCl solution. J Taiwan Inst Chem Eng 2023;147:104913.
[16] Arrousse N, et al. Synthesis, characterization, and evaluation of xanthene derivative as highly effective, nontoxic corrosion inhibitor for mild steel immersed in 1 M HCl solution. J Taiwan Inst Chem Eng 2021;120:344-359.
[17] Gu T, et al. Insight into the corrosion inhibition performance of Jasmine flower extract on copper in sulfuric acid medium using experimental and theoretical calculation methods. J Taiwan Inst Chem Eng 2023;150:105047.
[18] Tan B, et al. Insights into the inhibition mechanism of three 5-phenyltetrazole derivatives for copper corrosion in sulfuric acid medium via experimental and DFT methods. J Taiwan Inst Chem Eng 2019;102:424-437.
[19] Ren H, et al. Pumpkin Leaf Extract Crop Waste as a New Degradable and Environmentally Friendly Corrosion Inhibitor. Langmuir mars 2024;40(n 11): 5738-5752. https://doi.org/10.1021/acs.langmuir.3c03399.
[20] Wu Y, Gong Z, Guo L, AlObaid et AA. Batatas lam leaf extract as a biodegradable corrosion inhibitor for copper in 0.5 M H2SO4 solution. Sustain Chem Pharm 2024; 39:101601.
[21] Hassannejad et A. Nouri H. Sunflower seed hull extract as a novel green corrosion inhibitor for mild steel in HCl solution. J Mol Liq 2018;254:377-382.
[22] Olasunkanmi LO, Sebona MF, Ebenso et EE. « Influence of 6-phenyl-3 (2H)-pyridazinone and 3-chloro-6-phenylpyrazine on mild steel corrosion in 0.5 M HCl medium: experimental and theoretical studies. J Mol Struct 2017;1149:549-559.
[23] Alvarez PE, Fiori-Bimbi MV, Neske A, Brandan SA, Gervasi et CA. Rollinia occidentalis extract as green corrosion inhibitor for carbon steel in HCl solution. J Indus Eng Chem 2018;58:92-99.
[24] Ramezanzadeh M, Sanaei Z, Bahlakeh G, Ramezanzadeh et B. Highly effective inhibition of mild steel corrosion in 3.5% NaCl solution by green Nettle leaves extract and synergistic effect of eco-friendly cerium nitrate additive: experimental, MD simulation and QM investigations. J Mol Liq 2018;256:67-83.
[25] Mourya P, Banerjee S, Singh et MM. Corrosion inhibition of mild steel in acidic solution by Tagetes erecta (Marigold flower) extract as a green inhibitor. Corros Sci 2014;85:352-363.
[26] Deyab MA. Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution. J Indus Eng Chem 2015;22:384-389.
[27] Li Y, et al. Three piperazine compounds as corrosion inhibitors for copper in 0.5 M sulfuric acid medium. J Taiwan Inst Chem Eng 2021;126:231-243.
[28] Chevalier M, Robert F, Amusant N, Traisnel M, Roos C, Lebrini et M. Enhanced corrosion resistance of mild steel in 1 M hydrochloric acid solution by alkaloids extract from Aniba rosaeodora plant: electrochemical, phytochemical and XPS studies. Electrochim Acta 2014;131:96-105.
[29] Goulart CM, Esteves-Souza A, Martinez-Huitle CA, Rodrigues CJF, Maciel MAM, Echevarria et A. Experimental and theoretical evaluation of semicarbazones and thiosemicarbazones as organic corrosion inhibitors. Corros Sci 2013;67:281-291.
[30] P. Quezel et S. Santa, *Nouvelle flore de l'algerie et des regions desertiques meridionales: avec la collab. technique de Mme O. Schotter. Pref. du pr. L. Emberger*. Editions du CNRS, 1962.
[31] Zatout M, Berrekia R, Abdelguerfi et A. Contribution à l'étude des espèces spontanées du genre Trifolium L. en Algérie: répartition en fonction de quelques facteurs du milieu. XVI Congrès international des herbages Nice-France 1989: 281-282.
[32] Villax EJ. La culture des plantes fourragères dans la région méditerranéenne occidentale: maroc, portugal, tunisie, algérie, espagne, france, par edmond joseph villax…. Institut national de la recherche agronomique; 1963.
[33] A. Lapeyronie, *Les productions fourragères méditerranéennes*. 1982.
[34] Verma C, Olasunkanmi LO, Obot IB, Ebenso EE, Quraishi et MA. 2, 4-Diamino-5-(phenylthio)-5 H-chromeno [2, 3-b] pyridine-3-carbonitriles as green and effective corrosion inhibitors: gravimetric, electrochemical, surface morphology and theoretical studies. RSC Adv 2016;6(n 59). p. 53933-53948.
[35] da Silva MVL, de Britto Policarpi E, Spinelli et A. Syzygium cumini leaf extract as an eco-friendly corrosion inhibitor for carbon steel in acidic medium. J Taiwan Inst Chem Eng 2021;129:342-349.
[36] Engelmann NJ, Reppert A, Yousef G, Rogers RB, Lila et MA. In vitro production of radiolabeled red clover (Trifolium pratense) isoflavones. Plant Cell Tissue Organ Culture (PCTOC) 2009;98:147-156.
[37] Verma C, Olasunkanmi LO, Ebenso EE, Quraishi et MA. Substituents effect on corrosion inhibition performance of organic compounds in aggressive ionic solutions: a review. J Mol Liq 2018;251:100-118.
[38] Ponce MA, Scervino JM, Erra-Balsells R, Ocampo JA, Godeas et AM. Flavonoids from shoots and roots of Trifolium repens (white clover) grown in presence or absence of the arbuscular mycorrhizal fungus Glomus intraradices. Phytochemistry 2004;65(n 13):1925-1930.
[39] Ahmad et A. Zeb S. Phytochemical profile and pharmacological properties of Trifolium repens. J Basic Clin Physiol Pharmacol 2021;32(n 1):20200015.
[40] Toghan A, Gadow HS, Dardeer HM, Elabbasy et HM. New promising halogenated cyclic imides derivatives as potential corrosion inhibitors for carbon steel in hydrochloric acid solution. J Mol Liq 2021;325:115136.
[41] Verma C, Olasunkanmi LO, Ebenso EE, Quraishi et MA. Substituents effect on corrosion inhibition performance of organic compounds in aggressive ionic solutions: a review. J Mol Liq 2018;251:100-118. https://doi.org/10.1016/j.molliq.2017.12.055. févr.
[42] Luo Z-G, et al. Modified nano-lignin as a novel biomass-derived corrosion inhibitor for enhanced corrosion resistance of carbon steel. Corros Sci 2024;227:111705.
[43] Kaya F, Solmaz R, Geçibesler et İH. Investigation of adsorption, corrosion inhibition, synergistic inhibition effect and stability studies of Rheum ribes leaf extract on mild steel in 1 M HCl solution. J Taiwan Inst Chem Eng 2023;143: 104712.
[44] Solmaz R, Kardaş G, Çulha M, Yazici B, Erbil et M. Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media. Electrochim Acta 2008;53(n 20):5941-5952.
[45] Solmaz R, Kardaş G, Yazıcı B, Erbil et M. Adsorption and corrosion inhibitive properties of 2-amino-5-mercapto-1, 3, 4-thiadiazole on mild steel in hydrochloric acid media. Colloids Surf A Physicochem Eng Asp 2008;312(n 1):7-17.
[46] Liao LL, Mo S, Luo HQ, Li et NB. Corrosion protection for mild steel by extract from the waste of lychee fruit in HCl solution: experimental and theoretical studies. J Colloid Interface Sci 2018;520:41-49.
[47] Diaz-Ramos M, Roche V, Song R, Fan H, Bureau C, Lepretre et JC. Electrochemical Impedance Spectroscopy (EIS) of parylene coated magnesium stents in organic solvent to study early corrosion control. Corros Sci 2023;213:110932.
[48] Zhu H, Huo Y, Wang W, He X, Fang S, Zhang et Y. Quantum chemical calculation of reaction characteristics of hydroxyl at different positions during coal spontaneous combustion. Process Saf Environ Protect 2021;148:624-635. https://doi.org/10.1016/j.psep.2020.11.041. avr.
[49] Abd El-Lateef HM, Abu-Dief AM, Abdel-Rahman LH, Sañudo EC, Aliaga-Alcalde et N. Electrochemical and theoretical quantum approaches on the inhibition of C1018 carbon steel corrosion in acidic medium containing chloride using some newly synthesized phenolic Schiff bases compounds. J Electroanal Chem 2015;743: 120-133. https://doi.org/10.1016/j.jelechem.2015.02.023. avr.

[50] Fouda AE-AS, Molouk AF, Atia MF, El-Hossiany A, Almahdy et MS. Verbena officinalis (VO) leaf extract as an anti-corrosion inhibitor for carbon steel in acidic environment. Sci Rep 2024;14(n 1):16112. https://doi.org/10.1038/s41598-024-65266-z. juill.
[51] Şahin EA, Dursun YA, Geçibesler İH, Solmaz et R. Adsorption and corrosion inhibition ability of avocado seed (Persea americana) extract for copper corrosion in 0.5 M H2SO4 solution. Inorg Chem Commun 2024:112751.
[52] Adekunle AS, Olasunkanmi LO, Durodola SS, Oyekunle JAO, Olomola et TO. Investigation on Corrosion Inhibition of Mild Steel by Extract of Dracaena arborea Leaves in Acidic Medium. Chem Africa 2021;4(n 3):647-658. https://doi.org/10.1007/s42250-021-00246-8. sept.
[53] Dutta A, Saha SK, Adhikari U, Banerjee P, Sukul et D. Effect of substitution on corrosion inhibition properties of 2-(substituted phenyl) benzimidazole derivatives on mild steel in 1 M HCl solution: a combined experimental and theoretical approach. Corros Sci 2017;123:256-266.
[54] Garcia-Ochoa E, Guzmán-Jiménez SJ, Hernandez JG, Pandiyan T, Vásquez-Pérez JM, Cruz-Borbolla et J. Benzimidazole ligands in the corrosion inhibition for carbon steel in acid medium: DFT study of its interaction on Fe30 surface. J Mol Struct 2016;1119:314-324.
[55] de Britto Policarpi et A. Spinelli E. Application of Hymenaea stigonocarpa fruit shell extract as eco-friendly corrosion inhibitor for steel in sulfuric acid. J Taiwan Inst Chem Eng 2020;116:215-222.
[56] Salcı A, Yüksel H, Solmaz et R. Experimental studies on the corrosion inhibition performance of 2-(2-aminophenyl) benzimidazole for mild steel protection in HCl solution. J Taiwan Inst Chem Eng 2022;134:104349.
[57] Solmaz R, Salcı A, Dursun YA, Kardaş et G. A comprehensive study on the adsorption, corrosion inhibition efficiency and stability of acriflavine on mild steel in 1 M HCl solution. Colloids and Surf A Physicochem Eng Asp 2023;674:131908.
[58] Lai C, et al. Adsorption and Corrosion Inhibition Performance of 2-(p-bromobenzylthio)-1H-benzimidazole for Q235 Steel in HCl Solution. Int J Electrochem Sci 2016;11(n 12). p. 10462–10472.
[59] Okafor PC, Zheng Y. Synergistic inhibition behaviour of methylbenzyl quaternary imidazoline derivative and iodide ions on mild steel in H2SO4 solutions. Corros Sci 2009;51(n 4):850-859. https://doi.org/10.1016/j.corsci.2009.01.027. avr.
[60] Kaya F, Solmaz R, Geçibesler et İH. The use of methanol extract of Rheum Ribes (Işgın) flower as a natural and promising corrosion inhibitor for mild steel protection in 1 M HCl solution. J Indus Eng Chem 2023;122:102-117.
[61] Oulabbas A, Abderrahmane S, Salcı A, Geçibesler İH, Solmaz et R. Adsorption and Corrosion Inhibition of Cactus cladode Extract and Effect of KI Addition on Mild Steel in 0.5 M H_2SO_4. ChemistrySelect 2022;7(n 19):e202200212. https://doi.org/10.1002/slct.202200212. mai.
[62] Li et D. Lampner J. In-situ AFM study of pitting corrosion of Cu thin films. Colloids Surf A Physicochem Eng Aspects 1999;154(n 1-2):227-237.
[63] Nagalakshmi R, et al. Corrosion resistance of SS316L in artificial urine in presence of D-glucose. Int J Nano Corr Sci Engg 2014;1(n 1):39-49.