# Corrosion Inhibition of Oil Pipelines in Acidic Medium by Using Limon leaves Extract as an Environmentally Friendly Inhibitor

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## Abstract

Citrus Limon leaf ($CLL$) extract was used to produce an environmentally friendly anti-corrosion inhibitor when exposed to mild steel in $HCl$ at a $1\ M$ concentration. The effect of temperatures ($303, 313, 323, and\ 333\ K$) and inhibitor concentration was studied using a weight loss technique. The results obtained show that the inhibition efficiency increases with increasing extract concentration and increasing temperature. At higher inhibitor concentrations and temperatures, the inhibition effectiveness was increased to $91.11\%$. The inhibitory effect was confirmed by the absorption of the components of the extract, which was determined by the Langmuir adsorption isotherms. The values of the adsorption free energy were less than ($-20\ kJ.mol^{-1}$), indicating physical adsorption. The adsorption thermodynamic parameters that were calculated supported the physical adsorption of $CLL$ extract on a mild steel surface, as shown by the results. The inhibition was confirmed by testing the metal's surface morphology with $SEM$ and $AFM$.

Keywords: Citrus Limon leaf extract, Mild steel, Hydrochloric acid, Corrosion, Inhibitor Efficiency, Weight loss, Adsorption, SEM, AFM

## 1. Introduction

Metals used in oil and gas production are actually exposed to some very damaging industrial conditions owing to corrosion [1]. Corrosion is not only damaging, but it also causes billions of dollars in yearly losses due to the replacement of corroded equipment, product pollution, product loss from a corroded container, process interruptions induced by corrosion, and so on [2]. Corrosion in pipelines is among the most critical problems facing the global oil and gas sector. As a consequence, corrosion control or management has become a critical component of any business that relies on pipelines to transport materials [3]. Corrosion is an inherent danger of petroleum extraction and transportation. It is a product's damaging attack on its surroundings as a result of its contact with them. Corrosion may occur in practically any aquatic environment and occurs under a range of complex conditions throughout the production, processing, and transportation of petroleum. This process occurs when three things are available: an anode, a cathode, and an electrolyte. The anode is the location at which the metal corrodes. The electrolyte is the corrosive solution that allows the transfer of electrons between the anode and the cathode. The cathode is the conductor of electricity in the cell that is not corroded. Corrosion occurs when moist hydrocarbons are found in pipelines [4]. In an acidic environment, metals corrode rapidly. Corrosion is a natural and electrochemical process that occurs when the potential difference between the metal and the acid changes [5].

Utilizing inhibitors, which are compounds that decrease the rate of corrosion, is among the most efficient ways of protecting metals from corrosion. A corrosion inhibitor is a substance that is added in trace amounts to a corrosion environment to prevent it from corroding. The efficiency of an inhibitor in preventing foundation material corrosion, and even its environmental impact and cost, all play a role in its selection. Corrosion inhibitors made from green materials are non-toxic and biodegradable. Numerous research groups have established the efficacy of naturally occurring compounds in preventing metal corrosion in both acidic and alkaline environments [6].

Acids are widely used in industrial processes, with the most commonly used types being acid pickling, industrial chemical cleaning, acid descaling, as well as oil well acidizing. Due to the fact that acid liquids are often aggressive [3], the acid generally produces corrosion, which, if left without treatment, might shorten the life of the metal. Inhibitors are put in the acid solution to prevent the products from corrosion. While inorganic corrosion inhibitors including chromates, phosphates, and dichromate are useful, their use has been avoided owing to environmental impacts. Numerous reports have been conducted on the effectiveness of organic compounds, typically containing N, S, O, and P heteroatoms in addition to electrons in their chemical composition, as acid corrosion protectants, but their application has been limited because of the high price and complex synthesis methods [7]. The inhibitor's organic compounds adsorb on the metallic surface and obstruct the active surface area, resulting in a large

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reduction in corrosion rate [8].

So, in this study, citrus limon leaf extract obtained from acetone as an extractive solvent was tested for its ability to inhibit mild steel corrosion in hydrochloric acid, utilizing weight loss, $SEM$, and $AFM$ in support of ongoing research on green corrosion inhibitors in acid pickling processes for an oil well.

# 2. 2. Materials and Methods

## 2.1. Preparation of the Materials

### Metal Specimen

The metal sheets used in this current investigation were obtained from one of the pipes used by Iraqi petroleum companies.The chemical analysis of this pipe was as follows: $C$ (0.176%), $Si$ (0.261%), $Mn$ (0.955%), $P$ (<0.0005%), $S$ (<0.001%), $Cr$ (0.047%), $Mo$ (0.0358%), $Ni$ (0.024%), and the remainder is $Fe$. A sizeable rectangular sheet was actually formed from the tubing and then sliced into coupons with measurements of $3\,x\,1\,x\,0.1$ cm, exposing a total area of $6.8\ cm^2$ ($1.054\ inch^2$) to the corrosive acidic media. It was hardened for one hour at 600 °C in an electric furnace and then cooled to room temperature by using a desiccator [9]. The specimens' surfaces were prepared using emery papers of various grades ($220, 400, 600, 800, 1000, 1500,$ and $2000$). They were degreased in benzene, washed with water, dipped in acetone, and air-dried before being kept in moisture-free desiccators.

### Preparation of Plant Extracts

Citrus Limon leaves were gathered from Diyala Governorate orchards, rinsed with distilled water, and dried in the shade. The dry Citrus Limon leaves were crushed with a small electric grinder into a fine powder, and passed through a sieve ($75\ \mu m$) to make very small particles. The Soxhlet tool was used as a method for producing the extracts. It took 25 grams of dry powder and was used to make the extract. Then the product was filtered with a Whatman No. 1 filter, and the process was replicated many times to yield a certain quantity of leaf extracts. The extract was concentrated using a rotary vacuum evaporator at $40\ °C$. It was stored in the refrigerator at $4\ °C$ and was ready to be used [10].

### Preparation of HCl Solution

The acid electrolyte was prepared using laboratory-grade $37\%\ HCl$ with a molecular weight of $36.46\ g/mole$. To make a $1\ M\ HCl$ solution, the acid was precisely diluted with double distilled water.

### Weight loss measurements

For the weight loss measurements that were carried out at different temperatures $(303, 313, 323,$ and $333)\ K$, the mild steel six coupons were carefully weighed, tagged, and suspended via the hole on the coupon with the aid of twine rope and wooden sticks in the reaction beakers containing $250\ ml$ of $1\ M\ HCl$ maintained in a thermostated water bath for three hours. The beaker containing $250\ ml$ of $1\ M\ HCl$ without extract served as the blank for the acidic medium. The rest of the beakers are containing with different concentrations of Limon leaf extract as inhibitor ($2, 4, 6, 8,$ and $10\ ml/L$) of $HCl$ [11].

After three hours of immersion, the sample was scrubbed with a bristle brush under running water, rinsed in acetone, dried in warm air, and reweighed [12]. The weight loss was calculated in milligrams, the difference between the weight of the coupon before immersion and after immersion. From the weight loss values, the corrosion rate was calculated and expressed in ($mpy$) using the equation (2.1) [13].

$$CR(mpy) = \frac{534\ \Delta W}{DAT} \quad (2.1)$$

where $W$ denotes weight loss ($mg$), A denotes surface area ($inch^2$), $D$ denotes metal density ($g/cm^3$), and T is exposure period (hour).

Also, the inhibition efficiency ($IE$) was determined using the expression shown in the equation (2.2) [14]:

$$IE = 1 - \frac{W_{inh}}{W_{uninh}} * 100 \quad (2.2)$$

Where $W_{uninh}$ means weight loss without any of the inhibitor and $W_{inh}$ means weight loss with the inhibitor.

### Isotherm of Adsorption

Adsorption isotherms are critical for comprehending the process of corrosion inhibition. The term "adsorption isotherm" describes the relationship between the degree to which adsorbate molecules cover contact and the gas pressure or species concentrations in the solution. There are a lot of different types of adsorption isotherms, but the most common are the $Temkin$, $Freundlich$, $Frumkin$, $Florry\ Huggins$, $El - Awardy$, $Bockris–Swinkel$, and $Langmuir\ isotherms$ [15,16]. To determine the adsorption isotherm, the degree to which different inhibitor concentrations cover the surface must be calculated using equation (3.1) [17].

$$\theta = \left(1 - \frac{W_{inh}}{W_{uninh}}\right) \quad (3.1)$$

Where θ is coverage surface, $W_{uninh}$ implies weight loss without the use of the inhibitor, and $W_{inh}$ signifies weight loss with the use of the inhibitor.

The following equation can be used to figure out the adsorption free energy after figuring out which adsorption isotherm equation best fits the adsorption data.

$$\Delta G_{ads.} = -RT\ ln(55.5\ K_{ads.}) \quad (3.2)$$

where R denotes the ideal gas constant, T denotes the absolute temperature (in Kelvin), and 55.5 denotes the water concentration. Chemisorption generally requires roughly $-100\ kJ/mol$ of standard free energy, while physical adsorption requires a smaller number. [15,18].

# 3. Results and discussion

The corrosion rate, inhibition efficiency, and surface coverage were calculated using equations (2.1), (2.2), and (3.1) respectively, and the results are organized in the following table.

Table 1: The mild steel corrosion rate (mpy), inhibition efficiency (IE%), and surface coverage (θ) as a function of temperature and CLL extract concentration

| Cinh ml/L | Temperature | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 303K | | | 313K | | | 323K | | | 333K | | |
| | CR (mpy) | θ | IE% | $C_R$ (mpy) | θ | IE% | $C_R$ (mpy) | θ | IE% | $C_R$ (mpy) | θ | IE% |
| 0 | 66.691 | 0 | 0 | 133.354 | 0 | 0 | 445.231 | 0 | 0 | 1210.942 | 0 | 0 |
| 2 | 34.421 | 0.4838 | 48.38 | 66.691 | 0.5000 | 50.00 | 150.594 | 0.6618 | 66.18 | 292.582 | 0.7584 | 75.84 |
| 4 | 32.270 | 0.5161 | 51.61 | 51.632 | 0.6129 | 61.29 | 118.323 | 0.7342 | 73.42 | 210.831 | 0.8259 | 82.59 |
| 6 | 30.118 | 0.5483 | 54.83 | 49.480 | 0.6290 | 62.90 | 114.021 | 0.7439 | 74.39 | 174.258 | 0.8561 | 85.61 |
| 8 | 27.967 | 0.5806 | 58.06 | 43.026 | 0.6774 | 67.74 | 105.415 | 0.7767 | 77.67 | 150.594 | 0.8766 | 87.66 |
| 10 | 25.816 | 0.6112 | 61.12 | 38.724 | 0.7096 | 70.96 | 83.902 | 0.8125 | 81.25 | 107.567 | 0.9111 | 91.11 |

## Corrosion rate and inhibitor efficiency

The weight loss findings were used to determine the corrosion rate and inhibitor efficiency of mild steel coupons in 1 $M\ HCl$ with the absence and presence of $CLL$ extract at temperature degrees of $303$ to $333K$. $Table$ 1 summarizes the findings of 24 test runs. It is obvious that the rate of corrosion rose with increasing temperature and reduced with increasing inhibitor concentration. Numerous studies achieved similar findings when they investigated the inhibitory impact of plant extracts on carbon steel corrosion in 1 $M$ hydrochloric acid. They discovered that the corrosion rate and inhibition efficiency are affected by the concentration of the extracts and also the media temperature, and this was mentioned in previous literature. [19-23]

### The effect of temperature

The temperature has a great influence on the corrosion rate of both inhibited and uninhibited acids. Through the results recorded in Table 1, it was discovered that when the temperatures are increased from 303 to 333 $K$ in uninhibited acid, the corrosion rates increase, increasing from $66.691\ to\ 121.942\ mpy$ in mild steel, as shown in Fig.1. Another thing to note is that corrosion rates also rise with temperatures increasing with the presence of a certain concentration of inhibitor, but less than in the case of uninhibited acids, as shown in Fig. 2. This means that when temperatures rise, the rate of mild steel corrosion accelerates as the average kinetic energy of the interacting particles rises [24]. Fig. 3 shows that the mild steel inhibition efficiency in the solution containing a certain concentration of the above-mentioned inhibitors increases as the temperature rises, which is shown in figure. The inhibition efficiency maximum was at the highest temperature of the solution ($333K$).

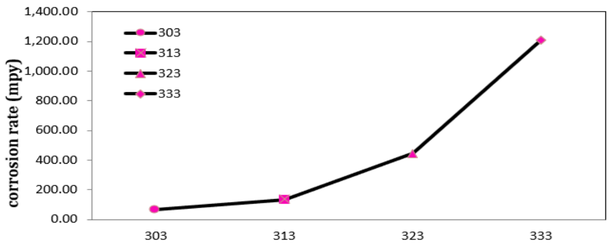


***Fig.*** **1**: *Effect of temperature on corrosion rates in the absence of inhibitor.*

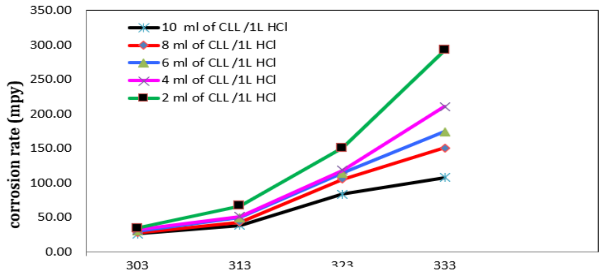


***Fig.*** **2**: *Effect of temperature on the corrosion rate of mild steel immersed in* $1M\ HCl$ *at different concentrations of* $CLL$ *extract as inhibitor.*

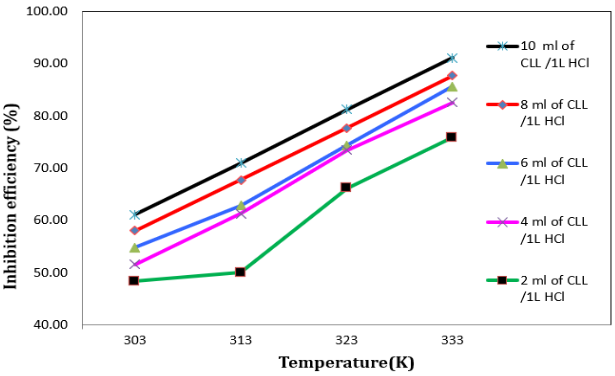


***Fig.*** **3**: *Effect of temperature on inhibition efficiency of* $CLL$ *extract as an inhibitor for mild steel corrosion in* $1M\ HCl$.

### The effect of inhibitor concentration

When mild steel was immersed in a 1 $M\ HCl$ solution, the presence of citrus Limon leaf extract significantly lowered the corrosion rate. Table 1 and Fig.4 illustrate the change in corrosion rate as a function of inhibitor concentration at various temperatures. At a particular temperature, it is self-evident that raising the inhibitor concentration reduces corrosion [25]. The extract's corrosion-inhibiting effect is thought to be related to the extract's different phytochemicals. However, it is unknown whether the extract's inhibitory action is due to a single component or a synergistic effect of the constituents. This is because certain extract constituents are well-known for their corrosion-inhibiting properties. [26]

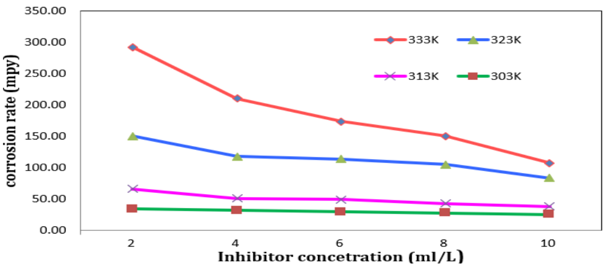


***Fig*.4**: *Effect of* $\boldsymbol{CLL}$ *extract concentration as an inhibitor on the corrosion rate of mild steel immersed in* $\boldsymbol{1\ M\ HCl}$.

## Inhibitor Performance and Adsorption Interpretation

When the inhibitor concentration was raised from 2 to 10 $ml/L$, the corrosion rate was seen to decrease to very low values. Fig. 4 illustrates this situation succinctly. The figure demonstrates that at a concentration of 10 ml/L of inhibitor, the corrosion rate reaches its minimum value. This might be because a 10 ml/L inhibitor concentration level is able to cover the metal surface between 303 and 333$K$. When the temperature was raised from 303 $to$ 333 $K$, the inhibition was larger at a concentration of 10 $ml/L$ than at a concentration of 8 ml/L. Thus, when the inhibitor concentration declines from 6 to 2 $ml/L$, the surface coverage reduces and the corrosion rate values rise, as seen in Fig. 4.

When studying adsorption properties, it is necessary to calculate the surface coverage ($\theta$) data. The surface coverage of an inhibitor at a given concentration was calculated using Equation (3.1). Corrosion rate data might be utilized to deduce the mechanism of adsorption. The Langmuir isotherm was a perfect isotherm for adsorption in the absence of interaction between the adsorbate and the adsorbent. According to Langmuir's assumptions, the inhibitor level of concentration (adsorbate concentration) ($C$) is proportional to the quantity of surface covering ($\theta$) through equation (5.1).

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (5.1)$$

where $\theta$ denotes the surface coverage, $C$ inhibitor concentration, and $K$ equilibrium constant of the adsorption process.

Table 1 may be utilized to assess the adsorption mechanism using the corrosion rate data by charting the values of $C/\theta$ vs. $C$ of $CLL$ extract in 1 $M\ HCl$ extract at different temps $(303, 313, 323, 333)$ $K$, the straight line which was created to represent the Langmuir isotherm, as seen in Fig. 5. Straight lines match the data, suggesting that inhibitors are adsorbed according to the Langmuir adsorption isotherm. The linear correlation coefficient ($R^2$) which is almost near to one and the slopes are quite close to one, indicating that this inhibitor was adsorbed onto the metal surface according to the Langmuir adsorption isotherm. To explain how the extracted molecules adsorbed on metallic surfaces, Langmuir's adsorption isotherm was utilized. This demonstrates the existence of a multimolecular layer of adsorption in which no contact between the adsorbate and adsorbent occurs [16, 27]. $K_{ads}$ values may be calculated by determining the intercept of a straight line on the $C/\theta$ axis and then substituting them into equation (3.2) to get $\Delta G^{\circ}_{ads}$.

The free energy of adsorption ($\Delta G^{\circ}_{ads}$) of the $CLL$ inhibitor on the mild steel surface was determined using the plot of the isotherms in Figure (4.14) The results obtained of $\Delta G^{\circ}_{ads}$ are reported in Table 2 . These are negative values ranging from $-9.184\ KJ/mol$ at 303 $K$ to $-12.398\ KJ/mol$ at 333 $K$ obtained from the Langmuir isotherm plot. The $\Delta G^{\circ}_{ads}$ values are all negative, suggesting that the inhibitor molecules adsorb spontaneously. The K values rise, indicating that the adsorption coefficient rises with temperature. This indicates that as temperature increases, so does adsorption and hence inhibitory efficiency [28]. In general, if $\Delta G^{\circ}_{ads}$values are less than or equal to $-20\ kJ.mol^{-1}$ (as obtained in this work), it implies compatibility with electrostatic interaction between the charged metal and ionic species (physical adsorption), while values larger than or equal to $-40\ kJ.mol^{-1}$ imply transfer or sharing of charges from the inhibitor molecule to the mild steel surface to establish a coordination bond (chemical adsorption) [29].

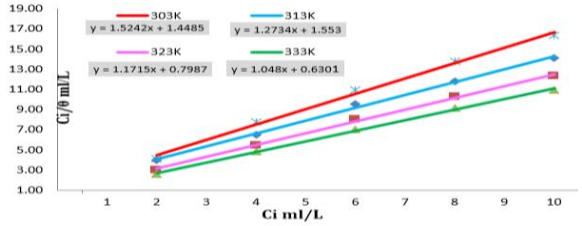


*Fig. 5: Langmuir adsorption isotherm of* $\boldsymbol{CLL}$ *extract on mild steel in* $\boldsymbol{1\ M\ HCl}$

Table 2: Equilibrium constant ($K_{ads}$) , standard adsorption free energy ($\Delta G^{\circ}_{ads}$), and coefficient of correlation ($R^2$) for Langmuir type adsorption isotherm of $CLL$ eetract on mild steel in 1 $M\ HCl$ at different temperatures

| ***Temperature* (*K*)** | **$K_{ads}$ (*L*/*ml*)** | **$\Delta G^{\circ}_{ads}\ KJ.mol^{-1}$** | **$R^2$** |
|---|---|---|---|
| **303** | 0.6903 | − 9.184 | 0.9955 |
| **313** | 0.6439 | − 9.306 | 0.9971 |
| **323** | 1.2520 | − 11.389 | 0.9976 |
| **333** | 1.5870 | − 12.398 | 0.9989 |
| Average value | 1.0433 | −10.569 | 0.9972 |

## Thermodynamic Studies

The impact of temperature on the inhibited acid–metal interaction may be represented using the Arrhenius equation (6.1), which states that the rate of corrosion is related to temperature, as shown in the following equation [16].

$$\ln(CR) = lnA - \frac{Ea}{RT} \quad (6.1)$$

Where $(A)$ denotes the frequency factor, $(Ea)$ denotes the activation energy $(KJ/mol)$, $(R)$ denotes the gas constant $(8.314\, J.mol^{-1}.K^{-1})$, and $(T)$ denotes the absolute temperature (K).

Additionally, the Arrhenius equation may be stated as follows:

$$\ln\left[\frac{CR}{T}\right] = \ln\frac{R}{Nh} + \left[\frac{\Delta S^*}{R}\right] - \left[\frac{\Delta H^*}{R}\right].\frac{1}{T} \quad (6.2)$$

Where h denotes the plank's constant $(6.63 * 10^{-34}$ $J.S)$, $N$ denotes Avogadro's number $(6.02 * 10^{23}$ $mol^{-1})$, $S^*$ denotes the entropy of activation, and $H^*$ denotes the enthalpy of activation.

Using equation (6.1), the experimental activation energy $(Ea)$ of mild steel corrosion in $(1\, M\, HCl)$ with and without $CLL$ extract was calculated. From the dataset of table 1, $(ln\, CR)$ versus $(1/T)$ Arrhenius plots yielded straight lines with slopes comparable to $(-Ea/R)$, as seen in Fig 6. The activation energy of mild steel was found to be $(81.912\, kJ/mol)$ in the absence of $CLL$ extract and lowered to $(42.069\, kJ/mol)$ in the concentration of $10\, ml/L$ (Table 3). The fact that the Ea values of inhibited systems are less than those of uninhibited systems indicates that the inhibitor has a high efficiency of inhibition at increased temperatures [30]. Adsorption is chemical if $Ea > 80\, kJ/mol$ and physical if $Ea < 80\, kJ/mol$ [31,32]. The average of the $Ea$ values less than $80\, KJ/mol$ and the $\Delta G^{\circ}_{ads}$values indicate that the inhibitor molecules adsorb onto the steel surface through a physical adsorption process. [33].

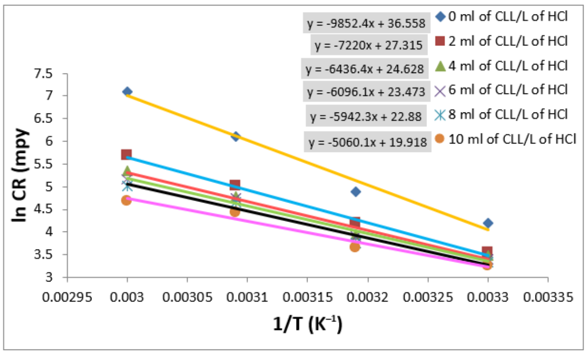


***Fig*.6**: *Arrhenius plot of the corrosion of mild steel in* $(1\, \boldsymbol{M\, HCl})$ *containing different concentrations of* $\boldsymbol{CLL\ extract}$ *at various temperatures.*

Experimental corrosion rates for mild steel corrosion only in (1M HCl) in the absence and availability of inhibitors have been determined using the weight-loss technique. For the activation enthalpy $(\Delta H *)$ and entropy $(\Delta S *)$, equation (6.2) was used. The values of $(\Delta H *)$ and $(\Delta S *)$ were obtained by graphing ln (CR/T) versus (1/T). As a result, the slope and intercept must be $(-\Delta H_{ads}/R)$ and $(\ln R/Nh + \Delta S_{ads} R)$, respectively as shown in Fig. 7, from which the values of $(\Delta H *)$ and $(\Delta S *)$ were computed and reported in Table 3. Endothermic dissolution is indicated by positive enthalpies $(\Delta H *)$ [34]. The positive and negative $(\Delta S *)$ values are an indication that the adsorbate molecules bind to the adsorbent surface in a different order than their shape in the solution [35]. Entropiese large and negative values of indicate that its activated complex in the rate-determining step denotes an association not dissociation step, implying that a reduction in disorder occurs when reactants are transferred to the activated complex. [36,37].

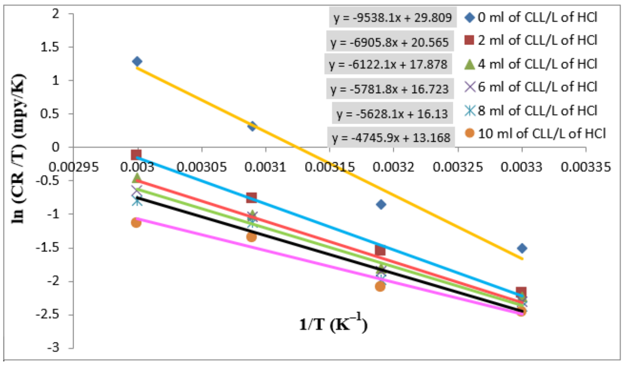


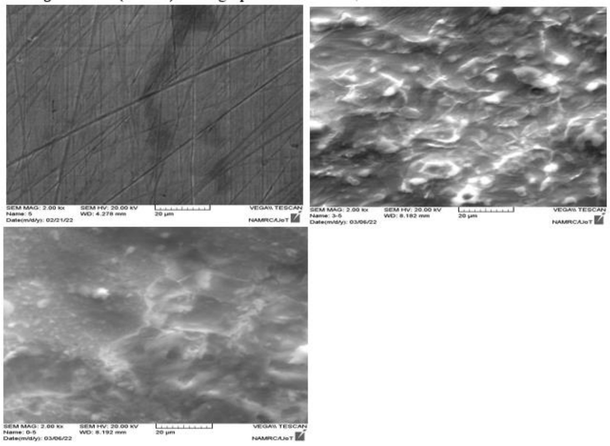
***Fig*.7**: *Transition state plot for mild steel corrosion in* $(\boldsymbol{1M\, HCl})$ *in absence and presence of different concentrations of* $\boldsymbol{CLL}$ *extract.*

Table 3: The values of the activation energy, enthalpy, and entropy of corrosion of mild steel in $\boldsymbol{1\, M\, HCl}$ in the absence and presenc of different concentrations of the $\boldsymbol{CLL}$ extract.

| $Ci(ml/L)$ | $Ea(kJ/mol)$ | ΔS^* (J /mol.K) | ΔH^* (kJ / mol ) |
|---|---|---|---|
| 0 | 81.912 | 50.2 | 79.299 |
| 2 | 60.027 | -26.5 | 57.414 |
| 4 | 53.512 | -48.9 | 50.898 |
| 6 | 50.682 | -58.5 | 48.069 |
| 8 | 49.404 | -63.4 | 46.792 |
| 10 | 42.069 | -88 | 39.457 |
| Average value | 56.267 | -55.9 | 53.654 |

## Scanning Electron Microscope ($\boldsymbol{SEM}$) study

A scanning electron microscope $(TESCAN\ type, Vega\ III\ model)$ was used to study the morphology of the mild steel (magnified images of 2.00Kx) in both inhibited and uninhibited systems as shown in Fig. 6. $SEM$ analysis is performed to see if absorption has occurred on the MS surface or not [38]. Fig. 6A depicts SEM micrographs of mild steel samples unimmersed. Because of the aggressive acid the sample immersed in $1\, M\, HCl$ only for $3\, h$ at temperature $333K$ was rough and severely destroyed, as shown in Fig. 6B,. also evidenced by the micrographs of mild steel immersed in $1\, M\, HCl$ for $3\, h$ at temperature $333K$ in the presence of the inhibitor at a concentration of 10 ml/L Fig. 6C, A smooth surface was seen. It is clear that the inhibitor has a significant effect on reducing corrosion, indicating that the surface was protected by the inhibitor. These consequences corroborate the results from weight loss experiments [39].



*$\boldsymbol{Fig}.\boldsymbol{8}$: SEM (2.00kx) micrographs of mild steel:*

(A) Before immersion in $1\ M\ HCl$.
(B) After immersion in $1\ M\ HCl$ and in the absence of an inhibitor at $333\ K$ for 3 h.
(C) After immersion in $1\ M\ HCl$ and in the presence of $CLL$ extract at a concentration of $10\ ml/L$ of $1M\ HCl$ at $333K$ for 3 h.

## Atomic Force Microscopy ($\boldsymbol{AFM}$) study

AFM is a useful tool for describing metal surfaces at the micro and nanoscales due to its high resolution [40].The images were analyzed and the values of the parameters were obtained as shown in table 4. Fig. 9 ($2D$ *and* $3D$) displays a chemically untreated mild steel surface, whereas Figs.10 and 11 ($2D$ *and* $3D$) show $AFM$ images of the mild steel surface after immersion in 1 M HCl without and with $CLL$ extract, respectively. The results shown in Table 4 indicated that the surface roughness ($Ra$) increased from $0.655\ nm$ in the case of the free surface to $3.66\ nm$ after immersion and the presence of $CLL$ extract but decreased from 3.66 nm in the case of immersion without inhibitor to $2.55\ nm$ after immersion and the presence of CLL extract, and the root mean square (grain-wise) value for a polished surface of chemically untreated mild steel was $0.655\ nm$, while the mild steel surface after immersion in $1\ M\ HCl$ was 3.66 without inhibitor and 2.55 with $CLL$ extract.

Through the results of the above examination, it was observed that the values of the roughness average ($Ra$) and the root mean square roughness ($Rms$) for a free surface are low (Fig. 9), and their values increased in the acidic medium in the absence of an inhibitor (Fig. 10). This means that the surface of the mild steel was more rough and corroded. While adding the inhibitor to the corrosive acid solution, the roughness average ($Ra$) and the mean square roughness ($Rms$) both went down, which means that the surface is smoother (Fig. 11). This is because the inhibitor components are absorbed into the mild steel or because the inhibitor molecules block the active sites on the surface of the mild steel, which reduces contact [41, 42].

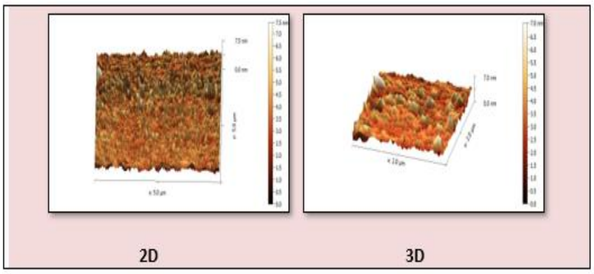


*Fig.9: $\boldsymbol{AFM}$ images ($\boldsymbol{2D}$ **and** $\boldsymbol{3D}$) for mild steel free surface without chemical treatment*

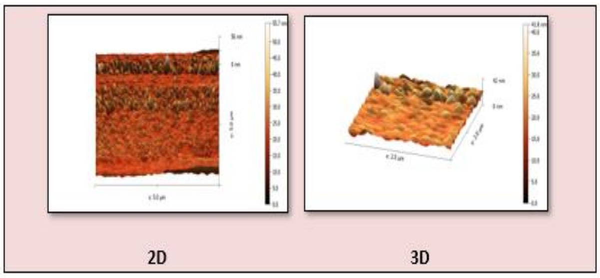


*Fig.10: $\boldsymbol{AFM}$ images ($\boldsymbol{2D}$ **and** $\boldsymbol{3D}$) for mild steel surface immersed in $\boldsymbol{1\ M\ HCl}$ for $\boldsymbol{3h}$ at temperature $\boldsymbol{333K}$*

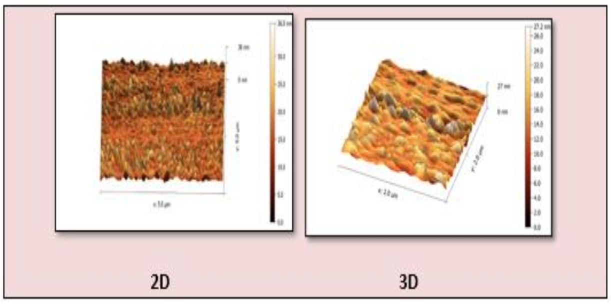


*Fig.11: $\boldsymbol{AFM}$ ($\boldsymbol{2D}$ **and** $\boldsymbol{3D}$) images of a mild steel surface immersed in $\boldsymbol{1\ M\ HCl}$ in the presence of $\boldsymbol{CLL}$ extract for $\boldsymbol{3\ h}$ at $\boldsymbol{333\ K}$.*

Table 4: Roughness parameters of thin films on mild steel surfaces

| Mask in use | Fig.9 | Fig.10 | Fig.11 |
|---|---|---|---|
| Average value | 3.519 nm | 21.80 nm | 16.54 nm |
| Minimum | 0.000 nm | 0.00 nm | 0.00 nm |
| Maximum | 7.451 nm | 55.73 nm | 36.04 nm |
| Median | 3.510 nm | 21.69 nm | 16.39 nm |
| Ra | 0.502 nm | 2.62 nm | 1.86 nm |
| Root mean square (Rms) | 0.655 nm | 3.66 nm | 2.50 nm |
| Rms (grain-wise) | 0.655 nm | 3.66 nm | 2.50 nm |
| Skew | 0.163 | 0.258 | 0.37 |
| Kurtosis | 1.12 | 3.45 | 2.29 |
| Surface area | 25.0188 $\mu m^2$ | 25.5702 $\mu m^2$ | 25.2832 $\mu m^2$ |
| Projected area | 25.0000 $\mu m^2$ | 25.0000 $\mu m^2$ | 25.0000 $\mu m^2$ |
| Inclination θ | 0.0 deg | 0.0 deg | 0.0 deg |
| Inclination ϕ | 51.2 deg | -91.6 deg | 106.0 deg |

## 4. Conclusion

The emergence of a new corrosion inhibitor for mild steel (which metal has huge applications in the petroleum industry), *Citrus Limon leaf* extract is an inhibitor natural and environmentally friendly. This inhibitor significantly reduces the decay of mild steel in a $1\,M\,HCl$ solution and has no adverse impact on the environment. Inhibition of mild steel corrosion by *Citrus Limon leaf* extract is believed to be effective through the presence of Active functional groups in its chemical constituents. These functional groups provide active sites for the adsorption of the inhibitor.

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