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Research Article

The Chemical Composition and Inhibitory Effect of the Essential Oil from *Lippia citriodora* Irrigated by wastewater on the Corrosion of Aluminum in 1 Molar Hydrochloric Acid

F. Bensabah* , S. Houbairi , M. Essahli , A. Lamiri , J. Naja

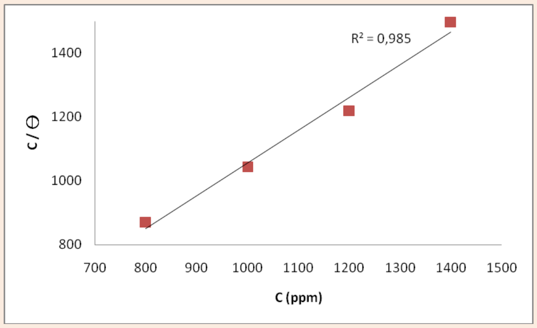
University Hassan 1, Faculty of Science and Techniques, Laboratory of Applied Chemistry and Environment,
B.P. 577, Settat, Morocco.

Abstract

The objective of this study is the valorization of essential oil (EO) of *Lippia citriodora* irrigated by urban wastewater from the city of Settat-Morocco, the corrosion inhibitor tested of aluminum in 1 M HCl using polarization method and weight loss measurements. The inhibition efficiency of *lippia citriodora* oil was calculated and compared. We note of good agreement between these methods. The results obtained revealed that the reduces tested inhibitor differently the kinetic of corrosion process of aluminum. Its efficiency increases with the concentration and attained 98.35% at 1200 ppm. The effect of temperature on the corrosion behaviour of aluminum in 1M HCl was also studied in the range 283 K and 313 K. The thermodynamic data of activation was determined.

Keywords: Corrosion inhibition, aluminum, *Lippia citriodora* , Essential oil and Wastewater

The analysis of *Lippia citriodora* oil, obtained by hydro-distillation, using gas chromatography (GC) showed that the major components were neral 13,85%, geranial 14,06% and limonene 28,32%.



***Correspondence**
F. Bensabah,
Email: bensabah_fati@yahoo.fr

1. Introduction

Aluminum and aluminum alloys represent an important category of materials due to their high technological value and wide range of industrial applications, especially in aerospace and house-hold industries [1] Owing to these applications of aluminum and its alloys, considerable attention has been devoted to the corrosion behaviour of these materials in various aggressive environments [2,3].

Over the last two decades, studies have focused on the application of non-toxic inhibitors, called green or eco-friendly environmental inhibitors. Extracts, oils, or pure compounds natural plants may be of major importance in keeping the environment more healthy, safe, and under pollution control. Among the variety of natural products, *ginger*[4], *jojoba* oil [5], *eugenol, acetyl-eugenol* [6], *eucalyptus* oil [7], *Mentha pulegium* [8], *Salvia aucheri Boiss. var. mesatlantica* [9], *argan* [10,11], *rosemary* oil [12,13], *prickly pear seed* oil [14], *chamomile* essential oil [15], *thymus* oil [16,17], *artemisia* [18,19], *lavender* oil [20], *fennel* (Foeniculum vulgare) essential oil [21] and *lippia citriodora* [22] have all been reported to be good inhibitors of corrosion of Aluminum in acidic solutions. Also we found the Mentha Spicata irrigated by wastewater has been good corrosion inhibitor of Aluminum in acidic solution (HCl 1 M) [23]**.** However, to the best of our knowledge, *lippia citriodora* irrigated by wastewater has not been used as a corrosion inhibitor for aluminum. In this work a variety of methods were used to investigate the inhibition of corrosion of aluminum in HCl solutions by *lippia ctridora* essential oil.

The efficiency of these organic corrosion inhibitors is related to the presence in the molecule of polar functions containing S, O, or N atoms, for example heterocyclic compounds, and p-electrons [24,25]. Acidic solutions are used in many industrial areas. The most important applications are acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing [26,27] . The use of inhibitors is one of the most practical methods for protection against corrosion and prevention of unexpected metal dissolution and acid consumption, especially in acid solutions [28].

The genus Lippia (Verbenaceae) includes approximately 200 species of herbs, shrubs and small trees [29]. Most of them are traditionally used as remedies for gastrointestinal and respiratory problems.Some species have shown antimalarial, antiviral and cytostatic properties. It is believed that their essential oils and phenolic compounds (flavonoids) are responsible for these properties [30]. It is cultivated mainly due to the lemon-like aroma emitted from its leaves that are utilized for the preparation of herbal tea, which is reputed to have antispasmodic, antipyretic, sedative and digestive properties [30,31, 32 and 33]. Lemon verbena has a long history of folk uses in treating asthma, spasms, cold, fever, flatulence, colic, diarrhea, indigestion, insomnia and anxiety [31 and 32].

2. Experimental Part

2.1. Plant material

Plantating was in may 2009 in experimental plots located in the Faculty of Sciences and Technics of Settat-Morocco (FSTS). Irrigation was done with the urban wastewater purified by lagoons from the city of Settat-Morocco. Harvests were made by hand. The quality of essential oils was also determined using a dried leaves of *Lippia citriodora* harvested.

2.2. Water quality irrigation

The physico-chemical parameters (temperature, pH and conductivity) were measured on site by means of a mercury thermometer (1/10°C), portable pH meter lutron (pH-206) and conductivity meter HANNA (HI-8733 with a margin of error of 2%. In the laboratory, the waters were analyzed for major ions (Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO^-_4 and HCO_3^-) and the nutritive salts. Chlorides and alkalinity were determined by titration (Appendix Table); Rodier 1996). The analysis of heavy metals was carried out by the technique of ICP.

2.3. Extraction of Lippia essential oil

The distillation apparatus consisted of a heating cap, a 1.5 L extraction flask, a cooling system and a receiver for hydrodistillate. Thirty grams of dried plant leaves and 800 mL of water were used and the distillation was carried out for 3 hours after the mixture reached boiling at 100°C. Hydrodistillation repetitions were done at least in duplicate depending on the availability of the spearmint leaves. The essential oil obtained was dried under anhydrous sodium sulfate and stored at 4 °C in the dark. After extraction essential oil has been divided into two parts, one was used for chemical analysis, while the second was used to study the Inhibitory tests.

2.4. Gas Chromatography-mass spectrometry

The essential oil was characterized using a gas chromatograph Trace GC Ultra equipped with an autoinjector (Triplus) directly interfaced with a mass spectrophotometer with a flame ionization detector (Pdains Q). Capillary column was DB-5 (5% of diphenyl and 95% of dimethypolysiloxane), 30m in length, 0.25mm thickness. Separation conditions were: 50°C for 2 min, 50–200°C at 5°C/min. Temperature of the injector was 220°C. The volume injected was 0.1 μL. The carrier gas was helium with a flow rate of 1.4 ml.min−1. The oil constituents were identified by comparison of their retention indices and their mass spectra with those of authentic samples. Quantitative analysis (in percent) was performed by peak area measurement.

2.6. Weight loss tests

The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37 % HCl with distilled water. Prior to all measurements, the aluminum samples were polished with different emery paper up to 1200 grade, washed thoroughly with distilled water, degreased with acetone and drying at room temperature.

The solution volume was 30 ml. The used aluminum specimens had a rectangular form, with a surface area of 7.5 cm^2. The immersion time for the weight loss was 1 h at 25°C. After the corrosion test, the specimen of aluminum were carefully washed in distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each case and the mean value of the weight loss was reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in $mg.cm^{-2}\ h^{-1}$

2.7 Rp, polarisation and EIS measurements

Electrochemical measurements were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) in the form of disc cut from aluminum has a geometric area of 1 cm^2. A saturated calomel electrode (SCE) and a disc platinum electrode were used respectively as reference and auxiliary electrodes, respectively. The temperature was thermostatically controlled at 25°C. The WE was abraded with different emery paper up to 1200 grade, degreased with acetone, and rinsed with distilled water before use.

Running on a compatible computer, the Voltab Master4 Software communicates with Instruments potentiostat–galvanostat model PGZ100 at a scan rate of 10 mV/sec. Before recording the polarization curves, the working electrode is maintained for 30 min to Ecorr. The resulting current is plotted as a function of the potential.

Polarization resistance (Rp) values were obtained from the current potential plot. The scan rate was 10 mV/sec.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with the electrochemical system which included a digital potentiostat model Volta lab PGZ 100 computer at Ecorr after immersion in solution, the circular surface of aluminum exposing of 1 cm^2 to the solution were used as working electrode. Frequencies between 100 kHz and 10 mHz were superimposed on the corrosion potential. The impedance diagrams are given in the Nyquist representation. Values of Rt and C_{dl} were obtained from Nyquist plots.

3. Results and Discussion

3.1. Physicochemical analysis of irrigation water

Throughout the experiment, the chemical composition of this water source of irrigation has been determined and detailed in table 1. The gravity irrigation planting is done 1 day / 3 source and water were analyzed at each irrigation.

Table 1 Characterization of wastewater purified by lagoons used for irrigation in the study.

Parameter	**Wastewater purified**	
	average value	**Norm**[(*)]
pH	7,63	6,5-8,4
Temperature /°C	29,36	35
Conductivity at 20 °C µs/cm	1313,64	1200
Biological Oxygen Demand mgO_2/L	27	-
Chemical Oxygen Demand mgO2/L	656,36	-

Parameter	**Wastewater purified**	
	average value	**Norm(*)**
NH_4^+ mg/L	11,25	-
Cl^- mg/L	850,7	350
Ca^{2+} mg/L	97,94	-
Mg^{2+} mg/L	53,63	-
HCO^-_3 mg/L	67,65	512
N-NO_2^- mg/L	0,09	30
PO_4^{3-} mg/L	3,27	-
SO_4^{2-} mg/L	124,00	350
Suspended matter mg/L	130,4	200
Cd mg/L	≤0.002	0,01
Cr mg/L	0.004	1
Cu mg/L	0,0075	0,2
Ni mg/L	0,012	2
Zn mg/L	0,089	2
Hg mg/L	≤0.01	0,001

(*): Standards of water quality for irrigation S.E.E.E-2007- Morocco (Secretariat of the Ministry of Energy, Mines, Water and Environment)

Wastewater physico-chemical analyzes showed that the chemical oxygen demand is high and the concentration of Cl^- ion exceeds the standard because urban water is responsible for by chloride ions. Other physico-chemical parameters meet the standards as metallic trace elements.

3.2. Chemical composition of lippie citriodora essential oil

The GC-MS analyzes of *lippia citriodora* essential oil irrigated by urban wastewater purified by lagoons from the city of Settat-Morocco are present in the table 2. The essential oil yield was 1.01% [34].

Table 2 Chemical composition of *Lippia citriodora* essential oil irrigated by wastewater from the city of Settat (Morocco) purified by lagoon

Compounds	Retention time	A
α-Pinene	8.62	1,06
Sabinene	10.00	2,42
Limonene	11.99	28,32
Trans- Ocimene	12.75	-
Nerol	17.77	1,40
Neral	19.55	13,85
Geranial	20.57	14,06
β-Caryophyllene	25.41	3,35
α-Curcumene	27.37	11,36
Neryl acetate	27.78	2,38
Copaene	28.28	2,38
α-Cadinene	28.59	-
Spathulenol	30.14	8,29
Caryophyllene oxide	30.29	7,07
ϒ-Cadinene	31.93	3,86

A: plots irrigated by wastewater from the city of Settat treated lagoon.

Lippia citriodora of Morocco still contains majority composed: limonene (28,32%), neral (13,85%) and geranial (14,06%). However, our results did not show the presence of p-cymene, camphor and thymol, which have been mentioned in other studies concerning *L. citriodora* [35,36].

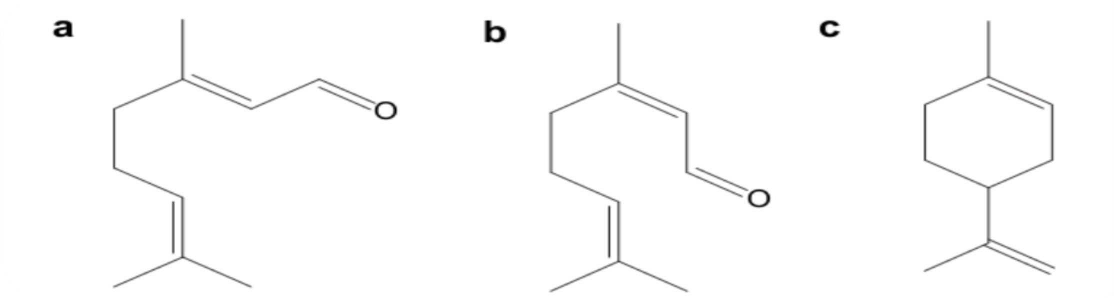


Figure 1 Molecular structures of geranial (a), neral (b) and limonene (c).

3.2. Weight loss tests

The corrosion rate (W_{corr}) of aluminum in 1M HCl solution at various contents of the natural oil tested was determined after 1 h of immersion period at 25°C. Values of corrosion rates and inhibition efficiencies are given in table 3. In the case of the weight loss method, the inhibition efficiency (E_w %) was determined by the following relation:

$$Ew\ \% = \frac{Wcorr - Wcorr(inh)}{Wcorr} \times 100 \qquad (1)$$

Where W_{corr} and Wcorr (inh) are the corrosion rates of aluminum in the absence and presence of the oil, respectively. The analysis of these results (table 3 and fig. 2) shows clearly that the corrosion rate decreases (W (mg/h.cm^2) while the inhibition efficiency (Ew (%)) increases with increasing inhibitor concentration reaching a maximum value of 98,35% at a concentration of 1200 ppm. This behaviour can be attributed to the increase of the surface covered θ (Ew % /100) and this is due to the adsorption of natural compounds on the surface of the metal as the inhibitor concentration increases. We can conclude that *lippia* oil is a good corrosion inhibitor for aluminum in 1M HCl solution.

3.3. Polarisation measurements

Current-potential characteristics resulting from cathodic polarisation curves of aluminum in molar HCl at various concentrations of the tested of *lippia* oil is evaluated. Fig. 3 shows the typical cathodic Tafel plots of the *lippia* oil at different concentrations.

Table 4 collects the corrosion kinetic parameters such as Ecorr, Icorr and β_c obtained from potentiodynamic polarization curves for aluminum in 1M HCl containing different concentrations of *lippia* oil. In the case of polarization method the relation determines the inhibition efficiency (EI %):

$$EI\ \% = \frac{Icorr - I\ corr\ (inh)}{Icorr} \times 100 \qquad (2)$$

where I_{corr} and Icorr (inh) are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

Table 3 Gravimetric results of aluminum in acid without and with addition of the natural oil at various contents (*t*= 1h. *T*= 25°C)

concentration /ppm	**W mg/cm^2.h**	**Ew /%**
Blank	1.5740	---
800	0.1284	91.84
1000	0.0667	95.76
1200	0.0259	98.35
1400	0.0259	98.35

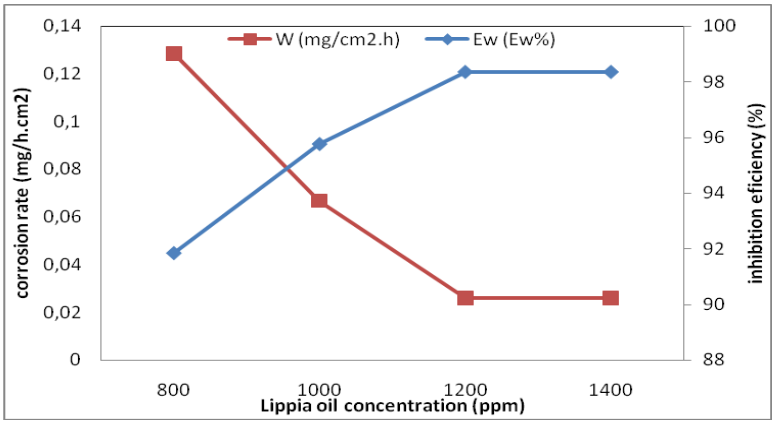


Figure 2 Variation of corrosion rate and inhibition efficiency of aluminum in 1M HCl without and with *lippia citriodora* oil

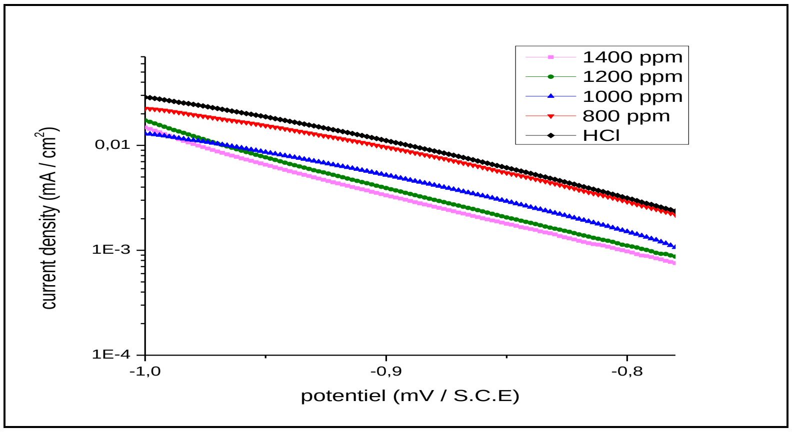


Figure 3 Cathodic plots of aluminum in 1M HCl at various concentrations of *lippia* oil

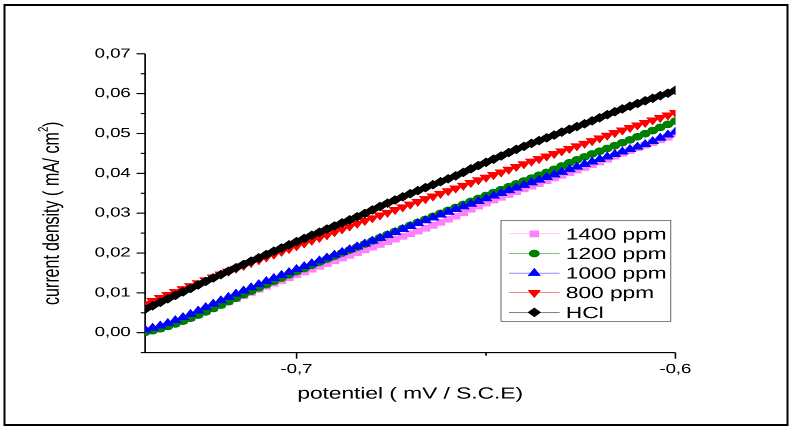


Figure 4 Anodic curves of aluminum in 1M HCl without and with *lippia* oil

Table 4 Electrochemical parameters of aluminum at various concentrations of *lippia* oil studied in 1M HCl at 25°C. Corresponding corrosion inhibition efficiencies

Inhibitor	concentration ppm	E_{corr} mV/SCE	Icorr mA/Cm^2	βc mV	Rp $ohm.cm^2$	E_I/%
Blank	----	-763	2.6693	-249.5	9.20	---
Lippia oil	800	-746.0	0.2056	-154	11.41	92.29
	1000	-772.4	0.0801	-165.8	17.42	96.99
	1200	-756.8	0.0395	-192.7	35.81	98.52
	1400	-758.6	0.0326	-181.1	40.06	98.77

From electrochemical polarisation measurements, it is clear that the addition of inhibitor causes a decrease of the current density. The values I_{corr} of aluminum in the inhibited solution are smaller than those for the inhibitor free solution (table 4). The parallel cathodic tafel plots obtained in fig.3 indicate that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of inhibitor. The addition of the inhibitor does not change the values of corrosion potential (Ecorr) and cathodic tafel slope (βc) when the concentration increases. These results demonstrate that the hydrogen evolution reaction is inhibited and that the inhibition efficiency increases with inhibitor concentration. In the anodic range (fig. 4), the polarisation curves of aluminum show that the addition of the natural oil decreases the current densities in large domain of potential. This result suggests that this compound act as a mixed-type inhibitor.

3.4. Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of aluminum in 1M hydrochloric acidic solution, in the absence and presence of *lippia* oil, is also investigated by the electrochemical impedance spectroscopy (EIS) at 25°C. The charge-transfer resistance (Rt) values are calculated from the diffenrence in impedance at lower and higher frequencies as suggested by Tsuru et al., 1978 [37]. The double layer capacitance (C_{dl}) and the frenquency at which the imaginary component of the impedance is maximal (-Zmax) are found as represented in equation:

$$C_{dl} = \frac{1}{.Rt} \text{ where } \omega = 2\pi\, .f_{max} \qquad (3)$$

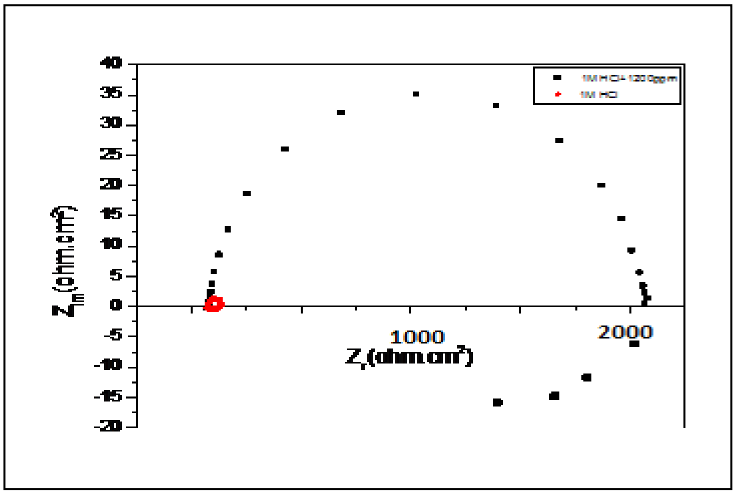


Figure 5 Nyquist plots of aluminum with and without *lippia* oil

Impedance diagrams are obtained for frequency range 100 KHz – 10 mHz for aluminum in 1M HCl in the presence and absence of *lippia* oil. Nyquist plots for aluminum in 1M HCl and in 1200 ppm concentration of lippia oil are presented in Figure 5.

Table 5 presents values of charge transfer resistance, Rt double-layer capacitance, $C_{dl,}$ and f_{max} derived from Nyquist plots and inhibition efficiency, the inhibition efficiency got from the charge-transfer resistance is calculated by the following relation:

$$E_{Rt}\,\% = \frac{R't - Rt}{R't} \times 100$$

Rt and R't are the charge-transfer resistance values without and with inhibitor respectively. Rt is the diameter of the loop

Table 5 Characteristic parameters evaluated from the impedance diagram for aluminum without and with of *lippia* oil

Inhibitor	**Rt ohm.cm^2**	**f_{max} / Hz**	**C_{dl} µF/cm^2**	**E_{Rt} / %**
blank HCL 1M	36.749	53.55	80.88	--------
***Lippia* oil 1200 ppm**	2000.12	2.455	32.41	98.16

From the impedance data (table 5), we conclude that the Rt values increase with inhibitor concentration and consequently the inhibition efficiency increases. As we notice, fig. 5, the impedance diagrams consists two capacitive loops. They are not perfect semicircles and this difference has been attributed to dispersion frequency. The impedance diagram consists of two capacitive loops.

The first capacitive loop is wide in high frequency can be attributed to the charge transfer. The second loop is in an area of low frequencies, it can be attributed to a diffusion phenomenon [38].

In fact, the presence of *lippia* oil is accompanied by the increase of the value of Rt in acidic solution indicating a charge transfer process mainly controlling the corrosion of aluminum. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor. The decrease in C_{dl} is due to the adsorption of the inhibitor on the metal surface leading to the formation of film or complex from acidic solution [39].

3.5. Effect of temperature

Table 6 Effect of temperature on the aluminum corrosion in the presence and absence of 1200 ppm oil for 1 hour

Temperature /°C	**W mg/cm^2.h**	**W' mg/cm^2.h**	**E/%**
10	0.1866	0.0306	83.60
20	0.8803	0.0445	94.94
30	2.2677	0.0194	99.14
40	2.8937	0.0112	99.61

The effect of temperature on the corrosion behaviour of aluminum in 1M HCl containing inhibitor at a concentration 1200 ppm is studied in the temperature range 10- 40°C using weight loss measurements. Table 6 regroups the corresponding obtained results.

It is obvious that the corrosion rate increases both in the uninhibited and inhibited acid solution with the rise of temperature. The presence of inhibitor leads to the decrease of the corrosion rate. E% which decreases with the increase of temperature.

The following relation can determine the apparent activation energy:

$$\text{Wcorr} = k \exp(-E_a / RT) \text{ and } W'\text{corr} = k' \exp(-E'_a / RT) \qquad (5)$$

W'corr and W_{corr} are the corrosion rates of aluminum with and without inhibitor, respectively. E'_a and E_a are the apparent activation energies in the presence and absence of inhibitor, respectively.

Arrhenius plots for the corrosion rates of aluminum are shown in Fig 4. The calculated values of activation energies from the slopes are 83.51 and 27,83 KJ/mol for free acid and with the addition 1800 ppm of lippia oil, respectively.

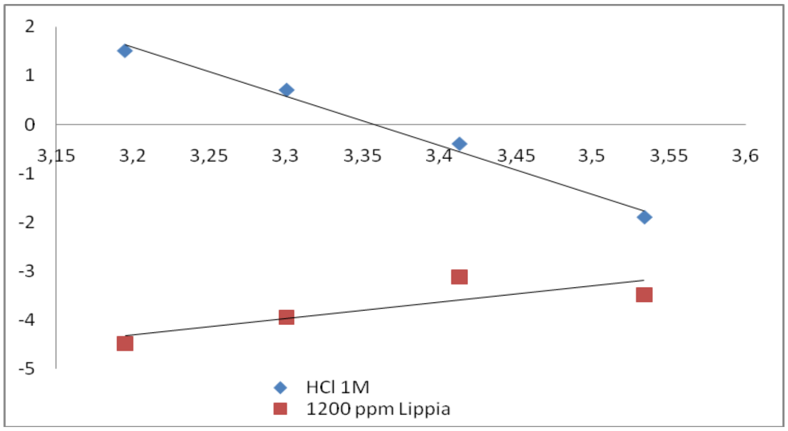


Figure 6 Arrhenius plots of aluminum in uninhibited and inhibited acid

In view of the compiled results we see that the activation in the presence of the inhibitor is less than the energy corresponding to HCl alone. This might indicate that the presence of the inhibitory mechanism of activation is attributed to the chemisorption of the aluminum surface [40].

3.6. Adsorption isotherm

It is found that the activation energy is increases in the presence of inhibitor. Furthermore, the decrease of E% is explained due to the physisorption of inhibitor molecule on the Aluminium surface [39]. The lower value of E_a of the corrosion process in an inhibitors presence when compared to that in its absence is attributed to its chemisorption [41].

The dependence of the fraction of the surface covered Θ obtained by the ratio E%/100 as function of the oil concentration (C) was graphically fitted for Langmuir, Temkin and Frumkin adsorption isotherms. Fig 7 shows the dependence of C/Θ as function of the oil concentration. The curve obtained clearly shows that the data fit well with Langmuir adsorption isotherm and this was found to be the best description of the adsorption behaviour of the studied inhibitor, which obeys:

$$\frac{C}{\Theta} = \frac{1}{Kads} + C \qquad (7)$$

C is the inhibitor concentration; Θ is the fraction of the surface covered, K_{ads} is the adsorption coefficient.

The literature shows that the adsorption of heterocyclic compounds occurs with the aromatic rings mostly perpendicular with respect of the metal surface at low concentration, but at elevated inhibitor concentration the molecules are reoriented to the parallel mod [40]. Besides, the adsorption phenomenon may be made by neral and geranial as the principal constituents of the essential oil of *lippia citriodora*. But as the natural oil contains so many components, the inhibitory action may also be due to synergistic intermolecular of the active molecules of this oil [42].

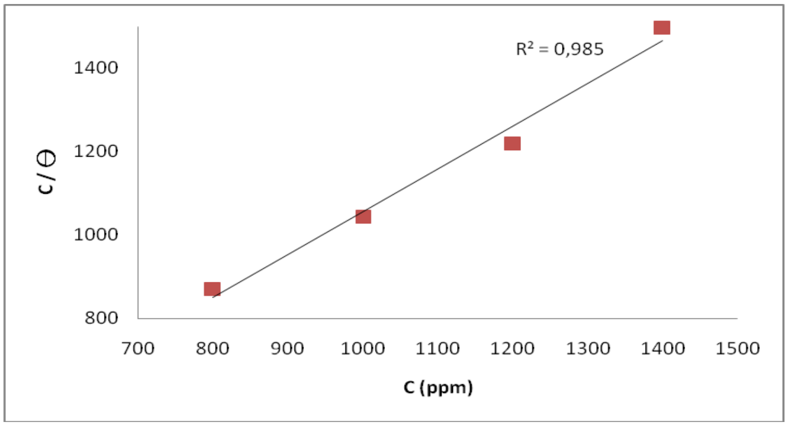


Figure 7 Langmuir adsorption isotherm of lippia oil on the aluminum surface

In aqueous acidic solutions, the natural components exist either as neutral molecules or in the form of cations (protonated species) leading to the establishment of the two modes of adsorption: chemisorptions and physical adsorption. The neutral species may adsorbed on metal surface via the chemisorp-tion mechanism, involving the displacement of water molecules from the metal surface and the sharing electrons between the heteroatoms as oxygen atom and Fe. The components can also adsorb on the surface of the metal on the basis of donor–acceptor interactions between p-electrons of aromatic ring and vacant d-orbitals of Fe. The protonated species facilitated the physical adsorption with the metal surface. The mixed inhibition discussed in polarization essays reinforced this assumption and we may introduce easily the phenomenon of intermolecular synergistic effects of the various constituents of verbena oil [41 and 43].

Conclusion

From the overall experimental results the following conclusions can be deduced:

- Chemical analysis showed limonene, neral and geranial as major components of *lippia citriodora* essential oil;
- *lippia citriodora* oil acts as good inhibitor for the corrosion of aluminum in HCl medium;
- The inhibition efficiency *of lippia citriodora* oil increases with concentration to attain 98,35% at 1200 ppm;
- The efficiency of *lippie citriodora* oil increases with the rise of temperature;
- The *lippia essential* oil acts on aluminum surface as mixed inhibitor with a physisorption mechanism.

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