

Improved Pitting Corrosion Resistance of Stainless Steel 304 by Lupine extract in Hydrochloric Acid

B. A. Abd-El-Nabey¹, S. El-Housseiny^{2,3}, M. A. Abd-El-Fatah^{4,*}

¹ Faculty of Science, Chemistry Department, Alexandria University, Alexandria, Egypt
ORCID Number: 0000-0001-3651-2449

² Faculty of Science, Chemistry Department, Jouf University, Jouf, Saudi Arabia

³ Faculty of Science, Chemistry Department, Kuwait University, Kuwait
ORCID Number: 0000-0001-9444-9121

⁴ Faculty of Education, Alexandria University, Alexandria, Egypt
ORCID Number: 0000-0001-5471-690X

*E-mail: marwaabozyada@gmail.com

Received: 22 February 2022 / Accepted: 2 June 2022 / Published: 10 September 2022

Improving pitting corrosion resistance of stainless steel 304 by Lupine investigated in 0.5 M HCl solution using Weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The polarization results showed that Lupine extract act as anodic -type inhibitor with a high protection efficiency of 92% at extract addition of 15 ppm. EIS measurements showed that the dissolution process of stainless steel occurs under diffusion control. The adsorption behavior of the main Lupine extract constituents on stainless steel surface was well described following Flory-Huggins isotherm and Kinetic-Thermodynamic model. Surface studies using SEM-EDX techniques supported the obtained chemical and electrochemical results.

Keywords: Stainless Steel 304, Inhibitor, Pitting Corrosion, Lupine extract, Hydrochloric acid, SEM, EDX, EIS, Polarization.

1. INTRODUCTION

Stainless steel is considered one of the main construction materials also; it is extensively used in many important industries, particularly in petroleum, energetics, food, medical, chemical and electrochemical sectors. Chromium oxyhydroxide film covers its surface and provides its resistance against corrosion in various aggressive environments. However, it suffers from corrosion in acidic solutions, such as hydrochloric and sulphuric acids, which are widely used for pickling treatments and acid-cleaning operations [1-5]. Different methods used to protect it against deterioration from corrosion, one of them being usage of corrosion inhibitors. Their action depends on the inhibitor ability

to react and adsorb on its surface to form a protective layer against aggressive ions [6]. Unfortunately, most of these compounds pollute the environment and have a very high toxicity if not properly treated, subsequently an intense effort was made to find an alternative [7-11].

The use of environmentally friendly materials, as green corrosion inhibitors was the best solution. So, it was gaining large preference and interest, due to its relatively abundant in nature, the safe effect, practical use and low cost. Extracts of plant materials are on the top of the green inhibitor's list. They utilize secondary metabolites of plant to reduce the rate of corrosion [12-14]. These metabolites compounds include alkaloids, flavonoids, tannins and nitrogen bases have heteroatoms (O, S, and N), double bonds, and electronegative groups function as ligands and centers of adsorption to bind metals. Several plant extracts have been shown to be effective in inhibiting the corrosion of various metals and alloys in acidic media, such as Aloe plant [2], Henna and Rosemary [14], *Cistus ladanifer* [13], Lupine, Hlffabar and Damssisa [15], *Salvia officinalis* leaves [16] and *Uncaria gambir* [17]. Novel approaches and current trends in the field of inhibition science and technology for corrosion protection of metals and alloys have been discussed in two recent articles [18,19].

In previous works [15, 20-25] the inhibition of corrosion of carbon steel, aluminum, zinc, copper and nickel metals in various media have been investigated using different plant extracts.

However, stainless steel 304 suffers from corrosion in acidic solutions, such as hydrochloric, for this reason, the aim of the current investigation is studying the effect of Lupine as natural extract on the corrosion resistance of stainless steel 304 in 0.5 M HCl solution, using the electrochemical techniques; potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and gravimetric technique (weight loss) as well as surface techniques, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDX). Theoretical fitting of different isotherms, Langumir, Florry-Huggins and the Kinetic-Thermodynamic model were tested to clarify the nature and mechanism of adsorption.

2. EXPERIMENTAL

2.1. Weight loss measurements

Rectangular specimens of stainless steel 304 with dimensions (2.5 cm x 1.0 cm x 1 mm) were used during the weight loss measurements. Its chemical composition was (wt. %): Cr 18.2; Ni 9.85; Mn 0.81; Si 0.59; Cu 0.075; C 0.067; P 0.031; and Fe in balance. The samples were prepared by abrading with a series of emery papers 320, 800, 1000 grades and washed with ethanol, rinsed in water and dried between filter paper. After weighting accurately, the specimens were immersed in 100 mL of 0.5 M HCl at 30°C without and with different concentrations of Lupine extract. The weight loss studies were carried out for 72 hours at 30°C. After 12 hours of immersion in the test solution, the sample is taken out of the solution and the difference in weight is taken and immersed again in the test solution and so on every 12 hours until we reach the last reading at 72 hours.

2.2. Electrochemical tests

Polarization and Impedance measurements were carried out with 604 Gill ACM instrument. Electrochemical measurements performed in a conventional three electrode cell with stainless steel as working electrode that had the chemical composition previously mentioned. Graphite is used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The stainless steel 304 used as working electrode is 7 mm diameter embedded in Teflon holder. Before polarization and EIS measurements, the working electrode was immersed into the test solution (0.5 M HCl with and without different concentrations of Lupine extract) and left for 15 min at the open circuit potential (OCP). Scan rate of potential was 30 mV min^{-1} and potential was scanned in the range of - 300 to +300 mV relative to the corrosion potential. Before each experiment, the working electrode was polished with a series of emery papers of different grit sizes (320, 800, and 1000). After polishing, the stainless steel electrode was washed with double distilled water and dried at room temperature. The frequency range for EIS measurements was $0.01 \leq f \leq 3 \times 10^4 \text{ Hz}$ with applied potential signal amplitude of 10 mV around the rest potential.

To test the reliability and reproducibility of the measurements, duplicate experiments were performed in each case of the same conditions. The results were consist within 2%.

2.3. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometer (EDS)

SEM was employed to characterize the surface morphology with JOEL instrument. Coupons with area 1 cm^2 stainless steel and with the same chemical composition of stainless steel samples used in the electrochemical measurements were used in the experiments. The elemental composition of the film formed on surface was analyzed by energy dispersive X-ray spectrometer (EDS, JEM-2100, Japan).

2.4. Plant

Lupine is an annual, erect, branched, bushy, short-hairy herb with a strong taproot. Leaves are alternate and compound with 5-9 leaflets, nearly smooth above and hairy beneath. Individual plants produce several orders of inflorescences and branches, resulting in clusters of long, oblong pods, each cluster having 3-7 pods, and each pod containing 3-7 seeds. Seed shape is slightly flattened, oval in shape, while seed color is light yellow, the hilum shape is groove, hilum elevation is sunken, and hilum position is basal. Seed texture is smooth, while seed outline is curved length and width almost the same in the two varieties (Giza1 and Giza 2) [26].

Lupine plant can grow on marginal agricultural lands in diverse environmental conditions. It has high nutritional, pharmaceutical and medicinal values. M.E. El-Awadi, studied the aqueous extract of whole Lupine seed in Egypt using Gas Chromatography-Mass Spectrometry (GC-MS). The results showed the occurrence of 47 compounds. It contains up to 50% protein, 20% lipids, and 5% quinolizidine alkaloids, lupanine (the most abundant), multiflorine and sparteine [27,28].

FTIR spectra of pure Lupine extract carried out by IR Affinity (Perkin-Elmer) spectrophotometer in the range 400–4000 cm^{-1} showed different functional groups such as the -OH stretching frequency at 3419 cm^{-1} , the -CH stretching frequency at 2933 cm^{-1} , the C=O stretching frequency appears at 1654 cm^{-1} , the -C=C stretching frequency appears at (1405-1547 cm^{-1}) (multiple bands), the -CN stretching frequency appears at 1246, 2923 cm^{-1} . This result confirmed the presence of chemically active ingredients which chemical structure represented in Figure 1. [29-31]

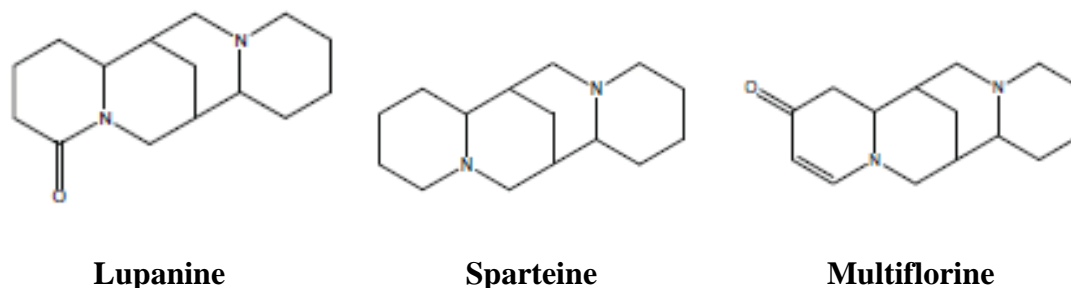


Figure 1. Chemical structures of the constituents of Lupine extract

2.5. Preparation of Lupine extract

Stock solution of Lupine was extracted by refluxing 10 g of the dry material in 250 mL distilled water for one hour at 60 °C. The refluxed solution was cooled and filtrated to remove any contamination. The concentration of the stock solution was calculated in g.L^{-1} by heating till dryness 5 mL of the stock solution and reweight after drying. The concentration of the stock solution was expressed in terms of ppm. Prior each experiment, 4 M HCl is added to an appropriate volume of the stock solution of the Lupine extract and double distilled water to obtain solution of 0.5 M HCl and the required concentration of the Lupine extract. The stock solution was prepared from analytical grade reagents and distilled water: 37% HCl, was purchased from Aldrich chemicals.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Figure 2 shows the variation of weight loss of stainless steel 304 in 0.5M HCl, in absence and presence of different concentrations of Lupine extract with exposure time up to 72 hours at room temperature. As seen, the weight loss increased with exposure time. The rate of corrosion, the slopes of the obtained lines, decreased sharply by the addition of the Lupine extract. The percentage inhibition (% P) was calculated using the following relationship:

$$\%P = [(R_0 - R) / R_0] \times 100$$

Where, R_0 and R are the values of corrosion rate ($\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$) in absence and presence of Lupine extract.

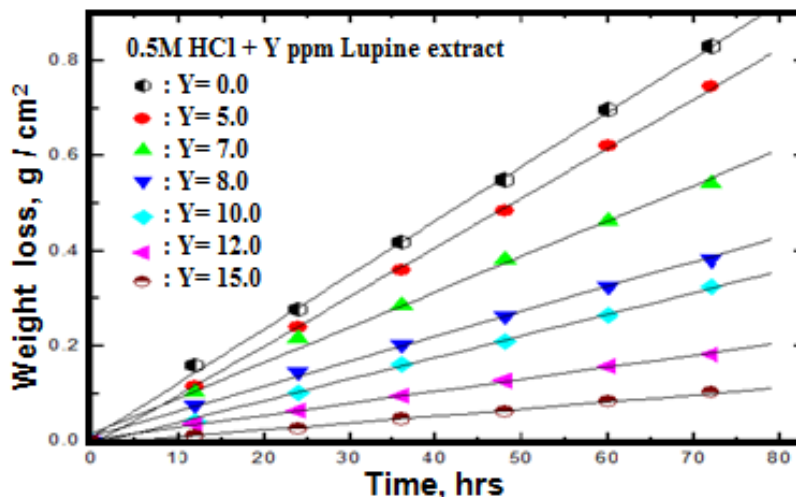


Figure 2. Variation of weight loss of stainless steel 304 against immersion time (72 hours) in absence and presence of different concentrations of Lupine extract at 30°C.

The values of corrosion rate (R) and inhibition efficiency ($\%P$) obtained from the weight loss for different Lupine extract concentrations in 0.5 M HCl solutions at 30°C are shown in table 1.

Table 1. Corrosion parameters obtained from weight loss of stainless steel 304 in 0.5 M HCl solutions containing different concentrations of Lupine extract at 30°C after immersion time 72 hours.

Conc., (ppm)	R , ($\text{g cm}^{-2}\cdot\text{hr}^{-1}$)	$\% P$
0	0.01143	--
5	0.00815	28.7
7	0.00446	61.0
8	0.00346	69.7
10	0.00255	77.7
12	0.00194	83.0
15	0.00136	88.1

The results show that R decreases clearly with an increase in Lupine extract concentration and $\%P$ increases reaching a maximum value 88.1 % at 15 ppm. This suggested that with increasing the adsorption of organic molecules from Lupine extract at the stainless steel surface increase, and consequently blocking the active sites and thereby protecting the metal from corrosion [32].

3.2. Potentiodynamic polarization measurements

Figure 3 shows the potentiodynamic polarization curves of stainless steel 304 in 0.5 M HCl solutions in absence and presence various concentrations of Lupine extract at 30°C. The polarization curves show activation behavior followed by formation of protective passive film on the stainless steel surface at the different passivation potentials (E_{pp}). During upward scanning, breakdown occurs, indicating starting of pitting corrosion as a result of the aggressive attack of Cl^- anions at the pitting potential (E_p) in the trans-passive region of the polarization curve, which evident by a sudden increase in the current density from the passive current level, which are evidenced by a shoulder in the current–potential plots at potentials less negative to their corresponding corrosion potential values [33].

It is known that the more noble the E_p obtained, the less susceptibility of the material to initiate the localized corrosion [34]. This is what extract did exactly as E_p values table 3 shifted to less negative with increasing extract concentration.

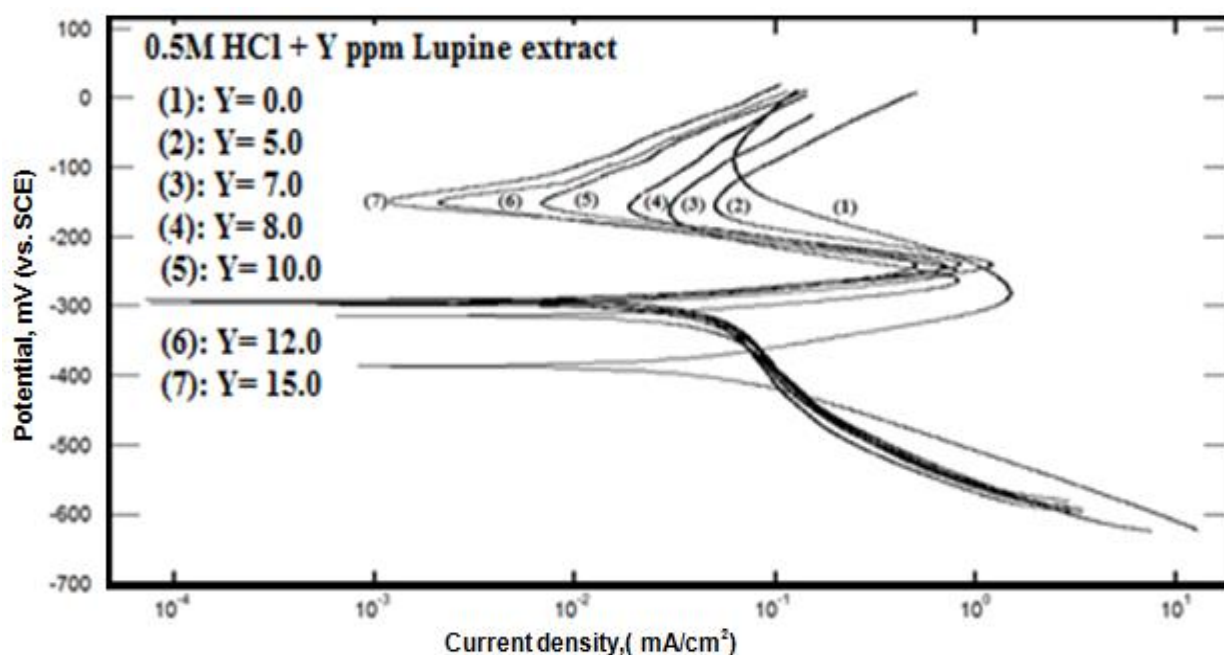


Figure 3. Polarization curves for stainless steel 304 in 0.5 M HCl solution in absence and presence of different concentrations of Lupine extract at 30°C.

Values of associated electrochemical parameters such as, corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (β_c), %P, E_p and i_{pass} are collected in table 2.

Table 2. Corrosion parameters obtained from potentiodynamic polarization curves of stainless steel 304 in 0.5 M HCl containing different concentrations of Lupine extract at 30°C.

Extract conc. (ppm)	$-E_{corr.}$ (mV vs. SCE)	$-E_p$ (mV vs. SCE)	R_p (Ohm.cm ²)	$i_{pass.}$ (μA.cm ⁻²)	$-\beta_c$ (mV.decade ⁻¹)	$i_{corr.}$ (μA.cm ⁻²)	%P
0.0	395	166	172	1460	141	1703.24	0.0
5.0	316	161	196	920	140	1110.62	34.8
7.0	302	159	214	613	146	591.13	65.3
8.0	295	157	234	327	145	434.12	74.5
10.0	294	153	281	201	144	291.11	82.9
12.0	291	150	267	114	138	225.27	86.8
15.0	287	148	301	57	141	133.85	92.1

In active region, the data reveals that the addition of Lupine extract decreases markedly the corrosion current and inhibits the general corrosion of stainless steel in 0.5 M HCl. The data show also that the increase of the corrosion of Lupine extract in the solution leads to markedly decrease of the passivating current (i_{pass}), markedly increase of the polarization resistance (R_p) and shift of the pitting potential (E_p) to more noble potentials. All these results indicate that Lupine extract act a good ecofriendly pitting corrosion inhibitor for corrosion of stainless steel in 0.5 M HCl solution.

3.3. Electrochemical impedance spectroscopy (EIS) results

Figure 4 manifested clearly distorted semicircles at high frequency followed by diffusion tail in low frequency which indicates that the corrosion process is controlled by diffusion.

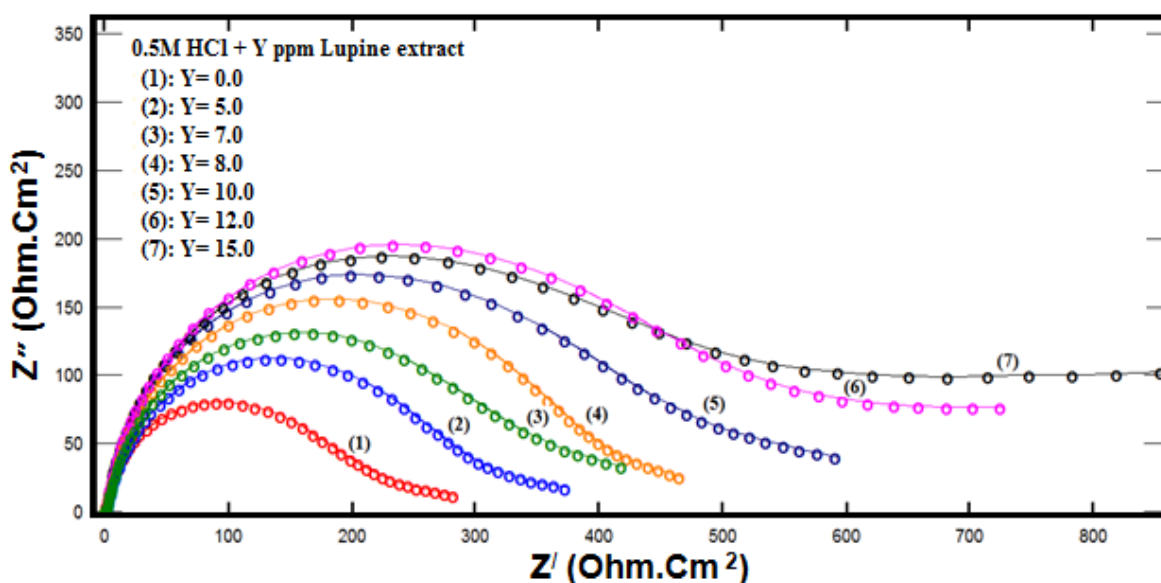


Figure 4. Nyquist plots for stainless steel 304 in 0.5 M HCl solution in absence and presence of different concentrations of Lupine extract at 30°C.

The increase in the size of the semicircle in presence of the extract gives indication of gradually barrier formation on stainless steel surface.

The impedance spectra were analyzed by fitting the experimental data to the equivalent circuit model shown in our recently research (Figure 6) [23].

The values of the electrochemical parameters obtained from EIS for stainless steel in 0.5 M HCl solution free from or containing different Lupine extract concentrations and the inhibition efficiency (% P) are given in table 3. The % P inhibitions were calculated from impedance measurements using the relation (9) in our recently research [23].

Table 3. Equivalent circuit parameters for stainless steel 304 in 0.5 M HCl solution in absence and presence of different concentrations of Lupine extract at 30°C.

Conc., (ppm)	R_s	Q_f ($\mu\text{F}\cdot\text{cm}^{-1}$)	n_1	R_p ($\text{Ohm}\cdot\text{cm}^2$)	R_{ct} ($\text{Ohm}\cdot\text{cm}^2$)	Q_{dl} ($\mu\text{F}\cdot\text{cm}^{-1}$)	n_2	R_2 ($\text{Ohm}\cdot\text{cm}^2$)	Q_3 ($\mu\text{F}\cdot\text{cm}^{-1}$)	n_3	% P
0.0	0.2	57	0.9	166	123	1387	0.6	212	4688	0.6	0.0
5.0	0.2	53	0.9	187	192	988	0.6	378	4469	0.6	35.9
7.0	0.2	49	0.9	192	382	842	0.6	457	4328	0.6	67.8
8.0	0.2	46	0.9	208	528	765	0.6	642	4168	0.6	76.7
10.0	0.2	41	0.9	244	825	637	0.6	912	4016	0.6	85.1
12.0	0.1	36	0.9	257	1156	512	0.6	1158	3627	0.6	89.4
15.0	0.2	31	0.9	287	1883	403	0.6	1295	3312	0.6	93.5

The data in the table show that:

1) On increasing Lupine extract concentration, the charge transfer resistance (R_{ct}) increased, suggesting decrease of the corrosion rate since the R_{ct} value, is a measure of electron transfer across the surface, and inversely proportional to the corrosion rate.

2) On increasing the concentration of Lupine extract the value of Q_{dl} decreases which can be attributed to the adsorption of active constituents of Lupine extract at the stainless steel surface to form an adherent film which increases the double layer thickness [35-37].

3.4. Application of adsorption isotherms

The experimental data have been tested with several adsorption isotherms including Langmuir isotherm, Flory-Huggins isotherm and Kinetic-thermodynamic model [20,38] to gain more information about the mode of adsorption of the extract on stainless steel surface. The values of surface coverage (Θ) were evaluated from weight loss method have been used.

The Langmuir isotherm, Flory-Huggins isotherm and the Kinetic-Thermodynamic model are given by the equations in our recently research [23]

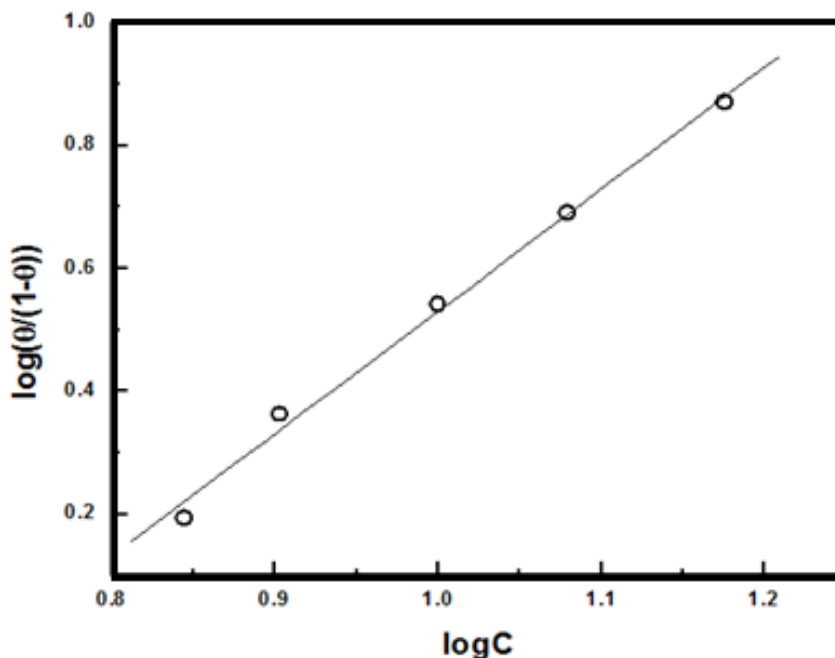


Figure 5. Linear fitting of the data of adsorption of Lupine extract to Kinetic-Thermodynamic model for stainless steel 304 in 0.5 M HCl solution at 30 °C.

Figure 5 shows the application of the Kinetic-Thermodynamic model to the data of Lupine extract obtained from weight loss method.

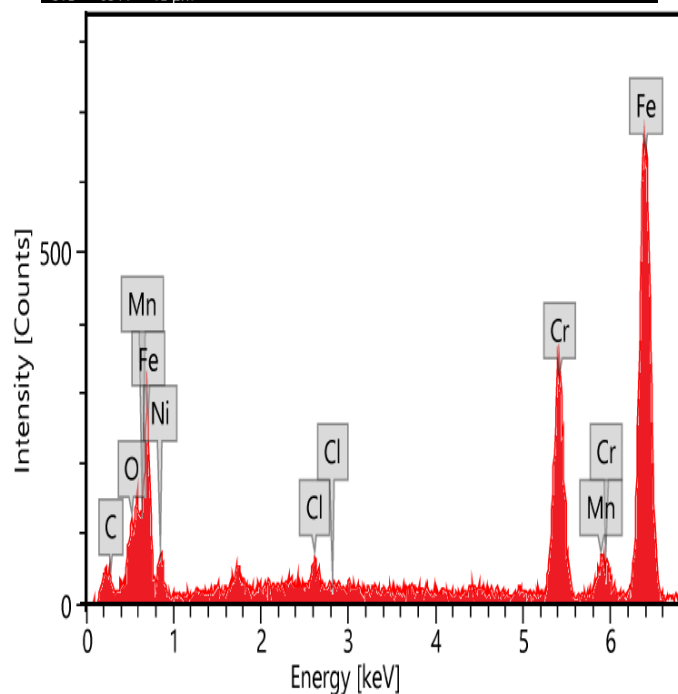
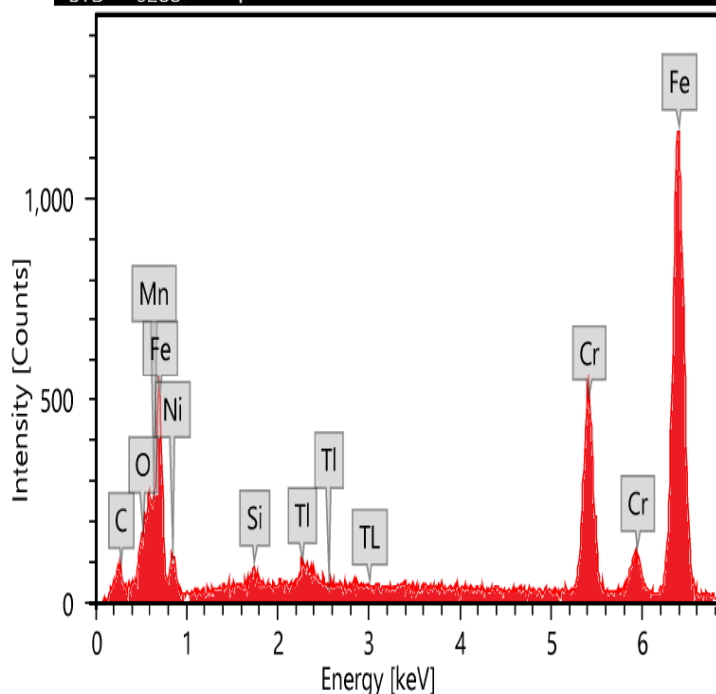
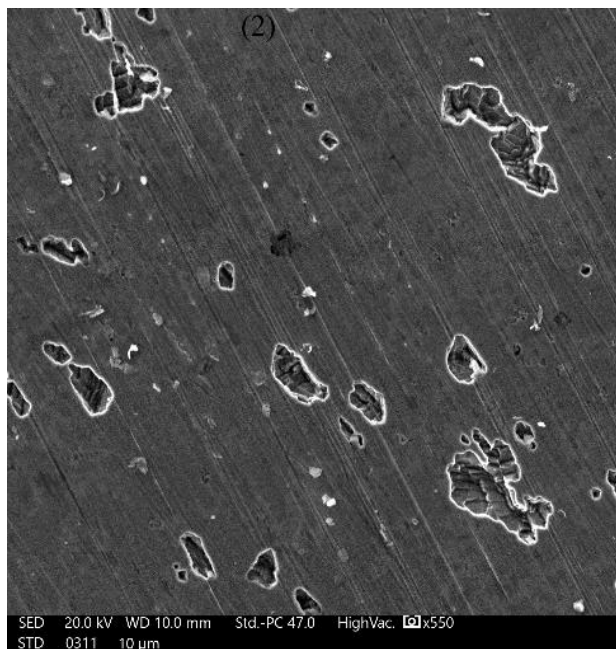
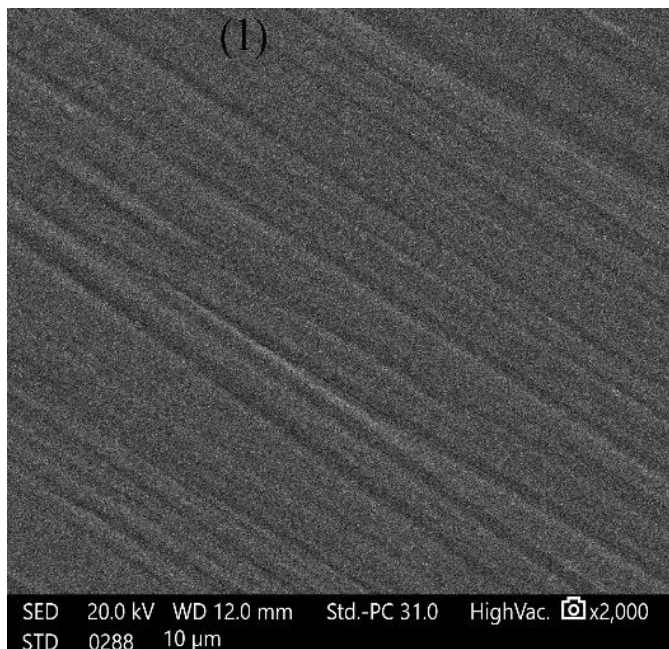
From our calculation's, Langmuir isotherm is not applicable to fit the data indicating that the adsorption process of Lupine extract on stainless steel surface in 0.5 M HCl is non-ideal. On the other hand, Flory-Huggins isotherm and Kinetic-thermodynamic model are found to be applicable. The value of Flory-Huggins size parameter $x = 0.34$ indicates that two adsorption of organic molecules from Lupine extract displace one adsorbed water molecule from the stainless steel surface. According to the Kinetic-thermodynamic model the term $1/y$ represents the number of active sites occupied by one inhibitor molecule. And equals 0.5 indicating that $y=2$ and two extract molecules occupy one active site of the stainless steel surface, i.e., this is a multilayer adsorption.

3.5. SEM Study and EDX Analysis

Figure 6 shows the micrographs of each of SEM and EDX of stainless steel 304 samples before and after immersion for 48 h and 72h in 0.5 M HCl solution in absence and presence of 15 ppm Lupine extract. Clear polished marks of the surface of stainless steel before immersion has been appeared in the SEM micrograph 1 which shows that the whole surface is smooth and homogeneous. Micrographs (2,3) show the surface of stainless steel after immersion for 48 h and 72 h in 0.5 M HCl solution ,while the surface of stainless steel after immersion for 48 h and 72 h in 0.5 M HCl solution containing 15 ppm of Lupine extract obtained in the micrographs (4,5).

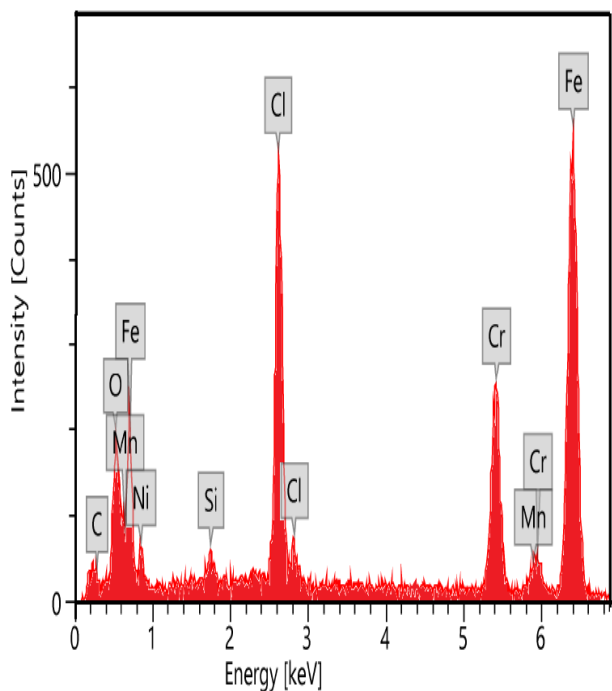
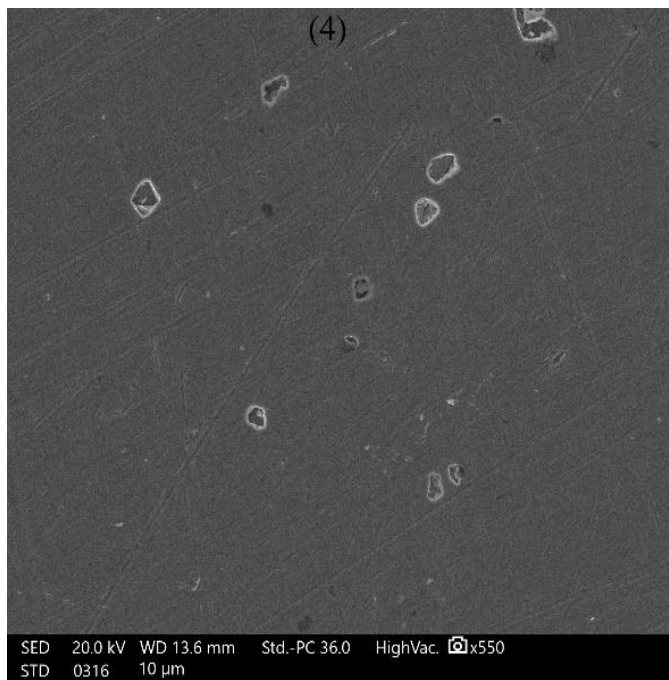
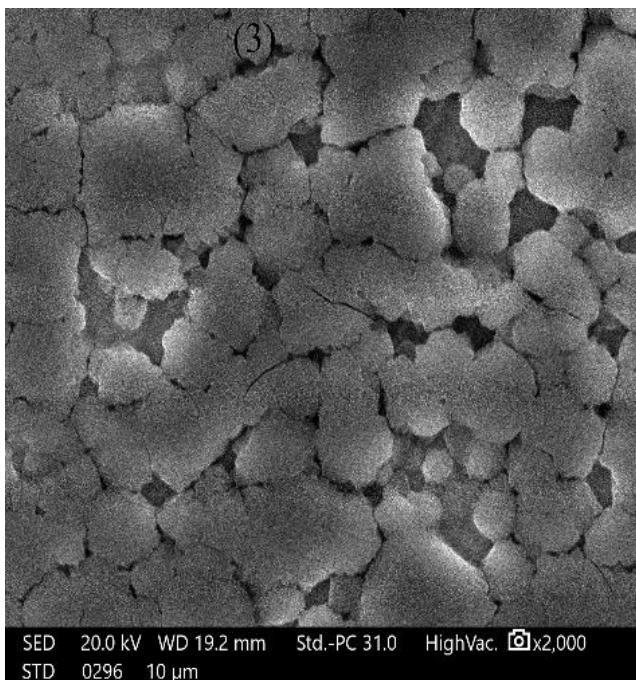
Micrographs (2,3) of stainless steel surface immersed for 48 h in 0.5 M HCl solution were observed as rough, porous, and damaged. It shows the formation of several pits randomly distributed

on the surface which increasing after immersion for 72 h indicating a vigorous corrosive attack on the surface. However, micrographs (4,5) show that Lupine extract exhibited less and smaller pits comparing to its analogue of free acid. This indicates that Lupine extract hindered the dissolution of iron and improve the resistance of stainless steel against the pitting corrosion in 0.5 M HCl solution [16,39].

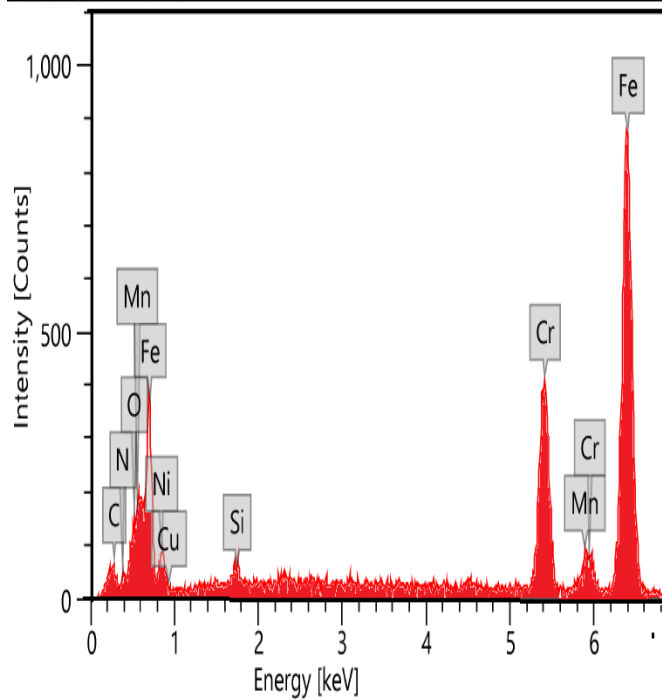


Stainless steel before immersion in 0.5 M HCl solution at 30 °C.

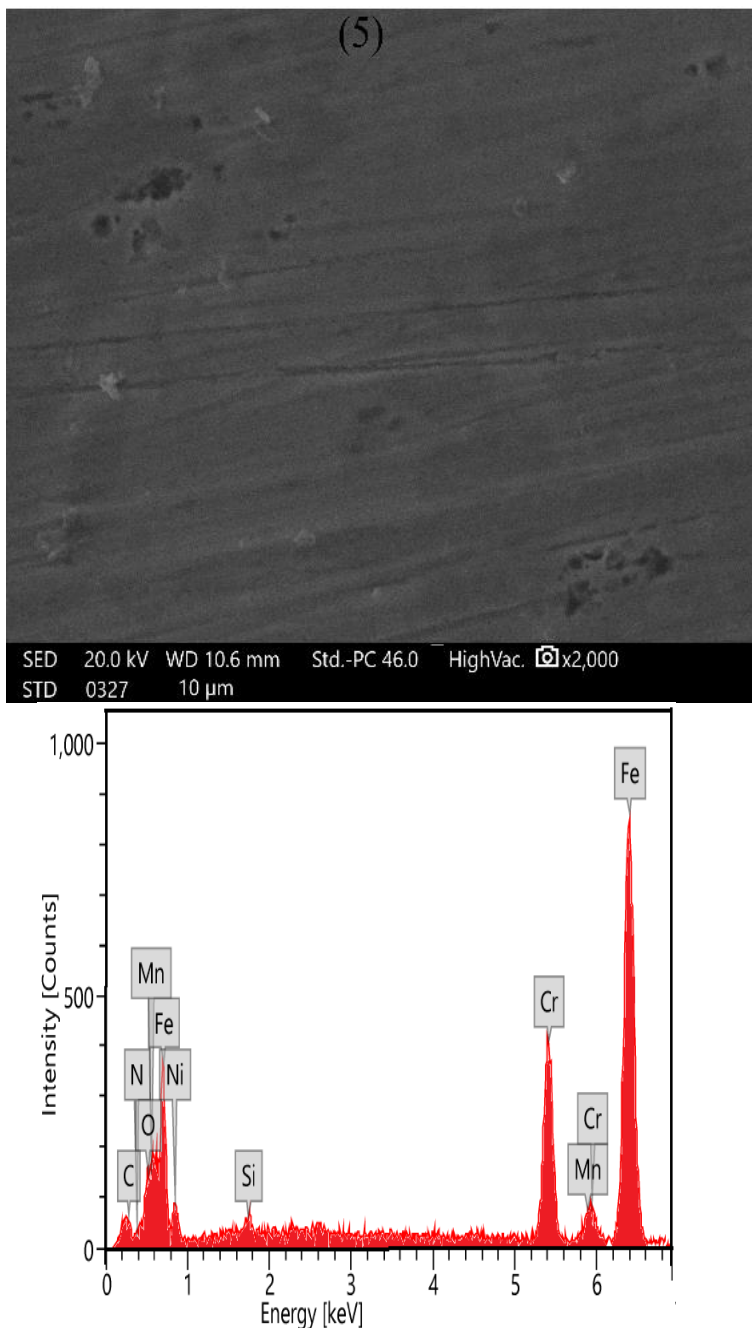
Stainless steel after immersion in 0.5 M HCl solution for 48h at 30 °C.



Stainless steel after immersion in 0.5 M HCl solution for 72h at 30 °C.



Stainless steel after immersion in 0.5 M HCl solution containing 15 ppm Lupine extract for 48h at 30 °C.



Stainless steel after immersion in 0.5 M HCl solution containing 15 ppm Lupine extract for 72h at 30 °C.

Figure 6. SEM images and EDX micrographs of stainless steel 304 before and after immersion for 48h and 72h in 0.5 M HCl solution in absence and presence of 15 ppm Lupine extract at 30 °C..

The EDX results show that the surface of stainless steel after immersion in 0.5 M HCl for 48 or 72 hours is free from nitrogen, however in presence of Lupine extract nitrogen is present on the surface and its Wt % decreases from 5.2 to 3.8 Wt % at 48 and 72 hours respectively.

The results can be discussed on the basis that:

- (i) The presence of nitrogen on the surface of the stainless steel indicating the adsorption of constituents of the extract on stainless steel surface.

(ii) The decrease of Wt % of N on the steel surface with increase of the time of immersion indicating the desorption of the constituents of the extract and the adsorption process is mainly physical in nature.

4. CONCLUSION

The results of this study show that:

The polarization results showed that Lupine extract act as anodic type inhibitor with high protection efficiency of 92% at extract addition of 15 ppm for corrosion of stainless steel 304 in 0.5 M HCl.

The weight loss of stainless steel increases with immersion time and was decreased in the presence of the extract compared to the free acid solution as a result of increasing the number of adsorbed extract molecules on stainless steel surface which blocking the active sites of acid attack and consequently protect the steel against corrosion.

Langmuir isotherm is not applicable to fit the experimental data indicating that the adsorption process of Lupine extract on stainless steel surface in 0.5 M HCl solution is non-ideal. On the other hand, Flory-Huggins isotherm and Kinetic-Thermodynamic model are found to be applicable and the data indicated that the adsorption of organic molecules from Lupine extract at stainless steel surface is a multilayer process.

The surface study, SEM and EDX results supported these obtained from the chemical and electrochemical techniques.

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to Prof. Dr. Beshir Ahmed Abd-EL- Nabey, Professor of Physical Chemistry, Chemistry Department, Faculty of Science, Alexandria University, for his guidance and constructive criticism during the various stages of this work and finalizing the paper in its present form.

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