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Grape Leaves and Ziziphus Spina-Christi, Extracts as a Green Inhibitors Corrosion for The Carbon Steel and Oil Pipelines in 1M H_2SO_4

مستخلصات أوراق العنب وأوراق السدر، كمثبطات خضراء للتآكل لأنابيب الصلب الكربوني و أنابيب النفط في 1مولار من حمض الكبريتيك

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Abstract

Metals suffer from corrosion by the surrounding fluids, which causes great economic losses and bad environmental effects, especially in oil pipelines or reservoirs. The extract of grape leaves (GL) and Sidr leaves, (Ziziphus spina-christi), (Zizi) were used as green corrosion inhibitors (CI) for carbon steel (CS), and Oil Pipelines in 1M H_2SO_4, these extracts showed varying capabilities in resisting corrosion. Corrosion rate was decreased with increase in inhibitor dose which could be due to enhanced surface coverage, as well as the effect of increasing the temperature on the percentage of the efficiency of inhibition, are decrease, and drawing the curves for that, as well as studying some physical properties related to the process of adsorption of extracts on the surface of (CS), such as the activation energy and entropy of the process of adsorption of the extracts on the surface of (CS), and calculating those values, and the extracts showed an efficiency that exceeded 90% at concentrations up to 400 ppm and a temperature of 313-343K. The activation energy associated with this process indicated surface interaction as the main mechanism and positive values of enthalpy change confirmed the endothermic nature. The potentiometric method showed the extent of voltage change with time for each concentration of extract of grape leaves for immersion time (2–24 h), and that the voltage increases with increasing concentration, which indicates a high ability of the inhibitor to adsorb to the metal..

Keywords: Grape Leaves- Green Corrosion Inhibitors- carbon steel - oil pipelines - Potentiometric method.

الملخص :

المعادن تعاني من التآكل بفعل السوائل المحيطة بها، مما يسبب خسائر اقتصادية كبيرة وتأثيرات بيئية سلبية، خاصة في خطوط أنابيب النفط أو الخزانات. تم استخدام مستخلص أوراق العنب (GL) وأوراق السدر-Ziziphus spina (christiكمثبطات تآكل خضراء للفولاذ الكربوني (CS)وخطوط الأنابيب النفطية في H2SO4 بتركيز 1 مولار، وأظهرت هذه المستخلصات قدرات متفاوتة في مقاومة التآكل. تم تقليل معدل التآكل مع زيادة جرعة المثبط والذي يمكن أن يكون نتيجة لتحسين تغطية السطح، وكذلك تأثير زيادة درجة الحرارة على نسبة كفاءة التثبيط، وهبوط منحنيات ذلك، ودراسة بعض الخصائص الفيزيائية المتعلقة بعملية امتزاز المستخلصات على سCS ، مثل طاقة التفعيل والإنتروبيا لعملية امتزاز المستخلصات على سطح CS، وحساب تلك القيم، وأظهرت المستخلصات كفاءة تفوقت عن 90% عند تراكيز تصل إلى 400 جزء في المليون ودرجة حرارة تتراوح بين 313-343 K. أشارت طاقة التفعيل المرتبطة بهذه العملية إلى التفاعل السطحي كآلية رئيسية وأكدت قيم موجبة لتغير الانثالبي ناتج التفاعل الداخلي الحراري. أظهرت الطريقة الجهدية مدى التغير في الجهد مع الوقت لكل تركيز من مستخلص أوراق العنب لفترة الغمر (2-24 ساعة)، وأن الجهد يزيد مع زيادة التركيز، مما يشير إلى قدرة عالية للمثبط على الامتزاز على المعدن.

الكلمات المفتاحية: ورق العنب – مثبطات التآكل الأخضر – الفولاذ الكربوني – أنابيب النفط – طريقة قياس الجهد.

1- Introduction

Several extracts from natural products are used as corrosion inhibitors (CI), green corrosion inhibitor extracted from the following: black pepper extract (BP), piperine used as (CI) in C38 steel in 1M HCl [1], Cumin extract (Cyminum) was used as (CI) for pure Al in 1N HCl [2], and also for mild steel (M.S) in seawater [3], Fenugreek seed extract was used as (CI) of steel in NaCl solution [4], and in carbon steel (CS) in HCl [5], Grape leaves rich in vitamins and minerals were used such as: vitamin A, 15.29%, beta-carotene, 32.39%, B vitamins About 5%, manganese, 14.28%, copper, 4.15%, and other vitamins [6], then beta-carotene was used as (CI) for (M.S) in acidic media [7], as well as vitamins such as nicotinic acid (B_3) and pyridoxine (B_6), and ascorbic acid (C) a) were used as (CI) for Fe in wet cement [8].

Licorice extract was used as (CI) for copper in 0.1M HCl [9], lavender oil extract was used as a (CI) for (M.S) in 1M HCl [10], Fig leaf extract was used as (CI) for (M.S) in a 2M acid solution [11], Black Cumin Oil was used as (CI) for Ni corrosion in 0.1M HCl using galvanostatic and strong dynamic techniques [12], Tangerine peel extract was used as (CI) for (M.S) in 1M HCl as a green inhibitor [13], Cinnamon Oil was used as (CI) for 304L stainless steel (SS) in 0.1 and 1.0 M HCl [14], and it was used as (CI) for steel which used in sulfide-contaminated brine [15], Thyme leaf extract was used as (CI) for (M.S) in 2M HCl [16], Artemisia annua extracts and Artemisinin (ATS) were used as (CI) for (M.S) in H_2SO_4 [17], Clove Oil extract was used as (CI) for Fe corrosion in HCl [18], Clove, Atlas cedar and Basil oil extracts were used as (CI) on (M.S) at 0.5 M H_2SO_4 [19], Moringa Oleifera leaf extract was used as (CI) for (SS) in 2M HCl [20], as well as Moringa was used as a (CI) for (CS) XC70 in 1M HCl [21], Turmeric and Ginger roots were used as (CI) for (M.S) corrosion in 1M HCl [22], and turmeric was used as a (CI) Corrosive to (MS) in 3.5% NaCl salt corrosion medium and seawater [23], Strictosamide was used as (CI)for steel in HCl [24], Aloe saponaria tannin (AST) extract was used as (CI) for bronze B66 in 3% NaCl [25], Aerial Parts extracted from Swertia chirata plant were used as (CI) of (CS) in 0.5M H_2SO_4 [26], Rose Petal (RP) and Lotus Petal (LP) extracts were used as (CI) for (MS) in 1M HCl [27], Arbutus unedo L. plant Leaves extract were used as (CI) of (M.S) in HCl [28], Walnut Green Husk Extract (WGHE) and potassium iodide (KI) were used as (CI) of cold rolled steel (CRS) in Cl_3CCOOH [29], Ziziphora leaves extract was used as (CI) for (MS) in HCl corrosion [30], Luffa cylindrica Leaf Extract (LCLE) was using as (CI) for (MS) in a 0.5 M HCl [31], Mustard seed extract using as (CI) for (MS) in HCl [32], Clove seed aqueous extract was used for (CI) of (MS) in 1M HCl [33], Garcinia fruit rind extract (GIW) was used as a green (CI) for (M.S) in HCl medium [34], Bistorta Officinalis extract was used as an green (CI) on the (CS) in cooling water systems [35], Asafoetida extract, used as (CI) of (M.S) in1M HCl [36], Garlic extract,used as corrosion inhibition of mild steel in well water, 3.5% NaCl, 1M HCl and 1M H_2SO_4 [37], Citrullus lanatus fruit (CLF) extract, used for (CI) of (M.S) in 1 M HCl [38], Nettle leaves extract, was used as (CI) of (M.S) in 3.5% NaCl [39], Brassica campestris,was used as (CI) for Cor-Ten steel in NaCl and acidic solutions [40], Coriandrum sativum L., was used as (CI) of Al 1.0 M H_3PO_4 [41], Tagetes erecta (Marigold flower) used as a (CI) for (M.S) in 0.5M H_2SO_4 [42], Ajwain seed extract, used as (CI) for Al in 0.5N HCl [43], Nigella Sativa L. was used as (CI) for Fe in acidic medium [44], Allium Jesdianum extract (AJE) used as (CI) for (M.S) in 1 M HCl [45], Salvia officinalis (S. officinalis) leaves, extract used as (CI) for 304 (SS) in 1M HCl [46], Murraya koenigii leaves, used as (CI) for mild steel in HCl and H_2SO_4 [47], Cnicus Benedictus, used as (CI) (M.S) corrosion in 0.5M HCl [48], Aegle Marmelos extracte was used as a green (CI) 1M H_2SO_4 [49], Nandina domestica Thunb extract (NDTE) was used as (CI) for (CS) in HCl [50], Turnip Peel Extract (TPE) as green bio-inhibitor for Cu corrosion in 3.5 wt% NaCl [51], Arabic gum (GA) was used as (CI) for (M.S) in 1 M HCl [52], Cannabis sativa L. seed oil (CSL) was used as (CI) for (CS) against corrosion in 1M HCl [53], Berry and Mango leaves extractes were used as (CI) for Fe, Cu and (CS) in 1M HCl and 1M of HNO_3 solutions[54], ($ZnSO_4$) and the extract Ziziphus spina-christi leaf (ZiZi) was used as (CI) for steel samples were evaluated in 3.5 wt % NaCl [55], (ZiZi), was used as (CI) for (CS) in acidic medium [56], (ZiZi), was applied to protect the surface of Al in acidic medium [57].

In this work Grape leaves, and Ziziphus spina-christi, extracts were studied as environmentally friendly (CI) for (CS) corrosion in 1M H_2SO_4.

2- EXPERIMENTAL

2.1. Materials and Chemicals

The (CS) sample with the following chemical composition, (wt%): C (0.200g), Si (0.003g), Mn (0.35g), P (0.02g) and Fe (Rest). The piece area was 1.23×10^{-3} m^2. The sample was embedded in a glass tube of just larger diameter than the sample. Epoxy resin (supplied from Ciba Co.) was used to stick the sample to the glass tube. Surface of (CS) electrode was mechanically rub off using sand papers, in different grades, for example 1200 grade, before used. The tests were used 1M H_2SO_4 (supplied from Sigma-Aldrich) with the addition of various concentrations of (GL), Zizi, extracts (100-400) ppm. All the test solutions were prepared from analytical chemistry grade chemical reagents prepared using distilled water, and used without further pure cation. For each hold, a freshly prepared solution was used. Temperature of solutions was thermostatically controlled at desired value, and all chemical material high purity about 99% [58].

2.2 Apparatus

All Potentiometric measurements were made at 25±1°C with an Orion (Model 720) pH/mV meter (Fisher scientific). Double junction Ag/AgCl reference electrode was used with digital multimeter (TMT480012). All chemicals were of analytical reagent grade unless otherwise stated and distilled water was used throughout. Testing was performed using dielectrode electrochemical cell with a volume of 250 ml. The working electrode was made of the (CS) with an exposed to solution area of 0.00123 m^2, the reference electrode was Ag/AgCl electrode, The inhibitors were added into the test solution. The current recorder by m A, the potential mV, and the time by min. The inhibitor measurements, the potential vs time dependences of (CS) in the H_2SO_4 1M solution without and with the addition of (GL), Zizi, extracts as inhibitors were recorded.

2.3 Tools and working method:

Voltage and current multimeter device, a glass beaker with a capacity of 250 ml, 1M H_2SO_4 acid titrated with Na_2CO_3 of accurate concentration, Ag /AgCl as a reference electrode prepared by dipping two silver electrodes in a 1M solution of HCl and passing a direct current between them from a 1.5 Volt battery, and the working electrode is (CS) electrode.

2.4 Cell preparation:

The cell consists of two electrodes, one of which is the silver electrode Ag/ AgCl electrode as a reference electrode, while the working electrode is (CS) electrode, an area immersed in acid $1.23 \times 10^{-3} m^2$. Voltage (mV) and current (mA) are measured every ten minutes for 2 hours, during which corrosion of (CS) takes place in the presence of 1M H_2SO_4 acid. Voltage, current and time are measured in the presence of different concentrations of GL and Zizi extracts were used as (CI) at concentrations of 100, 200, 300, 400, ppm and for a 2 hour for each concentration.

2.5. Weight loss measurements

Experiments were performed with different concentrations of the inhibitors. The immersion time for the weight loss is (2-24) h at 25 °C. The results of the weight loss experiments are the mean of three runs, each with a fresh specimen and 100 ml of fresh acid solution. The inhibition efficiency IE_w% and IE_e % were calculated.

Weight loss calculations are comprehensive corrosion tests for laboratory and field. Also, they help us to make a quantitative estimate of amount of corrosion. The corrosion behaviour of the metal in an aqueous environment is describe by the extent to which it dissolves in the water solution.

Calculated the weight of a specimen before and after precipitate and applying the following equation:

$$W = \frac{m1 - m2}{At} - - - - - - - - - - (1)$$

where m1 and m_2 – the mass of the sample before and after testing, respectively, g; A – area of the sample, m^2; t– exposure time, hours.

$$IE_w\% = \frac{W_0 - W}{W_0} \times 100 - - - - - - (2)$$

where W_0 and W – corrosion rate of (CS) in test solution without and with inhibitors, respectivelly.

All Potentiometric measurements were made at 25±1°C with an Orion (Model 720) pH/mV meter (Fisher scientific). Double junction Ag/AgCl reference electrode was used with digital multimeter (TMT480012). All chemicals were of analytical reagent grade unless otherwise stated and distilled water was used throughout. Testing was performed using dielectrode electrochemical cell with a volume of 250 ml. The working electrode was made of (CS) with an exposed to solution area of 0.00123 m^2, the inhibitor was added into the test solution, the effect of inhibition IE_e was determined by the formula:

$$IE_e = \frac{I_0 - I_{inh}}{I_0} \times 100 - - - - - (3)$$

where I_0 and I_{inh}. – corrosion current density of steel in test solution without, and with inhibitor, respectivelly, the current recorder by mA, the potential mV, and the time by min.

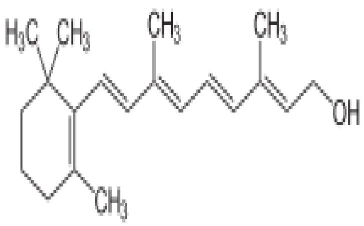
GL and Zizi extracts measurements, the potential vs time dependences of (CS) in the1M H_2SO_4 solution without and with the addition of GL and Zizi extracts inhibitors were recorded.

2.6. Preparation of expired GL and Zizi extracts solution

The liter of stock solution GL and Zizi extracts, was prepared by dissolving an accurately weighed quantity (1g) in (1L) (1000 ppm) in distilled H_2O, and then the desired concentrations (100 - 400) ppm are obtained by diluting the stock solution with the desired volume of distilled H_2O. The corrosive solution, 1M H_2SO_4 was prepared by diluting of high-grade H_2SO_4 (98 % w, d=1.84 g/ml, M. wt.= 98 g/mol.) with distilled water and dilute to up to 1M then titrate with 1M Na_2CO_3 standard solution to obtain exact 1M H_2SO_4 at suitable indicator. (CS) sample has area 1.23×10^{-3} m^2 was placed in 1M H_2SO_4 in a beaker devoid of, and with distinct quantities of the GL and Zizi extracts for (2-24) h at 298-323 K. Then they washed, desiccated, weighed after 10 min and measure the current and potential.

2. Preparation of Grape Leaves(GL) extract.

Wash grape leaves well with water and cut into small pieces and put 100 grams of them in a liter of distilled water and boil for an hour and then leave to cool for the next day, filter and concentrate the resulting extract to get rid of the water approximately and prepare solutions of 100-400 ppm [59]. Wash grape leaves well with water and cut into small pieces and put 100 grams of them in a liter of distilled water and boil for an hour and then leave to cool for the next day, filter and concentrate the resulting extract to get rid of the water approximately and prepare solutions of 100-400 ppm [55],

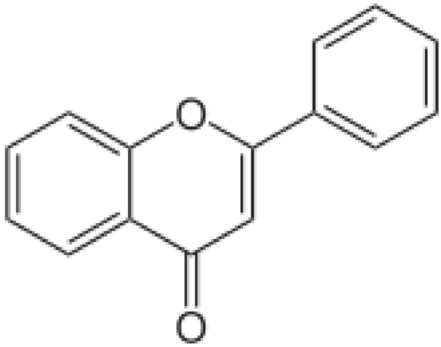


Vitamin A (divided to β- Carotene)

2. Preparation of Ziziphus spina-christi, (Zizi) extract.

From the leaves of Ziziphus spina-christi, the new flavonoid quercetin 3-xylosyl

(1⟶2) rhamnoside-4′-rhamnoside as well as rutin, hyperin and quercitrin were characterized [60].



Molecular structure of the flavone backbone (2-phenyl-1,4-benzopyrone).

To explain how GL and Zizi extracts molecules act as (CI) where GL and Zizi extracts molecules provide excellent surface coverage and protection as its molecules contain many electrons rich centers such as polar functional groups (OH), C=O, and aromatic rings through which they adsorb and act effectively as excellent (CI). The use of plants extraction which contain many of chemical compounds may be act as inhibitors of metal corrosion are one of the most effective, environmentally friendly and cheap things. This is due to its complex structures and large surface area. The effective functional groups in the extract molecules provide good coverage and protection for the surface [61].

2.3. Preparation of acid solutions

H_2SO_4 (1M) are prepared by analytical method,(1.8w/v, 98%) the volume of acid is divided into 6 bottles 50 ml for bulk solution and 20 ml of five different concentrations of nature extracts (50-250) ppm for acid with steel.

3. Results and discussion

3.1. Chemical Method (Weight-Loss Measurements) The activation energies (E_a) for the corrosion of steel in the absence and presence of different concentrations of BP extract was calculated using Arrhenius-type equation:

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$$W_{corr} = Ae^{\frac{-Ea}{RT}}$$

where E_a is the activation corrosion energy; R is the universal gas constant; A is the Arrhenius pre- exponential factor, T is the absolute temperature and W_{corr} is corrosion rate. Arrhenius plots for the corrosion rate of steel in 1 M H_2SO_4. Values of E_a for steel in were evaluated from the slope of log W versus 1/T plots. The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the corrosion of steel in HCl may be estimated using the transition-state equation:

$$W_{corr} = \frac{K_B\ T}{h} \exp^{\left(\frac{\Delta S^*}{R}\right)} \exp^{(-\frac{\Delta H^*}{RT})}$$

where k_B is the Boltzmann's constant and h is the Planck's constant. A plot of log(W/T) versus 1/T. Straight lines are obtained with a slope of $-\Delta H^*$ and from the intercepts of log(W/T)-axis, ΔS^* values were calculated.

The data was collected in **Table.1** indicate that the addition of (Ch. & Rh.) leads to an increase in the activation E_a and ΔH^* to values greater than that of the free solution. Moreover, the average difference value of the $E_a - \Delta H^*$ is 2.6 kJ/mol which is approximately equal to the value of RT (2.63 kJ/mol) at the average temperature (238 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known equation of perfect gas [62].

$$E_a - \Delta H^* = RT - - - - - (6)$$

It is pointed out in the literature that positive sign of the enthalpies reflects the endothermic nature of the (CS) dissolution process, the presence of inhibitors tested reveals that the corrosion process becomes more and more endothermic when compared to blank.

Table 1. Activation data of corrosion reaction of steel 1 M H_2SO_4 in the absence and presence GL and Zizi extracts.

	E_a (kJ/mol)	$\Delta H°_{ads}$ (kJ/mol)	$\Delta S°_{ads}$ (J/mol.K)
Blank	43.2	30.6	- 41.2
(GL)	69.3	66.7	-53.2
(Zizi)	78.2	71.4	-62.1

3.5. (GL)& Zizi extracts

The corrosion rate and inhibition efficiency for steel in 1 M H_2SO_4 solution at 25°C in the absence and presence of GL extract are given in Table10 . As the GL and Zizi extracts increases, the corrosion rate decreases. In other words, the inhibition efficiency of natural extract increases with the increase of its concentration to attain 97% and 90%.

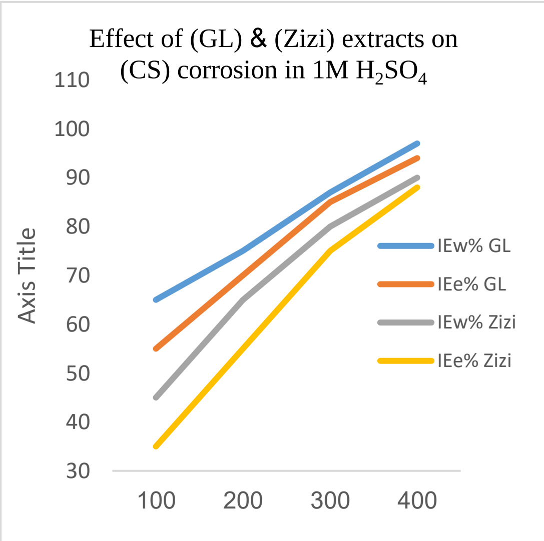

Fig. 1. Relationship between inhibition efficiency vs conc. of (GL) & (Zizi) extracts.

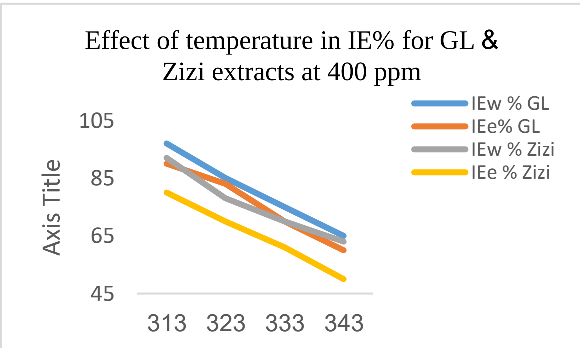

Fig.2. Effect of temperature in IE% for GL& Zizi extracts at 400 ppm.

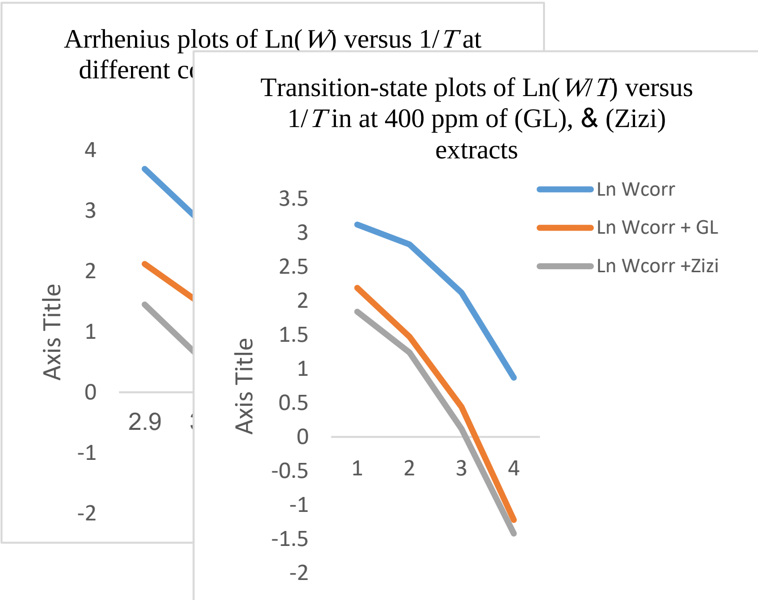

Fig.3. Arrhenius plots of Ln(W) versus 1/T at different conc. of (GL) & Zizi extracts.

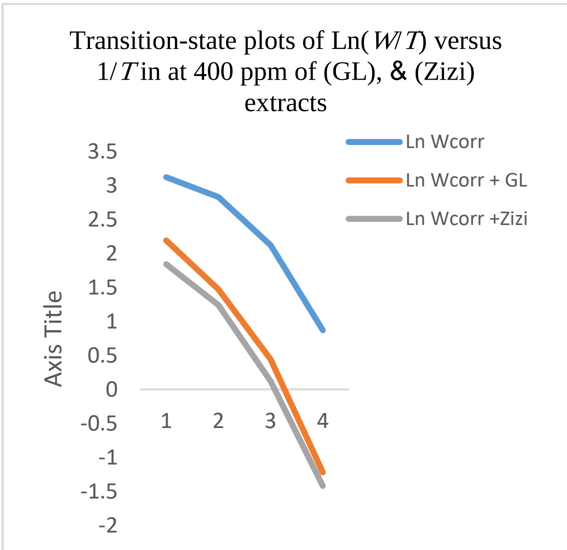

Fig.4. Transition-state plots of Ln(W/T) versus 1/T in at 400 ppm of (GL), and (Zizi) extracts.

The activation energies are $E^{*}a$ = 69.3 kJ mol^{-1} and $E^{*}a$ = 78.2 kJ mol^{-1} are the activation energies in the absence and presence of fenugreek, respectively. The low value of the activation energy (less than 80 kJ mol^{-1}) indicate physical adsorption of the extract molecules on metal surface. The decrease of % IE with temperature is explained by the adsorption of an organic adsorbate on the surface of a metal is regarded as a substitutional adsorption process between the organic compound in the aqueous phase, org_{aq}, and the water molecules adsorbed on the electrode surface H_2O_{suf}.

3.3. Potentiometric results

The activity of specific cations and anions can measure potentiometry with ion-selective microelectrodes at the solid/liquid interface from the solution side. Anodic and cathodic components of corrosion processes change the concentration of H^+, OH^- in local solution, ions of the supporting electrolyte, and metal cations [63].

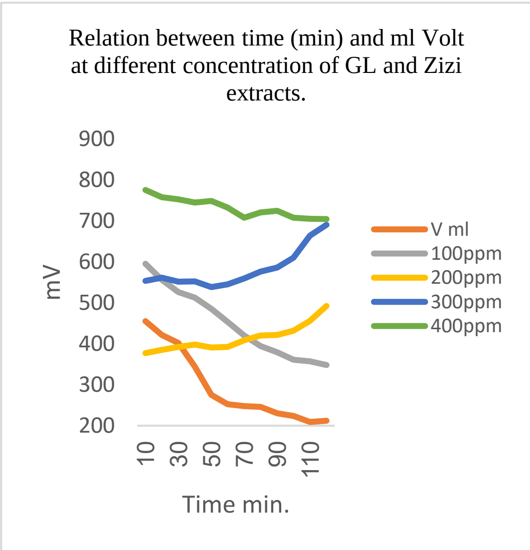

Fig.5. Relation between time (min) and ml Volt at different conc. of GL, and Zizi, extracts

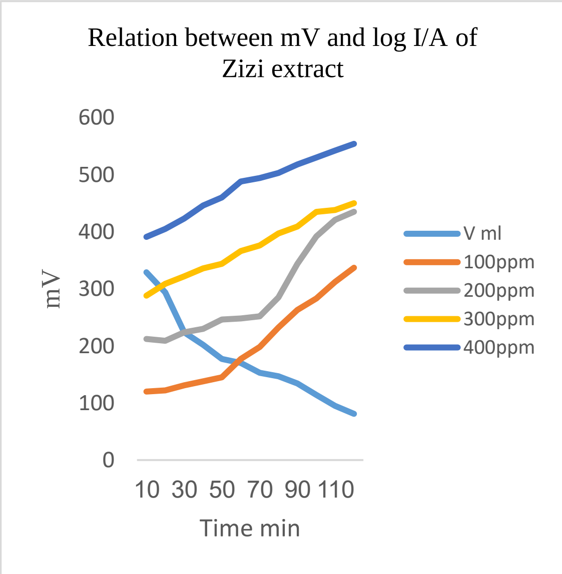

Fig.6. Relation between mV and log I/A of Zizi extract.

In Fig. 5,6. shows that the voltage during the corrosion process without adding GL and Zizi extracts which is used as a corrosion inhibitor in steel in the presence of H_2SO_4, we find that the voltage decreases with the increase in corrosion processes, and with the increase of time the voltage decreases to increase the formation of a layer of oxide that increases the conductivity of the solution. Then the voltage decreases between the working electrode and the reference electrode, while the voltage increases when (GL), and Zizi extracts were added as a result of adsorption of GL and Zizi extracts on the surface of (CS), which makes a protective layer between the steel and the solution, and it increases gradually with increasing time until two hours, and the voltage increases as the concentration of GL and Zizi extracts increases from a concentration of 100 ppm to 400 ppm.

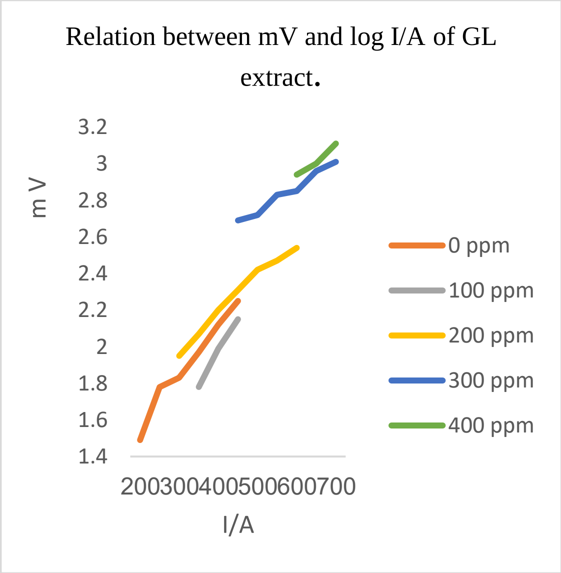

Fig.7. Relation between mV and log I/A of GL extract.

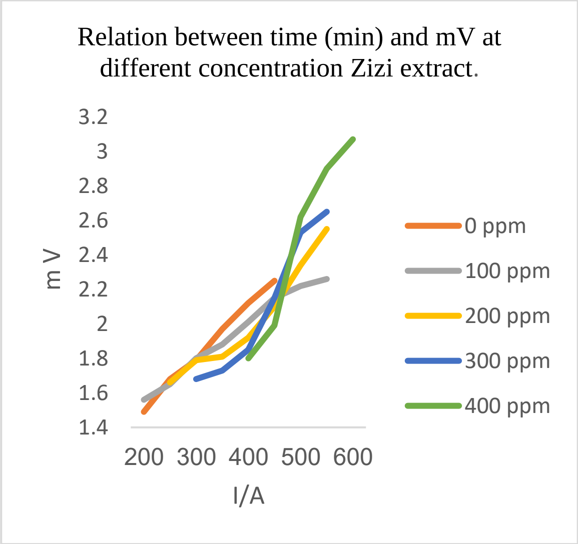

Fig.8. Relation between time (min) and mV at different conc. Zizi extract.

In Fig. 7,8. Shows the relationship between the voltage and the logarithm of the current density, which is the current intensity in A/ m^2. We note that the current density is higher when the solution is without an inhibitor (0 ppm), then it decreases as the concentration of the inhibitor increases at the same voltage, for example at a voltage of 500 mV, we find that the density decreases. The current increases with the concentration of the inhibitors, although it generally increases with the increase in the voltage, because the current generally increases with the increase in the voltage. It is noted here that the voltage increase is delayed at a concentration of 100 ppm and its decrease with time may be due to the fact that the layer formed at this concentration did not adhere sufficiently or because GL and Zizi extracts contained more than one compound (two compounds) that were not all of the same degree of efficiency in the process of adsorption or inhibition corrosion process, but it began to increase its efficiency by increasing the concentration up to 400 ppm.

4. Conclusion

The extracts of (GL), and Zizi extracts were studied as environmentally friendly (CI) for corrosion resistance in (CS) in 1M H_2SO_4. These extracts showed varying resistance to (CS) corrosion in H_2SO_4 because these extracts contain natural chemicals such as, vitamins A, from carotene in grape leaves, and flavones all of these substances have a high ability to adsorb on the surface of metal, especially on (CS), it is work to resist the corrosion. The Corrosion rate was decreased with increase in inhibitors concentration which could be due to enhanced surface coverage, the potentiometric method showed the extent of voltage change with time for each concentration of (GL), and Zizi extracts.

5. References

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