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**RESEARCH ARTICLE**

# Zygophllum coccineum L. Extract as green corrosion inhibitor for copper in 1 M $HNO_3$ Solutions

**A.S. Fouda[1], Y.M. Abdallah[2,*], G.Y. Elawady[1] and R.M. Ahmed[1]**

**1)** Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt,
**2)** Faculty of Oral and Dental Medicine, Delta University for science and Technology, Gamasa, Egypt,

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***Corresponding Author***

**Y.M.Abdallah**
**E-mail:**
**dr.ymostafa80@yahoo.com**

## *Abstract*

Zygophllum coccineum L. Extract (ZCE), was investigated as a green corrosion inhibitor for copper in 1 M $HNO_3$ solutions using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Surface morphology was tested using scanning electron microscope (SEM). The effect of the temperature on corrosion behavior with addition of different concentrations was studied in the temperature range of 25-45 ºC by weight loss method. Polarization curves reveal that the investigated extract is a mixed type inhibitors. The inhibition efficiency was found to increase with increase in the investigated extract concentration and decrease with raising solution temperature. The adsorption of the inhibitor on copper surface was found to obey the Langmuir's adsorption isotherm. The results obtained from chemical and electrochemical techniques are in good agreement.



## Introduction

Copper is a metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. The use of copper corrosion inhibitors in acid solutions is usually to minimize the corrosion of copper during the acid cleaning and descaling. The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated (Khaled, 2009, Kosec *et al*. 2008, Rahmouni *et al*. 2007).

Most well-known acid inhibitors are organic compounds containing nitrogen , sulfur, and oxygen atoms. Among them, organic inhibitors have many advantages such as high inhibition efficiency and easy production (Singh *et al*. 1993, Banerjee *et al*. 1992, Arab *et al*. 1993, Raspini 1993). Organic heterocyclic compounds have been used for the corrosion inhibition of copper (Villamil *et al*. 1999) in different corroding media. Although many of these compounds have high inhibition efficiencies, several have undesirable side effects, even in very small concentrations, due to their toxicity to humans, deleterious environmental effects, and high-cost (Parikh*et al*.2004).

Plant extract is low-cost and environmental safe, so the main advantages of using plant extracts as corrosion inhibitor are economic and safe environment. Up till now, many plant extracts have been used as effective corrosion inhibitors for copper in acidic media, such as: Zenthoxylum alatum (Chauhan, 2009), Azadirachta Indica (Sangeetha, *et al*. 2011) caffeine (Fernando Sílvio de Souza *et al*. 2012) Cannabis (Abd-El-Nabey*et al*. 2013). The inhibition performance of plant extract is normally ascribed to the presence of complex organic species, including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products in their composition. These organic compounds usually contain polar functions with nitrogen, sulfur, or oxygen atoms and have triple or conjugated double bonds with aromatic rings in their molecular structures, which are the major adsorption centers.

Zygophllum coccineum L, is a type genus of flowering plants in Zygophyllaceae family. The eleven species it contains are known generally as White Alratrit, is widely distributed in Mediterranean, The whole plant has great

medicinal importance, as Uses repellent worms, hypotensive , decrease the percentage of sugar in the blood and used as Antipyretic and anti-fever (Gibbons *et al*. 2001).
The present work was designed to study the inhibitory action of Zygophllum coccineum L extract for the corrosion of copper in 1 M $HNO_3$ using chemical and electrochemical techniques. Also, the surface morphology was tested using scanning electron microscope (SEM).

## Material and Methods

*2.1. Materials and Solutions*
Experiments were performed using copper specimens (99.98%) which were mounted in Teflon. An epoxy resin was used to fill the space between Teflon and copper electrode. The auxiliary electrode was a platinum sheet (1 $cm^2$), saturated calomel electrode (SCE) as reference electrode was connected to a conventional electrolytic cell of capacity 100 ml via a bridge with a Luggin capillary, the tip of which was very close to the surface of the working electrode to minimize the IR drop. The aggressive solution used was prepared by dilution of analytical reagent grade 70% $HNO_3$ with bidistilled water. The stock solution (1000 ppm) of ZCE was used to prepare the desired concentrations by dilution with bidistilled water. The concentration range of ZCE used was 50-500 ppm.

*2.2. Preparation of plant extracts*
Fresh aerial parts of ZCE sample were crushed to make fine powder. The powdered materials (250 g) were soaked in 500 ml of dichloromethane for 5 days and then subjected to repeated extraction with 5× 50 ml until exhaustion of plant materials. The extracts obtained were then concentrated under reduced pressure using rotary evaporator at temperature below 50°C. The dichloromethane evaporated to give solid extract that was prepared for application as corrosion inhibitor. Chemical studies have demonstrated that the ZCE contain:
Zygophyllin (28% in leaves, 0.18% in stems and 0.26% in fruits), Quinovic acid (0.36% in leaves, 0.31% in fruits and 0.47% in stems) and Flavonoids e.g. kaempfero1-3- rutinoside (El-Moghazy, 1957, Boulos, 2000).

*2.3. Weight lose measurements*
Seven parallel copper sheets of 1×1×0.2 cm were abraded with emery paper (grade 320–500–1200) and then washed with bidistilled water and acetone. After accurate weighing, the specimens were immersed in a 250 ml beaker, which contained 100 ml of $HNO_3$ with and without addition of different concentrations of ZCE. All the aggressive acid solutions were open to air. After 180 minutes, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of seven parallel copper sheets could be obtained. The inhibition efficiency (IE %) and the degree of surface coverage, θ of ZCE for the corrosion of copper were calculated as follows (Mu *et al*. 1996),

$$IE\% = \theta \times 100 = \left[1 - \frac{W}{W^{\circ}}\right] \times 100 \qquad (1)$$

where $W^o$ and W are the values of the average weight loss without and with addition of the inhibitor, respectively.

*2.4. Electrochemical measurements*
All the measurements were done in solutions open to atmosphere under unstirred conditions. All potential values were reported versus SCE. Prior to each experiment, the electrode was treated as before. Tafel polarization curves were obtained by changing the electrode potential automatically from (-0.8 to 1 V vs. SCE) at open circuit potential with a scan rate of 1 $mVs^{-1}$. Stern-Geary method (Parr *et al.* 1978), used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives (log $i_{corr}$) and the corresponding corrosion potential ($E_{corr}$) for inhibitor free acid and for each concentration of inhibitor. Then ($i_{corr}$) was used for calculation of inhibition efficiency (IE %) and surface coverage (θ) as in equation 2:

$$IE\ \% = \Theta \times 100 = \left[1 - \frac{i_{corr\ (inh)}}{i corr\ _{(free\ )}}\right] \times 100 \qquad (2)$$

where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively .
Impedance measurements were carried out in frequency range ($2x10^4$ Hz to $8x10^{-2}$ Hz) with amplitude of 10 mV peak-to-peak using ac signals at open circuit potential. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the charge transfer resistance $R_{ct}$ (diameter of high-frequency loop) and the double layer capacity $C_{dl}$. The inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements are calculated from equation 3:

$$IE\% = \theta \times 100 = \left[1 - \left(\frac{R^{\circ}_{ct}}{R_{ct}}\right)\right] \times 100 \qquad (3)$$

where $R^{o}_{ct}$ and $R_{ct}$ are the charge transfer resistance in the absence and presence of inhibitor, respectively.
Electrochemical frequency modulation (EFM) was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The large peaks were used to calculate the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_a$ and $\beta_c$) and the causality factors CF-2&CF-3 (Bosch *et al.* 2001). The electrode potential was allowed to stabilize 30 min before starting the measurements. All the experiments were conducted at 25°C.
All electrochemical measurements were performed using Gamry Instrument (PCI4/750) Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA 400. Gamry applications include DC105 software for potentiodynamic polarization, EIS300 software for electrochemical impedance spectroscopy, and EFM140 software for electrochemical frequency modulation measurements via computer for collecting data. Echem Analyst 6.03 software was used for plotting, graphing, and fitting data. To test the reliability and reproducibility of the measurements, duplicate experiments, which performed in each case at the same conditions.

*2.5. Surface morphology*
For morphological study, surface features (1 cm x 1 cm x 0.2cm) of copper were examined before and after exposure to 1 M $HNO_3$ solutions for 12 hours with and without ZCE. JEOL JSM-5500 scanning electron microscope was used for this investigation.

## Result and Discussion

*3.1. Weight loss measurements*

Weight loss measurements were carried out for copper in 1 M $HNO_3$ in the absence and presence of different concentrations of ZCE and are shown in Figure (1). The inhibition efficiency (IE %) values calculated are listed in Tables 1& 2. From these tables, it is noted that the IE% increases steadily with increasing the concentration of ZCE and decrease with raising the temperature from 25-45ºC. The inhibition efficiency (IE %) and surface coverage (θ) were calculated by equation (1).

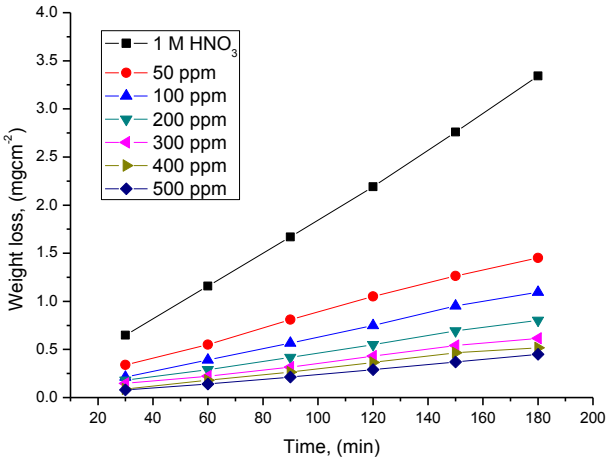


**Figure1:** Weight loss-time curves for the corrosion of copper in 1 M $HNO_3$ in the absence and presence of different concentrations of ZCE at 25°C

**Table 1: Corrosion rate (C.R.) and inhibition efficiency data obtained from weight loss measurements for copper in 1 M $HNO_3$ solutions without and with various concentrations of ZCE at 25°C**

| Conc., ppm | Weight loss, Mg $cm^{-2}$ | C.R., mg $cm^{-2}$ $min^{-1}$ | θ | %IE |
|---|---|---|---|---|
| **1 M $HNO_3$** | 3.44 | 0.027 | --- | --- |
| **50** | 1.10 | 0.019 | 0.680 | 68.0 |
| **100** | 0.80 | 0.017 | 0.767 | 76.7 |
| **200** | 0.50 | 0.006 | 0.855 | 85.5 |
| **300** | 0.47 | 0.004 | 0.863 | 86.3 |
| **400** | 0.43 | 0.003 | 0.875 | 87.5 |
| **500** | 0.31 | 0.001 | 0.91 | 91.0 |

**Table 2:** Data of weight loss measurements for copper in 1 M $HNO_3$ solution in the absence and presence of different concentrations of ZCE at 25–45°C

| Conc., ppm | Temp., °C | C.R., mg$cm^{-2}$$min^{-1}$ | θ | IE% |
|---|---|---|---|---|
| 50 | 25 | 0.019 | 0.680 | 68.0 |
| | 30 | 0.065 | 0.620 | 62.0 |
| | 35 | 0.083 | 0.536 | 53.6 |
| | 40 | 0.120 | 0.473 | 47.3 |
| | 45 | 0.237 | 0.410 | 41.0 |
| 100 | 25 | 0.017 | 0.767 | 76.7 |
| | 30 | 0.022 | 0.638 | 63.8 |
| | 35 | 0.042 | 0.548 | 54.8 |
| | 40 | 0.053 | 0.490 | 49.0 |
| | 45 | 0.062 | 0.453 | 45.3 |
| 200 | 25 | 0.006 | 0.855 | 85.5 |
| | 30 | 0.017 | 0.793 | 79.3 |
| | 35 | 0.027 | 0.685 | 68.5 |
| | 40 | 0.038 | 0.543 | 54.3 |
| | 45 | 0.050 | 0.496 | 49.6 |
| 300 | 25 | 0.004 | 0.863 | 86.3 |
| | 30 | 0.016 | 0.809 | 80.9 |
| | 35 | 0.023 | 0.743 | 74.3 |
| | 40 | 0.035 | 0.694 | 69.4 |
| | 45 | 0.060 | 0.547 | 54.7 |
| 400 | 25 | 0.003 | 0.875 | 87.5 |
| | 30 | 0.015 | 0.832 | 83.2 |
| | 35 | 0.021 | 0.773 | 77.3 |
| | 40 | 0.028 | 0.753 | 75.3 |
| | 45 | 0.036 | 0.621 | 62.1 |
| 500 | 25 | 0.001 | 0.910 | 91.0 |
| | 30 | 0.011 | 0.848 | 84.8 |
| | 35 | 0.017 | 0.805 | 80.5 |
| | 40 | 0.023 | 0.782 | 78.2 |
| | 45 | 0.037 | 0.653 | 65.3 |

The observed inhibition action of the ZCE could be attributed to the adsorption of its components on copper surface. The formed layer, of the adsorbed molecules, isolates the metal surface from the aggressive medium which limits the dissolution of the latter by blocking of their corrosion sites and hence decreasing the corrosion rate, with increasing efficiency as their concentrations increase (Zhang *et al.* 2009).

*3.2. Polarization measurements*

Figure 2 shows potentiodynamic polarization curves recorded for copper in 1 M $HNO_3$ solutions in the absence and presence of various concentrations of ZCE at 25ºC.

Lee and Nobe (Lee *et al.* 1986) reported the occurrence of a current peak between the apparent-Tafel and limiting-current regions during potential sweep experiments. The presence of ZCE shifts both anodic and cathodic branches to the lower values of corrosion current densities and thus causes a remarkable decrease in the corrosion rate. The parameters derived from the polarization curves in Figure 2 are given in Table 3. In 1 M $HNO_3$ solution, the presence of ZCE causes a remarkable decrease in the corrosion rate i.e., shifts both anodic and cathodic curves to lower current densities. In other words, both cathodic and anodic reactions of copper electrode are retarded by ZCE in 1 M $HNO_3$ solution. The Tafel slopes of $\beta_a$ and $\beta_c$ at 25ºC do not change remarkably upon addition of ZCE, which indicates that the presence of ZCE does not change the mechanism of hydrogen evolution and the metal dissolution process. Generally, an inhibitor can be classified as cathodic type if the shift of corrosion potential in the presence of the inhibitor is more than 85 mV with respect to that in the absence of the inhibitor (Tao *et al* 2009, Ferreira *et al.* 2004). In the presence of ZCE, $E_{corr}$ shifts to less negative but this shift is very small (about 20-30 mV), which indicates that ZCE can be arranged as mixed type inhibitor. Since $\beta_c > \beta_a$, ZCE is classified as mixed type inhibitor but the cathode is more polarized than the anode when an external current was applied.

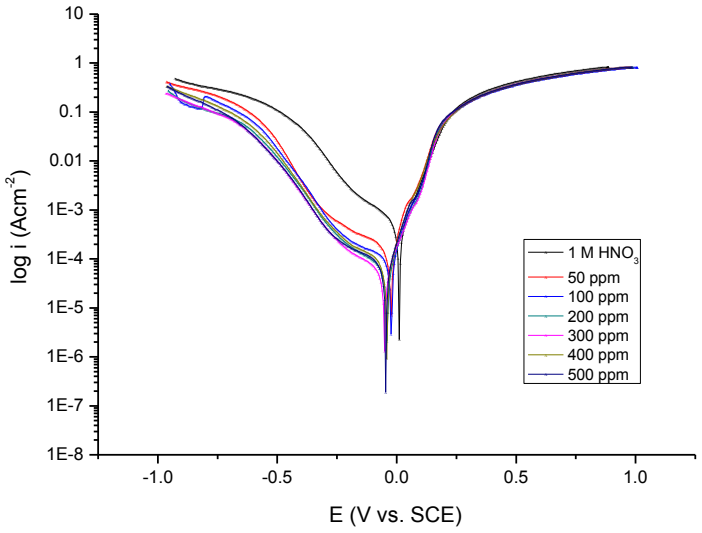


**Figure 2:** Potentiodynamic polarization curves for the corrosion of copper in 1 M $HNO_3$ solution without and with various concentrations of ZCE at 25˚C.

**Table 3**: Effect of concentration of ZCE on the electrochemical parameters calculated using potentiodynamic polarization technique for the corrosion of copper in 1 M $HNO_3$ at 25˚C.

| Concentration, ppm | $i_{corr}$, $\mu A\ cm^{-2}$ | $-E_{corr}$, mV vs. SCE | $\beta_a$, $mVdec^{-1}$ | $\beta_c$, $mVdec^{-1}$ | CR, $mm\ y^{-1}$ | θ | η % |
|---|---|---|---|---|---|---|---|
| 1 M $HNO_3$ | 363.0 | 10.7 | 86 | 207 | 179.30 | -- | -- |
| 50 | 124.0 | 20.4 | 77 | 287 | 61.22 | 0.658 | 65.8 |
| 100 | 120.0 | 24.6 | 77 | 234 | 59.39 | 0.669 | 66.9 |
| 200 | 56.5 | 22.9 | 73 | 224 | 27.86 | 0.844 | 84.4 |
| 300 | 54.1 | 40.0 | 69 | 224 | 26.68 | 0.851 | 85.1 |
| 400 | 42.7 | 42.9 | 76 | 214 | 21.06 | 0.882 | 88.2 |
| 500 | 36.3 | 50.0 | 80 | 212 | 17.94 | 0.900 | 90.0 |

*3.3. Electrochemical impedance spectroscopy (EIS)*

EIS is well-established and powerful technique in the study of corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from impedance diagrams (Silverman *et al*. 1988, Lorenz *et al*. 1981, Macdonald *et al*. 1982, Mansfeld 1981, Gabrielli 1982) Figure 3 and Figure 4 show the Nyquist and Bode plots respectively, obtained at open-circuit potential both in the absence and presence of increasing concentrations of ZCE at 25°C. The increase in the size of the capacitive loop with the addition of ZCE extract shows that a barrier gradually forms on the copper surface. From the Bode plots (Fig.4), the total impedance increases with inhibitor concentration (log Z vs. log f). But (log f vs. phase) the continuous increase in the phase angle shift, obviously correlating with the increase of inhibitor adsorbed on Cu surface. The Nyquist plots do not yield perfect semicircles as expected from the theory of EIS. The deviation from ideal semicircle was generally attributed to the frequency dispersion (El Achouri *et al*. 2001) as well as to the in homogeneities of the copper surface.

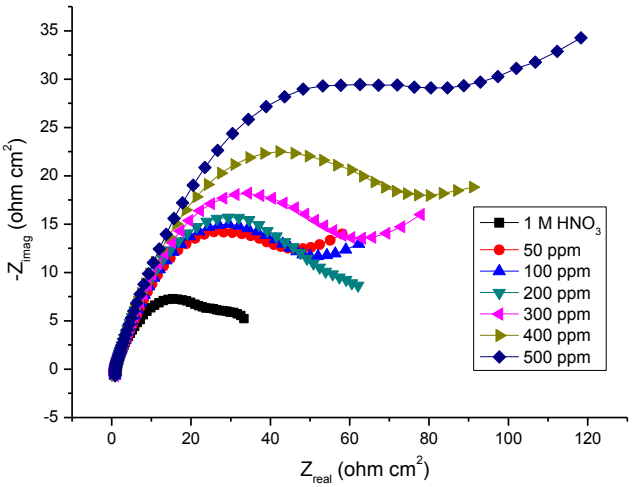


**Figure 3.**Nyquist plots recorded for copper in 1 M $HNO_3$ without and with various concentrations of ZCE at 25˚C

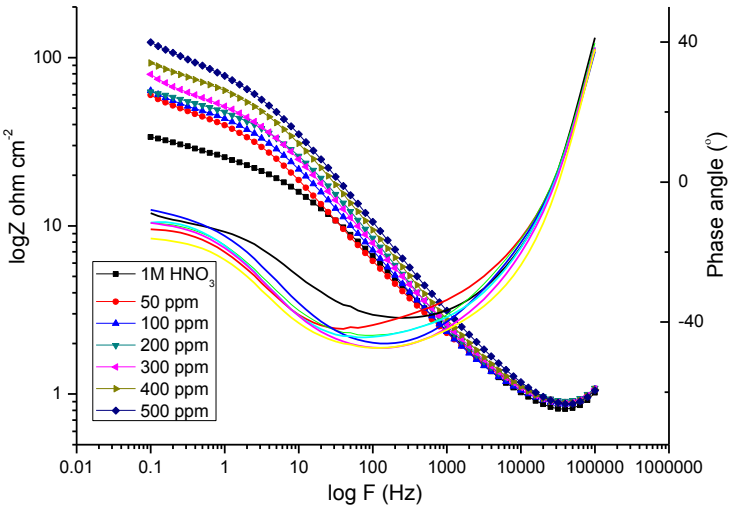


**Figure 4.** Bode plots recorded for copper in 1 M $HNO_3$ without and with various concentrations of ZCE at 25˚C

EIS spectra of the investigated extract were analyzed using the equivalent circuit in Figure 5, which represents a single charge transfer reaction and fits well with our experimental results. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit (Macdonald *et al*. 1987).The double layer capacitances, $C_{dl}$, for a circuit including a CPE parameter ($Y_0$ and n) were calculated from the following equation (Tao *et al.*2009):

$$C_{dl} = Y_0 (\omega_{max})^{n-1} \quad (4)$$

where$Y_0$ is the magnitude of the CPE, $\omega_{max}= 2\pi f_{max}$, $f_{max}$ is the frequency at which the imaginary component of the impedance is maximal and the factor n is an adjustable parameter that usually lies between 0.5 and 1.0. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charged-transfer controlled (Mertens *et al.* 1997, Trabanelli *et al*. 2005). The general shape of the curves is very similar for all samples (in presence or in absence of ZCE at different immersion times) indicating that no change in the corrosion mechanism (Trowsdate *et al.* 1996). From the impedance data (Table 4), we conclude that the value of $R_{ct}$ increases with increase in concentration of the ZCE and this indicates an increase in % IE .

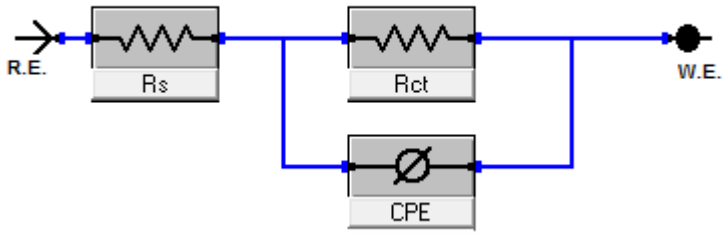


**Figure 5.** Electrical equivalent circuit used to fit the impedance data

**Table 4.** Electrochemical kinetic parameters obtained from EIS technique for copper in 1M $HNO_3$ solution containing various concentrations of ZCE at 25˚C.

| Conc., ppm, | $R_{ct}$, Ω $cm^2$ | $C_{dl}$, µF $cm^{-2}$ | θ | IE % |
|---|---|---|---|---|
| 1 M $HNO_3$ | 20.84 | 874.8 | --- | --- |
| 50 | 60.46 | 814.5 | 0.655 | 65.5 |
| 100 | 69.65 | 783.5 | 0.701 | 70.1 |
| 200 | 73.56 | 732.3 | 0.717 | 71.7 |
| 300 | 75.45 | 700.9 | 0.724 | 72.4 |
| 400 | 87.19 | 657.8 | 0.761 | 76.1 |
| 500 | 119.8 | 632.7 | 0.826 | 82.6 |

The presence of ZCE enhances the value of $R_{ct}$ in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of ZCE and the decrease in the values of CPE follows the order similar to that obtained for $i_{corr}$ in this study. The decrease in CPE/$C_{dl}$ results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggesting that ZCE extract inhibit the copper corrosion by adsorption at metal/acid (Reis *et al.* 2006, Lagrenee *et al*.2002, McCafferty *et al.* 1972). The inhibition efficiency is calculated from the charge–transfer resistance data as shown in equation 3 (.Ma *et al*. 2002)

*3.4. Electrochemical frequency modulation (EFM)*

EFM is a nondestructive corrosion measurement technique that can directly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring (Kus *et al*. 2006). The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality

factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Figure 6 show the frequency spectrum of the current response of pure copper in 1 M $HNO_3$ solution, contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The EFM intermodulation spectrums of Cu in 1 M $HNO_3$ solution containing (50ppm- 500ppm) of the ZCE extract at 25°C is shown in Figure 6. The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 200 µA, are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 mA). The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the "activation" model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode (Caigman *et al*. 2000). The larger peaks were used to calculate the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_c$ and $\beta_a$) and the causality factors (CF-2 and CF-3).These electrochemical parameters were simultaneously determined by Gamry EFM140 software, and listed in Table 5 indicating that this extract inhibit the corrosion of copper in 1 M $HNO_3$ through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality (Abdel–Rehim *et al*. 2006). The inhibition efficiencies $IE_{EFM}$ % increase by increasing the studied extract concentrations and was calculated as follows:

$$IE\,\%_{EFM} = \left(1 - \frac{i_{corr}}{i^{o}_{corr}}\right) \times 100 \qquad (5)$$

where $i^{o}_{corr}$ and $i_{corr}$ are corrosion current densities in the absence and presence of ZCE extract, respectively.

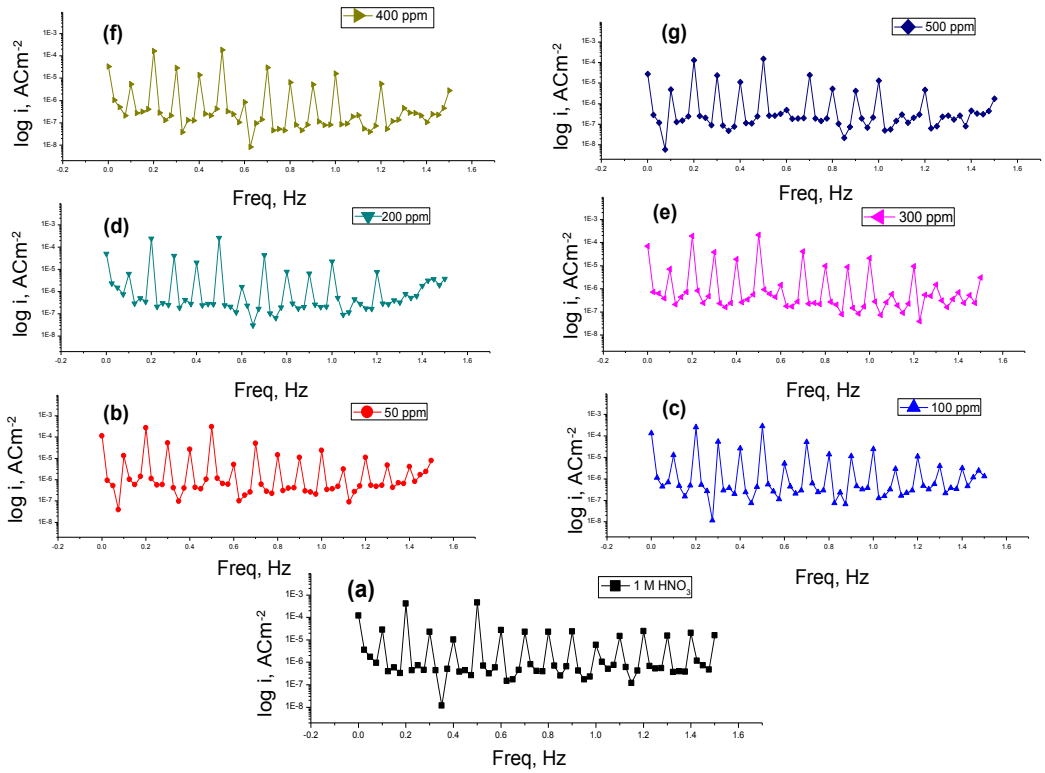


**Figure 6 (a-g):** Intermodulation spectrums for the corrosion of copper in 1 M $HNO_3$without and with various concentrations of ZCE at 25˚C

**Table 5:** Electrochemical kinetic parameters obtained by EFM technique for Cu in1 M $HNO_3$ solutions containing various concentrations of ZCE at 25°C.

| Conc., ppm | $i_{corr}$, $\mu Acm^{-2}$ | $\beta_a$ mV $dec^{-1}$ | $\beta_c$ mV $dec^{-1}$ | C.R. mpy | CF-2 | CF-3 | θ | IE% |
|---|---|---|---|---|---|---|---|---|
| 1 M $HNO_3$ | 319.6 | 44.800 | 52 | 158 | 1.76 | 2.80 | --- | --- |
| 50 | 183.6 | 47.730 | 102 | 140 | 1.91 | 2.92 | 0.426 | 42.6 |
| 100 | 167.6 | 46.650 | 107 | 132 | 2.07 | 3.10 | 0.476 | 47.6 |
| 200 | 134.8 | 49.700 | 110 | 125 | 1.93 | 2.92 | 0.578 | 57.8 |
| 300 | 105.2 | 48.280 | 114 | 106 | 2.00 | 3.24 | 0.671 | 67.1 |
| 400 | 63.3 | 56.250 | 117 | 98 | 1.97 | 3.10 | 0.802 | 80.2 |
| 500 | 38.7 | 54.520 | 129 | 83 | 2.00 | 3.13 | 0.879 | 87.9 |

*3.5. Adsorption Isotherm*

The mode and interaction degree between an inhibitor and a metallic surface have been widely studied with the application of adsorption isotherms. The adsorption of an organic molecule occurs because the interaction energy between an inhibitor and a metallic surface is higher than that between water molecules and metallic surface (Bockris*et al*. 1964, Saleh *et al.* 2006). To obtain the adsorption isotherms, the degree of surface coverage (θ) obtained from weight loss method was determined as a function of inhibitor concentration. The values of θ were then plotted to fit the most suitable model of adsorption (Narvez *et al.* 2005). Attempts were made to fit experimental data to various isotherms including Frumkin, Langmuir, Temkin, Freundlich, isotherms. By far the results were best fitted by Langmuir adsorption isotherm as seen in Figure 7 (Li *et al*. 2009):

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

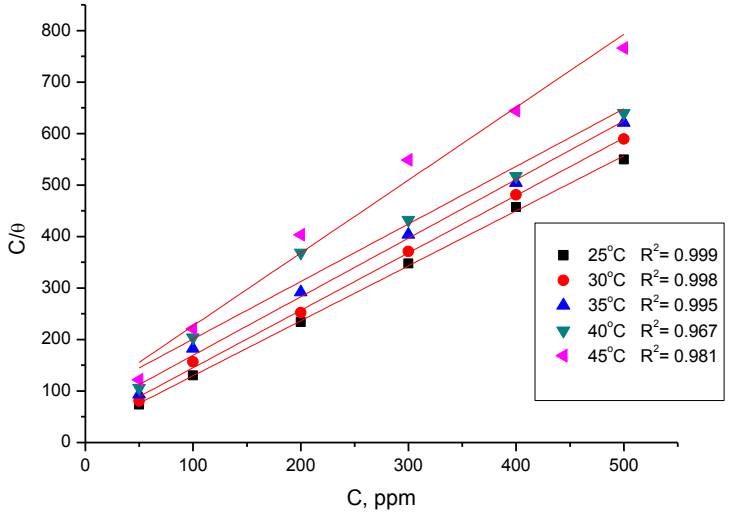


**Figure 7:** Langmuir adsorption plots for copper in 1 M $HNO_3$ containing various concentrations of ZCE at 25°C

*3.6. Kinetic-thermodynamic corrosion parameters*

Weight loss method was carried out at different temperature (25°C–45°C) in the presence of different concentration of ZCE. It has been found that he corrosion rate increases with the increase in temperature for ZCE (Table 2). The corrosion rate of copper in the absence of ZCE increased steeply from 25 to 45°C whereas; in the presence of ZCE the corrosion rate decreased slowly. The inhibition efficiency was found to decrease with temperature. The corrosion parameter in the absence and presence of extract in the temperature range 25–45°C has been summarized in Table 2.The apparent activation energy ($E^*_a$) for dissolution of copper in 1M $HNO_3$ was calculated from the slope of plots by using Arrhenius equation:

$$\log k = \frac{-E_a^*}{2.303\ R\ T} + \log A \qquad (7)$$

where k is rate of corrosion, $E^*_a$ is the apparent activation energy is the universal gas constant, T is absolute temperature and A is the Arrhenius pre-exponential factor.

By plotting log k against 1/T the values of activation energy ($E^*_a$) has been calculated ($E^*_a$ = (slope) 2.303 x R) (Figure 8). Activation energy for the reaction of copper in 1M $HNO_3$increases in the presence of extract (Table 6). This increasing in activation energy $E^*_a$ indicates the formation of energy barrier which. However, the extent of the rate increment in the inhibited solution is higher than that in the free acid solution. Therefore, the inhibition efficiency of the ZCE decreases markedly with increasing temperature. This result supports the idea that the adsorption of extract components on the copper surface may be physical in nature. Thus, as the temperature increases the number of adsorbed molecules decreases leading to decrease in the inhibition efficiency. The obtained results suggest that ZCE inhibits the corrosion reaction by increasing its activation energy. This could be done by adsorption on the copper surface making a barrier for mass and charge transfer. Moreover, the relatively low value of activation energy in presence of ZCE suggests a physical adsorption process.

The values of change of entropy ($\Delta S^*$) and change of enthalpy ($\Delta H^*$) can be calculated by using the formula:

$$k = \left(\frac{RT}{Nh}\right) exp\left(\frac{\Delta S^*}{R}\right) exp\left(\frac{\Delta H^*}{RT}\right) \quad (8)$$

where k is rate of corrosion, h is Planck's constant, N is Avogadro number, $\Delta S^*$ is the entropy of activation, and $\Delta H^*$ is the enthalpy of activation. A plot of log (k/T) vs. 1/T (Figure 9) should give a straight line, with a slope of ($\Delta H^*$/2.303R) and an intercept of [log (R/Nh)+$\Delta S^*$/2.303R], from which the values of $\Delta S^*$ and $\Delta H^*$ can be calculated (Table 6).The negative value of $\Delta S^*$ for the inhibitor indicates that activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of transition from reactant to the activated complex (Saliyan *et al.* 2007) The negative sign of $\Delta H^*$ indicates that the adsorption of inhibitor molecules is an exothermic process. Generally, exothermic process signifies either physisorption, chemisorption's or a combination of both.

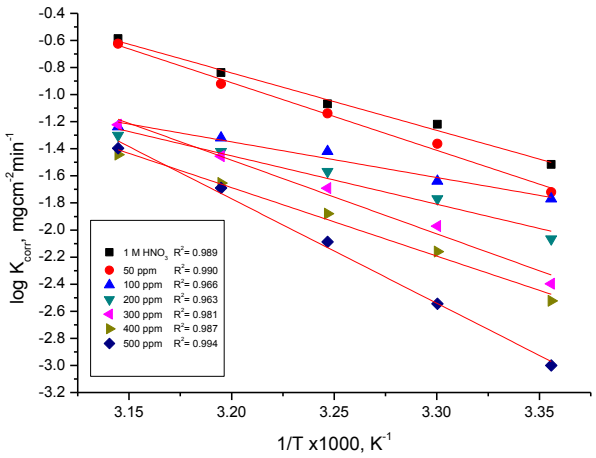


**Figure 8:** log k (corrosion rate) – 1/T curves for copper in 1 M $HNO_3$ in the absence and presence of different concentrations of ZCE

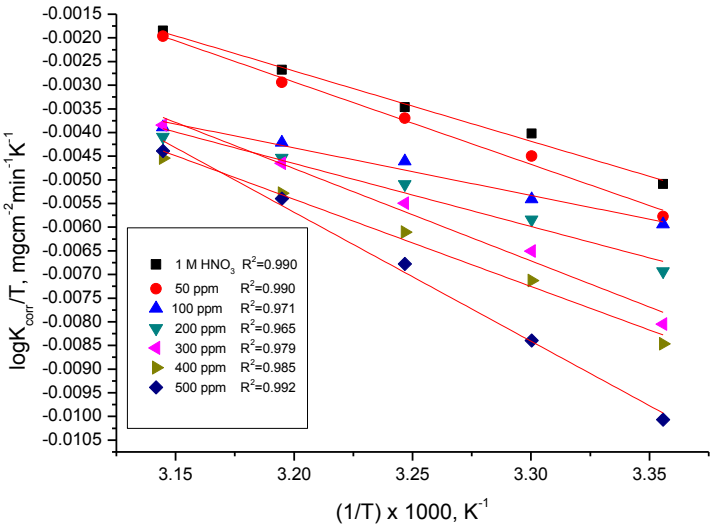


**Figure 9:** log k (corrosion rate) /T – 1/T curves for copper in 1 M $HNO_3$in the absence and presence of different concentrations of ZCE.

**Table 6:** Activation parameters for dissolution of copper in the absence and presence of different concentrations of ZCE in 1 M $HNO_3$ in the range of 25-45°C.

| Conc. ppm | $E_a^*$, kJ $mol^{-1}$ | $\Delta H^*$, kJ $mol^{-1}$ | $-\Delta S^*$, J $mol^{-1}K^{-1}$ |
|---|---|---|---|
| 1.0 M $HNO_3$ | 50.41 | 83.63 | 196.71 |
| 50 | 68.49 | 110.57 | 196.56 |
| 100 | 81.24 | 123.37 | 197.04 |
| 200 | 95.63 | 144.74 | 196.85 |
| 300 | 96.85 | 153.06 | 196.47 |
| 400 | 104.30 | 162.12 | 196.55 |
| 500 | 147.66 | 226.55 | 196.01 |

*3.7. Surface analysis by SEM*

Figure10 shows an SEM photograph recorded for copper samples Polished (A) and exposed for 12 h in 1M $HNO_3$ solution without (B) and with 500 ppm of ZCE at 25°C. A photograph of the polished copper surface before immersion in 1 M $HNO_3$ solution is shown in Figure 10a. The photograph shows the surface was smooth and without pits. The SEM micrographs of the corroded copper in the presence of 1 M $HNO_3$ solution are shown in Figure 10b. The faceting seen in this figure was a result of pits formed due to the exposure of copper to the acid. The influenced of the inhibitor addition 500 ppm on the copper in 1 M $HNO_3$ solution is shown in Figure 10c. The morphology in Figure 10c shows a rough surface, characteristic of uniform corrosion of copper in acid, as previously reported (Li *et al*. 2005), that corrosion does not occur in presence of inhibitor and hence corrosion was inhibited strongly when the inhibitor was present in the nitric acid, and the surface layer is very rough. In contrast, in the presence of 500 ppm of ZCE, there is much less damage on the copper surface, which further confirm the inhibition action. Also, there is an adsorbed film adsorbed on copper surface (Figure 10c).In accordance, it might be concluded that the adsorption film can efficiently inhibits the corrosion of copper.

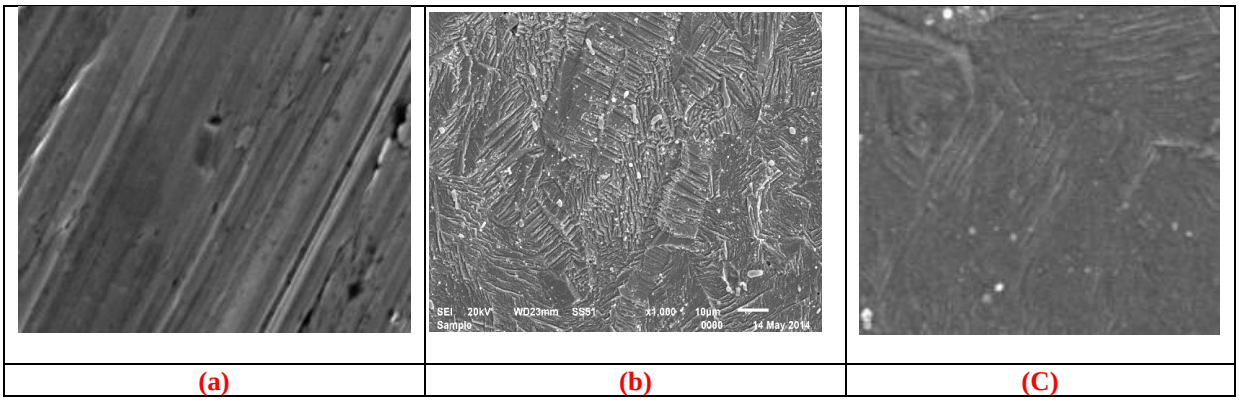


**Figure 10:** SEM micrographs of copper surface (a) before of immersion in 1 M $HNO_3$, (b) after 12 h of immersion in 1 M $HNO_3$and (c) after 12 h of immersion in 1 M $HNO_3$ + 500 ppm of ZCE at 25°C

*3.8. Mechanism of the corrosion inhibition*

Most of organic inhibitors contain at least one polar group with an atom of nitrogen, oxygen, sulphur or in some cases selenium and phosphorus. The inhibiting properties of many compounds are determined by the electron density at the reaction center (Anand *et al.* 1965).

With increase in electron density in the center, the chemisorption between the inhibitor and the metal are strengthened (Cook *et al*. 1951, Bordeaux *et al*. 1957).The plant extract ZCE is composed of numerous naturally occurring organic compounds. Accordingly, the inhibitive action of ZCE could be attributed to the adsorption of its components on the copper surface. The main phytochemical constituents of ZCE are Zygophyllin (28% in leaves, 0.18% in stems and 0.26% in fruits), Quinovic acid (0.36% in leaves, 0.31% in fruits and 0.47% in stems) and Flavonoids e.g. kaempfero1-3- rutinoside. Most of these phytochemicals are organic compounds that have center for π-electron and presence of hetero atoms such as oxygen and nitrogen; hence, the adsorption of the inhibitor on the copper surface is enhanced by their presence (Ebenso *et al.* 2008) reported that Quinovic acid and flavonoids are major constituents of plant that enhance the inhibition potentials of plant extracts. Therefore, the inhibition efficiency of methanol extracts of ZCE is due to the formation of multi-molecular layer of adsorption between copper surface and some of these phytochemicals. Results of the present study have shown that ZCE extract inhibits the acid induced corrosion of copper by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of the metal, inhibitor concentration, and temperature as well as inhibitor adsorption abilities, which is so much dependent on the number of adsorption sites. The mode of adsorption (physisorption) observed could be attributed to the fact that ZCE contains many different chemical compounds, which some can be adsorbed physically. This observation may derive the fact that adsorbed organic molecules can influence the behavior of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes (Singh *et al*. 2010).

## Conclusions

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

1. The ZCE shows good performance as corrosion inhibitor in 1 M $HNO_3$.
2. The results obtained from weight loss showed that the inhibiting action increases with the ZCE concentration and decreases with the increasing in temperature.
3. Double layer capacitances decrease with respect to blank solution when the plant extract is added. This fact confirms the adsorption of plant extract molecules on the copper surface.
4. The ZCE inhibits the corrosion by getting adsorbed on the metal surface following Langmuir adsorption isotherm.
5. The inhibition efficiencies determined by weight loss, potentiodynamic polarization and EIS techniques are in reasonably good agreement.

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