

Adsorption and inhibitive properties of methanol extract of *Euphorbia Heterophylla* for the corrosion of copper in 0.5 M nitric acid solutions

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The adsorption and the inhibitive properties of methanol extract of *Euphorbia heterophylla* on copper in 0.5 M HNO₃ have been studied by weight loss method at different temperatures (30–50°C), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Also, the surface morphology was analyzed by scanning electron microscopy (SEM). It was found that the inhibition efficiency increases with increasing extract doses and decreased with increasing temperature. The polarization data revealed that this extract acts as mixed type inhibitor. The adsorption process was more favored at lower temperatures with larger negative standard free energy. The extract was adsorbed physically on the copper surface followed Frumkin isotherm.

Keywords: acid corrosion, copper, green inhibitor, adsorption, kinetic parameters.

INTRODUCTION

Metals are most commonly unstable in the atmosphere. Corrosion is the process of a metal returning to the material's stable thermodynamic state. Primary reasons for concern about corrosion are safety, economics and conservation¹. Corrosion is both costly and dangerous. Billions of dollars are spent annually for the replacement of corroded structures, machinery and components. Premature failure of these can result in human injury, loss of life and collateral damage. Corrosion of metallic surfaces can be controlled or reduced by the addition of chemical compounds to the corrodent². Most practical methods for protection against the successive dissolution of metal by corrosion are the use of inhibitors. The use of organic compounds containing O, S and N to reduce corrosion of copper has been studied, but pose environmental crisis, as they are toxic and expensive³. However, the extracts of the plant contain mixtures of compounds having O, S and N element and are eco-friendly. These compounds having nitrogen and sulphur as constituent atoms were studied as the corrosion inhibitor in various acid media. Literature reveals that not much work has been done on the inhibition of copper in 0.5 M nitric acid using plant extract. A variety of plant extracts has been employed as a corrosion inhibitor for metal and metal-based alloys^{4–14}. The bioactive compounds present in the plant extract are as effective as synthetic inhibitors. These compounds act as inhibitors in the acid solution which interact with metals and affect the corrosion reaction in a number of ways. Photochemical analysis of *Euphorbia heterophylla* revealed the presence of reducing sugar, alkaloids, flavonoids, saponins, sterols, tannins and triterpenoids in the whole plant (Fig. 1). Some of them are well known to possess biological activities¹⁵.

Thus attempt has been made to investigate the inhibitive action, adsorption kinetics of *Euphorbia Heterophylla* extract as a low cost, natural and non-toxic corrosion inhibitor for copper in HNO₃ over a range of temperature from 25 to 40°C.

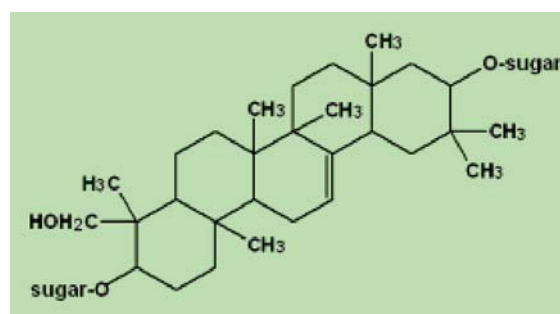


Figure 1. Saponins nucleus

EXPERIMENTAL PROCEDURE

Preparation of specimens

Copper specimens (0.001% Sn, 0.001% Ag, 0.01% Fe, 0.0005% Bi, 0.002% Pb, 0.0002% other elements and copper is the remainder) of dimensions 30×10 x 2 mm were abraded to a mirror finished and degreased using methanol¹⁵.

Solutions

The aggressive solutions used were made of AR grade HNO₃ (7 M) and its concentration was checked using standardized NaOH. 0.5 M of acid was prepared by dilution using bidistilled water. 100 ml stock solutions (10³ ppm) of investigated plant extracts were prepared by dissolving an accurately weighed quantity of plant extract (1 g) in an appropriate volume (1 L) of absolute methanol, and then the required doses (5–25 ppm) were prepared by dilution with bidistilled water.

Preparation of extract

149 g of *Euphorbia heterophylla* powder was weighed and differently soaked in nearly 900 mL of methanol. The mixture was kept for two weeks to enhance proper mixing of the solvent with the powder at room temperature, and then poured into the air-tight glass container, and allowed to dry under shade. The mixtures were first filtered with cheese cloth, then with What Man No 1 filter paper (24 cm). The filtrates were then separated, kept in front of a fan at room temperature to evaporate

the solvent and to concentrate the filtrates to complete dryness. The extract was stored in an air-tight glass at room temperature and left for use.

Weight loss method

Copper specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the extract for three hours. The weight of the specimens before and after immersion was determined using analytical balance to the nearest 0.0001 g and the weight loss per unit area was calculated as:

$$\Delta W = \frac{W_1 - W_2}{a} \quad (1)$$

Where W_1 and W_2 are the weights in grams of the test piece before and after immersion, respectively, and (a) is the surface area in cm^2 . The degree of surface coverage (θ) and the inhibition efficiency (Eff. %) were calculated from the following equation:

$$\text{Eff. \%} = \theta \times 100 = \left[1 - \frac{\Delta W}{\Delta W'} \right] \times 100 \quad (2)$$

Where ΔW and $\Delta W'$ are the weight losses in the presence and absence of extract, respectively

Tafel polarization tests

A three electrode set up was employed with Pt foil as the auxiliary electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode was in the form of a square cut from copper sheet of equal composition embedded in the epoxy resin of polytetrafluoroethylene so that the flat surface area was 1 cm^2 prepared as described in the gravimetric experimental method. Before tests, the electrode was immersed in the solution for 30 min until a steady state was reached. The potentials were swept at the rate of 1 mVs^{-1} , primarily from more negative potential than open circuit potential (E_{ocp}) to a more positive potential than E_{ocp} through, corrosion potential (E_{corr}). All experiments were carried out in freshly prepared solutions at 25°C and results were always repeated at least three times to check the reproducibility. Then i_{corr} was used for the calculation of inhibition efficiency and surface coverage (θ) as below:

$$\text{Eff. \%} = \theta \times 100 = 1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (3)$$

Where i_{corr}^0 and i_{corr} are corrosion current densities in the absence and presence of the extract, respectively.

Impedance tests

The electrochemical impedance spectroscopy (EIS) measurements were carried out using the same cell setup employed for the Tafel polarization. The measurements were carried out in the frequency range of 10^5 to 10^{-2} Hz. at the open circuit potential by superimposing a sinusoidal AC signal of small amplitude, 5 mV, after immersion for 30 min in the corrosive media. The double layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}) were determined from the impedance plots as before¹⁶. R_{ct} is inversely proportional to i_{corr} , it was used to determine the inhibition efficiency (Eff. %) using the relationship:

$$\text{Eff. \%} = \left[1 - \frac{R_{\text{ct}}^0}{R_{\text{ct}}} \right] \times 100 \quad (4)$$

Where R_{ct} and R_{ct}^0 are the charge transfer resistance values in the uninhibited and inhibited solutions, respectively

Electrochemical Frequency Modulation (EFM) tests

EFM experiments were performed by applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The larger peaks were used to calculate the i_{corr} , the Tafel slopes (β_c and β_a) and the causality factors CF-2 and CF-3. The electrode potential was allowed to stabilize for 30 min before starting the measurements. All the experiments were conducted at 25°C .

Tafel polarization, EIS and EFM measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ ZRA (PCI4-G750). This includes Gamry applications, DC105 software for DC corrosion, EIS300 software for EIS, and EFM140 for measurements along with a computer for collecting data. Echem analyst v 6.03 software was used for plotting, graphing, and fitting data.

Surface morphology

For the morphological study, surface features ($2 \times 2 \times 0.2 \text{ cm}$) of copper were abraded and treated as in weight loss method, then were examined before and after exposure to 0.5 M HNO_3 solutions for 24 hrs. with and without the extract. JEOL JSM-5500 scanning electron microscope was used for this investigation.

RESULTS AND DISCUSSION

Gravimetric method

Figure 2 represents the variation of weight loss with time for copper in 0.5 M HNO_3 in the absence and presence of different doses of *Euphorbia heterophylla* extract. It is clear that by increasing the doses of this extract, the weight loss of copper sample is decreased and hence, the Eff. % increases. The maximum corrosion inhibition was found at 25 ppm. This means that the presence of this extract retards the corrosion of copper

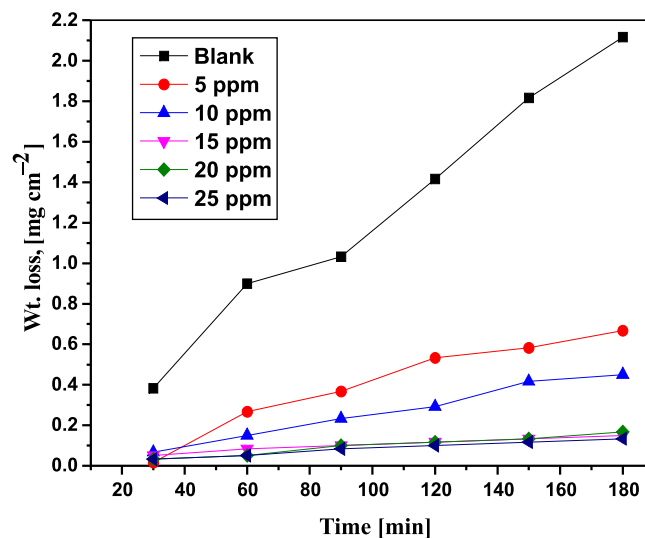


Figure 2. Weight loss – time curves for the dissolution of copper in the absence and presence of different doses of *E. heterophylla* plant extraction at 25°C

in 0.5 M nitric acid or in other words, this extract acts as the inhibitor. The increase of Eff.% by increasing doses of the targeted extract showed that the inhibition process is affected by the adsorption of extract molecules onto the copper surface. In the absence of any surface films, the extract components are first adsorbed onto the metal surface and thereafter impede corrosion by merely blocking the reaction.

Effect of temperature

The effect of temperature on the corrosion rate of copper in 0.5 M HNO₃ solution in absence and presence of different doses of the *Euphorbia heterophylla* plant extract was studied at different temperatures (25–40°C) by weight loss method. It is clear that from Table 1 that the weight loss values increase at all doses with raising the temperature. This may be attributed to desorption of plant extract components from the surface of copper at higher temperatures. The increase in weight loss values with increasing temperature is suggestive of physical adsorption¹⁷ of these extract components on the surface of copper metal.

Table 1 shows the effect of temperature on the Eff.% at different doses for the tested extract. Inspection of this table it was found that the Eff.% decreases with raising the temperature. Also, the Eff.% increases with increasing the concentration of plant extract.

The increase in temperature might stimulate larger metal surface kinetic energy, which has an adverse effect on the adsorption process where it weakens the adsorption process and encourage desorption process, hence the equilibrium shift towards desorption¹⁸.

The thermodynamic parameters of the corrosion process were calculated from Arrhenius-type equation [Eq. (5)] and transition-state equation [Eq. (6)] as follows¹⁹:

$$\text{Rate}(k) = A e^{\frac{-E_a^*}{RT}} \quad (5)$$

$$\text{Rate}(k) = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \quad (6)$$

Where E_a^* represents the apparent activation energy, R is the gas constant, T is the absolute temperature, A is the pre-exponential factor, k is the corrosion rate, ΔS^* is the entropy of activation, ΔH^* is the enthalpy of activation, h is Planck's constant and N is the Avogadro's number. Figure 3 represents the plot of the log rate vs. 1/T and Figure 4 represents plots of the log (rate/T) vs. 1/T. The calculated values of the apparent E_a^* , ΔS^* and ΔH^* are given in Table 2. Inspection of these data revealed that the apparent activation energy in HNO₃ solution in the absence of extract was 58.2 kJ mol⁻¹ which is in good agreement with the values obtained by Fouda et al²⁰ in which they found that the activation energy of copper in 3 M HNO₃ is 72.4 kJ mol⁻¹. Also, since the activation energy (E_a^*) was more than 40 kJ mol⁻¹, the

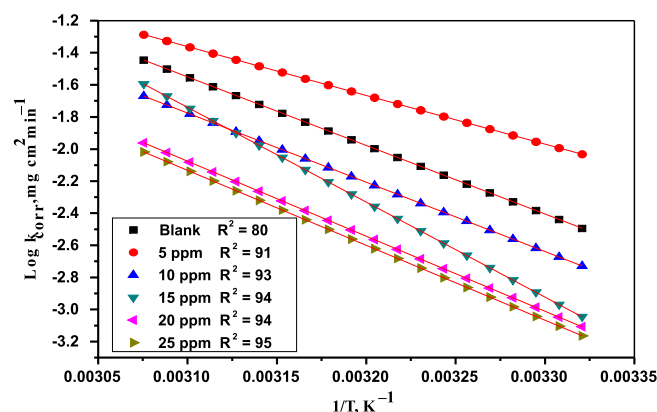


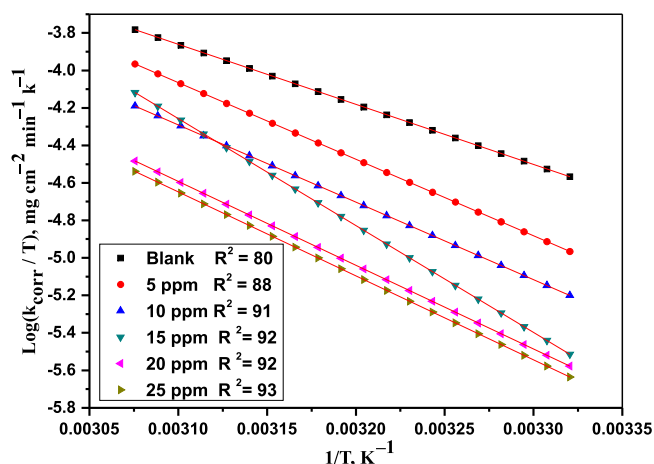
Figure 3. Log corrosion rate vs. 1/T curves for copper dissolution in absence and presence of different doses of *E. heterophylla* plant extract

Table 1. Percentage inhibition efficiency of plant extracts at different doses of extract as determined from gravimetric method at different temperatures, duration of the experiment: 120 min immersion

Temperature [°C]	C _{inh} [ppm]	W [mg]	CR [mgcm ⁻² min ⁻¹]	θ	[%] Eff.
25	B	2.086	0.017	–	–
	5	0.793	0.007	0.620	62.0
	10	0.483	0.004	0.769	76.9
	15	0.414	0.003	0.802	80.2
	20	0.241	0.002	0.885	88.5
	25	0.207	0.002	0.901	90.1
30	B	1.650	0.014	–	–
	5	0.897	0.007	0.456	45.6
	10	0.576	0.005	0.651	65.1
	15	0.483	0.004	0.707	70.7
	20	0.259	0.002	0.843	84.3
	25	0.241	0.002	0.854	85.4
35	B	4.828	0.040	–	–
	5	2.897	0.024	0.400	40.0
	10	1.699	0.014	0.648	64.8
	15	1.520	0.013	0.685	68.5
	20	0.777	0.006	0.839	83.9
	25	0.718	0.006	0.851	85.1
40	B	5.600	0.047	–	–
	5	3.472	0.029	0.380	38.0
	10	1.976	0.016	0.647	64.7
	15	1.959	0.016	0.650	65.0
	20	1.016	0.008	0.819	81.9
	25	0.838	0.007	0.850	85.0

Table 2. Activation parameters, pre-exponential factor (A), activation energy (E_a^*), enthalpy (ΔH^*) and entropy (ΔS^*) of dissolution of copper in 0.5 M HNO_3 containing various doses of the extract

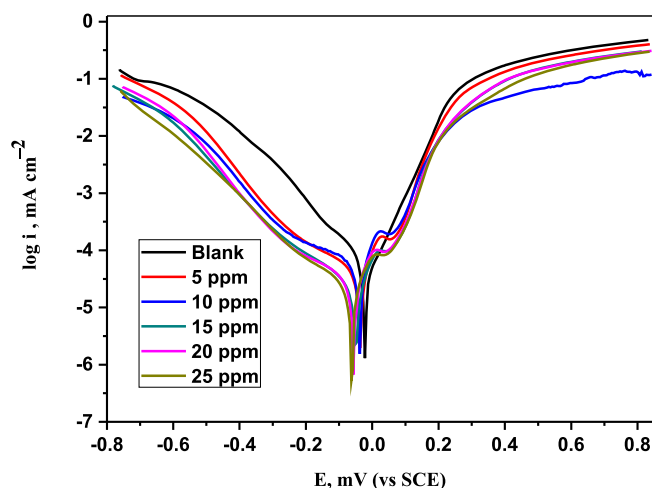
Dose [ppm]	A [$\text{mg cm}^{-2} \text{min}^{-1}$]	E_a^* [kJ mol^{-1}]	ΔH^* [kJ mol^{-1}]	$-\Delta S^*$ [$\text{J mol}^{-1} \text{K}^{-1}$]
0.0	8.06	58.2	26.6	81.5
5	11.70	81.9	33.9	32.9
10	11.61	82.7	34.3	34.6
15	16.59	113.2	47.4	59.4
20	12.41	89.4	37.2	20.2
25	12.35	89.5	37.3	20.6

**Figure 4.** Log corrosion rate/T vs.1/T curves for copper dissolution in the absence and presence of different doses of *E. heterophylla* plant extract

process is diffusion controlled. The increase of E_a^* in the presence of the extract indicated the physical adsorption or weak chemical bonding between the extract component molecules and copper surface²¹. Higher values of E_a in the presence of extract could also be correlated with the increase in thickness of the double layer that enhances the E_a of the corrosion process²². The entropy of activation in the absence and presence of extract was negative. This implied that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place in going from reactants to the activated complex²³. It was observed that the shift of ΔS^* to more positive values on increasing the concentration of the extract is the driving force that can overcome the barriers for the adsorption of extract onto the copper surface. The positive sign of ΔH^* indicated that the corrosion process is endothermic one.

Polarization studies

Both the anodic and cathodic polarization curves of copper in 0.5 M HNO_3 in the absence and presence of different doses of *E. heterophylla* are shown in Figure 5. It is clear that the polarization behavior of copper in

**Figure 5.** Potentiodynamic polarization curves for the corrosion of copper in 0.5 M HNO_3 in the absence and presence of different doses of *E. heterophylla* plant extract at 25°C

this media follows almost similar pattern. Various corrosion kinetic parameters such as E_{corr} , i_{corr} , and Tafel slopes β_a and β_c derived from the polarization curves are given in Table 3. From these data it was concluded that this extract behaved, did not as mixed-type inhibitor (the presence of extract does not prominently shift the corrosion potential) and also the presence of this extract caused a remarkable decrease in the corrosion rate (Hence increase in Eff.) i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be attributed to adsorption of the extract over the corroded surface. Both β_a and β_c change upon addition of the extract, and which indicates that the extract affects both anodic and cathodic reactions²⁴. The data of Table 3 show the increasing of the % Eff. of this plant extract with increasing of concentration and the decrease of corrosion rate (CR) obtained from polarization method at 30°C. For anodic polarization in the presence of different doses, higher anodic currents were produced, indicating the desorption of adsorbed extract components from the electrode surface. The almost unchanged Tafel slopes in the presence of the extract indicated that the extract

Table 3. The effect of concentration of *E. heterophylla* on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (% Eff.), degree of surface coverage (θ) and corrosion rate for the corrosion of copper in 0.5 M HNO_3 at 25°C

Dose [ppm]	$-E_{\text{corr}}$ [mV vs SCE]	i_{corr} [mA cm^{-2}]	$-\beta_c$ [mV dec^{-1}]	β_a [mV dec^{-1}]	θ	[%] Eff.	C.R. [mm^{-1}]
0.0	23	146.0	233	226	–	–	80.99
5	40	34.7	219	205	0.762	76.2	19.19
10	36	28.5	195	197	0.805	80.5	15.74
15	56	18	191	198	0.877	87.7	9.93
20	52	21.7	204	194	0.851	85.1	11.97
25	62	22.0	207	202	0.849	84.9	12.20

acted by merely blocking the reaction sites of the metal surface without changing the anodic and cathodic reaction mechanisms. There was a good agreement between the results obtained from the weight loss and potentiodynamic polarization measurements.

Adsorption isotherms

Attempts were made to fit θ values to various isotherms including Frumkin, Langmuir and Temkin. By far the best fit was obtained with Frumkin isotherm²⁵. This Frumkin model has been used for other inhibitor systems²⁶. According to this isotherm θ is related to the concentration of inhibitor via:

$$KC = \frac{\theta}{1-\theta} e^{(-2a\theta)} \tag{7}$$

Or its linear form:

$$\ln \left[\frac{C \theta}{1-\theta} \right] = \ln K + 2a\theta \tag{8}$$

where (K) is the equilibrium constant of the adsorption reaction, (C) is the extract concentration in the bulk of the solution, (a) is the parameter of interaction between molecules adsorbed on the metal surface. The surface coverage, i.e., the fraction of the surface covered by the inhibitor molecules, θ was calculated.

Figure 6 represents the linear relationship of the Frumkin adsorption isotherm. By plotting $\ln [\theta / (1 - \theta) C]$ vs. θ straight lines were obtained for investigated extract (data obtained from weight loss method). The equilibrium constant (K) is related to the free energy of adsorption (ΔG°_{ads}) by:

$$K = \frac{1}{55.5} e^{\frac{\Delta G^\circ_{ads}}{RT}} \tag{9}$$

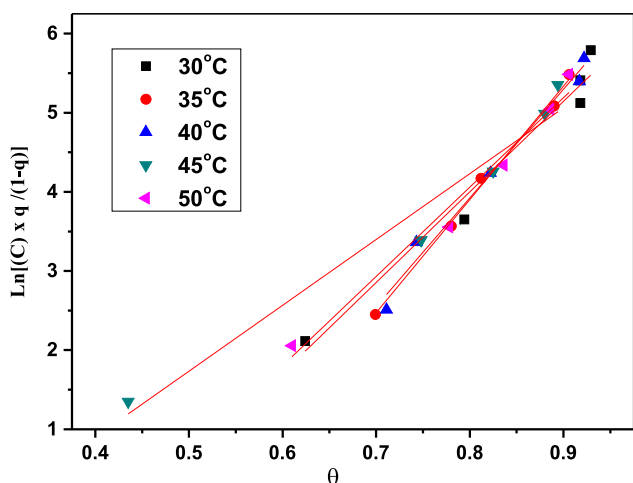


Figure 6. Linear form of Frumkin adsorption isotherms for copper corrosion in 0.5 M HNO₃ in the presence of different doses *E. heterophylla* plant extract from weight loss measurements at different temperatures

Table 4. Interaction parameter (a), adsorption equilibrium constant (K), free energy (ΔG°_{ads}) and regression constant (R^2) of Cu dissolution in the presence of investigated plant extract at 25°C in 0.5 M HNO₃

Temperature [°C]	a	K [M ⁻¹]	$-\Delta G^\circ_{ads}$ [kJ mol ⁻¹]	R ²
30	11.44	5.15	14.0	0.98846
35	14.31	7.55	15.0	0.99772
40	13.73	7.06	14.8	0.9917
45	8.32	2.42	12.1	0.98291
50	11.28	4.96	13.9	0.98945

where 55.5 is the molar concentration of water in solution in mol L⁻¹. The linear fitting slope for the Frumkin isotherm gave the values of (a) and the intercepts gave the values of (K) for the investigated extract. The results are given in Table 4. The increasing values of K reflect the increasing capability, due to the structural formation, on the metal surface²⁷, and also, the lower values of ΔG°_{ads} (< 20 kJ mol⁻¹) indicated that this extract is physically adsorbed on the copper surface.

Electrochemical Impedance Spectroscopy (EIS) studies

Figures 7 and 8 showed the Nyquist and Bode plots for copper in 0.5 M HNO₃ solution in the absence and presence of different doses of *E. heterophylla* extract. The obtained Nyquist impedance diagram in most cases did not show perfect semicircle, generally attributed to the frequency dispersion²⁸ as a result of roughness and inhomogeneities of the electrode surface. The data revealed

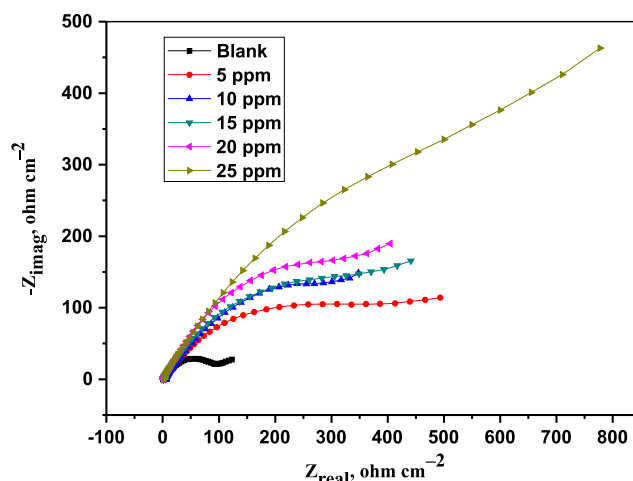


Figure 7. The Nyquist plot for copper metal in 0.5 M HNO₃ solution in the absence and presence of different doses of *E. heterophylla* extract at 25°C

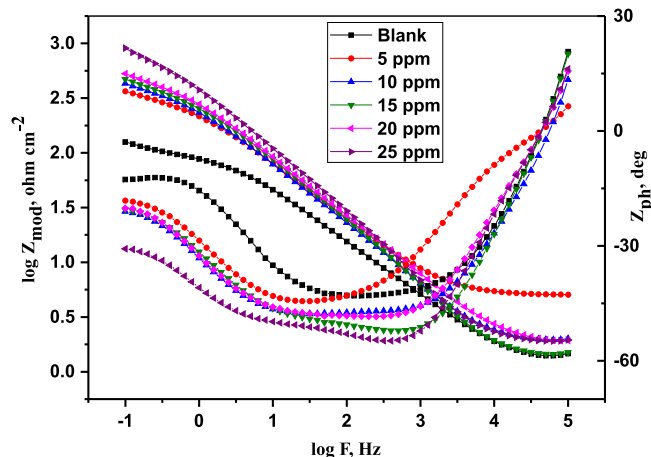


Figure 8. The Bode plot for copper in 0.5 M HNO₃ solution in the absence and presence of different doses of *E. heterophylla* at 25°C

that each impedance diagram consists of a large capacitive loop with low frequencies dispersion (inductive arc). The increase in the capacitive loop size with the addition of extract shows that a barrier gradually forms on the Cu surface, protecting it from corrosion. In most cases, the capacitive loops are depressed semicircles rather than regular ones, which are related to a phenomenon called the dispersion effect. In the high frequency region, a charge-transfer process controls the electrode reaction. A Warburg diffusion tail was observed at low frequency values. The tails are inclined at an angle of 45° to the real-axis at the low frequencies, a diffusion controlled process therefore exists. As known in the literature²⁹ the diffusion process is controlled by diffusion of the O_2 from the bulk of solution to the electrode surface. Even at the high concentration of the extract the diffusion tail still appears. This means that the corrosion behavior of Cu with and without the extract is influenced by mass transport. The impedance spectra for different Nyquist and Bode plots were analyzed by fitting the experimental spectra data to equivalent circuit model, Figure 9, which included, W stands for the Warburg impedance, the solution resistance (R_s) and the double layer capacitance (C_{dl}) which is placed in parallel to charge transfer resistance element, (R_{ct}). Values of elements fitted with the equivalent circuit in Figure 9 are listed in Table 5. From the impedance data given in Table 5, it was concluded that:

- As the impedance diagram obtained has a semicircle appearance, it showed that the corrosion of copper is mainly controlled by a charge transfer process
- The value of R_{ct} increased with increase in the concentration of the extract. This is due to the adsorption of the extract components on the electrode surface leading to a film formation on the copper surface and this indicated the increase in the corrosion inhibition efficiency in acidic solution
- The value of C_{dl} decreased by increasing the extract concentration. This is due to the increase in dielectric constant resulting from the replacement of extract components by the water molecules adsorbed on Cu surface and also due to the increase in the thickness of the adsorbed layer
- It was observed that the value of % IE increases with increase in the extract concentration up to 25 ppm reaching a maximum 89.6%. This result suggests that this extract is good inhibitor for Cu

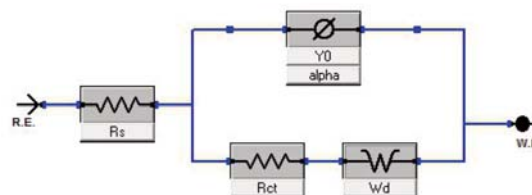


Figure 9. Equivalent circuit model used to fit the impedance data

in HNO_3 . Values of R_{ct} , C_{dl} and % IE calculated from impedance plots were in good agreement with that obtained from weight-loss and polarization measurements.

Electrochemical Frequency Modulation (EFM) studies

Results of EFM experiments is a spectrum of current response as the function of frequency. The spectrum is called the “inter modulation spectrum” and an example was shown in Figure 10. The corrosion parameters such

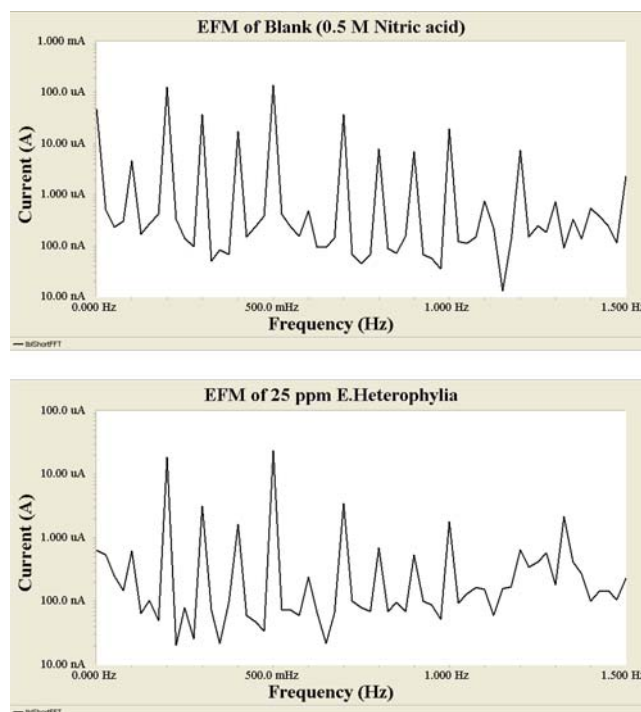


Figure 10. EFM spectra for copper in the absence and presence of 25 ppm of *E. heterophylla* extract in 0.5 M HNO_3

Table 5. Electrochemical kinetic parameters obtained by EIS technique for the corrosion of copper in 0.5 M HNO_3 at different doses of investigated plant extract at $25^\circ C$

Dose [ppm]	R_{ct} , [$\Omega \text{ cm}^2$]	C_{dl} , [$\mu F \text{ cm}^{-2}$]	W , $\times 10^{-3}$	θ	[%] Eff.
0.0	105.2	4.24	44.80	—	—
5	351.9	3.96	12.70	70.9	0.709
10	356.4	3.93	5.62	71.2	0.712
15	396.5	3.13	8.32	73.5	0.735
20	512.3	2.64	8.66	80.6	0.806
25	545.8	2.21	8.18	81.4	0.814

Table 6. Electrochemical kinetic parameters obtained by EFM for copper in the absence and presence of various doses of plant extracts as inhibitors in 0.5 M HNO_3 at $25^\circ C$

Conc [ppm]	i_{corr} , [$\mu A \text{ cm}^{-2}$]	β_c , [$mV \text{ dec}^{-1}$]	β_a , [$mV \text{ dec}^{-1}$]	CF2	CF3	θ	[%] Eff.	CR , [$\mu m \text{ yr}^{-1}$]
0.0	163.40	253	47	2.01	4.86	0.00	—	90.35
5	55.65	147	49	1.91	3.55	0.659	65.9	30.77
10	45.64	152	51	1.88	1.90	0.721	72.1	25.23
15	42.60	116	46	1.94	3.36	0.739	73.9	23.56
20	34.36	109	46	1.91	3.23	0.790	79.0	19.00
25	26.23	133	58	1.95	2.64	0.839	83.9	14.50

as % Eff., i_{corr} , β_a , β_c and causality factors (CF-2 and CF-3), at different doses of additive extract in 0.5 M HNO_3 solution at 25°C are presented in Table 6. Table 6 the corrosion current densities decreased by increasing the concentration of *E. heterophylla* extract. The causality factors indicated that the measured data are of good quality. If the causality factors are approximately equal to the predicted values of 2 and 3, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable³⁰. When CF-2 and CF-3 were in the range 2 and 3, respectively, then the EFM data is valid. The deviation of causality factors from their ideal values might be due to that the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well³¹. Figure 11 showed the inhibition efficiencies recorded for *E. Heterophylla*, at various doses using the four different techniques,

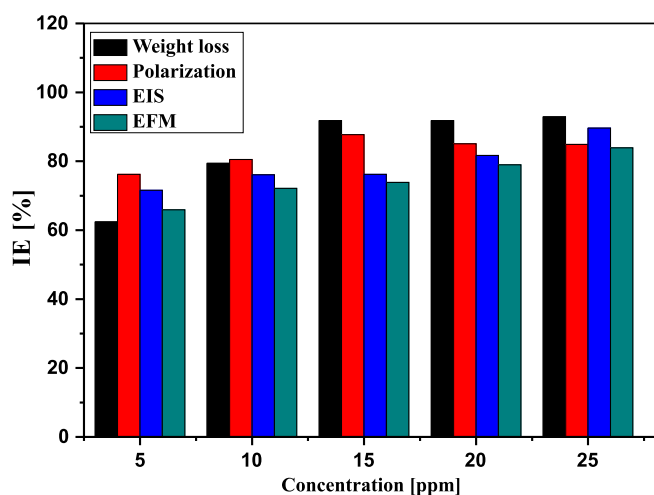


Figure 11. Effect of dose of extract on the inhibition efficiency obtained from different techniques

namely weight loss, Tafel polarization, EIS and EFM. The calculated inhibition efficiencies obtained are in good agreement.

Surface morphological examination

The morphology of the corroded surface of each specimen was studied using scanning electron microscope

(SEM). All micrographs of corroded specimens were taken at a magnification of (x500). Scanning electron micrographs Figure 12 are achieved for copper metal surface immersed for 12 hours in 0.5 M HNO_3 solution in the absence (a) and presence of 25 ppm *E. heterophylla* plant extract (b). The results are shown in Figure 12a revealed that the copper specimen exhibits a very rough surface in the absence of extract due to corrosive attack by the acid solution. In the presence of the extract Figure 12b surface roughness the inhibiting effect of the extract. The attack was relatively uniform with slight evidence of selective corrosion.

Mechanism of inhibition

Adsorption process can occur through the replacement of solvent molecules from the metal surface by ions and molecules accumulated near the metal/solution interface. Ions can accumulate at the metal/solution interface in excess of those required to balance the charge on the metal at the operating potential. These ions replace solvent molecules from the metal surface and their centers reside at the inner Helmholtz plane. This phenomenon is termed specific adsorption³². Photochemical analysis of *E. heterophylla* revealed the presence of reducing sugar, alkaloids, flavonoids, saponins, sterols, tannins and triterpenoids in the whole plant. These chemical constituents are rich in hetero atoms, functional group, and π -electrons. Corrosion inhibition by *E. heterophylla* can be regarded as a synergistic process involving these chemical constituents. The structures of one of the constituents of *E. heterophylla* extract are given in Figure 1. The high performance *E. heterophylla* extract could also be due to the large size of the constituent molecules, which covered larger areas on the metal surface, thus retarding corrosion³³. Also, the high inhibition efficiency shown by *E. heterophylla* extract could be attributed to the presence of hetero atoms and CH_3 groups which enhanced the inhibition efficiency. It was not possible to consider a single adsorption mode between inhibitor and metal surface because of the complex nature of adsorption and inhibition of a given inhibitor. The adsorption of main constituents of *E. heterophylla* extract could be attributed to the presence of O-atoms, π -electrons, and aromatic/heterocyclic rings. Therefore, the possible reaction centers are unshared electron pair of hetero atoms

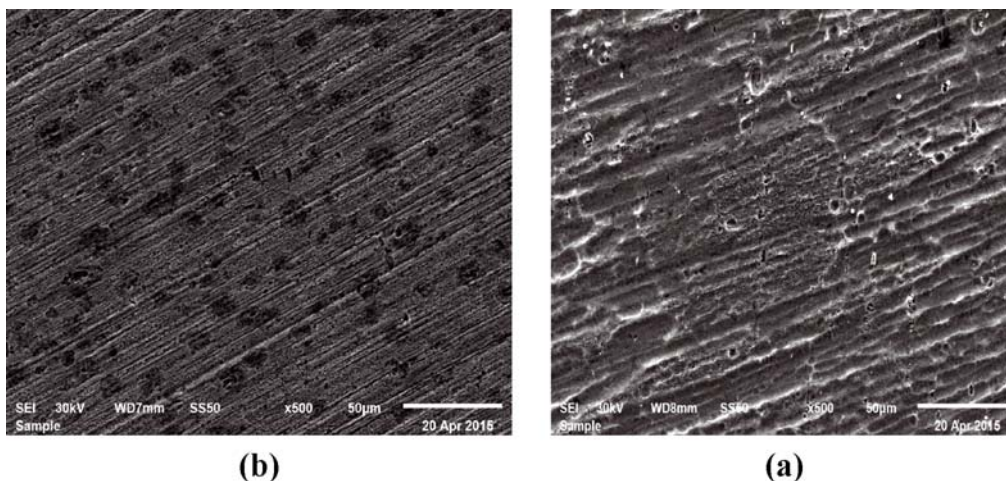


Figure 12. (a) SEM micrograph (x500) of copper immersed in 0.5M HNO_3 at 25°C (b) SEM. micrograph (x500) of copper immersed in 0.5 M HNO_3 at 25°C in presence of *E. heterophylla* of concentration 25 ppm

and π -electrons of the aromatic/heterocyclic ring. In aqueous acidic solutions, main constituents exist either as neutral molecules or as protonated molecules (cations). The constituents may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed NO_3^- ions, (ii) donor-acceptor interaction between the π -electrons of the aromatic ring and vacant d-orbital of surface iron atoms, and (iii) interaction between unshared electron pairs of hetero atoms and vacant d-orbital of iron surface atoms. It is well known that the copper surface bears positive charge in acid solution³⁴, so it was difficult for the protonated molecules to approach the positively charged copper surface (H_3O^+ /metal interface) due to the electrostatic repulsion. Thus, inhibition of copper corrosion in 0.5 M HNO_3 was due to the adsorption of extract constituents on the copper surface.

CONCLUSIONS

The following conclusions could be drawn:

E. heterophylla plant extract was found to act as save corrosion inhibitor for the corrosion of Cu in 0.5 M HNO_3 . The results of the investigation show that the inhibiting properties of the extract depend on concentration and temperature. The adsorption of the extract components on Cu surface was found to follow Frumkin adsorption isotherm. The values of E_a^* and $\Delta G_{\text{ads}}^\circ$ indicated the physical adsorption of this extract on the copper surface. Potentiodynamic polarization studies have shown that this extract acts as the mixed-type inhibitor. Thermodynamic parameters also revealed that the adsorption process is spontaneous. EIS and EFM measurements are in good agreement with weight loss results. Scanning electron microscope (SEM) showed that *E. heterophylla* extract was acting as good inhibitor

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