Corrosion Inhibition of Copper in Nitric Acid Using *Lawsonia* Extract as Green Inhibitor

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Abstract

The inhibitive action of henna leaves (*Lawsonia Inermis*) extract on corrosion of copper in nitric acid solution was investigated through weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic methods at different temperature. The effect of inhibitor concentrations on different acid concentrations was investigated. The present study revealed that the percentage of inhibition efficiency is enhanced with increase of inhibitor concentration and decrease with increase in temperature. The inhibitive action of the extract is discussed in view of adsorption of *Lawsonia* molecules on the metal surface. It was found that the adsorption follows Langmuir adsorption isotherm. Tafel plot of polarization study indicate that the *Lawsonia* extract acts as a mixed type inhibitor. Inhibition efficiency of *Lawsonia* extract was found up to 98%.

Keywords: Corrosion; Copper; *Lawsonia* extract; Nitric acid; Inhibitor.

1. Introduction

Corrosion of metal can be defined as the deterioration of materials due to their reaction with the environment. Copper and its alloys are widely used material for its excellent electrical and thermal conductivities in many industrial applications such as electronics and in the manufacture of integrated circuits. Copper is a relatively noble metal, requiring strong oxidants for its corrosion or dissolution; its corrosion resistance becomes less while the aggressive solution concentration increases [1, 2]. Copper corrosion in nitric acid solution induced a great deal of research [3, 4]. It is noticed that presence of heteroatom such as nitrogen [5, 6], oxygen [7, 8], phosphorus [9] and sulphur [10, 11] in the organic compound molecule improves its action as corrosion inhibition. However, as a result of their high cost, toxicity and increasing awareness of health and ecological risks, attention is being drawn towards finding highly efficient, cheaper and non-toxic inhibitors. The present trend in research on environmental friendly corrosion inhibitors is concentrating on products of natural origin due principally to their low cost and eco-friendliness.

The aim of the present work is to develop eco-friendly corrosion inhibitors, with good inhibition efficiency (IE) at low risk of environmental pollution [12]. From many decades, plant extracts have attracted attention in the field of corrosion inhibition. As natural products, they are a source of non-toxic, eco-friendly, bio-degradable and of potentially low cost inhibitors for preventing metal corrosion [13]. Most of the naturally occurring substances are safe and can be extracted by simple procedure. The inhibitive action of leaves extract of *Azadirachta indica* on copper corrosion in HNO_3 solutions was studied using weight loss and electrochemical techniques [14]. The results obtained indicated that the extracts functioned as good inhibitors in HNO_3 solutions.

Henna (*Lawsonia Inermis*), a herb which has interesting dyeing properties used for centuries in Asia and North Africa for traditional decoration of the skin and hair. *Lawsonia Inermis* has anti-inflammatory, antipyretic and analgesic effect [15-16]. Henna has been used as corrosion inhibitor for aluminium and steel in aggressive solution [17], iron in hydrochloric acid [18] and aluminium in hydrochloric acid [19-20]. El- Etre A.Y. et al. [21] studied the inhibiting action of *Lawsonia* extract on the corrosion of different metals. The corrosion inhibition efficacy of these extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as their acid hydrolysis products.

In the present work, inhibitive action of *Lawsonia* leaves extract as a cheap, eco friendly and naturally occurring substance on corrosion behavior of copper in HNO_3 solution has been investigated through weight loss, polarization measurements and electrochemical impedance spectroscopy methods.

2. Experimental section

2.1. *Sample and Solution preparation*

The copper specimens of the size 4.5 × 2.0 × 0.178 cm having an effective area 0.1988 dm^2 with a chemical composition (99.99 % Cu and 0.01% S) was used. The specimens mechanically abraded using different grades of emery papers, cleaned by washing with distilled water, degreased with acetone, washed once more with distilled water and finally dried and weighted by using electronic balance. The corrosive solutions were prepared by dilution of analytical grade of 69% HNO_3 (Merck) using distilled water.

2.2. *Extract preparation*

Lawsonia inermis leaves were dried, crushed and extracted in boiled water for 2 h. The extracted solution was then filtered and concentrated until the water from the extract evaporates [22]. This extract was used to study the corrosion inhibition properties and to prepare the required concentrations of *Lawsonia inermis* varied from 0.6, 0.8, 1.0 and 1.2 g/L.

2.3. *Weight loss measurement*

For weight-loss experiment, the copper coupons were each suspended completely in 0.5, 0.75 and 1.0 M HNO_3 solutions without and with different concentrations of *Lawsonia* extract with the help of glass hooks at 301±1 K for 24h (1 day). The volume of solution kept 230 ml. The coupons were retrieved after 24 h, washed by distilled water, dried well and reweighed. From the weight loss data, corrosion rate in mg/dm^2d was calculated.

2.4. *Temperature effect*

To study the effect of temperature on corrosion rate, the copper coupons were completely immersed in 230 ml of 1.0 M HNO_3 solution without and with different concentrations of *Lawsonia* extract at 313, 323 and 333 K for 2h. From the data, inhibition efficiency, energy of activation (E_a) and heat of adsorption (Q_{ads}) were calculated.

2.5. *Electrochemical measurements*

Electrochemical measurements were carried out by using an electrochemical work station (CHI608C-series, U.S. Model with CH instrument). In electrochemical experiment Ag/AgCl was used as a reference electrode, platinum as an auxiliary electrode and copper metal was used as a working electrode. For polarization study, copper specimens having an area of 1 cm^2 exposed to 230 ml 0.5 M HNO_3 in absence and presence of *Lawsonia* extract and allowed to establish a steady-state open circuit potential (OCP) for about 30 minutes. Test coupons were then polarized by the application of potential drift of −250 mV cathodically and +250 mV anodically with respect to the OCP at a scan rate of 5.0 mV/s. The potentiodynamic polarization plots (Tafel curves) were developed simultaneously. Anodic and cathodic polarization curves give anodic and cathodic Tafel lines correspondingly. The intersect point of Tafel lines gives the corrosion potential (E_{corr}) and corrosion current (i_{corr}) [21]. The electrochemical impedance studies were carried out in the same setup using potentiodynamic polarization studies described above. Impedance studies were carried out at steady-state open circuit potential (OCP). A small amplitude (5.0 mV) sinusoidal ac Voltage, in wide frequency range 1 to 100 KH_z was applied over the system. A graph was drawn by plotting real impedance (Z') versus imaginary impedance (Z″). From the Nyquist plots the charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) were calculated. Impedance measurements were carried out both in the absence and presence of *Lawsonia* extract.

3. Results and discussion

3.1. *Weight loss experiment*

The corrosion rate of copper in 0.5, 0.75 and 1.0 M of HNO_3 solution without and with different concentration of *Lawsonia* extract 0.6, 0.8, 1.0 and 1.2 g/L at 301±1 K for an exposure period of 24h (1 day) was calculated from the weight loss data using following equation:

$$\mathrm{CR}\ (\mathrm{mg/dm^2 d}) = \frac{\text{Weight loss (gm) x 1000}}{\text{(metal surface area) dm}^2 \text{ x day}} \tag{1}$$

The Inhibition efficiency (IE) was calculated by using following formula,

$$\mathrm{IE}(\%) = \frac{W_{uninh} - W_{inh}}{W_{uninhi}} \text{ x } 100 \tag{2}$$

where, W_u = Weight loss without inhibitor, W_i = Weight loss with inhibitor.

The degree of surface coverage (θ) for different concentration of the inhibitor in acidic media have been evaluated from weight loss experiments using this equation,

$$\theta = \frac{W_{uninh} - W_{inh}}{W_{uninhi}} \tag{3}$$

Table 1. Corrosion rate for copper in various HNO_3 concentrations in the absence and presence of different concentrations of *Lawsonia* extract from weight loss measurements at 301±1 K.

Inhibitor concentration (g/L)	Acid concentration					
	0.5 M		0.75 M		1.0 M	
	CR (mg/dm^2d)	IE (%)	CR (mg/dm^2d)	IE (%)	CR (mg/dm^2d)	IE (%)
Blank	90.52	–	281.55	–	1030.67	–
0.6	20.11	77.78	80.45	71.43	477.65	53.66
0.8	15.08	83.34	60.33	78.57	236.31	77.07
1.0	10.06	88.89	45.25	83.93	181.00	82.44
1.2	4.02	95.56	20.11	92.86	105.59	89.76

Results showed in Table 1 indicate that as the concentration of acid increases corrosion rate was increases. The corrosion rate was 90.52, 281.55 and 1030.67 mg/dm^{2}d for 0.5, 0.75 and 1.0 M HNO_3 concentrations respectively for an immersion period of 24 h at 301±1 K.

At constant acid concentration, the IE increases with increase *Lawsonia* extract concentrations, e.g. *Lawsonia* extract in 0.5 M HNO_3 solution, the IE found to be 77.78, 83.34, 88.89 and 95.56 % with respect to 0.6, 0.8, 1.0 and 1.2 g/L inhibitor concentrations (Table 1). At constant inhibitor concentration, the IE was decreases as the acid concentration increases, e.g. for 0.6 g/L *Lawsonia* extract, the IE was found to be 77.78, 71.43 and 53.66 % with respect to 0.5, 0.75 and 1.0 M HNO_3 solution (Table 1).

Table 2. Corrosion rate (log ρ) of copper in 0.5 M HNO_3 in absence and presence of *Lawsonia* extract for an immersion period of 24 h at 301 ± 1K.

Inhibitor concentration (C) (g/L)	CR (ρ)	log ρ	IE (%)	surface coverage (θ)	1–θ
Blank	90.52	1.9567	–	–	–
0.6	20.11	1.3034	77.78	0.7778	0.2222
0.8	15.08	1.1784	83.34	0.8334	0.1666
1.0	10.06	1.0026	88.89	0.8889	0.1111
1.2	4.02	0.6042	95.56	0.9556	0.0444

The results obtained were presented in Table 2 and in Fig. 1&2, which indicates that with increase in inhibitor concentration from 0.6 to 1.2 g/L the corrosion rate was decreased from 20.11 to 4.02 mg/dm^{2}d while IE increases from 77.78 to 95.56 %. It can be concluded that IE is directly proportional to the inhibitor concentration.

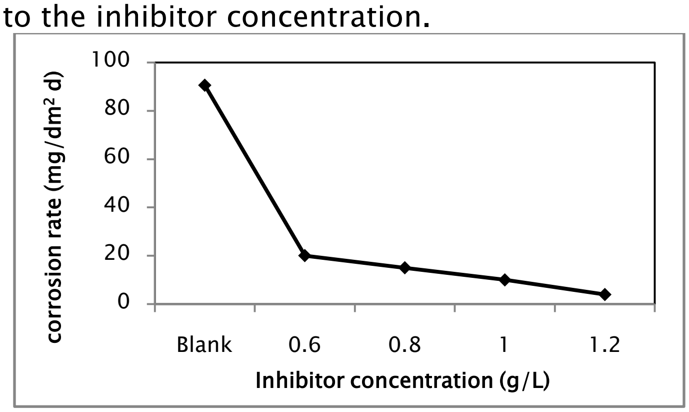

Fig.1. Corrosion rate of copper corrosion in 0.5 M HNO_3 solution in absence and presence of different concentration of *Lawsonia* extract for an immersion period of 24h (1 day).

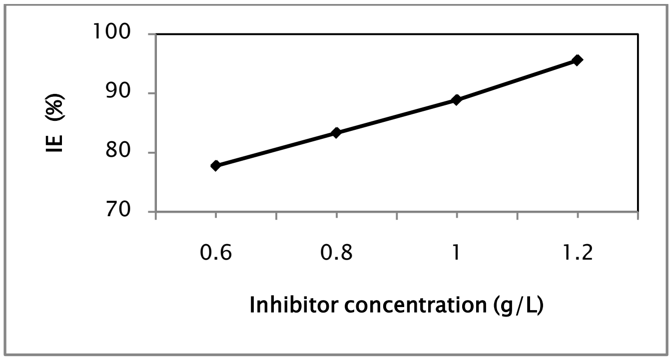

Fig.2. IE of copper corrosion in 0.5 M HNO_3 solution in presence of different concentration of *Lawsonia* extract for an immersion period of 24h (1 day).

3.2. *Temperature effect*

To investigate the influence of temperature on corrosion of copper, the weight-loss experiments were carried out at temperature 313, 323 and 333K in 1.0 M HNO_3 without and with *Lawsonia* extract for an immersion period of 2 h. The results in Table 3 shows that corrosion rate increase with rise in temperature, the corrosion rate was 5309.52, 9050.22 and 23530.58 mg/dm^{2}d with respect to 313, 323 and 333 K. The IE was decrease with increase in temperature, e.g. for 1.2 g/L *Lawsonia* extract the IE was 95.45, 90.00 and 82.05 % for 313, 323 and 333 K temperature respectively (Fig. 5). The value of energy of activation (E_a) has been calculated with the help of following Arrhenius equation [23].

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4}$$

where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

Table 3. Temperature effect on corrosion rate (CR), inhibition efficiency (IE) and activation energy (E_a) for copper in 1.0 M HNO_3 in absence and presence of *Lawsonia* extract for an immersion period of 2 h.

Inhibitor concentration (g/L)	Temperature						Energy of activation (E_a) (kJ/mol)			(E_a) from Arrhenius plot (kJ/mol)
	313 K		323 K		333 K		313–323 K	323–333K	Mean	
	CR (mg/dm^{2}d)	IE (%)	CR (mg/dm^{2}d)	IE (%)	CR (mg/dm^{2}d)	IE (%)				
Blank	5309.52	–	9050.22	–	23530.58	–	44.83	85.46	65.15	64.33
0.6	2232.36	57.95	5550.84	38.67	17376.48	26.15	76.58	102.07	89.32	88.82
0.8	1086.00	79.55	4042.44	55.33	14540.76	38.21	110.50	114.49	112.49	112.45
1.0	362.04	93.18	1568.76	82.67	6516.12	72.31	123.27	127.36	125.32	125.27
1.2	241.32	95.45	905.04	90.00	4223.40	82.05	111.13	137.78	124.45	123.96

The value of E_a were also calculated from the slope of the Arrhenius plot (Fig. 3), i.e. log ρ Versus $1/T \times 10^3$ [23]. (ρ=corrosion rate, T=absolute temperature)
It was found that, the values of E_a were found higher in inhibited acid ranging from 89.32 to 125.32 kJ/mol than E_a values for uninhibited acid 65.15 kJ/mol. The higher values of E_a indicate physical adsorption of the inhibitor on the metal surface and the adsorption of inhibitor causes an increase in the E_a of the process [24].

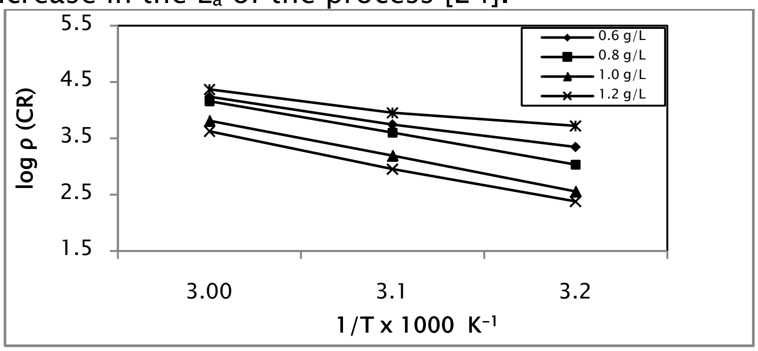

Fig.3. Arrhenius plot for corrosion of copper in 1.0 M HNO_3 in absence and presence of different concentration of *Lawsonia* extract for an immersion period of 2 h.

The mean value of E_a was 65.15 kJ/mol in uninhibited acid and the value calculated from the slop of the Arrhenius plot was found 64.33 kJ/mol, which was found almost similar (± 1.0 kJ/mol).

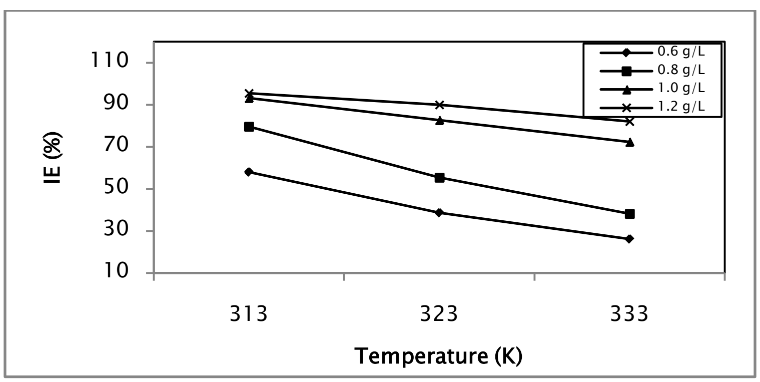

Fig.4. Effect of temperature on IE for copper corrosion in 1.0 M HNO_3 at different concentration of *Lawsonia* extract for immersion period of 2 h.

The values of heat of adsorption (Q_{ads}) were calculated by following equation [25].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1T_2}{T_2-T_1}\right] \qquad (5)$$

where, θ_1 and θ_2 are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively. From Table 4, it is evident that in all cases, the Q_{ads} values are negative and ranging from –51.61 to –96.21 kJ/mol. The negative values shows that the adsorption and hence the IE decreases with rise in temperature.

The IE was correlated to surface coverage (θ) and a 100 % efficiency suggesting to full coverage (θ=1). The degree of surface coverage values were used to determine its adsorption characteristics in HNO_3 solution. The plot of C_{inh}/θ versus C_{inh} gives straight lines with slope values equal to unity (Fig. 5). All the regression coefficients are very close to one which indicates that the inhibitors cover both the anodic and cathodic region through general adsorption following Langmuir isotherm [26]. This isotherm can be represented as,

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + c_{inh} \tag{6}$$

where, K_{ads} = equilibrium constant of the adsorption process and C_{inh} = inhibitor concentration.

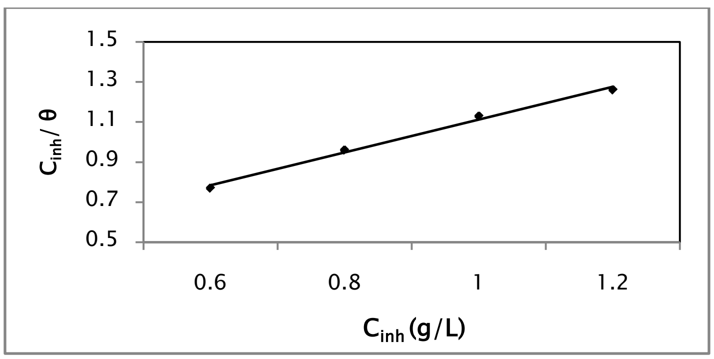

Fig.5. Langmuir adsorption isotherm for corrosion of copper in 0.5 M HNO_3 solution containing different concentration of *Lawsonia* extract for an immersion period of 24 h.

Free energy of adsorption (ΔG_a^o) was determined by the Langmuir isotherm was given by a plot of C_{inh}/θ Vs C_{inh} [27] (Fig. 5). From the intercepts of the straight lines on the C_{inh}/θ axis, K_{ads} can be calculated which was related to ΔG_a^o, as given by following equation. The ΔG_a^o value of the inhibitors on copper surface can be calculated from the following equation [28,29].

$$\Delta G_a^o = -RT \ln (55.5\ K_{ads}) \tag{7}$$

where, R is the gas constant, T is the absolute temperature (K), and the value 55.5 in the above equation is the concentration of water in solution in Molar [30], K_{ads} is the equilibrium constant of the adsorption/desorption process. The ΔG_a^0 values were almost negative in all cases indicated the spontaneous adsorption of *Lawsonia* extract on copper surface and strong interactions between inhibitor molecules and the metal surface. The enthalpy of adsorption (ΔH_a^o) and entropy of adsorption (ΔS_a^o) were calculated using the equations (8) & (9).

$$\Delta H_a^0 = E_a - RT \tag{8}$$

$$\Delta S_a^0 = \Delta H_a^0 - \Delta G_a^0/T \tag{9}$$

Table 4. The values of physical parameters Heat of adsorption (Q_{ads}), Free energy of adsorption (ΔG_a^0), Enthalpy of adsorption (ΔH_a^0) and Entropy of adsorption (ΔS_a^0) for copper in 1.0 M HNO_3 in the absence and presence of different concentration of *Lawsonia* extract for an immersion period of 2 h.

Inhibitor concentration (g/L)	Q_{ads} (kJ/mol)		ΔG_a^0 (kJ/mol)			ΔH_a^0 (kJ/mol)		ΔS_a^0 (kJ/mol K)	
	313–323 K	323–333 K	313 K	323 K	333 K	313 K	323 K	313 K	323 K
Blank	–	–	–	–	–	42.22	82.78	–	–
0.6	−65.74	−51.61	−10.68	−9.51	−8.46	73.98	99.39	0.27	0.34
0.8	−96.21	−62.13				107.90	111.81	0.38	0.38
1.0	−88.46	−53.89				120.67	124.68	0.42	0.42
1.2	−71.14	−60.59				108.52	135.10	0.38	0.45

The results revealed that ΔH_a^o values were positive and increase in presence of inhibitor indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the copper corrosion reaction. The enthalpy change ΔH_a^o was positive and ranging between 73.98 to 135.10 kJ/mol indicating the endothermic nature of the reaction suggests that higher temperature favors the corrosion process. Positive value of ΔS_a^o, lie between 0.27 to 0.45 kJ/mol K indicate the affinity of the adsorbent for the inhibitor and the corrosion process is thermodynamically favorable.

3.3. *Potentiodynamic polarization measurements*

Figure 6 represents the Potentiodynamic polarization curves for copper in 0.5 M HNO_3 in the absence and presence of *Lawsonia* extract. Associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (i_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and percentage inhibition efficiency were given in Table 5. From Fig. 6 and Table 5, it was observed that the addition of *Lawsonia* extract in HNO_3 solution, the significant decrease in the corrosion current density (i_{corr}) and decrease in the corrosion rate with respect to the blank. There is significant change in the anodic and cathodic slopes after the addition of the inhibitor and slightly shifted towards cathodic region. This Tafel curves indicate that *Lawsonia* function as a mixed-type inhibitor with the predominant cathode effectiveness.

Table 5. Potentiodynamic polarization parameters for copper in 0.5 M HNO_3 and in absence and presence of 1.2 g/L *Lawsonia* extract.

System	E_{corr} (mV)	i_{corr} (μA/cm^2)	Tafel Slope mV/decade		IE (%) calculated from	
			Anodic β_a	Cathodic β_c	Polarization method	Weight loss Method
Blank	−28.2	2062	169.87	429.74	–	–
***Lawsonia* extract**	−33.3	219.3	103.83	200.56	89.36	95.56

Inhibition efficiency (IE) from (i_{corr}) was calculated using following equation [31].

$$IE(\%) = \frac{i_{corr\ (uninh)} - i_{corr\ (inh)}}{i_{corr\ (uninhi)}} \text{ x } 100 \qquad (10)$$

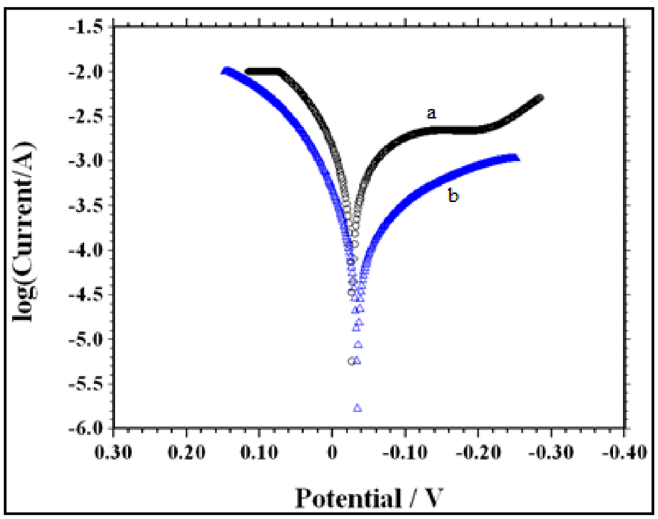

Fig.6. Potentiodynamic polarization curves for copper in (a) 0.5 M HNO_3 and (b) 0.5 M HNO_3 containing 1.2 g/L *Lawsonia* extract.

3.4. *Electrochemical impedance spectroscopy (EIS) measurements*

Corrosion of copper in 0.5 M HNO_3 solution in the presence of *Lawsonia* extract was investigated by EIS at room temperature. Nyquist curves for copper obtained in the absence and presence of extract were shown in Figure 7 and EIS parameters were shown in Table 6. It was observed from Figure 7 that the impedance diagram is almost semicircular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion. The semicircular nature of the plots indicates that the corrosion of copper is mainly controlled by charge transfer process.

Table 6. EIS parameters for the corrosion of copper in 0.5 M HNO_3 in absence and presence of 1.2 g/L *Lawsonia* extract.

System	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	IE (%) calculated from	
			EIS Method	Weight loss method
Blank	85	53.52	–	–
***Lawsonia* extract**	539	2.53	84.23	95.56

The charge transfer resistance (R_{ct}) values were calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum was found as presented in the following equation [32].

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{11}$$

Where f_{max} is the frequency at maximum height of the semicircle on the imaginary axis [33].

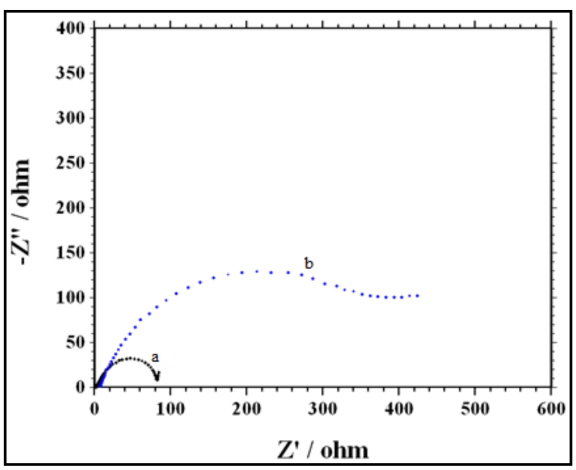

Fig.7. Nyquist plot for copper in (a) 0.5 M HNO_3 alone and (b) 0.5 M HNO_3 containing 1.2 g/L *Lawsonia* extract.

Inhibition efficiency from R_{ct} values was calculated by using the following equation [32].

$$IE(\%) = \frac{R_{ct\,(inh)} - R_{ct\,(uninh)}}{R_{ct\,(inh)}} \times 100 \tag{12}$$

The addition of inhibitor, increase R_{ct} value while decreases in C_{dl} values which is due to the adsorption of inhibitor on the metal surface. The above results can be explained on the basis that the electrostatic adsorption of inhibitor species at the metal surface leads to form a physical protective film that retards the charge transfer process and therefore inhibits the corrosion reactions, leading to increase R_{ct} values. Moreover, the adsorbed inhibitor species decrease the electrical capacity of electrical double layer values at the electrode/solution interface and therefore decrease the values of C_{dl} [34].

From the result, IE of *Lawsonia* extract for copper in HNO_3 solution obtained by weightloss, polarization and EIS methods were almost similar.

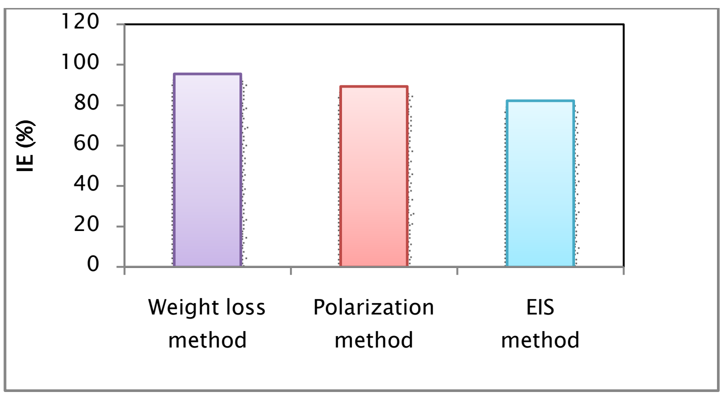

Fig. 8. Comparison of inhibition efficiency (IE) values obtained by weight loss, polarization and EIS method for copper in 0.5 M HNO_3 solution containing 1.2 g/L *Lawsonia* extract.

3.5. *Mechanism of corrosion*

Being a strong oxidizing agent, HNO_3 is capable of attacking copper. Copper is corroded to Cu^{+2} in HNO_3 solution and no oxide film is formed to protect the surface from the attack of the corrosive medium. The electrochemical reaction for copper in HNO_3 solution may be described as follows.

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)} \tag{13}$$

Anodic reaction:

$$Cu \rightarrow Cu^{+2} + 2e^{-} \tag{14}$$

Cathodic reaction:

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O \tag{15}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2\,H_2O \tag{16}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2\,H_2O \tag{17}$$

3.6. *Mechanism of inhibition*

It was reported that *Lawsonia inermis* leaves extract contain soluble matter, lawsone (2-Hydroxy-1, 4-naphthoquinone), resin and tannin, coumarins, gallic acid and sterols [25]. The main components of *Lawsonia inermis* extract are hydroxy aromatic compounds such as tannin and lawsone.

The main constituent of the extract is lawsone (Fig. 9) which is present in a relatively higher amount. Lawsone amounts to 1.02 % in the leaves [35]. The coloring matter is quinone. Lawsone molecule is a ligand that can chelate with various metal cations forming complex compounds. Therefore, the formation of insoluble complex compounds, by combination of the metal cations and the lawsone molecules adsorbed on the metal surface [22], is a probable interpretation of the observed inhibition action of lawsone. In the acidic medium, delocalization of the lone pair of electrons on hydroxyl group takes place resulting in the rearrangement shown in Fig. 11. Such a rearrangement, in the presence of metal cations, enhances the complex formation reaction Fig. 10. This could be the reason for the observed high inhibition efficiencies in the acidic medium.

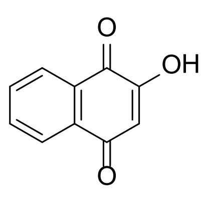

Fig.9. Structure of *Lawsone.*

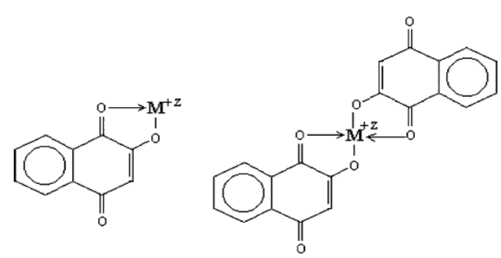

Fig.10. Forms of M-*Lawsonia* complexes. M is Cu.

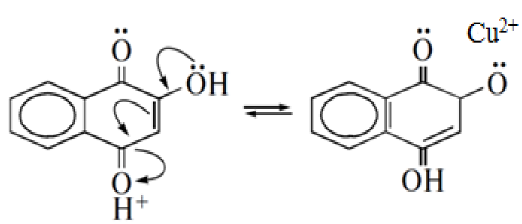

Fig.11. Process of delocalization on *Lawsone* molecule.

The inhibitive action of tannin was attributed to the formation of a passivating layer of tannates on the metal surface [36,37]. Tannins are also known to form complex compounds with different metal cations, especially in the basic media. It can be concluded then, due to the higher amount of lawsone in *Lawsonia inermis* extract, it can be attributed to the main constituent is responsible for inhibition. Moreover, in the presence of henna extract the values of corrosion potential E_{corr} are nearly constant; therefore, henna extract could be classified as a mixed type inhibitor with the predominant cathode effectiveness.

4. Conclusion

The present study shows that *Lawsonia* was found to be a good eco-friendly inhibitor for the corrosion control of copper in HNO_3 solution. Corrosion rate increases as HNO_3 concentration increase. The inhibition efficiency increases with increase in *Lawsonia* extract concentration. *Lawsonia* adsorbed on metal surface follows Langmuir adsorption isotherm. Tafel plot indicates *Lawsonia* acts as a mixed type inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. All three techniques give almost identical values of inhibition efficiency for copper in HNO_3 solution.

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