

Lawsonia Extract as a Green Corrosion Inhibitor for Copper in Nitric Acid Solution

K. K. Patel, R. T. Vashi*

Department of Chemistry, Navyug Science College, Surat, Gujarat-395009, India

Author of correspondence: Email: ketan140187@gmail.com (K.K.Patel); Phone: +0261 2781404

Abstract

The inhibition effect of henna leaves (*Lawsonia inermis*) extract for the corrosion of copper in nitric acid solution has been studied by using 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 this adsorption follows Langmuir adsorption isotherm in all tested systems. Tafel plot of polarization study indicates that the extract acts as a mixed type inhibitor. It was found that the extract acts as a good corrosion inhibitor for all the tested systems and the inhibition efficiency was obtained 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; 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, but these compounds are highly toxic. 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. Henna (*Lawsonia inermis*) has anti-inflammatory, antipyretic and analgesic effect [14–15]. Henna has been used as corrosion inhibitor for aluminium and steel in aggressive solution [16], iron in hydrochloric acid [17] and aluminium in hydrochloric acid [18–19]. El-Etre et al. [20] studied the *Lawsonia* extract for corrosion inhibition of some metals. The present work carried out to investigate the inhibition efficiency of an extract of *Lawsonia* leaves, for controlling corrosion of copper in nitric acid solution by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) methods.

2. Experimental Section

2.1 Sample and Solution preparation

The copper specimens of the size $4.5 \times 2.0 \times 0.178$ 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 solution was prepared by diluting analytical grade of HNO_3 purchased from Merck using double distilled water.

2.2 Extract preparation

The powder of the crushed leaves is extracted in boiled water for 20 min. After filtration, the water was evaporated from the extract. The solid residue was used for preparation of the tested concentrations of lawsonia [20].

2.3 Weight loss measurement

For weight-loss experiment, the copper coupons having an area of 0.1988 dm^2 were each suspended completely in 230 ml of HNO_3 solution with and without different concentrations of *Lawsonia* extract with the help of glass hooks at $301 \pm 1 \text{ K}$ for 24h (1 day). The coupons were retrieved after 24h, washed by distilled water, dried well and reweighed. From the weight loss data, corrosion rate in mg/dm^2 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 M HNO_3 solution with and without 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 cm² exposed to 230 ml 0.5 M HNO₃ with and without 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 mVs⁻¹. 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 K Hz 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 weight loss experiments was carried out for corrosion study of copper in different concentrations 0.5, 0.75 and 1.0 M of HNO₃ solution containing different concentration of *Lawsonia* extract 0.6, 0.8, 1.0 and 1.2 g/l at 301±1 K for exposure period of 24h (1 day) was investigated.

Results showed in Table 1 indicate that as the concentration of acid increases corrosion rate increases while inhibition efficiency decreases.

Inhibition efficiency (IE) was calculated by using the formula,

$$\% \text{ IE} = [W_u - W_i / W_u] \times 100 \quad (1)$$

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

Table 1: Effect of nitric acid concentration on corrosion rate (CR) and inhibition efficiency (IE) of copper metal having different inhibitor concentration at the temperature 301±1 K.

Inhibitor concentration g/l	Acid concentration					
	0.5 M		0.75 M		1.0 M	
	CR mg/dm ² d	IE %	CR mg/dm ² d	IE %	CR mg/dm ² d	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

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,

$$\theta = W_u - W_i / W_u \quad (2)$$

Table 2: Corrosion rate (log ρ) of copper in 0.5 M HNO₃ in absence and presence of *Lawsonia* extract for an immersion period of 24 h at 301±1 K.

Inhibitor concentration (g/l)	CR (ρ)	log ρ	IE (%)	surface coverage (θ)	1- θ	log($\theta/1-\theta$)
Blank	90.52	1.9567	–	–	–	–
0.6	20.11	1.3034	77.78	0.7778	0.2222	0.5441
0.8	15.08	1.1784	83.34	0.8334	0.1666	0.6992
1.0	10.06	1.0026	88.89	0.8889	0.1111	0.9031
1.2	4.02	0.6042	95.56	0.9556	0.0444	1.3329

The results obtained were presented in Table 2 and in Figure 1, 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 4.02mg/dm²d while inhibition efficiency increases from 77.78 to 95.56 %. It can be concluded that inhibition efficiency is directly proportional to the inhibitor concentration.

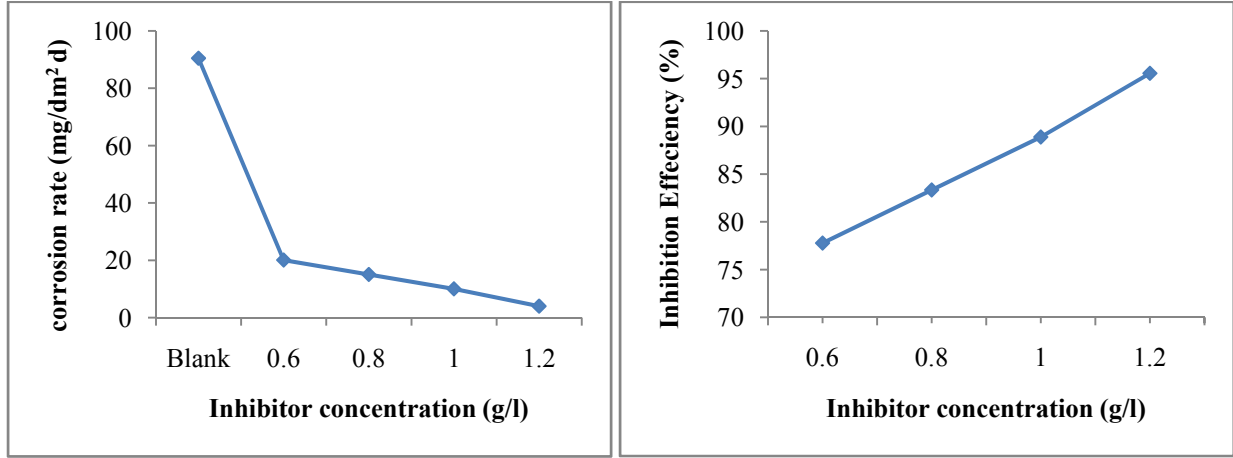


Figure 1: Corrosion rate and IE of copper corrosion in 0.5 M HNO₃ solution in presence of different concentration of *Lawsonia* extract for an immersion period of 24 h (1 day).

The surface coverage θ value was calculated by using equation 2. The plot of inhibitor concentration C_{inh} versus C_{inh}/θ is presented in Figure 2, straight line with almost unit slope was obtained indicates that the system follows Langmuir Adsorption Isotherm [22]. This isotherm can be represented as,

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (3)$$

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

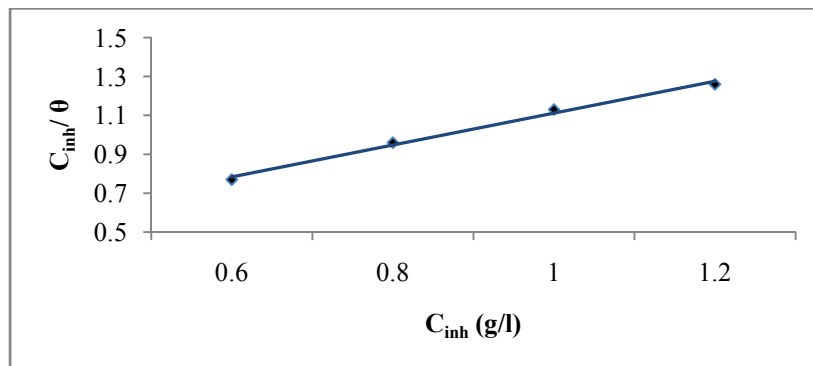


Figure 2: Langmuir adsorption isotherm for corrosion of copper in 0.5 M HNO₃ solution containing different concentration of *Lawsonia* extract for an immersion period of 24 h.

Linear plot obtained from Figure 2 Shows that constituents of *Lawsonia* extract on a copper surface making a barrier for charge and mass transfer between the metal and environment follows Langmuir adsorption isotherm which shows inhibition effect.

3.2 Temperature effect

To investigate the effect of temperature on corrosion rate, the weight-loss experiments were carried out at temperature 313, 323 and 333K in 1M HNO₃ for an immersion period of 2h.

The value of energy of activation (E_a) has been calculated from the slope of $\log \rho$ versus $1/T \times 10^3$ and also with the help of Arrhenius equation [22].

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

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 M HNO₃ in absence and presence of *Lawsonia* extract for an immersion period of 2h.

Inhibitor Concentration (g/l)	Temperature						Mean (E _a) from Eq. (1) (kJ/mol)	(E _a) from Arrhenius plot (kJ/mol)
	313 K		323 K		333 K			
	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	–	65.15	64.33
0.6	2232.36	57.95	5550.84	38.67	17376.48	26.15	89.32	88.82
0.8	1086.00	79.55	4042.44	55.33	14540.76	38.21	112.49	112.45
1.0	362.04	93.18	1568.76	82.67	6516.12	72.31	125.32	125.27
1.2	241.32	95.45	905.04	90.00	4223.40	82.05	124.45	123.96

As data given in Table 3, the values of E_a were found higher in inhibited acid ranging from 89.32 to 124.45 kJ/mol than uninhibited acid 65.15 kJ/mol, which indicate that the inhibitor induces energy barrier for the corrosion reaction and the inhibitor was strongly adsorbed on metal surface.

From the data of Table 3 and Figure 4, as temperature increases, rate of corrosion increase while percentage of inhibition efficiency decreases. The value of E_a were also calculated from the slope of the Arrhenius plot of $\log \rho$ versus $1/T \times 10^3$ (Figure 4), shows good agreement with the calculated values.

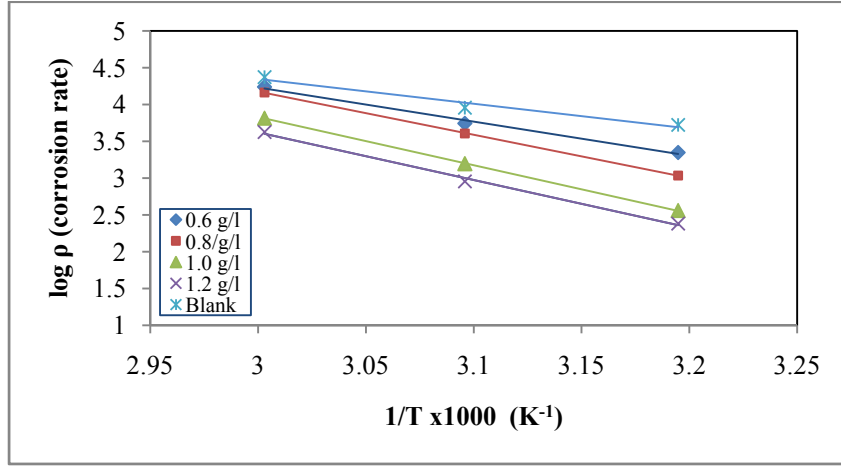


Figure 3: Arrhenius plot for corrosion of copper in 1 M HNO₃ in absence and presence of different concentration of *Lawsonia* extract for an immersion period of 2 h.

It was evident from Figure 1 that as temperature increases from 313 to 333 K the inhibition efficiency of *Lawsonia* extract was decreases.

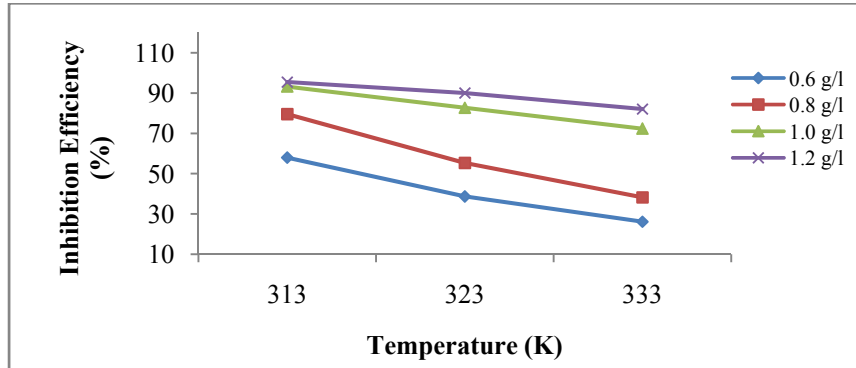


Figure 4: Effect of temperature on IE for copper corrosion in 1 M HNO₃ at different concentration of *Lawsonia* extract for immersion period of 2 h.

The values of heat of adsorption (Q_{ads}) were calculated by following equation [23].

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

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 -58.67 to -79.17 kJ/mol.

The values of free energy of adsorption (ΔG_a^0) were calculated with the help of following equation (6).

$$\log C = \log (\theta/1-\theta) - \log B \quad (6)$$

Where, $\log B = -1.74 - (\Delta G_a^0/2.303R)$ and C is the inhibitor concentration. The mean ΔG_a^0 values were almost negative in all cases and lie in the range of -10.81 to -11.66 kJ/mol indicated the spontaneous adsorption of *Lawsonia* extract on copper surface and strong interactions between inhibitor molecules and the metal surface.

Table 4: The values of physical parameters Q_{ads} , ΔG_a^0 , ΔH_a^0 and ΔS_a^0 for copper in 1M 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 (J/Kmol)
0.6	-58.67	-10.81	86.67	0.30
0.8	-79.17	-11.01	109.84	0.38
1.0	-71.17	-11.50	122.66	0.42
1.2	-65.86	-11.66	121.80	0.41

The enthalpy of adsorption (ΔH_a^0) and entropy of adsorption (ΔS_a^0) were calculated using the equations (7) & (8).

$$\Delta H_a^0 = E_a - RT \quad (7)$$

$$\Delta S_a^0 = \Delta H_a^0 - \Delta G_a^0 / T \quad (8)$$

The enthalpy change ΔH_a^0 was positive and ranging between 86.67 to 122.66 kJ/mol indicating the endothermic nature of the reaction suggests that higher temperature favors the corrosion process. The entropy ΔS_a^0 values were positive and lie between 0.30 to 0.42 J/k.mol confirming that the corrosion process is entropically favorable.

3.3 Potentiodynamic polarization measurements

Figure 5 represents the Potentiodynamic polarization curves for copper in 0.5 M HNO_3 in the presence and absence of *Lawsonia* extract. Associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and percentage inhibition efficiency were given in Table 5.

Table 5: Potentiodynamic polarization parameters of copper in 0.5 M HNO₃ and in presence and absence of 1.2 g/l *Lawsonia* extract.

System	E _{corr} mV	I _{corr} μA/cm ²	Tafel Slope mV/decade		IE (%) calculated from	
			Anodic	Cathodic	Polarization	Weight loss
			β _a	β _c	method	method
Blank	-28.2	2062	169.87	429.74	–	–
<i>Lawsonia</i> extract	-33.3	219.3	103.83	200.56	89.36	95.56

From Figure 5 and Table 5, it was observed that the addition of *Lawsonia* extract in acid solution indicates 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. This Tafel curves indicate that *Lawsonia* function as a mixed-type inhibitor.

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

$$\% \text{ IE} = (i_{corr} - i_{corr(inh)} / i_{corr}) \times 100 \quad (9)$$

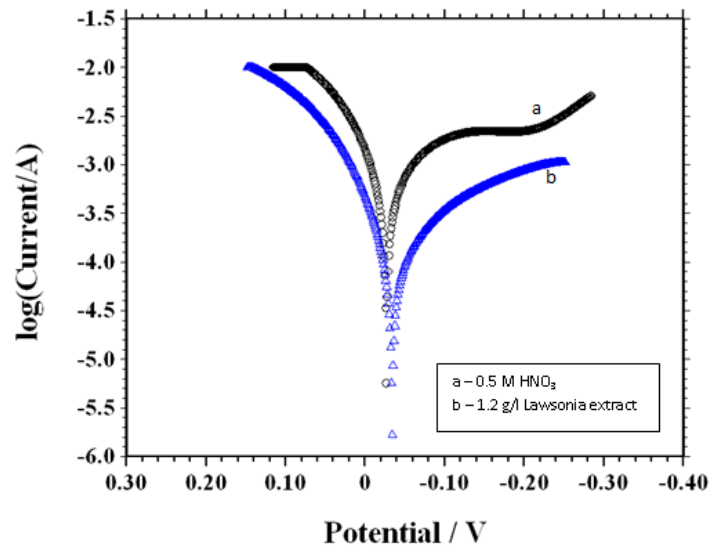


Figure 5: Potentiodynamic polarization curves for copper in (a) 0.5 M HNO₃ and (b) 0.5 M HNO₃ in the presence of 1.2 g/l *Lawsonia* extract.

3.4 Electrochemical impedance spectroscopy (EIS) measurements

Corrosion of copper in 0.5 M HNO₃ 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 are shown in Figure 6 and EIS parameters were shown in Table 6. It is observed from Figure 6 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 HNO₃ in presence and absence 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	–	–
<i>Lawsonia</i> extract	430	2.82	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 [24].

$$C_{dl} = 1 / 2\pi f_{max} R_{ct} \quad (10)$$

Where f_{max} is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [25].

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

$$\% IE = (R_{ct(inh)} - R_{ct} / R_{ct(inh)}) \times 100 \quad (11)$$

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} [26].

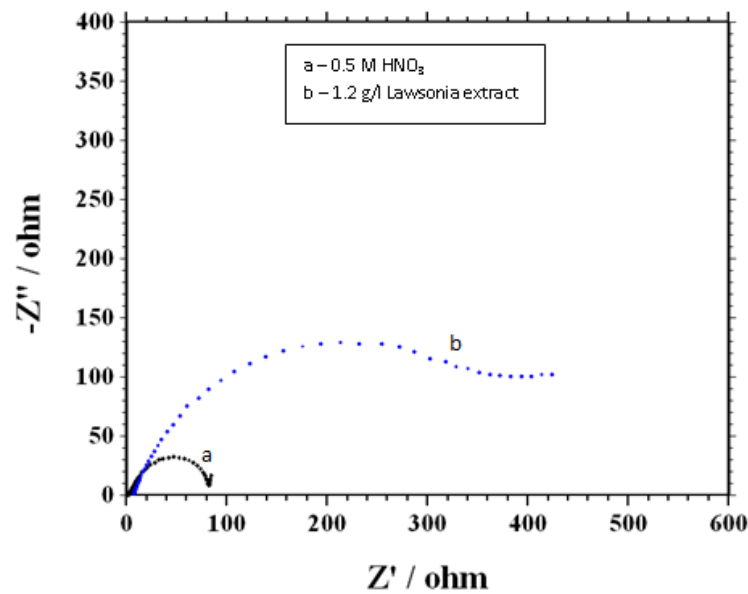


Figure 6: Nyquist plot for copper in (a) 0.5 M HNO_3 alone and (b) 0.5 M HNO_3 in presence of 1.2 g/l *Lawsonia* extract.

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.



3.5.1. Anodic reaction

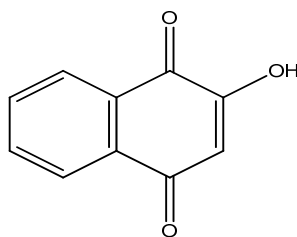


3.5.2. Cathodic reaction



3.6 Mechanism of inhibition

It was reported that *Lawsonia* leaves contain soluble matter, Lawson (2-hydroxy-1, 4-naphthoquinone) resin and tannin, coumarins, gallic acid and sterols[23]. Lawsone amounts to 1.02% in the leaves [27]. The coloring matter is quinone. The structure of Lawsone was shown below. It contains benzene unit, p-benzoquinone unit and phenolic group.



2-hydroxynaphthalene-1,4-dione

The main components of *Lawsonia* leaves extract are hydroxy aromatic compounds such as tannin and lawsone. The inhibitive action of tannin was attributed to the formation of passivating layer of tannates² on the metal surface [28–29]

The other constituent of the extract is lawsone which is present in relatively higher amount. Lawson molecule is a ligand, which can chelate with various metal cations forming complex compounds. Therefore, the formation of insoluble complex compounds, by combination of the metal cations and lawsone molecule adsorbed on the metal surface, it is a probable interpretation of the observed inhibition action of lawsone.

4. Conclusions

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 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 nitric acid.

Acknowledgement—The authors are thankful to the Department of Chemistry, Navyug Science College, Surat for providing laboratory facilities.

References

1. M. A. Elmorsi, A. M. Hassanein, *Corros. Sci.*, **41**, pp2337, 1999.
2. F. Zucchi, V. Grassi, A. Frignani, G. Trabanelli, *Corros. Sci.*, **46**, pp2853, 2004.
3. A. S. Fouda, H. A. Wahed, *Arab. J. Chem.*, 2011.
4. K. F. Khaled, M. A. Amin, *Corros. Sci.*, **51**, pp2098, 2009.
5. A. Zarrouk, B. Hammouti, A. Dafali, F. Bentiss, *Ind. Eng. Chem. Res.*, **52**, pp2560–2568, 2013.
6. R. T. Vashi, H. M. Bhajiwala, S. A. Desai, *Der PharmaChemica*, **3**, 2, pp 80, 2011.
7. R. T. Vashi, H. M. Bhajiwala, S. A. Desai, *E-Journal of Chemistry*, **7**, 2, pp 665, 2010.
8. A. Doner, A. O. Yuce, G. Kardas, *Ind. Eng. Chem. Res.*, **52**, pp 9709–9718, 2013.
9. G. Tansug, T. Tuken, E. S. Giray, G. Findikkiran, G. Sigircik, O. Demirkol, M. Erbil, *Corros. Sci.*, **84**, pp2, 2014.
10. R. T. Vashi, P. S. Desai, *Anti corrosion methods and materials*, **58**, 2, pp70, 2011.
11. P. Mourya, S. Banerjee, R. Rastogi, M. Singh, *Ind. Eng. Chem. Res.*, **52**, pp12733–12747, 2013.
12. L. R. Chauhan, G. Gunasekaran, *Corros. Sci.*, **49**, pp1143, 2007.
13. A. M. Abdel-Gaber, B. A. Abd-El-Nabey, I. M. Sidahmed, A. M. El-Zayady, M. Saadawy, *Corros. Sci.*, **48**, pp2765, 2006.
14. B. H. Ali, A. K. Bashir, M. O. M. Tanira, *Pharmacology*, **51**, pp356, 1995.
15. M. Al-Tufail, P. Kraham, H. Hassam, T. Mahier, S. T. Al-Sedairy, *Toxicol Environ Chem., Print.*, **71**, pp241, 1999.
16. M. Al. Sehaibani, Mater Wissen, *Werkst tech.*, **31**, pp1060, 2000.
17. A. Chetouani, B. Hammouti, *Bulletin of Electrochemistry*, **19**, pp23, 2003.
18. A. Petchiammal, S. Selvaraj, *Int. J. Chem. Tech. Res.*, **5**, 4, 2013.
19. W. B. Wan Nik, F. Zulkifli, R. Rosliza, M. M. Rahman, *IJMER*, **1**, 2, pp723–728.
20. A. Y. El-Etre, M. Abdallah, Z. E. El-tantawy, *Corros. Sci.*, **47**, 2, pp385–395, 2005.
21. A. Singh, I. Ahamad, M. A. Quraishi, *Arabian J. of Chem.*, 2012.
22. G. R. Bruker, P. B. Phipps, *Corrosion Chemistry ACS*, pp293, 1979.

- 23.R. H. Thomson, *Naturally Occurring Quinones*, third ed., Academic Press, London, New York, pp74, 1971.
- 24.E. Khamis, M. A. Ameer, N. M. Al-Andis, G. Al-Senani, *Corrosion*, **56**, 2, pp127, 2000.
- 25.C. A. C. Souza, J. E. Mayb, A. T. Machado, A. L. R. Tacharda, E. D. Bidoiac, *Surf. Coat. Tech.*, **75**, pp190, 2005.
- 26.F. Ansfield, *Corrosion Mechanism*, Marcel Dekker, New York, pp119, 1987.
- 27.J. J. Khorrami, *Q. J. Crude Drug Res.*, **17**, pp131, 1979.
- 28.K. S. Rajagopalam, N. Subramanyam, M. Sundaram, *Ind. J. Appl. Chem.* **107**, pp414, 1969.
- 29.G. H. Booth, S. J. Mercer, *Corros. Sci.*, **4**, pp425, 1964.