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Investigation of Withania Somnifera Extract as Corrosion Inhibitor for Copper in Nitric Acid Solutions

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Corrosion inhibitive effect of Withania Somnifera extract has been studied in 0.5 M nitric acid for Copper (Cu). The studies were done at different temperatures (30-50^{o}C). The thermodynamic parameters were determined. Withania Somnifera has been found to be more effective corrosion inhibitor at lower temperatures and inhibition efficiency (IE) reached 91.8% at 25 ppm. Adsorption isotherm was determined and was found to follow Frumkin adsorption isotherm. Inhibition efficiencies at different Withania Somnifera concentrations were determined using chemical and electrochemical techniques. Polarization data revealed that this extract acts as a mixed-kind inhibitor. The obtained inhibition efficiencies were in a high agreement, confirming the validity of the used techniques in testing the inhibitory action of Withania Somnifera for Cu corrosion in nitric acid medium.

Keywords: Withania Somnifera, Nitric acid, Frumkin adsorption isotherm, EIS, SEM.

1. INTRODUCTION

Cu is a widely used metal in an industry as it has good characteristics, and shows high resistance against chemicals, and atmospheric factors. However, it can be corroded when exposed to aggressive media such as acids. Cu corrosion prevention can be attained using inhibitors. Inorganic compounds [1], and organic compounds like azoles [2-26], amines [27-33] amino acids [34, 35] and plant extracts [36-40] have been examined as Cu corrosion inhibitors in various corrosive media. The presence of hetero atoms like O, N, S, P in the organic compound molecule improves its inhibition action, as it can form coordination bonds with vacant d orbitals in a metal atom. Rings of conjugated bonds, π electrons, can also improve the action of these inhibitors. According to these results, a lot of compounds having numerous heteroatoms and functional groups were developed. Withania Somnifera (W. Somnifera) is a plant used as an herb in Ayurvedic medicine. W. Somnifera has known commonly as winter cherry [41] or Indian ginseng [42]. It is cultivated in many of the drier regions around the world. W. Somnifera was examined as an inhibitor for acidic metals corrosion [43, 44]. The target of this work is to investigate the inhibitory action of W. Somnifera as a green corrosion inhibitor towards Cu in 0.5 M HNO_3 (corrosive solution) using different techniques.

2. EXPERIMENTAL TECHNIQUES

2.1. Materials and solutions

The chemical composition (weight%) of the tested Cu metal was given in Table 1.

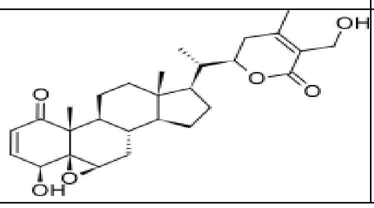
Table 1. Weight % of the tested Cu metal

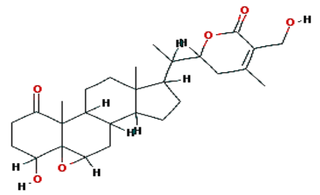
weight %						
Bi	Sn	Pb	Ag	Fe	Other elements	Cu
0.0005	0.001	0.002	0.001	0.01	0.0002	Rest

7 M HNO_3 (a stock solution) was prepared by dilution of the concentrated chemical AR grade acid using bidistilled water. The acid titration was done using standardized NaOH solution. Exactly 0.5 M HNO_3, which used as a corrosive solution throughout the experiments, was obtained by dilution of the stock solution using bidistilled water.

245.7 gm of W. Somnifera powder was soaked in 900 ml of methanol (70% BDH), and the mixture was kept at room temperature. After two weeks, the mixture was left to dry in shade in an air-tight vessel. The dried samples were converted into a fine powder using an electric blender, filtrated using cheesecloth and filter papers, and stored at room temperature in air-tight vessels. Gas chromatography and mass spectroscopy analysis were carried out in methanolic extract of W. Somnifera and the structures of main chemical constituents, that isolated from W. Somnifera plant, were characterized as shown in Table 2.

Table 2. Some photo components identified in the methanolic extract of W. Somnifera plant

Name	Structural formula	IUPAC Name	Molecular formula	Molecular weight g/mol
Withaferine A		(4β,5β,6β,22R)-4,27-Dihydroxy-5,6:22,26-diepoxyergosta-2,24-diene-1,26-dione	$C_{28}H_{38}O_6$	470.60

Dihydrowithaferin-A		2,3-Dihydrowithaferin-A	$C_{28}H_{40}O_6$	472.6136

2.2. Wight loss (WL) method

For WL measurements, the Cu metal coupons were cut into 3×1×2 cm^2 pieces and were polished using different grades of emery papers up to 1200 grit size. The pieces were cleaned by acetone and bidistilled water, dried using filter papers, and then weighed. Seven pieces of Cu were hanging in test solutions without and with different concentrations (5-25 ppm) of W. Somnifera using suitable glass hooks. After a definite interval time, the pieces were taken out from the solutions, rinsed, dried, and weighed again. The WL for each piece was then taken. The % IE of W. Somnifera and surface coverage of Cu (θ) were determined using the following equation:

$$\%IE = \theta \times 100 = [(W_{free} - W_{inh})/ W_{free}] \times 100 \quad (1)$$

where W_{free} is the WL of the metal without W. Somnifera and W_{inh} is the WL of the metal with W. Somnifera.

2.3. Electrochemical techniques

The electrochemical techniques have been performed using PCI4-G750 Potentiostat/Galvanostat and a personal computer with Gamry PCI4-G750 software for calculations. The used electrical circuit consists of three electrodes (SCE reference electrode, Pt auxiliary electrode, and Cu electrode). 1 cm^2 of the Cu electrode is prepared and cleaned as illustrated in WL method. The pre-immersion oxide film was reduced by giving a time period of about 20 minutes for open circuit potential (OCP). All electrochemical studies were performed at 30 ±1 °C.

Potentiodynamic polarization (PP) is a useful method because they give more information about the corrosion mechanism and the factors affecting the corrosion process and inhibition behavior of the inhibitor. This is done by measuring the potential- current characteristics of the metal/ solution system. In PP measurements, electrode potential from –1000 to 1000 mV was applied at scanning rate 1 mV s^{-1}. %IE and θ from PP measurements were determined by applying the following equation:

$$\% IE = \theta \times 100 = [(i_{corr\,(free)} - i_{corr(inh)})/ i_{corr\,(free)}] \times 100 \quad (2)$$

where $i_{corr\ (free)}$ is the corrosion current density without W. Somnifera and $i_{corr(inh)}$ is the corrosion current density with W. Somnifera.

In the electrochemical impedance spectroscopy (EIS) process, the frequency range is between 100 kHz and 0.1 Hz and the AC signal is 10 mV peak to peak. % IE and θ were obtained by employing the following relation:

$$\%IE = \theta \times 100 = [(R_{ct(free)} - R_{ct(inh)}) / R_{ct(free)}] \times 100 \quad (3)$$

where $R_{ct(free)}$ is the charge transfer resistance without W. Somnifera and $R_{ct(inh)}$ is the charge transfer resistance with W. Somnifera.

In electrochemical frequency modulation (EFM), the larger peaks were used to obtain i_{corr}, causality factors (CF-2 & CF-3) and Tafel slopes (βc & βa). θ and % IE from EFM measurements were calculated using equation (2).

2.4. Surface analysis

For surface analysis, the Cu specimens had been exposed to the test solutions for 24 hours. JEOL scanning electron microscope (SEM) model T-200 was used to study morphology at an enlargement of (x500). Energy dispersive X-ray (EDX) was used to detect the elements on the Cu surface

3. RESULT AND DISCUSSION

3.1. Weight loss (WL) method

Figure 1 illustrates the curves of WL - time at 30^{o}C for Cu in corrosive solution without and with different W. Somnifera concentrations. As shown from this Figure, by raising the W. Somnifera concentration the WL of the Cu sample decreases. This means that W. Somnifera acts as an inhibitor for Cu in nitric acid medium.

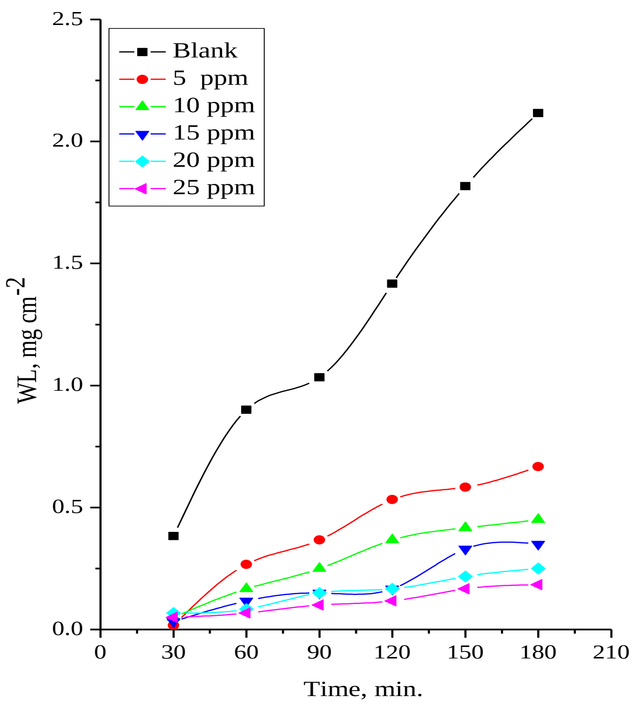


Figure 1. Curves of WL - time for Cu in corrosive solution without and with W. Somnifera extract at 30^{o}C

3.2. Temperature effect

The temperature effect on Cu dissolution in corrosive solution without and with different W. Somnifera concentrations has been studied in the temperature range (30-50^{o}C) by WL, and illustrated in Figure 2. The Figure showed that the WL increases with raising the temperature at all W. Somnifera concentrations. This may be referred to molecules desorption from the metal surface at higher temperatures. Increasing of WL with a temperature rising is suggestive of physical adsorption [45]. Table 3 displays the temperature effect on the corrosion rate (CR), θ, and %IE for Cu in corrosive solution. As shown, CR of Cu metal increases while %IE decreases with rising temperature.

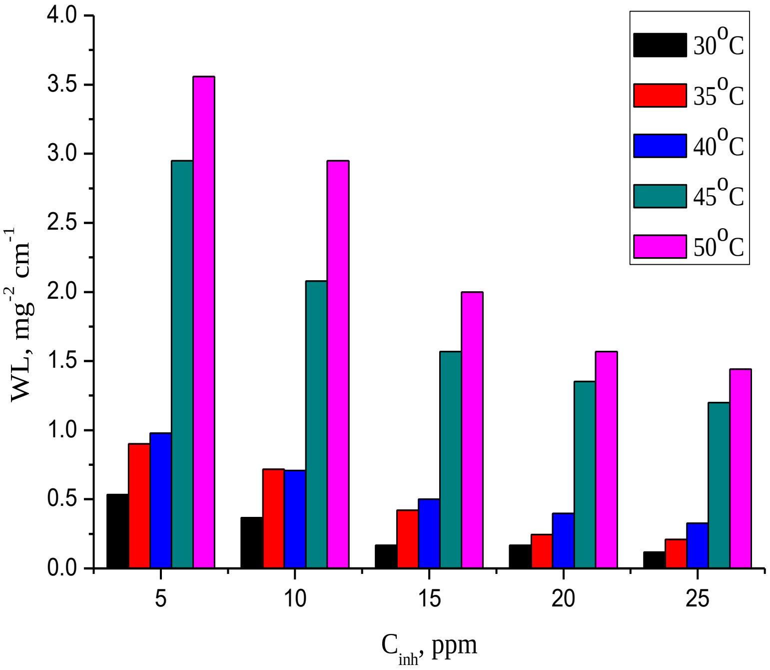


Figure 2. WL of Cu in corrosive solution with different W. Somnifera concentrations at different temperatures

Table 3. Temperature effect on CR, θ, and %IE for Cu in corrosive solution without and with different W. Somnifera concentrations

Temp., ^{o}C	30		
$C_{inh,}$ ppm	CR, mg cm^{-2} min^{-1}	θ	% IE
Blank	0.012	—	—
5	0.004	0.624	62.4
10	0.003	0.741	74.1
15	0.001	0.882	88.2
20	0.001	0.882	88.2

25	0.001		0.918		91.8	
Temp., ^{o}C	35			40		
$C_{inh,}$ ppm	CR, mg cm^{-2} min^{-1}	θ	% IE	CR, mg cm^{-2} min^{-1}	Θ	% IE
Blank	0.017	—	—	0.014	—	—
5	0.008	0.567	56.7	0.008	0.407	40.7
10	0.006	0.656	65.6	0.006	0.572	57.2
15	0.004	0.799	79.9	0.004	0.697	69.7
20	0.002	0.883	88.3	0.003	0.759	75.9
25	0.002	0.899	89.9	0.003	0.801	80.1
Temp., ^{o}C	45			50		
$C_{inh,}$ ppm	CR, mg cm^{-2} min^{-1}	θ	% IE	CR, mg cm^{-2} min^{-1}	Θ	% IE
Blank	0.040	—	—	0.047	—	—
5	0.025	0.389	38.9	0.030	0.365	36.5
10	0.017	0.569	56.9	0.025	0.474	47.4
15	0.013	0.675	67.5	0.017	0.643	64.3
20	0.011	0.720	72.0	0.013	0.720	72.0
25	0.010	0.751	75.1	0.012	0.743	74.3

The activation energy (E_a^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation were determined using the Arrhenius-type equation (4) and transition-state equation (5) [46-49]:

$$CR = A \exp(-E_a^*/RT) \qquad (4)$$

$$CR = RT / Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \qquad (5)$$

Where R is gas constant, T is Kelvin temperature h is Planck's constant, A is the frequency factor and N is the number of Avogadro. Plots of log CR vs. 1/T (Figure 3) and log (CR /T) vs. 1/T (Figure 4) give straight lines. Values of E_a^*, $\Delta S^*$and ΔH^* were determined from the slopes and intercepts of these lines and given in Table 4. Increasing E_a^* in inhibited corrosive solution compared to that without inhibitor together with the decrease in % IE with the temperature rising, can be referred to physisorption [50]. The positive values of ΔH^* indicate that the Cu dissolution process is of endothermic nature. The negative values of ΔS^* indicate an increase in ordering ongoing from reactants to the activated complex. The shift of ΔS^* values to more positive values with rising W. Somnifera concentration is referred to the driving force that can overcome the adsorption barriers for W. Somnifera on the Cu surface.

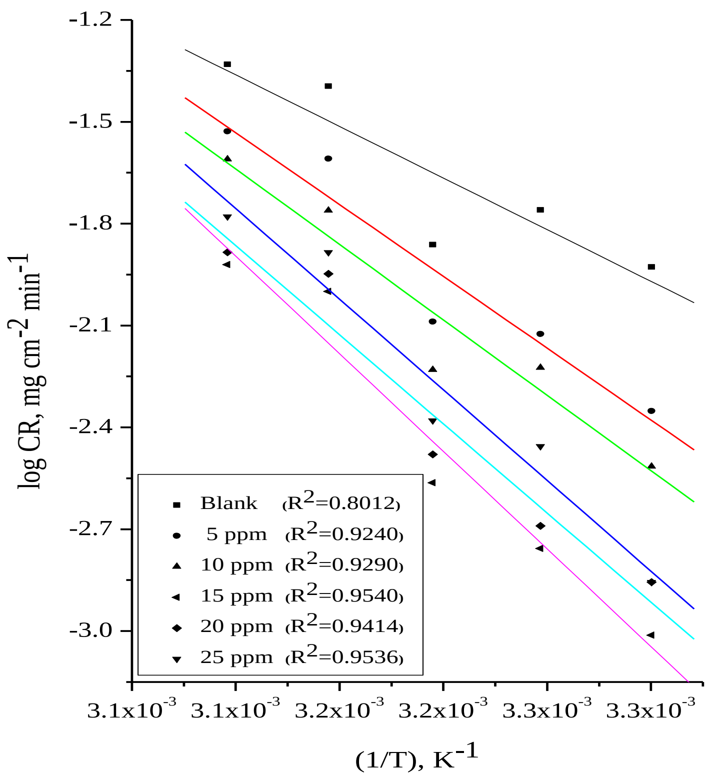


Figure 3. log CR against 1/T for Cu in corrosive solution without and with different W. Somnifera concentrations

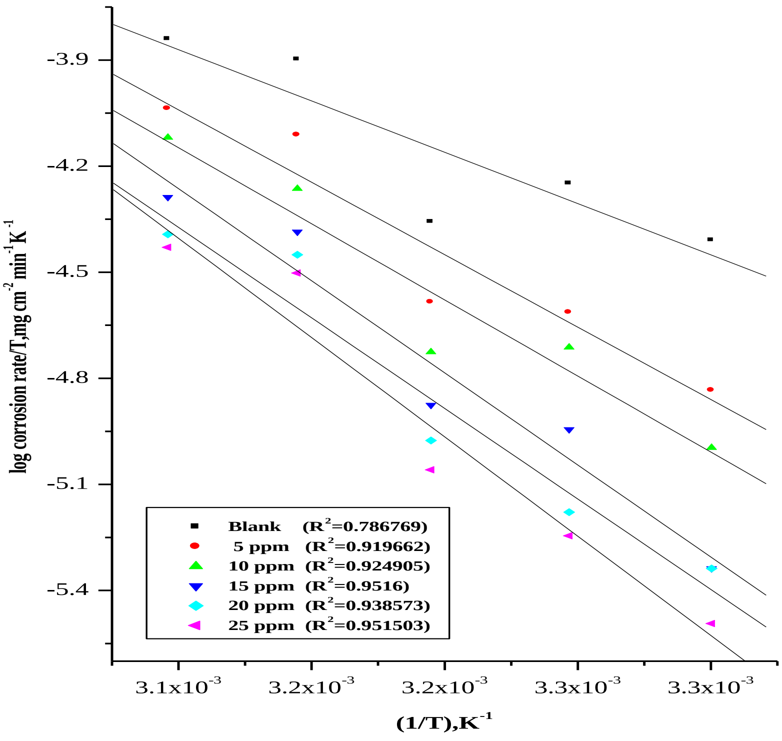


Figure 4. log (CR/T) against 1/T for Cu in corrosive solution without and with different W. Somnifera concentrations

Table 4. Activation parameters for Cu in corrosive solution without and with different W. Somnifera concentrations

C_{inh}, ppm	A, mg cm^{-2} min^{-1}	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}
Blank	8.061	58.2	26.6	-81.5
5	11.581	81.0	34.1	-31.8
10	12.131	85.1	35.8	-21.5
15	14.798	102.2	43.3	+29.9
20	14.418	100.6	42.6	+22.6
25	15.932	110.1	46.7	+51.5

3.3. Adsorption isotherms

Among numerous of adsorption isotherms, Frumkin adsorption isotherm [51], that given by the following equation, was the best fit:

$$K_{ads}C_{inh} = \theta / 1 - \theta \exp(-2 a \theta) \quad (6)$$

Or its linear form:

$$\ln[(C_{inh}\theta) / (1 - \theta)] = \ln K_{ads} + 2a\theta \quad (7)$$

where K_{ads} is adsorption constant and a is the interaction parameter between adsorbed molecules. Plotting ln $[C_{inh}\theta / (1 - \theta)]$ against θ gives straight lines (Figure 5) according to the linear Frumkin form. Values of (a) and (ln K_{ads}) can be obtained from the slopes and intercepts of these plots. K_{ads} is connected to the standard free energy of adsorption ($\Delta G°_{ads}$) through the following relation [52,53]:

$$\ln K_{ads} = \ln 0.018 - \Delta G°_{ads.} / RT \quad (8)$$

where 0.018 is the water molarity in solution. Standard enthalpy of adsorption (ΔH^o_{ads}) was obtained by plotting log K_{ads} against 1/T (Figure 6) according to the following relation [54]:

$$\ln K_{ads} = (- \Delta H^{\circ}_{ads} / RT) + \text{constant} \quad (9)$$

Entropy changes of adsorption process (ΔS^o_{ads}) were attained as follows [55]:

$$\Delta S°_{ads} = (\Delta H°_{ads} - \Delta G°_{ads})/T \quad (10)$$

The adsorption results were given in Table 5. The positive (a) values signalize that there are attractive forces between the adsorbed species on the surface. Lowering of $\Delta G°_{ads}$ values indicates that W. Somnifera was physically adsorbed on the Cu surface. Negative values of ΔH^o_{ads} indicate exothermic adsorption process [56]. Values of ΔS^o_{ads} were negative as accompanied by exothermic adsorption process [57].

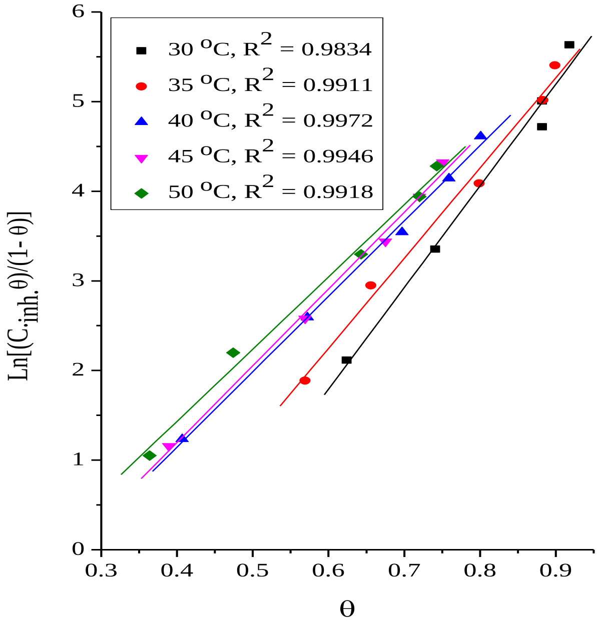


Figure 5. Plotting ln [$C_{inh}\theta$ / (1 – θ)] vs. θ for Cu in corrosive solution with W. Somnifera at different temperatures

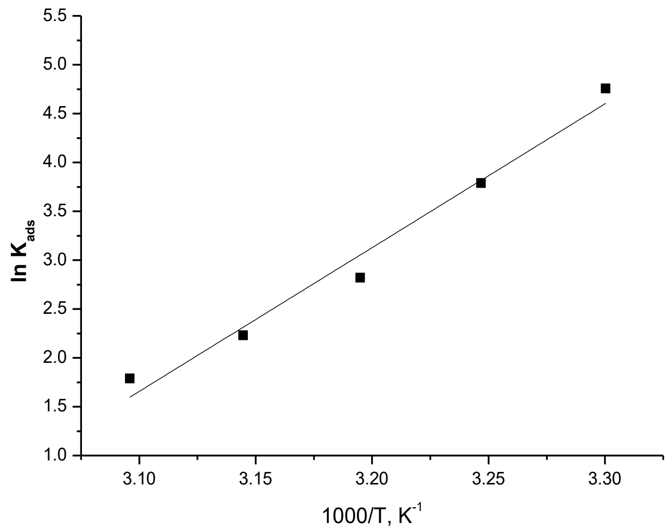


Figure 6. ln K_{ads} vs. 1/T for Cu in corrosive solution with W. Somnifera

Table 5. Frumkin adsorption results at different temperatures for Cu in corrosive solution with W. Somnifera

Temp.,°C	A	ln K_{ads}, M^{-1}	-ΔG^o_{ads}, kJ mol^{-1}	-ΔH_{ads}, kJ mol^{-1}	-ΔS_{ads}, J $mol^{-1}K^{-1}$
30	11.3	5.0	22.8	122.3	328.6
35	10.1	3.8	20.0		332.3
40	8.4	2.2	16.2		339.0
45	8.6	2.2	16.5		332.8
50	8.5	1.8	15.6		330.5

3.4. Potentiodynamic polarization (PP) measurements

PP curves without and with different W. Somnifera concentrations for Cu in corrosive solution were illustrated in Figure 7. The variation of corrosion potential (E_{corr}), i_{corr}, β_a, β_c, CR, θ and % IE with W. Somnifera concentration were given in Table 6. Experimental results indicate that i_{corr} is significantly decreased with increasing W. Somnifera concentration. Both the anodic and cathodic curves were affected by the presence of W. Somnifera, i.e. W. Somnifera limited both the anodic and cathodic reactions (mixed type inhibitor), but largely affected the cathodic one. The almost unchanged Tafel slopes indicate that W. Somnifera acts by just blocking the metal surface reaction sites without changing the mechanisms of the anodic and cathodic reaction.

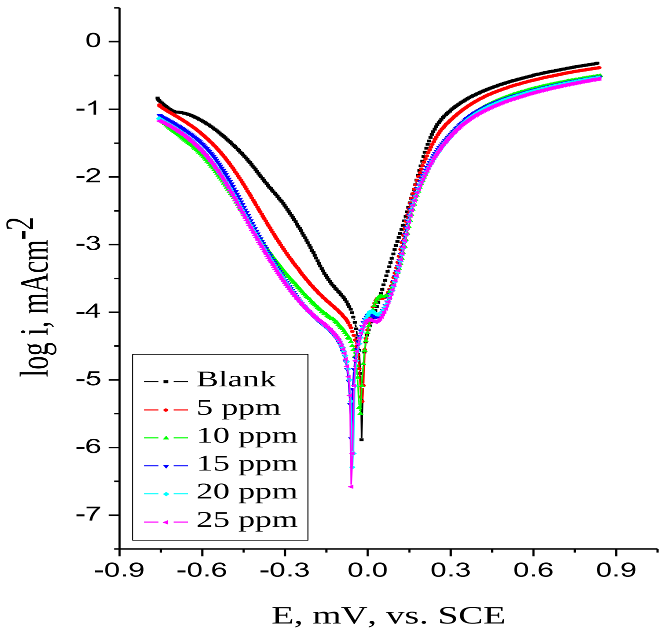


Figure 7. PP curves without and with different W. Somnifera concentrations for Cu in corrosive solution

Table 6. Effect of W. Somnifera concentration on E_{corr}, i_{corr}, β_a , β_c, CR, θ, and % IE for Cu in corrosive solution

C_{inh}, ppm	$-E_{corr}$, mV vs SCE	i_{corr}, mA cm^{-2}	$-\beta_c$, mV dec^{-1}	β_a, mV dec^{-1}	CR, mmy^{-1}	θ	% IE
Blank	23	146.0	233	226	81.0	—	—
5	25	52.4	211	207	29.0	0.641	64.1
10	32	31.3	215	204	17.3	0.786	78.6
15	64	24.6	189	206	13.6	0.832	83.2
20	57	21.5	191	202	11.9	0.853	85.3
25	59	22.3	193	205	12.3	0.847	84.7

3.5. Impedance (EIS) measurements

Figure 8 presents the Nyquist plots for Cu dissolution in corrosive solution without and with different W. Somnifera concentrations. The Nyquist diagrams do not display ideal semicircle, this referred to the frequency dispersion [58] which results from the surface roughness. The inductive arc of the diagrams (large capacitive loops with low frequencies dispersion) referred to adsorbed intermediates ruling the anodic process [59-61]. In corrosive solution without and with W. Somnifera, the diagrams show the same capacitive loop, but its diameter increases with rising W. Somnifera concentration. The impedance spectrum was analyzed by using the simple equivalent circuit model shown in Figure 9. The circuit has the solution resistance R_s and the double layer capacitance C_{dl} that put parallel to R_{ct} [62]. R_{ct}, is attained from the diameter of the high-frequency loop, while C_{dl} is obtained as follow:

$$C_{dl} = 1/\,(2\pi\, f_{max} R_{ct}) \qquad (11)$$

where f_{max} is the maximum frequency and π =3.14. Table 7 includes the obtained impedance data. As shown, R_{ct} increases while C_{dl} decreases with the increase in W. Somnifera concentration. That is because adsorption of the W. Somnifera on the Cu surface, forming a film on it. Bode plots of W. Somnifera on Cu in corrosive solution were presented in Figure 10. The higher frequency indicates (R_s), while the lower frequency indicates (R_s+R_{ct}). Nyquist and Bode results show high conformity.

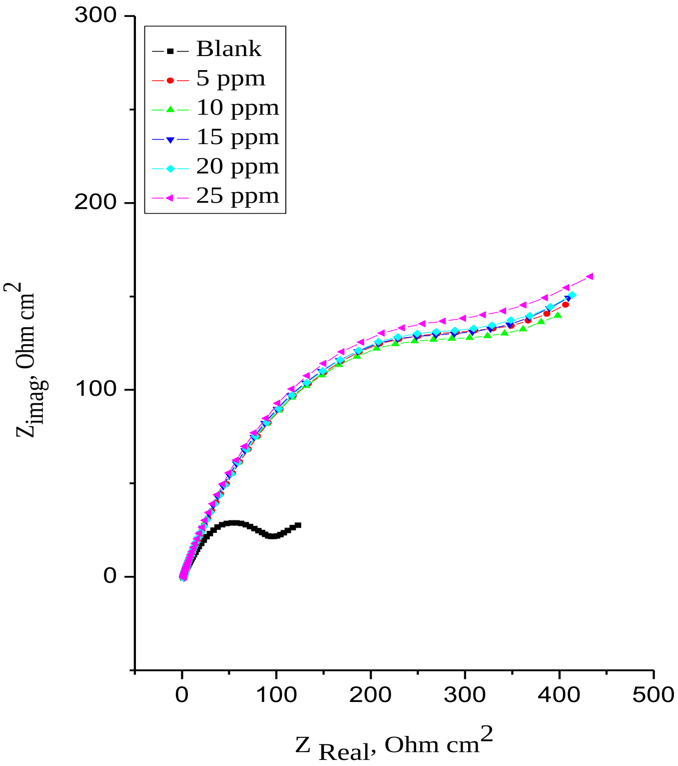


Figure 8. Nyquist plots Cu in corrosive solution without and with different W. Somnifera concentrations

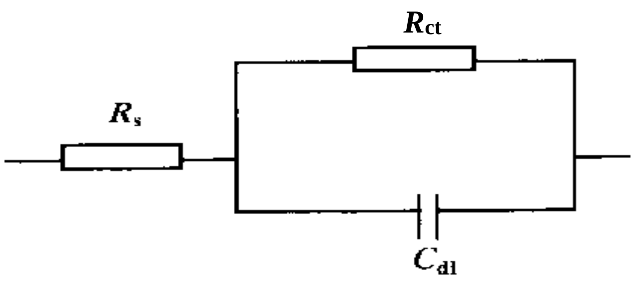


Figure 9. The circuit used in EIS results

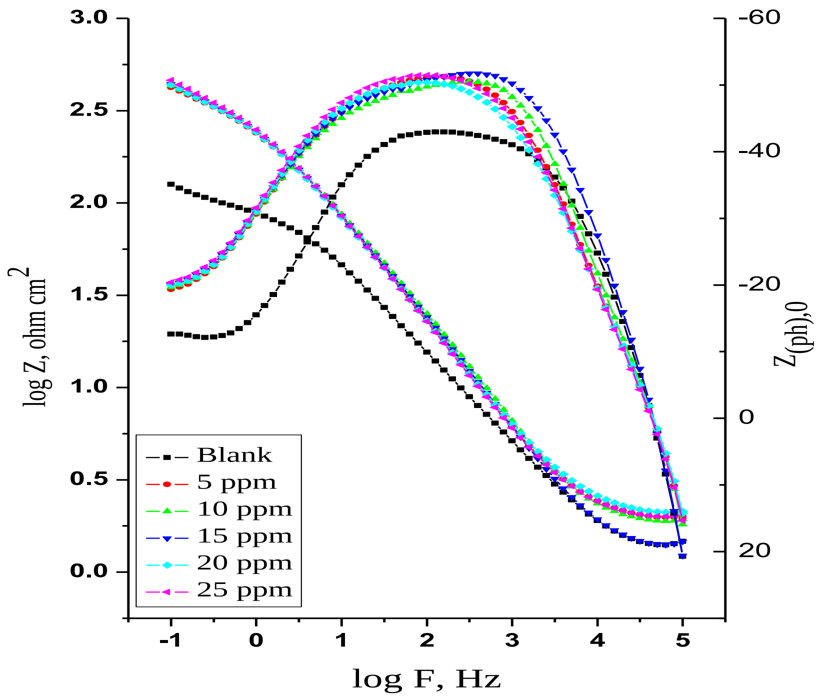


Figure 10. Bode plots for Cu in corrosive solution without and with different W. Somnifera concentrations

Table 7. EIS results for Cu in corrosive solution without and with different W. Somnifera concentrations

C_{inh}, ppm	C_{dl}, μF cm^{-2}	R_{ct}, Ω cm^{-2}	θ	% IE
Blank	389	119.4	—	—
5	410	456.7	0.739	73.9
10	405	467.9	0.745	74.5
15	406	468.7	0.745	74.5
20	455	483.0	0.753	75.3
25	441	500.6	0.761	76.1

3.6. Electrochemical frequency modulation (EFM) measurements

EFM for Cu in corrosive solution without and with W. Somnifera was presented in Figure 11. Data obtained from EFM were recorded in Table 8. It is observed that i_{corr} decreases by increasing the

W. Somnifera concentration. Also, CF-2 and CF-3 values were very approached to the theoretical values and this agrees with the EFM theory [63] and guarantees the rightness of Tafel slopes and i_{corr}.

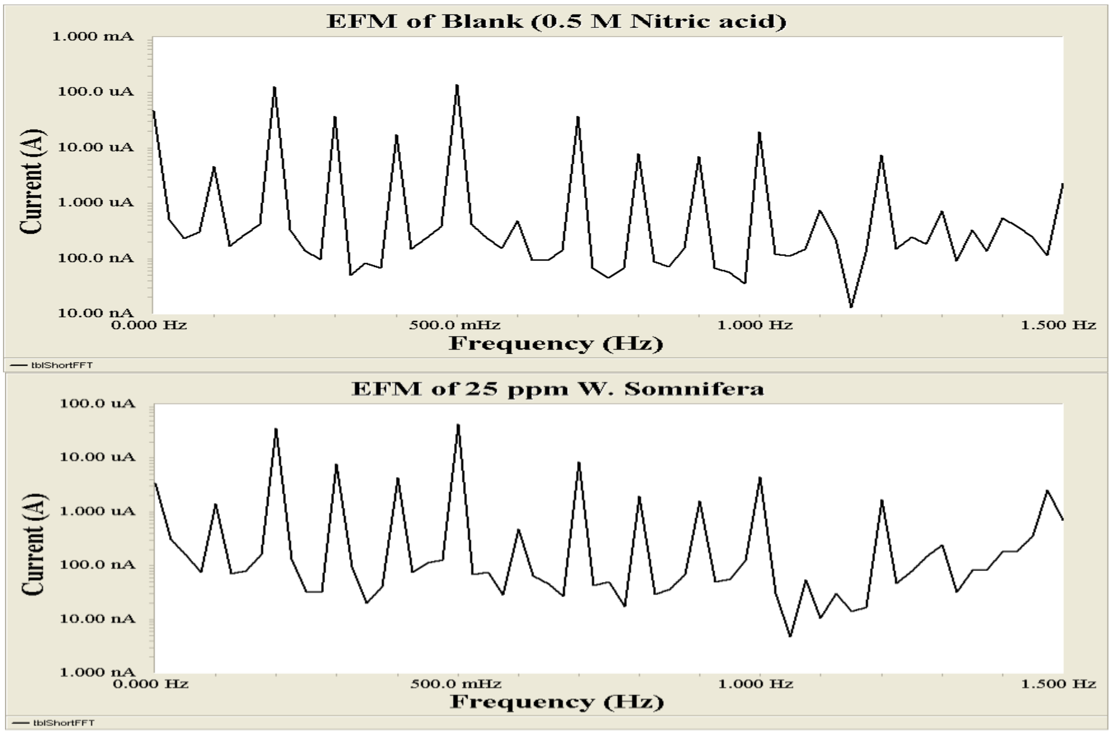


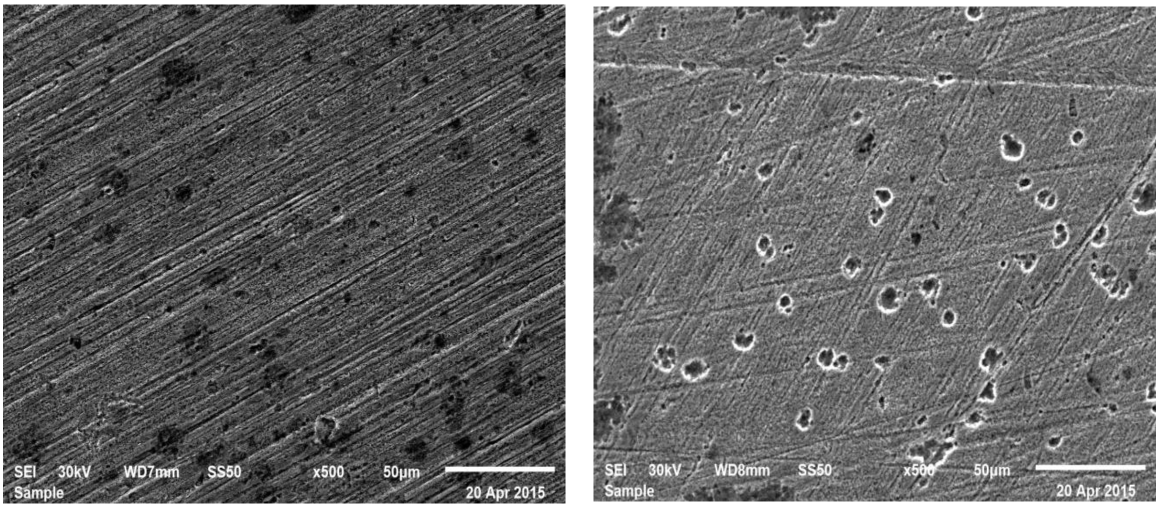
Figure 11. EFM spectra for Cu in corrosive solution without and with 25 ppm of W. Somnifera

Table 8. EFM results for Cu in corrosive solution without and with different W. Somnifera concentrations

C_{inh}, ppm	i_{corr}, μAcm^{-2}	β_c, $mVdec^{-1}$	β_a, $mVdec^{-1}$	CF-2	CF-3	CR , μmy^{-1}	Θ	% IE
Blank	163.4	253	47	2.01	4.86	90.35	—	—
5	47.97	141	52	1.90	3.54	26.52	0.706	70.6
10	46.59	131	48	1.92	3.63	25.76	0.715	71.5
15	46.31	130	50	1.90	2.98	25.61	0.717	71.7
20	46.09	139	50	1.90	2.89	25.48	0.718	71.8
25	42.5	132	49	1.87	2.84	23.50	0.740	74.0

3.7. Scanning electron microscopy (SEM) analysis

SEM for Cu metal surface without and with 25 ppm of W. Somnifera was illustrated in Figure 12 (a & b). In Figure 12 (a) (without W. Somnifera), the micrographs displayed an extended etching contains green and dark areas with some white areas. The green areas indicate the protective film that contains mainly Cu and its oxides, while the dark areas indicate the Cu corroded areas. In Figure 12 (b)(with 25 ppm of W. Somnifera), it is clear that W. Somnifera provided good protection at the surface of the Cu metal as it forms a protective film on the surface.

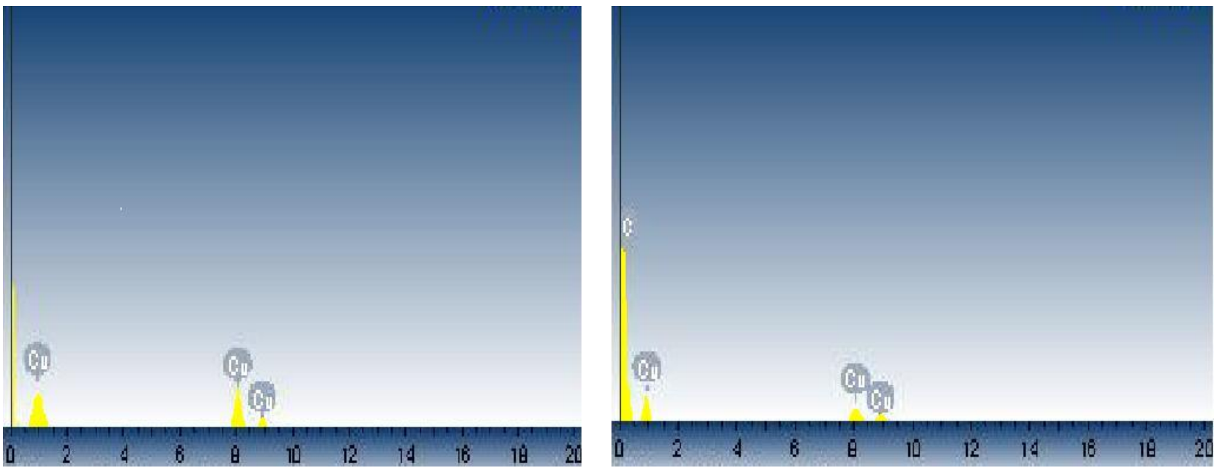


(a) (b)

Figure 12. SEM for Cu (a) in corrosive solution and (b) in corrosive solution with 25 ppm of W. Somnifera

3.8. Energy dispersive X-ray (EDX) analysis

EDX for Cu without W. Somnifera (Figure 13(a)) revealed that only Cu is present. EDX analysis of Cu with 25 ppm of W. Somnifera (Figure 13(b)) showed an additional line of C, indicates the protective film of W. Somnifera on the Cu surface. Table 9 presented the weight % (wt %) of Cu and carbon atoms in the protective films on the Cu surface without and with 25 ppm of W. Somnifera as obtained from EDX. It is clearly shown that Cu% on the surface was decreased in the presence of W. Somnifera compared with the blank, while C% increased because of the adsorption of W. Somnifera on the Cu surface.



(a) (b)

Figure 13. EDX analysis of Cu surface after exposure to the corrosive solution (a) without W. Somnifera (b) with 25 ppm of W. Somnifera

Table 9. Wt % of substances obtained from EDX for Cu surface without and with 25 ppm of W. Somnifera

C_{inh}, ppm	Wt%	
	Cu %	C %
Blank	100	——
25	20.99	79.01

Figure 14 shows a comparison of %IE at different W. Somnifera concentrations as recorded using the different techniques. It is clear that the obtained %IE values were in good agreement, this guarantees the validity of these techniques in determining the inhibitory effect of W. Somnifera on Cu dissolution in 0.5 M HNO_3

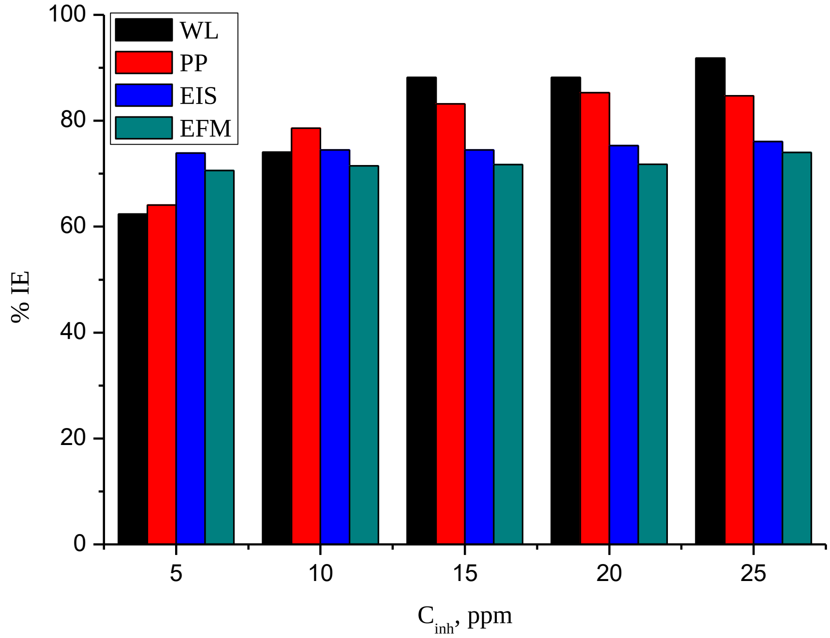


Figure 14. Comparison of %IE (recorded using WL, PP, EIS and EFM measurements) obtained for Cu in corrosive solution with different W. Somnifera concentrations

3.9. Corrosion inhibition mechanism

The inhibitory action of W. Somnifera on corrosion of Cu in 0.5 M HNO_3 can be clarified mainly on adsorption. It is apparent from photochemical analysis of W. Somnifera that the chemical constituents which identified in the methanolic extract of W. Somnifera plant (Table 2), contain a lot of heteroatoms (O atoms), functional group (OH group), and π-electrons, which widely aid in the adsorption process, and so in inhibition action. Since Cu has the ability to form coordinative bonds with atoms able to share with electrons like O atoms, W. Somnifera adsorption on Cu surface can be referred to coordination with O atoms and rings having π electrons. Also, the inhibitory action can be illustrated on the basis of the molecular weight, where molecules with large size will cover larger surface areas, so delaying corrosion [64]. Since the chemical constituents identified in the methanolic extract of W. Somnifera plant have large molecular weights (Withaferine A has molecular weight = 470.60 g/mol and Dihydrowithaferin-A has molecular weight = 472.6136 g/mol), they will cover large Cu surface areas and so delaying its corrosion. Table 10 shows a comparison between %IE of some plant extracts for Cu corrosion in HNO_3. As shown from the table, W. Somnifera can be used effectively as Cu corrosion inhibitor in HNO_3.

Table 10. Comparison between %IE of some plant extracts for Cu in HNO_3

Extract	C_{inh}	$[HNO_3]$	%IE	Reference
Trigonella stellate extract	250 ppm	1 M	63.3	65
Azadirachta Indica (AI) leaves extract	1.2 g/l	0.5 M	94.5	66
Euphorbia heterophylla extract	25 ppm	0.5 M	90.1	67
Withania Somnifera extract	25 ppm	0.5 M	91.8	Our results

4. CONCLUSIONS

W. Somnifera was examined as a Cu corrosion inhibitor in 0.5 M HNO_3 using WL, PP, EIS, EFM, SEM, and EDS techniques. The brief of the obtained results is as follows:

As W. Somnifera concentration increases, the Cu weight loss decreases. Desorption of W. Somnifera molecules from the metal surface takes place by increasing temperature. Adsorption of W. Somnifera on Cu surface is physically and followed Frumkin isotherm. Increasing W. Somnifera concentration causes little shift in PP curves toward both positive and negative potentials, indicating a mixed type mechanism. By adding more of W. Somnifera, R_{ct} increases while C_{dl} decreases. W. Somnifera makes the Cu surface smoother. The results from the used techniques showed a similar range of %IE, indicating the validity of the studied techniques.

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