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Methanol Extract of Slanum Nigrum as Eco-Friendly Corrosion Inhibitor for Zinc in Sodium Chloride Polluted Solutions

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In this work, *Slanum Nigrum* extract has been tested as eco-friendly green dissolution inhibitor for zinc in 3.5% NaCl and 16 ppm Na_2S solution by using mass loss, Tafel polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The surface morphology of zinc specimens in absence and presence of *Slanum Nigrum* extract has been evaluated by SEM and AFM measurements. The obtained results has been illustrated that *Slanum Nigrum* extract functioned as an effective and good inhibitor. The inhibition efficiency has been found to improve with improvement of extract dose but decreases with improvement in temperature reaching maximum inhibition efficiency 81.5% at 30°C at 500 ppm after 180 min immersion. Tafel curves illustrated that the polarization discovered that the extract coordination are mixed type and has been followed Langmuir Adsorption isotherm. The adsorption of the extract molecules on zinc metal surface has been agreed with Freundlich and Langmuir adsorption isotherms.

Keywords: *Slanum Nigrum*, 3.5% NaCl and 16 ppm Na_2S solution, Zinc corrosion, Mass loss, Tafel Polarization, EIS, EFM, SEM, AFM.

1. INTRODUCTION

Corrosion has been defined as metal properties dissolution due to its chemical and electrochemical reactions with its environment. Dissolution leads to harm effects on metal properties such as malleability, ductility and electrical conductivity are lost. Synthetic organic compounds have been used as corrosion inhibitors for dissolution prevention of many metals and alloys in various aggressive environments. Because of their hazardous nature, researchers focus their attention on developing cheap, biodegradable, non-toxic, and environment friendly natural products of plant origin as corrosion inhibitors [1-10]. Plant materials Extract involving nitrogen, oxygen and /or sulphur atoms were used to prevent dissolution of Zn and others metals in different corrosion medium such as NaCl, HCl [11-16].

Zinc metal electrochemical properties had been exercised to a large extent. Its imposition in batteries (secondary silver-zinc, primary alkaline zinc battery and both primary and secondary zinc-air batteries) [17] Sacrificial protection of mild steel, especially in automobile bodies and building construction [18] and in solar energy application [19].

Solanum nigrum is a medicinal plant has been extensively used traditionally to treat various impairments such as inflammation, fever and pain has been also applied in the oriental systems of medicine for various objectives – as an antitumorigenic, antioxidant, epatoprotective, diuretic, antipyretic agent, a strong sudorific, analgesic and sedative with powerful narcotic properties [20-25]. Structures of some of the previously isolated phytoconstituents from *Solanum nigrum* are shown in scheme 1.

In present work extract leaves and grains of *Solanum nigrum* had been applied as dissolution inhibitor as an example for green chemistry for zinc metal in 3.5% NaCl and 16 ppm Na_2S solution using chemical and electrochemical tests.

2. EXPERIMENTAL

2.1. Sample Material Composition

The chemical composition of zinc (BDH grade) has been used in this investigation:

Element	Pb	Fe	Cd	Cu	Zn
weight%	0.001	0.002	0.001	0.003	Rest

2.2. Solutions

Dissolution medium employed has been 3.5% NaCl and 16 ppm Na_2S designed from analytical grade and bidistilled water has been utilized in preparation of solutions. A stock solution of sodium chloride (3M) has been prepared by using distilled water. Dissolve 175.5 g of anhydrous sodium chloride in 500 ml freshly prepared distilled water then dilute to 1000 ml with the distilled water then withdrawal 20 ml from stock solution then dilute to 100 ml to prepare 3.5% sodium chloride. A stock solution of sodium sulfide (1000 ppm) has been prepared using bi-distilled water. Launder crystals of sodium sulfide with de-ionized water to eject oxidation products contaminants and patch dry the crystals with a tissue. Dissolve 1g of anhydrous sodium sulfide in 250 ml freshly prepared distilled water then dilute to 1000 ml with the distilled water then withdrawal 1.6 ml from stock solution then dilute to 100 ml to prepare 16 ppm sodium sulfide.

2.3. Plant Extract production

Solanum nigrum plant has been gained from local market. It has been scour under tap water to remove and scour mud particles. The plant leaves and grains have been dried in a furnace for 2 hours at 100^{o}C to get powder form of material. About 50 g of the powder has been soaked in a 250 ml of methanol under cold percolation method. At regular intervals of time the extract has been filtered and distillation has been carried out to collect the crude extract. The extract has been stored in an amper bottle and refrigerated [26].

2.4. Measuring Tests

2.4.1. Mass loss tests:

Tested pieces were 20 x 20 x 2 mm. The pieces have different scales of emery papers were first abraded (up to 1200 grit size) to obtain a soft surface, pursued by ultra-sonically degreasing with ethanol, then swilled with bidistilled water, dried between two filter papers and weighted.

In mass loss tests, pre-weighed zinc metal specimens have been hanging in a 100 ml beaker containing 50 ml of 3.5% NaCl and 16 ppm Na_2S solutions for 180 minutes. Then metal specimens had been ejected from corrosive medium, swilled by bidistilled water, scour, dried and reweighted. From this metal mass loss has been determined the difference between the initial weight and weight after 180 minutes inundation in acid media. The tests had been repeated with both mediums in absence and in presence of inhibitors with various concentrations. Each test has been repeated thrice and the average of the three values was taken as the final value. The efficiency of inhibition (IE%) and the surface coverage degree (θ) have been calculated using equation (1).

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

Where W_o and W_i are mass losses per unit area in absence and presence of examined extract.

2.4.2. Electrochemical tests:

Zinc electrodes have been cut from zinc plates, thickness 0.088 mm. Electrodes dimensions are 10 x 10 mm and have been weld from one side to a copper wire in order to electric connection and had been coated with epoxy resin, to expose geometrical surface areas of 1 cm^2. Prior to these tests, the exposed surface has been pretreated in the same manner as for mass loss tests.

2.4.3. Potentiodynamic polarization test

Electrochemical tests have been achieved in a three electrode electrochemical cylindrical Pyrex glass cell with a platinum counter electrode and saturated calomel electrode (SCE) as reference. The working electrode had the form of a square cut from Zn sheet (1 cm^2). The exposed area has been treated as before. A duration time 30 min has been given for the system to attain a steady state and the open circuit potential (OCP) was noted. Both anodic and cathodic polarization curves have been registered potentiodynamically by changing the electrode potential between -0.5V and -2V, at scan rate of 1 mVs-1, inhibition efficiency (IE%) and surface coverage degree (θ) have been calculated from the electrochemical tests by equation (2):

$$\% IE = \Theta \times 100 = [1-(i_{inh}/i_{free})] \times 100 \quad (2)$$

Where, i_{inh}. = Corrosion current in presence of inhibitor and i_{free} Corrosion current in absence of inhibitor.

2.4.4. EIS and EFM tests

EIS tests experiments have been connected in frequency range of 100 kHz to 10 mHz at open circuit potential (OCP). The amplitude has been 5 mV. EFM tests Experiments have been achieved using two frequencies 2 and 5 Hz. The base frequency was 1Hz with 32 cycles, so the waveform repeats after 1s. A perturbation signal with amplitude of 10 mV has been used.

Electrochemical measurements have been achieved using Potentiostat/Galvanostat/Zera analyzer (Gamry PCI 300/4). This involves Gamry framework system based on the ESA400, and a personal computer with DC 105 software for potentiodynamic polarization, EIS 300 software for EIS, and EFM 140 software for EFM tests. Echem Analyst 5.58 software has been utilized for plotting, graphing and fitting data.

3. RESULTS AND DISCUSSION

3.1. Mass loss tests

3.1.1. Effect of inhibitors concentrations and inundation time

Mass loss of zinc in 3.5% NaCl and 16 ppm Na_2S in absence and presence of different concentrations of *Solanum Nigrum* extract (50-500 ppm**)**, have been specified at different times of immersion (30 to 180 min.) at 30°C. Table 1 illustrated that values of the inhibition efficiency raised with increasing of *Solanum Nigrum* extract concentration this action should be referred to the raise of the surface area covered by the adsorbed molecules of extract with the improve of its concentration [27, 59, 60]. To elucidate the effect of immersion time on corrosion rate of zinc, the data have been obtained from mass loss measurements for different periods illustrated in Fig. 1, mass loss of zinc enhances with immersion time. On the other hand, by improving the concentration of *Solanum Nigrum* extract, the mass loss of zinc samples have been decreased. This means that *Solanum Nigrum* extract act as inhibitor. *Solanum Nigrum* extract gives maximum inhibition efficiency of 81.5% at 500 ppm concentration and 30^{o}C after 180 min inundation.

Table 1. Mass loss of zinc dissolution in 3.5% NaCl and 16 ppm Na_2S solution containing different concentrations of *Solanum Nigrum* extract after 180 min immersion at 30°C.

Solanum Nigrum Conc., ppm	50	100	200	300	400	500
% IE	37.8	49.6	58.0	65.9	74.7	81.5

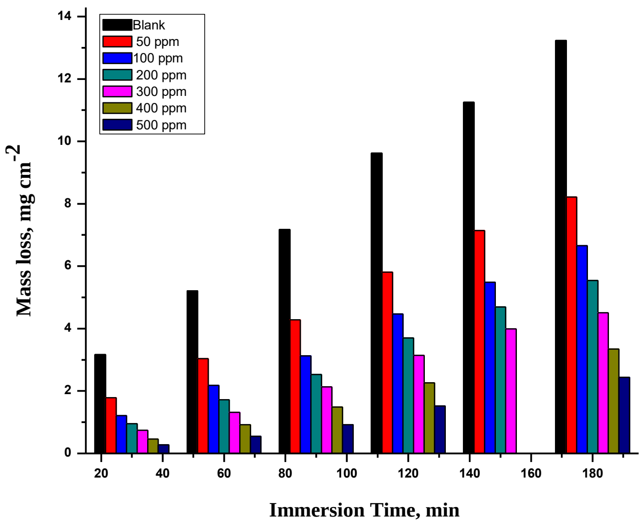


Figure 1. Mass-loss versus immersion time for Zn in 3.5% NaCl and 16 ppm Na_2S solution in absence and presence various concentrations of *Solanum Nigrum* at 30°C.

3.1.2. Adsorption Isotherm

Examining mechanism of *Solanum Nigrum* corrosion inhibition, efforts have been made to fit data available to various adsorption isotherms. Adsorption of *Solanum Nigrum* on zinc metal surface has been agreed with Freundlich and Langmuir adsorption isotherm Fig. 2 and Fig. 3 (R^2 is nearly to unity), Freundlich isotherm has been the earliest known relationship characterizing the sorption equation. The fully favorable empirical isotherm can be utilized for non-ideal sorption that comprises heterogeneous surface energy system and has been expressed by the following equation [28, 59, 60].

$$\Theta = K_{ads} C^n \qquad (3)$$

where C is the inhibitor concentration, K is the adsorption equilibrium constant denoting the strength of interaction in the adsorbed layer and ‘n’ is a constant such that $0 \leq n \leq 1$.

The Langmuir adsorption model hypothesizes that there is no interaction between adsorbed molecules and adsorption energy is independent on the surface coverage (Θ) and maximum adsorption corresponds to the saturated monolayer of Langmuir equation may be described by equation (4),[29, 30].

$$C/\Theta = 1/K + C \qquad (4)$$

ΔG^o_{ads} value for Freundlich adsorption of *Solanum Nigrum* extract components found to be -4.483 kJ mol-1. The negative and low sign of adsorption free energy mentions that adsorption of *Solanum Nigrum* extract at Zn surface is a spontaneous process and physical adsorption [31]. Positive and large values of K_{ads} gained (0.11 x 103 mol^{-1}) suggest significantly strong interaction between the adsorbed components of *Solanum Nigrum* extract and is independent of all factors except temperature [32, 59, 60]. The experimental data fit to above isotherms has been hinted that interaction with metal surface through electrostatic attraction (physical adsorption) [33,34]. Value of ΔG^o_{ads} for Langmuir -21.4813 kJ mol^{-1} the negative value gained of ΔG^o_{ads} that *Solanum Nigrum* extract has been spontaneously physisorbed on metal surface [35,36].

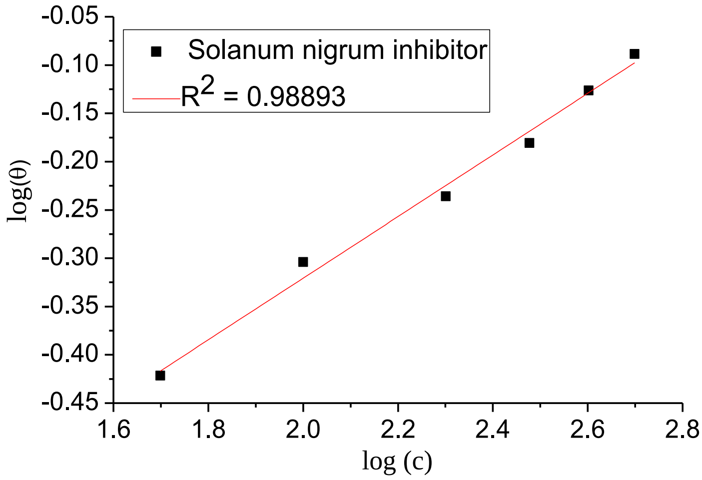


Figure 2. Freundlich adsorption isotherm plotted as logΘ vs. logC of *Solanum Nigrum* extract for corrosion of Zn in 3.5% NaCl and 16 ppm Na_2S solution at 30°C.

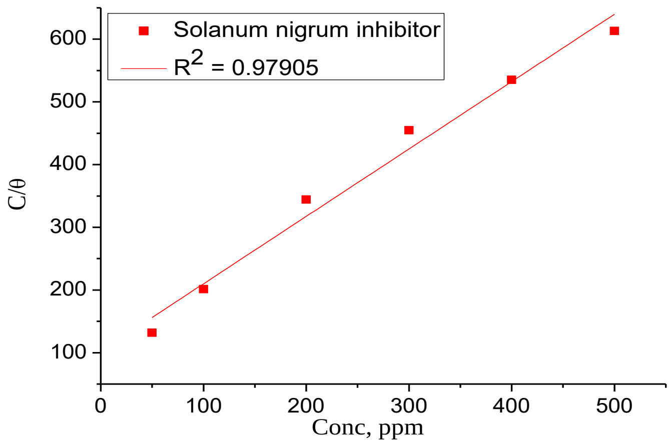


Figure 3. Langmuir adsorption isotherm plotted as C/Θ vs C of *Solanum Nigrum* extract for corrosion of Zn in 3.5% NaCl and 16 ppm Na_2S solution at 30°C.

3.1.3. Effect of temperature

Temperature effect on the % IE of the *Solanum Nigrum* inhibitor has been specified by mass loss test at various concentrations & various temperatures (30-50°C) for a fixed inundation time of 180 minutes has been illustrated in Fig. 4. Data in Table 2 appeared that the inhibition efficiency reduced by raising temperature, due to desorption of adsorbed inhibitor components on Zn surface. This appearing that extract components are physically adsorbed on the metal surface.

Table 2. Effect of temperature on % IE of the *Solanum Nigrum* extract at various concentrations and at various temperatures (30-50°C) after 180 min.

	Solanum Nigrum Conc., ppm					
Temp,^{o}C	50	100	200	300	400	500
	% IE					
30	37.8	45.8	52.3	60.7	66.3	73.2
35	33.2	42.5	49.8	57.9	63.8	70.6
40	30.9	39.8	47.5	55.8	60.2	68.4
45	26.9	35.5	44.3	52.1	57.2	65.7
50	22.5	31.2	40.6	48.5	54.9	60.5

3.1.4. Thermodynamic calculations

The apparent activation energy (E^*_a) of metal corrosion in acid media must be calculated from Arrhenius equation (5).

$\ln k = (E^*_a)/RT + A$ (5)

Where k is the corrosion rate, (E^*_a) is the apparent activation energy for the corrosion of Zn, R is the universal gas constant, A is Arrhenius pre exponential factor and T is the absolute temperature. The values of the activation energies, E^*_a, has been calculated from slopes of the straight lines of Fig.4. Activation energies values, E^*_a, for dissolution of zinc in absence and presence of *Solanum Nigrum* extract in 3.5 % NaCl + 16 ppm Na2S solution have been presented in Table 3.

An alternative formulation of Arrhenius equation is transition state equation (6) [37, 59, 60].

$k = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$ (6)

where h is Planck's constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Fig. 5 show a plot of log k/T against 1/T.A straight line has been obtained with slopes of ($-\Delta H^*/2.303R$) and an intercept of ($\log R/Nh + \Delta S^*/2.303R$) [38], from which ΔH^* and ΔS^* values were calculated, respectively. The calculated values of the apparent activation energy, Ea^*, activation enthalpies, ΔH^* and activation entropies, ΔS^* have been reported in Table 3 which reported that these values denote that presence of *Solanum Nigrum* extract improving activation energy, (E_a^*) and activation enthalpy, ΔH^* and reduces activation entropy, ΔS^* for corrosion process. The raising in the activation energy denoting that a strong adsorption of inhibitor molecules on Zn surface and denote the energy barrier caused by adsorption of *Solanum Nigrum* molecules on Zn surface. The raising in activation enthalpy (ΔH^*) in presence of the inhibitors implies that addition of inhibitors to the 3.5 % NaCl and 16 ppm Na_2S solution improving height of energy barrier of corrosion reaction to an extent depends on type and concentration of present inhibitor. The entropy of activation (ΔS^*) in blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step [39-42].

The (E_a^*) high value in presence of *Solanum Nigrum* extract matching to that in its absence and the reduce in the %IE with rising temperature is explicate as indication of physisorpation [43–45]. The ΔH^* positive values displays that inhibitor adsorbs onto zinc surface through endothermic nature of zinc dissolution process and it mentions that dissolution of zinc is difficult. The ΔS^* negative values mentions that inhibitor molecules in bulk solution are adsorbed in an orderly fashion onto zinc surface resulting in a reduce in entropy.

Table.3. Activation parameters for Zn dissolution in absence and presence of various concentrations of *Solanum Nigrum* extract in 3.5% NaCl and 16 ppm Na_2S.

Extract	Conc., ppm	Activation parameters		
		Ea^*	ΔH^*	$-\Delta S^*$
Blank	3.5 % NaCl + 16 ppm Na_2S	18.8	8.1	157.3
Solanum nigrum extract	50	27.5	11.9	132.6
	100	30.9	13.4	123.0
	200	31.9	13.8	121.0
	300	34.4	14.9	114.3
	400	42.6	18.5	89.7
	500	49.7	21.5	69.1

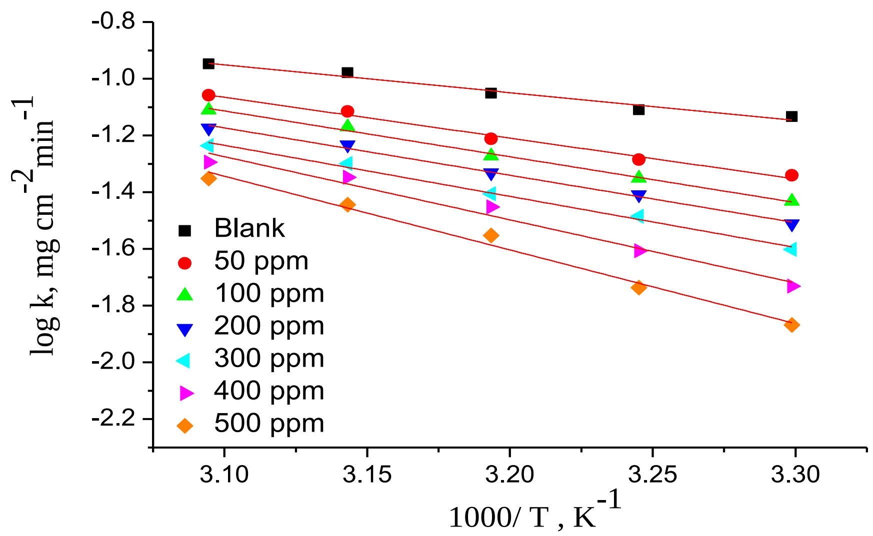


Figure 4. Arrhenius plots (logk *vs*. 1000/T) for Zn in 3.5% NaCl and 16 ppm Na_2S in absence and presence of various concentrations of *Solanum Nigrum* extract.

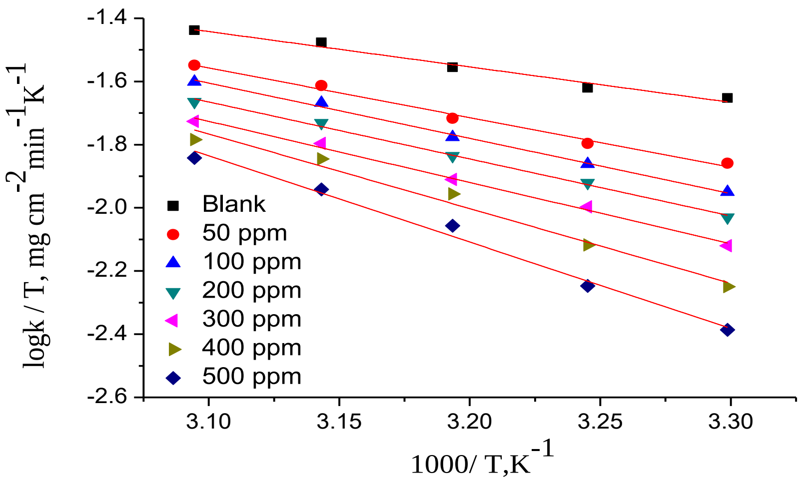


Figure 5. Arrhenius plots (log k/T *vs.* 1/T) for Zn in 3.5% NaCl and 16 ppm Na_2S in absence and presence of various concentrations of *Solanum Nigrum* extract.

3.2. Electrochemical tests

3.2.1. Potentiodynamic polarization tests

Zinc potentiodynamic polarisation curves in 3.5% NaCl and 16 ppm Na_2S solution with and without different concentrations of *Solanum Nigrum* extract has been illustrated in Fig. 6, Kinetic parameters of electrochemical corrosion obtained via Tafel extrapolation method have been showed in Table 4.

Table 4. Corrosion parameters of Zn electrode in 3.5% NaCl and 16 ppm Na_2S solution in absence and presence of various concentrations of *Solanum Nigrum* extract at 25^{o}C.

Conc., ppm	$-E_{Corr}$ mV vs SCE	i_{corr} mA cm^{-2}	Tafel slopes		R_p Ω cm^2	Θ	%IE
			$-\beta_a$ mVdec^{-1}	β_c mVdec^{-1}			
Blank	963.9	0.7319	34	173	29.12	--	--
50	964.1	0.5123	32	153	41.71	0.303	30.3
100	964	0.4091	29	109	52.92	0.441	44.1
200	964.1	0.3024	28	104	70.68	0.586	58.6
300	963.9	0.2351	27	69	90.7	0.678	67.8
400	964	0.1808	25	60	119.9	0.752	75.2
500	964.2	0.1332	18	33	156.6	0.818	81.8

In corrosion potential (E_{corr}) no definite shift has been discovered, although there was no specific relation between E_{corr} and inhibitor concentration. It can be seen from Fig. 6 that anodic and cathodic reactions have been affected by presence of the extract indicating that *Solanum Nigrum* extract acts as mixed-type inhibitor. *Solanum Nigrum* extract addition to 3.5 % NaCl and 16 ppm Na_2S solution therefore decreases anodic dissolution of Zn and also block the hydrogen evolution cathodic reactions. It can be seen from the polarization results that the corrosion current density (i_{corr}) decreased with increasing in inhibitor concentration, due to raise in blocked fraction of the metal surface by adsorption. The polarization resistance (R_p) has been improved with increasing in *Solanum Nigrum* extract concentration. The inhibition efficiencies have been calculated from the corrosion current density and the polarization resistance has been increased with the inhibitor concentration reaching a maximum value 81.5 % at 500 ppm [46, 53-58].

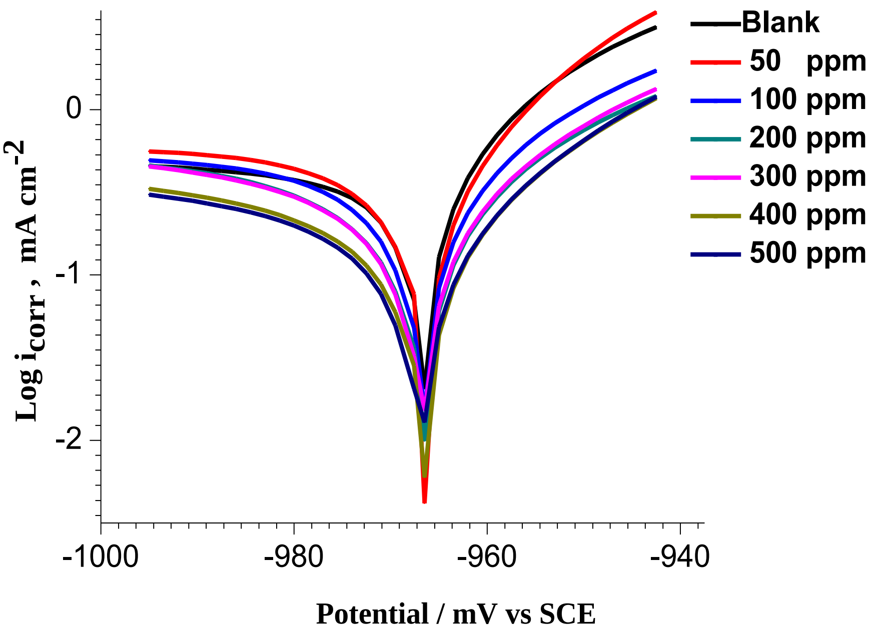


Figure 6. Potentiodynamic polarization curve for zinc corrosion in 3.5% NaCl and 16 ppm Na_2S in absence and presence of various concentrations of *Solanum Nigrum* extract at 25^{o}C.

3.2.2. EIS tests

Electrochemical Impedance Spectroscopy (EIS), have been presented to be an efficient and convincing tool for analyzing dissolution behavior of metals. The Impedance diagrams Nyquist plot & bode plot have been obtained for Zn in absence and presence of various concentrations of *Solanum Nigrum* extract in 3.5 % NaCl and 16 ppm Na_2S solution illustrated in Fig. 7 & Fig. 8. As a result, the semicircle in presence of inhibitor is greater than that in absence of inhibitor (Blank) and raises as inhibitor concentrations have been raised. This confirms that the impedance of inhibited Zn substrate has been improves with raising *Solanum Nigrum* extract concentration. Electrochemical impedance parameters have been calculated from the Nyquist plots and are reported in Table 5. Charge transfer resistance values (R_{ct}**)**, % IE raise and double layer capacitance (C_{dl}**)** reduce with improving extract concentration. This is referred to a great resistance shown by adsorbed extract components at metal – solution interface and raise in thickness of electrical double layer due to adsorption of extract components. Hence, it is deduced that extract molecules gradually substitute water molecules by adsorption at metal/solution interface, which progress to formation of a protective film on Zn surface and thus deduces the extent of the dissolution reaction [47, 53-58]. The equivalent circuit drawn in Fig. 9 has been utilized to test the impedance spectra for *Solanum Nigrum*.

Table 5. Impedance parameters and inhibition efficiency for zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in absence and presence of various concentrations of *Solanum Nigrum* at 25°C.

Conc, ppm	R_{ct} ohm cm^2	C_{dl} µF cm^{-2}	Θ	%IE
Blank	82.3	1.80	--	--
50	131.4	1.76	0.378	37.8
100	162.4	1.62	0.493	49.3
200	197.9	1.51	0.584	58.4
300	240.6	1.42	0.658	65.8
400	316.8	1.33	0.740	74.0
500	415.5	1.27	0.815	81.5

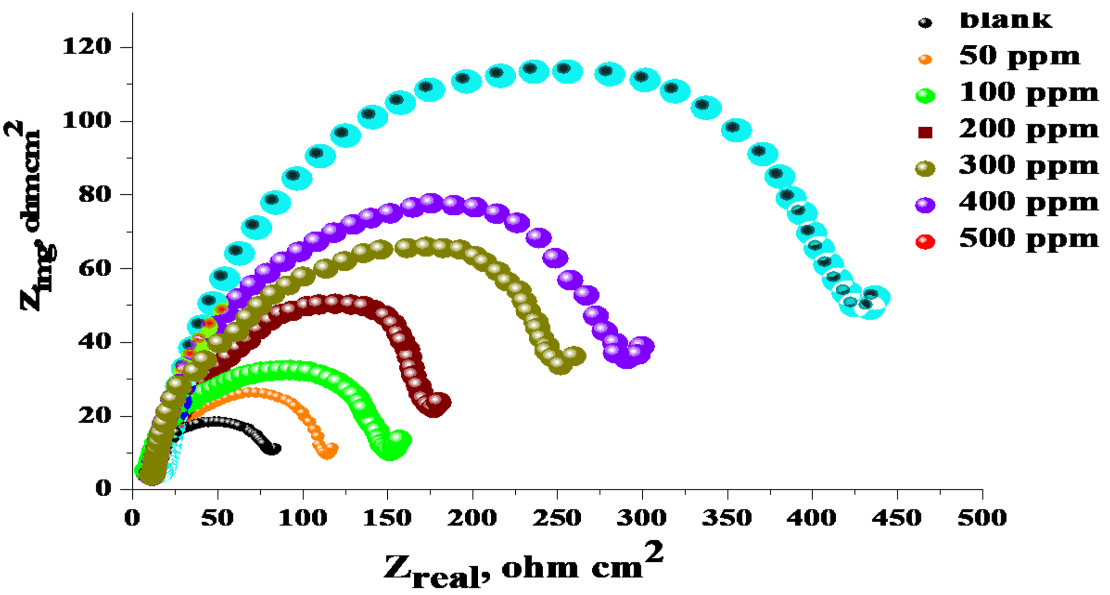


Figure 7. Nyquist plots for Zn corrosion in 3.5% and 16 ppm Na_2S solution in absence and presence of various concentrations of *Solanum Nigrum* at 25°C.

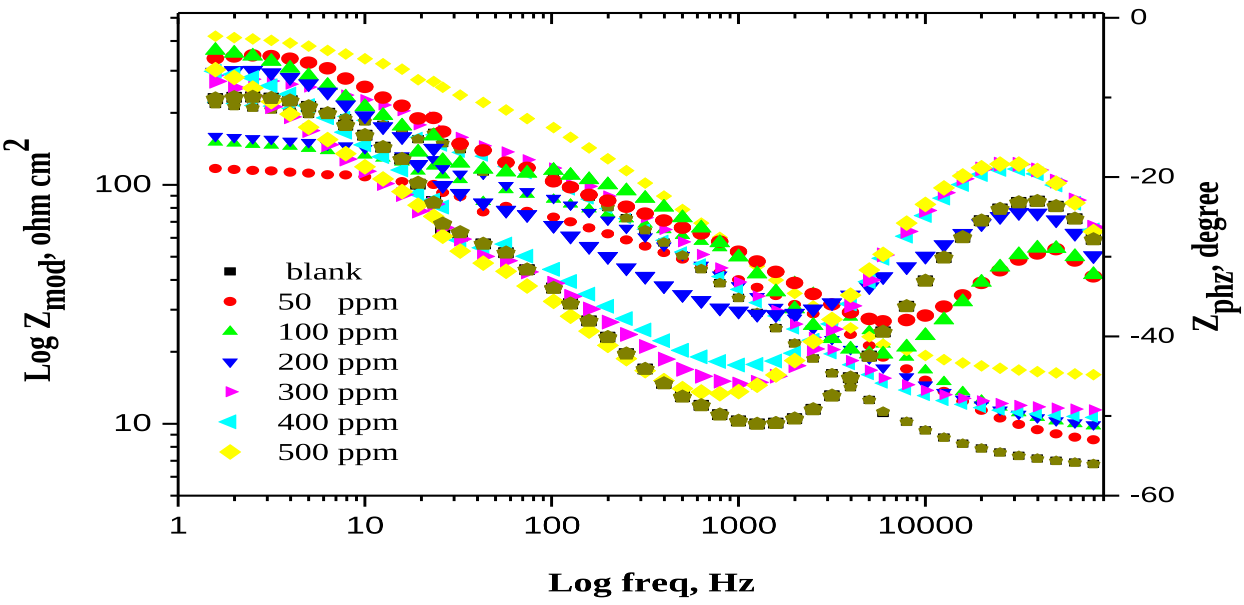


Figure 8. Bode plots gained from zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in absence and presence of various concentrations of *Solanum Nigrum* at 25°C.

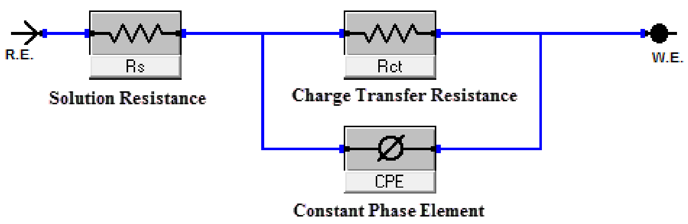


Figure 9. Equivalent circuit model used to fit experimental EIS data

3.2.3. EFM tests

The electrochemical frequency modulation **(**EFM) hasn't destructive technique of corrosion test that can directly allow values of corrosion current without prior knowledge of Tafel constants [48,49, 53-58]. Fig. 10 has been illustrated the intermodulation spectra gained from EFM tests of zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in absence of investigated *Solanum Nigrum* extract, and Fig. 11 has been illustrated the intermodulation spectra gained from EFM tests of zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in presence of 500 ppm *Solanum Nigrum* extract. The calculated corrosion kinetic parameters at various concentrations of the *Solanum Nigrum* in 3.5% NaCl and 16 ppm Na_2S at 25^{o}C has been illustrated in Table 6. From this Table, the corrosion current density reduces and the inhibition efficiency has been improved by raising concentration of investigated extract. The major strength of EFM is the causality factor, which avails as an internal check on the validity of the EFM test [50]. CF-2 and CF-3 standard values are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might due to that the perturbation amplitude was too small or that the frequency spectrum resolution has not high enough.

Table 6. EFM spectra of zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in absence and presence of various concentrations of *Solanum Nigrum* at 25°C.

Conc., ppm	$i_{corr.}$ μA cm^{-2}	β_a mV dec^{-1}	β_c $mVdec^{-1}$	CR mpy	CF2	CF3	ϴ	% IE
Blank	331.5	71	52	305.5	2.249	2.161	--	--
50	208.2	31	54	213.9	2.33	1.023	0.371	37.1
100	166.2	32	52	153.1	2.428	1.103	0.498	49.8
200	138.4	36	49	146.5	2.249	2.161	0.580	58.0
300	115.1	43	47	101.7	2.454	2.412	0.653	65.3
400	85.0	49	46	88.39	2.302	1.62	0.743	74.3
500	60.2	51	52	48.33	2.033	6.420	0.818	81.8

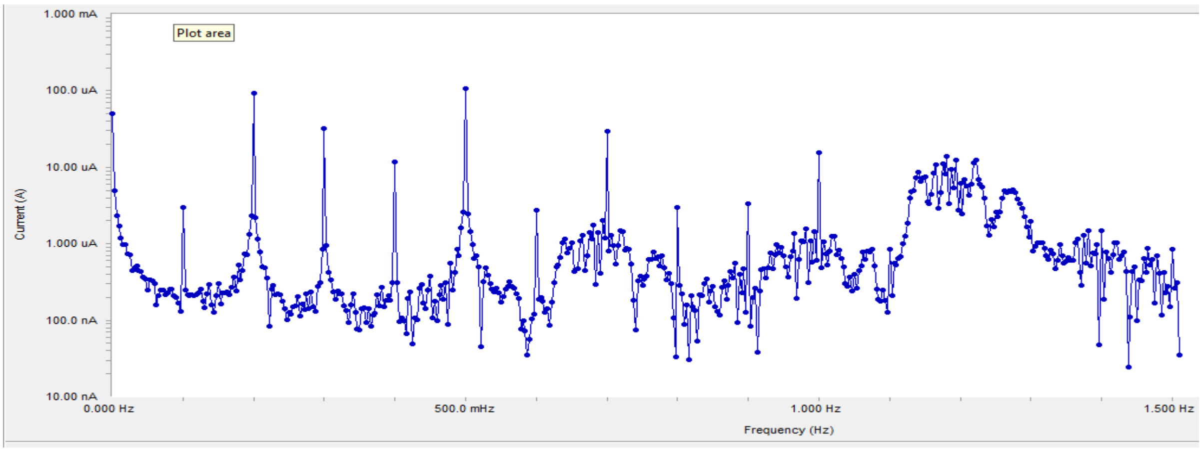


Figure 10. EFM spectra gained from zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in absence of *Solanum Nigrum* at 25°C.

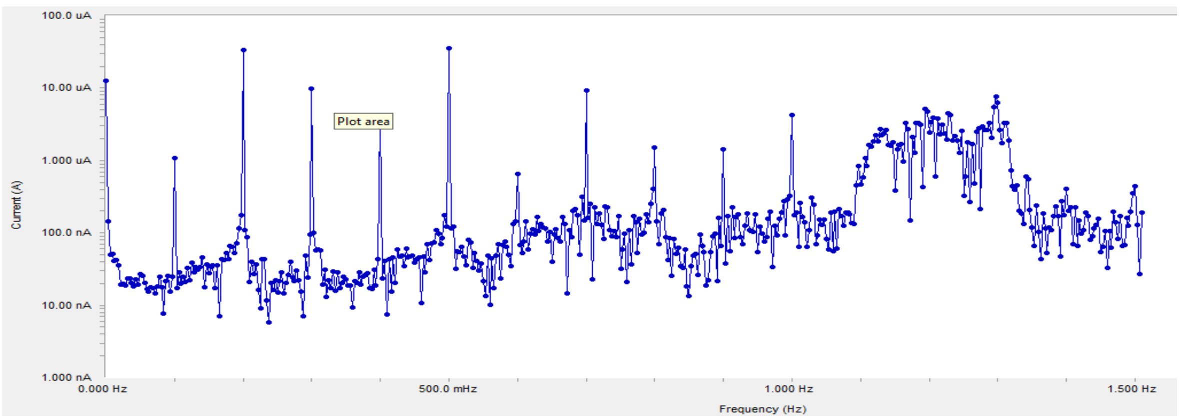


Figure 11. EFM spectra gained from zinc corrosion in 3.5% NaCl and 16 ppm Na_2S solution in presence of 500 ppm of *Solanum Nigrum* at 25°C.

3.2.4. Surface examination measurements

3.2.4.1. SEM Studies

Fig. 12 illustrate an Scanning Electron Microscopy **(**SEM) photograph gained from Zinc Polished samples (A) and immersed in 3.5% NaCl and 16 ppm Na_2S solution for 12 h (B) and with 500 ppm of *Solanum Nigrumm* extract at 25°C. The polished zinc surface photograph before immersion in 3.5% NaCl and 16 ppm Na_2S solution has been illustrated in Figure 12a. The photograph displays that surface was very soft and without any cavity. SEM micrograph of corroded zinc in presence of 3.5% NaCl and 16 ppm Na_2S solution has been illustrated in Figure 12b. There are facts have been seen in this figures was a result of cavity created due to the inundation of zinc in 3.5% NaCl and 16 ppm Na_2S solution. The influence of the inhibitor addition 500 ppm on the zinc in 3.5% NaCl and 16 ppm Na_2S solution has been illustrated in Figure 12c. The morphology in Figure 12c give protective film has ben formed on the surface of zinc, characteristic of uniform corrosion of zinc, as previously reported [51], that corrosion has not happen in presence of inhibitor and hence corrosion has been inhibited hardly when inhibitor has been existed in 3.5% NaCl and 16 ppm Na_2S solution, and surface layer is very coarse. In contrast, in presence of 500 ppm of *Solanum Nigrumm* extract, there is much less deterioration on the zinc surface, which further assure the inhibition action. Also, there is an adsorbed film dsorbed on zinc surface Figure 12c. In conformity, it might be complemented that the adsorption film can efficiently prevents corrosion of zinc.

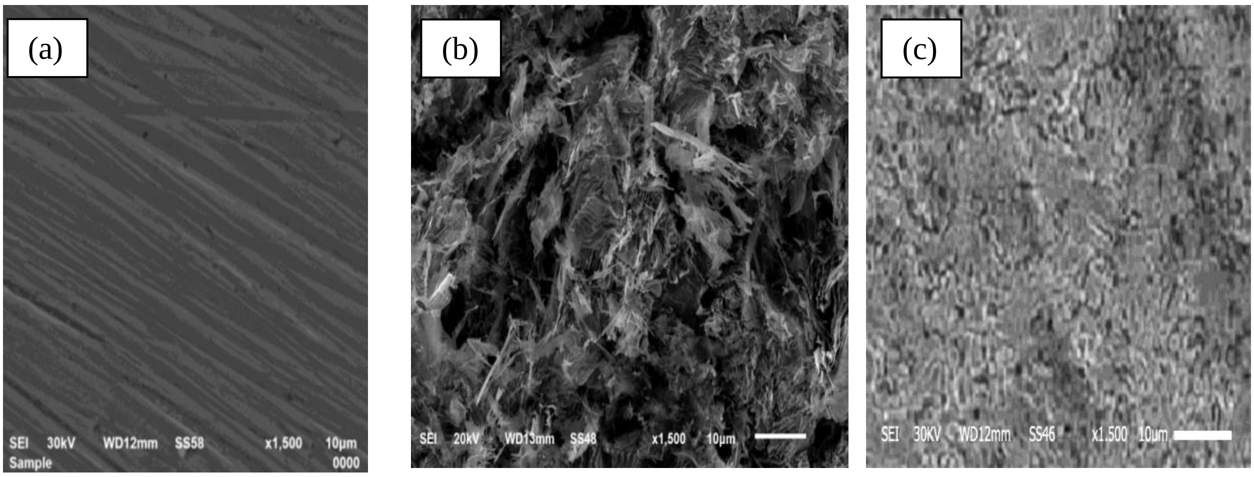
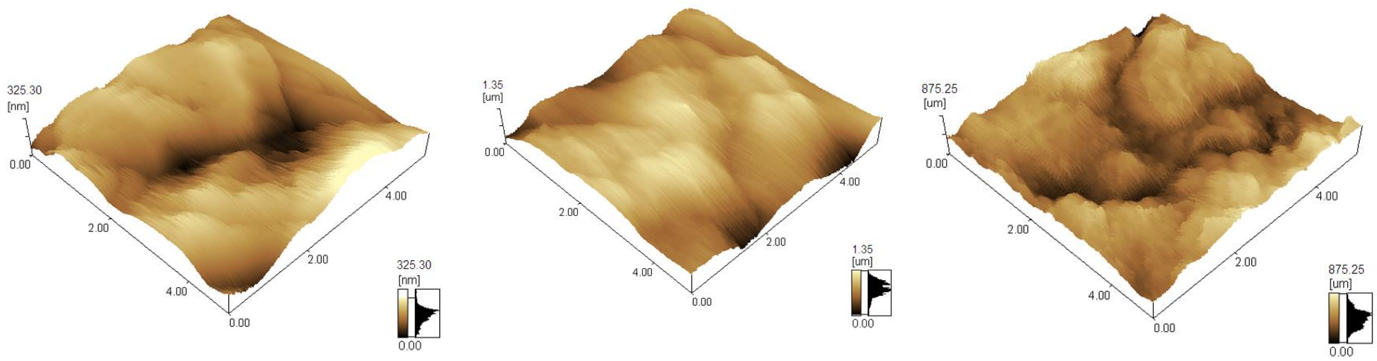


Figure 12. SEM micrographs of Zinc surface (a) before of inundation in 3.5% NaCl and 16 ppm Na_2S solution, (b) after 12 h of inundation in 3.5% NaCl and 16 ppm Na_2S solution (c) after 12 h of inundation in 3.5% NaCl and 16 ppm Na_2S solution + 500 ppm of *Solanum Nigrumm* extract at 25°C.

3.2.4.2. AFM Studies

The surface morphology of zinc surface has been tested by atomic force microscopy (AFM). In Fig. 13 (a-c) has been illustrated the surface (3D) morphology of the zinc surfaces, zinc sample specimens without and with inhibitor in 3.5% NaCl and 16 ppm Na_2S solution respectively.



(A) Zinc metal surface

(B) 3.5% NaCl and 16 ppm Na_2S solution (Blank)

(C) Tested solution containing 500 ppm of *Solanum Nigrumm* extract

Figure 13. AFM micrographs of zinc surface (a) Polished fresh specimens b) Immersed in 3.5% NaCl and 16 ppm Na_2S solution c) Immersed in 3.5% NaCl and 16 ppm Na_2S solution containing 500 ppm *Solanum Nigrumm* extract for 12 h at 25°C.

The average roughness of zinc sample polished surface (figure 13A), zinc in 3.5% NaCl and 16 ppm Na_2S solution without and with inhibitor (figures 13B-C) was reported to be 0.30, 1.35 and 0.88 μm respectively. It is clearly from the figure 13B that corroded zinc sample has been presented a coarse surface due to 3.5% NaCl and 16 ppm Na_2S solution corrosion. However in presence of inhibitor, the corrosion rate is restrained and inhibited zinc specimens surface get smoothened as shown in figure 13C. The reduce in coarseness due to formation of an adsorbed *Solanum Nigrumm* extract film on zinc surface [52].

4. CONCLUSION

The mass loss and electrochemical measurements recorded that *Solanum Nigrum* extract acts as a good green corrosion inhibitor and exhibited good inhibition efficiency for zinc in 3.5% NaCl and 16 ppm Na_2S solution. Inhibition efficiency has been improved with raising *Solanum Nigrum* extract concentration and reducing of temperature. It displayed a maximum inhibition efficiency of 81.5% at 500 ppm concentration. The inhibitor molecules adsorption on metal surface has been agreed with Freundlich and Langmuir adsorption isotherms.

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