Research Article

Corrosion Inhibition by an Aqueous Extract of Sansevieria Roxburghiana for Carbon Steel in 60 ppm of Chloride Environment

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Abstract

The corrosion inhibition efficiency(IE) of the *sansevieria roxburghiana*(SR) extract – Zn^{2+} system control the corrosion of carbon steel in 60 ppm chloride environment has been investigated by weight loss method. It is observed that The formulation consisting of 6 ml *sansevieria roxburghiana*(SR) extract, 100 ppm of sodium potassium tartarate(SPT) and 300 ppm of Zn^{2+} offers 97% inhibition efficiency. The synergistic effect exists between *sansevieria roxburghiana*(SR)– Zn^{2+} system. Polarization study reveals that this formulation controls the anodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. The value of the separation factor R_L, indicated the *sansevieria roxburghiana*(SR) system was favourable adsorption. The *sansevieria roxburghiana*(SR) extract – Zn^{2+} system may find in cooling water system.

Keywords: Corrosion, inhibition efficiency, *sansevieria roxburghiana*, synergistic effect
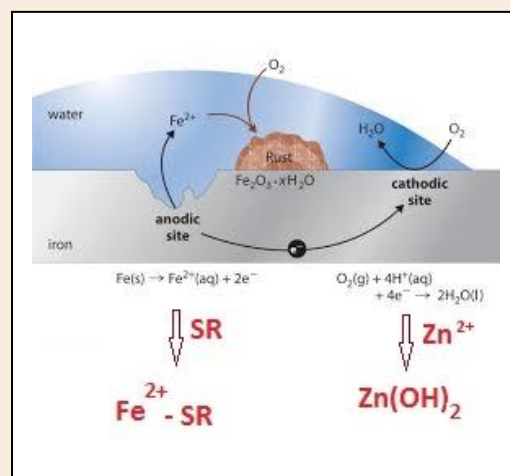
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Introduction

Corrosion is the deterioration of a metal by chemical or electrochemical reaction with its environment. The Cooling systems are exposed to many types of corrosion from general electrochemical corrosion, to pitting caused by deposits, electrolysis, or microorganisms. Corrosion can reduce the life-span of equipment by years, requiring expensive replacement. It can lead to costly equipment repairs and production downtime. Corrosion related deposits lead to reduced capacity and wasted energy because of heat transfer efficiency losses. In order to prevent or minimize corrosion, the corrosion inhibitors are usually used in flow cooling water systems.

Most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environment. Therefore, it is desirable to source for environmentally safe inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. A lot of natural products have been previously used as corrosion inhibitors[1-5] for different metals in various environments The plant extracts are environmentally friendly, non- toxic and readily available. These extracts contain many ingredients. They contain several organic compounds which have polar atoms such as O, N, P and S[6-11].

The present work is undertaken:

1. To evaluate the inhibition efficiency (IE) of an aqueous extract *sansevieria roxburghiana*(SR) in controlling the corrosion of carbon steel in aqueous medium containing 60 ppm of chloride ions in the absence and presence of Zn^{2+}
2. To understand the mechanistic aspects of corrosion inhibition by polarization studies and AC impedance analysis
3. To analysis the protective film formed on the carbon steel by Langmuir and Freundlich isotherm
4. To propose a suitable mechanism for corrosion inhibition.

Materials and Methodology

Preparation of plant extract

An aqueous extract of *sansevieria roxburghiana* (SR) was prepared by grinding 50g of *sansevieria roxburghiana*(SR) with double distilled water, filtering the suspending impurities, and making up to 500ml. The extract was used as corrosion inhibitor in the present study.

Preparation of the specimen

Carbon steel (0.026%S, 0.06%P, 0.4%Mn, 0.1% C, and the rest Fe) specimen of dimension 1 cm x 4 cm x 0.2 cm were used for weight loss study. Carbon steel rod of the same composition, encapsulated in Teflon was polished to a mirror finish and degreased with trichloroethylene.

Weight loss method

Carbon steel specimens in triplicate were immersed in 100 ml of distilled water containing 60 ppm of chloride ions with test solution containing various concentrations of the inhibitors, in the absence and presence of and Zn^{2+} ions, for a period of three days. The weight of the specimens before and after immersion was determined using Shimadzu balance, AY62 model. The corrosion products were cleansed with Clarke's solution[12]. From the change in weight of the specimens, corrosion rates were calculated with the help of the following relationship:

Where,

$$CR = \frac{\Delta m}{A * t} \qquad\qquad (1)$$

CR - corrosion rate
Δm - loss in weight (mg)
A - surface area of the specimen (dm^2)
t - period of immersion (days)]

The inhibition efficiency (IE) was then calculated using the equation

$$IE = 100 \left(1 - \frac{W_2}{W_1} \right) \qquad\qquad (2)$$

Where, W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively

Polarization study

Polarization studies were carried out in on H & CH electrochemical work station impedance analyzer model CHI 660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. According to the stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current

$I_{corr} = b_a \times b_c / 2.303 (b_a + b_c) R_p$

Where, R_p is polarization resistance

AC impedance study

The instrument used polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance(R_t) and the double layer capacitance(C_{dl}) were calculated.

$R_t = (R_s + R_t) - R_s$

Where, R_s = solution resistance

$C_{dl} = \frac{1}{2} \pi R_t f_{max}$

Where, f_{max} = maximum frequency

Surface examination

The carbon steel specimens were immersed in various test solutions for a period of Three days, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic and adsorption studies.

Surface coverage area

$1/\theta = \theta/1-\theta, \ 1/C-\theta$
$C/\theta = C/1-\theta/\theta.B$

Where, θ =surface coverage area of metal ion solution at equilibrium,

C = equilibrium concentration of the metal ion,
$1-\theta$ = rate of adsorption,
B = constant related to the energy of adsorption.

Langmuir Adsorption isotherm model

The Langmuir model was developed based on assumption of the formation of a monolayer of the metal ion solution onto the surface of the *sansevieria roxburghiana*(SR), It has also been assumed that surface sites are completely heterogeneous. The study of Langmuir isotherm is essential in assessing the adsorption efficiency of the *sansevieria roxburghiana*(SR). In this regard the Langmuir isotherm is important, through the restriction and the limitation if this model has been well recognized.

Freundlich Adsorption isotherm Model

The Freundlich isotherm is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy system and is expressed by the following equation
$$IE = K_F SPT^{1/n}$$

Where, K_F is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The essential characteristics of Langmuir and freundlich isotherm can be expressed in terms of dimension less constant, separate ion factor or equilibrium parameter R_L, which is defined by $R_L = C_o / 1+bC_o$ is the initial metal ion concentration and b is the Langmuir constant the parameter indicates the shape of isotherm as follows.

R_L	Types of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The applicability of Langmuir and Freundlich model to then chosen metal ion solution system was studied in the present work.

Result and Discussion

Analysis of Results of Weight-Loss Method

Corrosion rates(CR) of carbon steel immersed in an aqueous medium containing 60 ppm of chloride ions in the absence and presence of inhibitor at various concentrations obtained by the weight - loss method are given in Tables 1 to 4. The corrosion inhibition efficiencies(IE) of *sansevieria roxburghiana*(SR) – Zn^{2+} system are also given in these Tables. It is evident from the Table 1 that SR by itself is poor corrosion inhibitor[13-15]. In the presence of Zn^{2+}, good inhibition efficiencies are obtained. As the concentration of Zn^{2+} increases, IE also increases. (Table 2 to 3). For example 6ml of SR has 17% IE, 300 ppm of Zn^{2+} has 22% IE.

Table 1 Corrosion Rate (CR) of carbon steel immersed in 60 ppm chloride ion environment and Corrosion Inhibition Efficiencies (IE) obtained by weight loss method**.**

S.No.	SR Extract ml	IE %	CR mdd
1	0	-	28.00
2	1	-2	28.56
3	2	1	27.72
4	3	2	27.44
5	4	11	24.92
6	5	13	24.36
7	6	17	23.24

Inhibitor system: SR alone; Immersion period: 3 days

Table 2 Corrosion Rate (CR) of carbon steel immersed in 60 ppm chloride ion environment and Corrosion Inhibition Efficiencies (IE) obtained by weight loss method

S.No.	Zn^{2+} ppm	IE %	CR mdd
1	0	-	28.00
2	1	3	27.16
3	2	6	26.32
4	3	8	25.76
5	4	10	25.20
6	5	15	23.80
7	6	22	21.84

Inhibitor system : Zn^{2+} alone; Immersion period : 3 days

Table 3 Corrosion Rate (CR) of carbon steel immersed in 60 ppm chloride ion environment and Corrosion Inhibition Efficiencies (IE) obtained by weight loss method

S.No.	SR ml	Zn^{2+} ppm	IE %	CR mdd
1	0	0	--	28.00
2	1	10	2	22.40
3	2	50	24	21.28
4	3	100	33	18.76
5	4	150	42	16.24
6	5	200	52	13.04
7	6	300	68	8.96

Inhibitor system: SR-Zn^{2+} system alone; Immersion period: 3 days

However, interestingly the formulation consisting of 6ml of SR and 300 ppm of Zn^{2+} has 68% IE. This is due to synergistic effect exist between SR - Zn^{2+} system. A thin interference film is observed on the surface of the inhibited metal during the weight loss experiment.

Effect of sodium potassium tartarate(SPT) on the inhibition efficiency of the SR – Zn^{2+} System.

The formulation consisting of 6 ml of SR and 300 ppm of *sansevieria roxburghiana*(SR) shows 68% IE. The various concentration of SPT is added on the above mentioned formulations to get excellent IE(Table 4). The formulation consisting of 6ml of SR, 300 ppm of Zn^{2+} and 100 ppm has 97% IE. This is due to synergistic effect exist between SR - Zn^{2+}-SPT system. This is found to be the maximum inhibition efficiency offered by this system.

Table 4 Corrosion Rate (CR) of carbon steel immersed in 60 ppm chloride ion environment and Corrosion Inhibition Efficiencies (IE) obtained by weight loss method

S.No.	SR ml	Zn^{2+} ppm	SPT ppm	IE %	CR mdd
1	0	0	0	--	28.00
2	6	300	100	97	0.84
3	6	300	200	89	3.08
4	6	300	300	87	3.64
5	6	300	400	85	4.20
6	6	300	500	84	4.48
7	6	300	600	80	5.60

Inhibitor system: SR-Zn^{2+} - SPT system; Immersion period: 3 days

Influence of pH on the inhibition efficiency of the SR - Zn^{2+} System

The influence of pH on the inhibition efficiency of the SR- Zn^{2+} -SPT system is given in Table 5. When pH is lowered from 7 to 5 (addition of H$_2$SO$_4$), the inhibition efficiency is slightly lowered. For example, the system consisting of 6 ml of SR, 300 ppm of Zn^{2+} and 100 ppm SPT, the inhibition efficiency decreases from 97 to 89%. It is interestingly to find that at higher pH 9, the inhibition efficiency drastically decreases. The decrease in inhibition efficiency at higher pH values (addition of NaOH solution) may be due to the formation of Zn(OH)$_2$ precipitate in the bulk of the solution. Hence, the inhibition efficiency decreases.

**Table 5** The influence of various pH on the inhibitors is obtained by weight loss method

S.No.	SR ml	Zn^{2+} ppm	SPT ppm	pH 5		pH 7		pH 9	
				IE %	CR mdd	IE %	CR mdd	IE %	CR mdd
1	0	0	0	--	31.00	--	28.00	--	22.00
2	6	300	100	89	3.41	97	0.84	-34	28.16
3	6	300	200	87	4.03	89	3.08	-28	29.28
4	6	300	300	85	4.65	87	3.64	-18	25.96
5	6	300	400	84	4.96	85	4.20	-16	25.52
6	6	300	500	80	6.20	80	5.60	-11	24.42
7	6	300	600	78	6.82	80	5.60	-10	24.20

Inhibitor system: SR - Zn^{2+} - SPT system; Immersion period: 3 days

Analysis of the results of Polarization curves

The potentiodynamics polarization curve of carbon steel immersed in 60 ppm of chloride solution in the presence and absence of inhibitors are shown in Figure 1. The corrosion parameters are given in Table 6. When the carbon steel immersed in 60 ppm of chloride ion solution, the corrosion potential is (E$_{corr}$) − 507 mV vs SCE. The formulation consisting of 6 ml of SR extract, 100 ppm of SPT and 300 ppm of Zn^{2+} shifts the corrosion potential to -527 mV vs

SCE, i.e. corrosion potential shifts to anodic direction (from -507 mV to -525mV). This suggests that the anodic reaction is controlled predominantly indicating the reduction resolution of metal as more inhibitors are transported to the anodic sides in the presence Zn^{2+} ions. The corrosion current (I_{corr}) for 60 ppm of chloride environment is 2.645 x 10^{-5} A cm^{-2}. It is defused to 2.098 x 10^{-5} A cm^{-2} by the addition best formulation inhibitors system. The current of the iron dissolution is decreased significantly indicating that the metal surface was passive by the formed inhibitor layer. The significant reduction in corrosion current for inhibitor formulation may indicate more adsorption of the inhibitors and better inhibitions performance. This result suggests that a protective film is formed on the metal surface[16-19]. This protects the metal from corrosion.
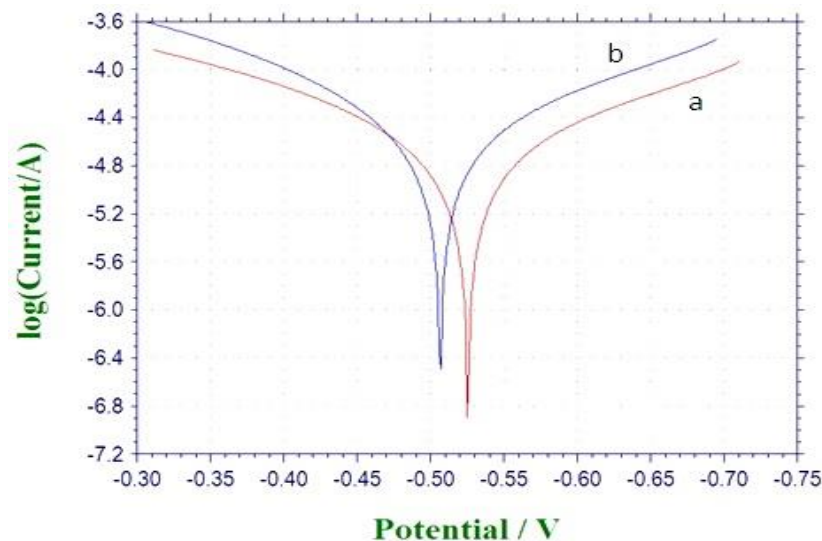
Figure 1 Polarization curves of carbon steel immersed in various test solution

Table 6 Corrosion parameters of carbon steel in 60 ppm chloride environment in the presence and absence of inhibitor system obtained from Potentiodynamic Polarization study

S.No	System	E_{corr} mV	I_{corr} A cm^{-2}	b_a mV decade^{-1}	b_c mV decade^{-1}
1	60 ppm of Cl⁻ solution	-507	2.645×10^{-5}	610	517
2	60 ppm of Cl⁻ + 300 ppm of Zn^{2+} + 6 mL of SR extract + 100 ppm of SPT	-525	2.098×10^{-5}	543	507

a. 60 ppm of Cl⁻ solution; b. 60 ppm Cl⁻ + 300 ppm Zn^{2+} + 6 ml SR + 100 ppm SPT

Analysis of the results of AC impedance studies

The AC impedance spectra of carbon steel immersed in 60 ppm of chloride ion solution containing the formulation are shown in Figure 2. The AC impedance parameters namely charge transfer resistance(R_t) and the double layer

capacitance(C_{dl}) are given in the table I. When the carbon steel immersed in 60 ppm of chloride ion, the charge transfer resistance(R_t) value is found to be 329 Ω cm^2. The double layer capacitance(C_{dl}) value is 2.858 x 10^{-7} F/cm^{-2}. When the carbon steel immersed in the formulation consisting of 6 ml of SR extract, 100 ppm of SPT and 300 ppm of Zn^{2+}, the R_t value increased from 329 Ω cm^2 to 452 Ω cm^2 and the C_{dl} value has decreased from 2.858 x 10^{-7} F/cm^{-2} to 1.517 x 10^{-7} F/cm^{-2}. The increase in R_t values obtained from impedance studies justify the good performance of a compound as an inhibition in chloride solution[21-26]. This behavior means that the film obtained act as a barrier to the corrosion process that clearly proves the formation of the film.
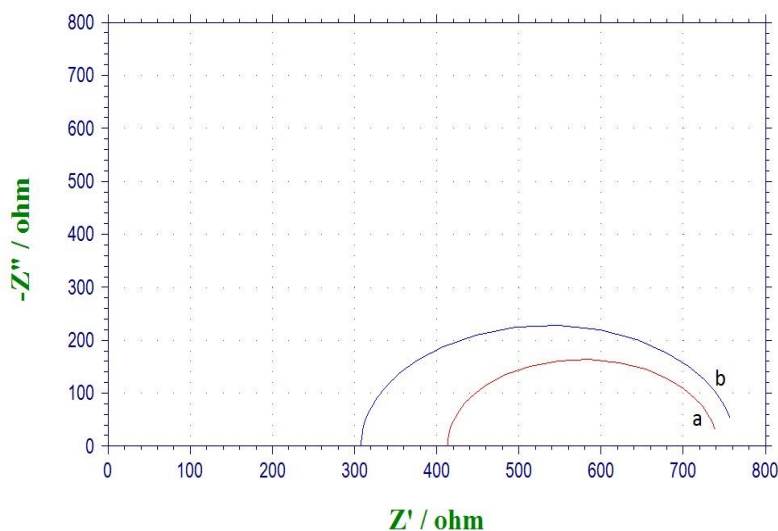
Figure 2 Polarization curves of carbon steel immersed in various test solution
a.60 ppm of Cl⁻ solution b. 60 ppm Cl⁻ + 300 ppm Zn^{2+} + 6 ml SR + 100 ppm SPT

Table 7 Corrosion parameters of carbon steel in 60 ppm chloride environment in the presence and absence of inhibitor system obtained from AC impedance study

| S.NO	Environment	R_t (Ωcm^2)	C_{dl} (F/cm^2)
1	60 ppm of Cl⁻ solution	329	2.858 x 10^{-7}
2	60 ppm of Cl⁻ + 300 ppm of Zn^{2+} ion + 6 mL of SR extract + 100 ppm 0f SPT	452	1.517 x 10^{-7}

Langmuir adsorption isotherm Model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to the saturated monolayer of Langmuir equation can be described by

$C/\theta = 1/\theta.B + (1/\theta)$

Where C is the equilibrium concentration of the metal ion solution, θ is the surface coverage area of the metal ion, B is the Langmuir constant related to adsorption capacity and rate of adsorption, respectively.
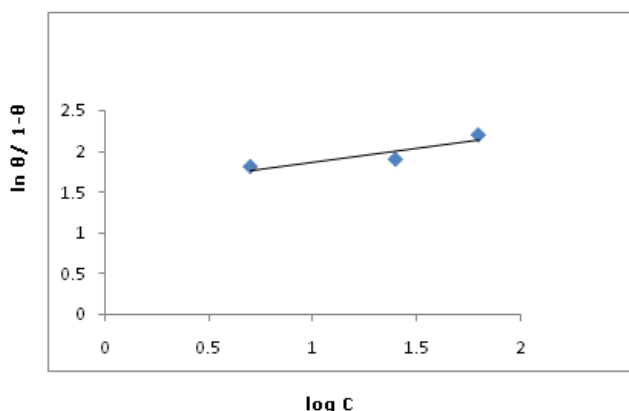
Figure 3 Langmuir isotherm for Zn^{2+} Solution on to *sansevieria roxburghiana*(SR)

The linear plot of specific adsorption (C/θ) against the equilibrium concentration (C) of Figure 3 Shows that the adsorptions obey the Langmuir model. The Langmuir constant B was determined from the slope and intercept of the plot and are presented in Table 8.

Table 8 Langmuir Isotherm for Zn^{2+} Solution on *sansevieria roxburghiana*(SR)

S.No	Zn^{2+} ppm	SR ml	SPT ppm	ln C	θ	$\theta/1-\theta$	ln $\theta/1-\theta$
1	300	6	1	0.0	0.97	22.33	3.48
2	300	6	2	0.7	0.86	6.14	1.81
3	300	6	3	1.1	0.84	5.25	1.66
4	300	6	4	1.4	0.87	6.69	1.90
5	300	6	5	1.6	0.81	4.26	1.45
6	300	6	6	1.8	0.90	9.00	2.20

The R^2 values (0.9566) suggest that the Langmuir isotherm provides a good fit to the isotherm data. The essential characteristics if the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L given by the equation

$R_L = 1/1+bC_0$

Where C_0 is the highest initial concentration of *sansevieria roxburghiana*(SR) and b is Langmuir constant. The parameter R_L, indicates the nature of shape of isotherm accordingly.

Freundlich adsorption isotherm Model

The Freundlich isotherm is the earliest known relationship describing the sorption equation (shown in Table 9). The fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy system and is expressed by the following equation

$IE = K_F SPT^{1/n}$

Where, K_F is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. In general as the K_F value increases the adsorption capacity of *sansevieria roxburghiana*(SR). Value $n>1$ represents favourable adsorption condition.
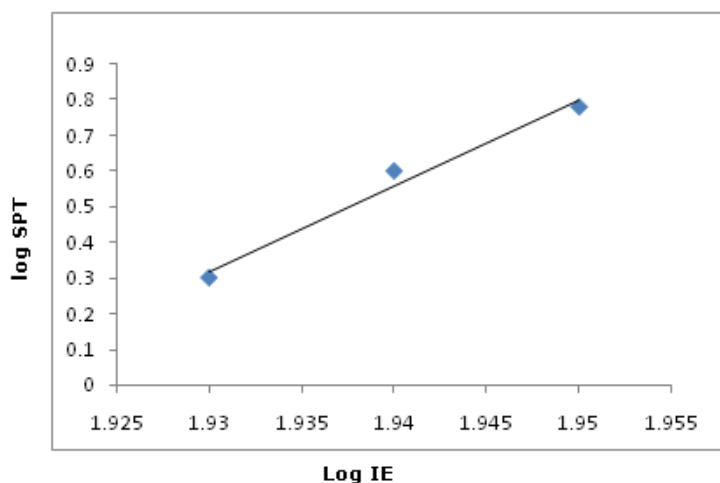
Figure 4 Freundlich isotherm for Zn^{2+} solution on *to sansevieria roxburghiana*(SR)

The Linear form of equation is given below

$\log IE\% = \log K_F + (1/n) \log SPT$

Values of K_F and n are calculated from the intercept and slope of the plot Figure 4 and are listed in Table 10.

Table 9 Freundlich isotherm for Zn^{2+} solution on *sansevieria roxburghiana*(SR)

S.No	Zn^{2+} ppm	SR ml	SPT ppm	IE %	log IE %	log SPT
1	300	6	1	97	1.99	0.00
2	300	6	2	89	1.93	0.30
3	300	6	3	87	1.92	0.48
4	300	6	4	85	1.94	0.60
5	300	6	5	84	1.90	0.70
6	300	6	6	80	1.95	0.78

Table 10 Langmuir and Freundlich isotherm constant and correlation Co-efficient for
Adsorption of Zn^{2+} Solution Concentration

| Langmuir isotherm	
K_F	0.000
$1/n$	2.000
R^2	0.9566
R_L	0.1851
Freundlich isotherm	
K_F	0.030
$1/n$	8.000
R^2	0.0372
R_L	0.1424

The R^2 value (0.0372) is lower than Langmuir isotherm. The best equilibrium model is determined based linear square regression correlation co-efficient R^2 from Figure 4. It was observed that the equilibrium sorption data were very best fit isotherm expression conform the monolayer coverage process of *sansevieria roxburghiana*(SR)on to Zn^{2+}.

**Mechanism of Corrosion Inhibition**

The weight – loss study reveals that the formulation consisting of 300 ppm of Zn^{2+}, 6 ml of *sansevieria roxburghiana*(SR)and 100 ppm of SPT has 97 % inhibition efficiency. In order to explain the above observations, the following mechanism of corrosion inhibition is proposed[27-28].

When the environment consisting of 300 ppm of Zn^{2+}, 6ml of SR and 100 ppm of SPT are prepared, there is a formation of Zn^{2+} -SR complex and Zn^{2+} - SPT complex.

When Carbon steel is introduced in this solution there is diffusion of Zinc complex towards the metal surface.
On the metal surface Zinc complex is converted into iron complex on the anodic site.
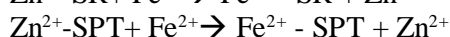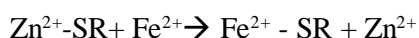
Zn^{2+}-SR+ Fe^{2+}→ Fe^{2+} - SR + Zn^{2+}
Zn^{2+}-SPT+ Fe^{2+}→ Fe^{2+} - SPT + Zn^{2+}
The released Zn^{2+} combined with OH^- to form $Zn(OH)_2$ on the cathodic Sites.
$Zn^{2+} + 2OH^-$ → $Zn(OH)_2\downarrow$
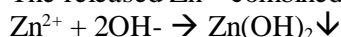
Thus protective film consists of Fe^{2+} - SR, Fe^{2+}-SPT complexes on anodic sites of metal surface and $Zn(OH)_2$ formed on cathodic sites of metal surface.

Conclusion

The present study leads to the following conclusions:
- The formulation consisting of 6 ml *sansevieria roxburghiana*(SR) extract, 300 ppm of Zn^{2+} and 100 ppm of sodium potassium tartarate (SPT) offers 97% inhibition efficiency;
- The synergistic effect exists between *sansevieria roxburghiana*(SR)– Zn^{2+} system;
- Polarization study reveals that this formulation controls the anodic reaction predominantly;
- AC impedance spectra reveal that a protective film is formed on the metal surface;
- The value of the separation factor R_L, indicated the *sansevieria roxburghiana* (SR) system was favourable adsorption.

Acknowledgement

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