

Study of the Inhibitive and Adsorptive Properties of Mild Steel in H₂SO₄ - *Boscia senegalensis* Plant Environment

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Abstract

The inhibitive and adsorption properties of ethanol extract of *Boscia senegalensis* for the corrosion of mild steel in H₂SO₄ were investigated using weight loss, linear polarization, and scanning electron microscopy techniques. From the result, it was found that the corrosion rate of mild steel to decrease with an increase in the concentration of the inhibitor as well as increase with an increase in temperature of the environment. The inhibition efficiency of the inhibitor increases with increasing concentration but decreases with increasing temperature. The inhibition potential of ethanol extract of *Boscia senegalensis* is attributed to the presence of saponnin, tannin, phlobatanins, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid in the extract. The adsorption of the inhibitor on mild steel surface was found to be exothermic, spontaneous and is best described by Freundlich and Temkin adsorption model. The calculated values of activation energy, enthalpy of activation, entropy of activation, free energy of adsorption and the trend in the variation of inhibition efficiency with temperature, the mechanism of adsorption of the inhibitor by physical adsorption. Ethanol extract of *Boscia senegalensis* is a good adsorption inhibitor for the corrosion of mild steel in H₂SO₄. Tafel polarization analyses indicated that studied plant extract is a mixed type inhibitor.

Keywords: *boscia senegalensis*; polarization; adsorption.

1. Introduction

The studies of mild steel corrosion in acidic, basic and neutral media have received more and more attention both in academics and industrial processes because of its wide applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes (Eddy *et al.*, 2008). The electrochemical corrosion is generally caused by dissymmetry potentials between metal and strong acid. The aggressiveness of hydrogen ion is inevitable in uninhibited acid. H⁺ and Dissolved O₂ are named natural motors of corrosion (Putilova *et al.*, 1960; Amin *et al.*, 2007). Consequently, the metal is prone to attack by corrosion, which depends on the concentration of the aggressive medium, operating temperature, period of contact, the presence or absence of inhibitors, etc. (Obot and Obi-Egbedi, 2009).

As a result of the viability of mild steel, the high cost of production and installations, several steps have been adopted to protect the metal against corrosion (Oguzie *et al.*, 2010). However, one of the most practical and preferred methods are the use of corrosion inhibitors (Ita, 2004, 2005; Ita and Offiong 1995; Ebenso *et al.*, 2004, 1998; Ebenso, 2004; Elayyoubi *et al.*, 2004; Odoemelam and Eddy, 2008). Most efficient inhibitors are organic compounds containing electronegative functional groups and pi-electrons in triple or conjugated double bonds. The presence of heteroatoms such as sulphur, phosphorus, nitrogen, and oxygen as well as aromatic rings in their structures is the major adsorption centers (Wang *et al.*, 2007; El Ashry *et al.*, 2006). However, it has been found that the inhibition efficiency of an organic inhibitor does not only depend on structural characteristics of the inhibitor, but also on the nature of the metal and the environment. Therefore, the selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitor and environmental requirements. In recent times, there is increasing concern about the toxicity of most corrosion inhibitors because the toxic effects do not only affect living organisms, but also poison the environment (Eddy and Ebenso, 2008; Eddy *et al.*, 2008; Ebenso *et al.*, 2008; Ekop and Eddy, 2009; Eddy *et al.*, 2009; Umoren and Ebenso, 2008). Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds (Umoren *et al.*, 2008). Plant extracts and oils have become important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention; therefore, finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance (Satapathy *et al.* 2009; Raja and Sethuraman, 2008) may give a vivid account of natural products which are used as corrosion inhibitors for various metal and alloys in aggressive media. They stated that natural plant have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. Successful use of naturally occurring substances for the inhibition of the corrosion of metals in acidic and alkaline media has been reported by some research groups (Yurt *et al.*, 2004; Gomez *et al.*, 2006; Obot and Obi-Egbedi, 2010; Kumar *et al.*, 2011; Okafor and Ebenso, 2007; Okafor *et al.*, 2007; Oguzie *et al.*, 2007; Eddy and Ekop, 2005; Ebenso *et al.*, 2008; Ekop and

Eddy, 2009; Eddy *et al.*, 2009 and Yurt *et al.*, 2004) . In spite of the large numbers of green corrosion investigated and tested, literature is scanty on the inhibitive and adsorptive properties of ethanol extract of *Boscia senegalensis* for the corrosion of mild steel in H₂SO₄. Therefore the objective of the study is to investigate the inhibitive and adsorptive properties of ethanol extract of *Boscia senegalensis* leaves for the corrosion of mild steel in H₂SO₄.

2. Materials and Method

Materials used for the study were mild steel sheet of composition (wt%) Mn (0.6), P (0.36), C (0.15), and Si (0.03) and the rest Fe (determined by quantitative method). The sheet was mechanically pressed cut into different coupons, each of dimension, 3mm x 2mm x 0.11 mm. Each coupon were polished with different size of emery paper grids (600 – 1200), and were later degreased by washing with ethanol, rinsed with acetone and allowed to dry in air before they were preserved in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation.

2.1 Plants Extraction

Samples of *Boscia senegalensis* leaves were obtained from Zango - Shanu a location and later taken to Ahmadu Bello University, Samaru Campus, Zaria albertum for identification and also batch number. The leaves were dried, ground, and soaked in a solution of ethanol for 48 hours. After 48 hours, the samples were cooled and filtered. The filtrates were further subjected to evaporation at 352 K in order for the sample to be free of ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5 g of the extract in 1L of 2.5 M H₂SO₄, respectively. For gravimetric analysis as well as linear polarization analysis, the concentration of H₂SO₄ used for the preparation of the inhibitor-acid solutions was 0.5 M.

2.2 Chemical analysis

Phytochemical analysis of the ethanol and aqueous extract of the sample was carried out according to the method reported elsewhere (Qureshi and Eswar, 2010). Frothing and Na₂CO₃ tests were used for the identification of saponin, bromine water, and ferric chloride tests were used for the identification of tannin while Leberman's and Salkowski's tests were used for the identification of cardiac glycosides while Dragendorf, Hagger, and Meyer reagent tests were used for the identification of alkaloid.

2.3 Scanning Electron Microscopy (SEM)

Morphological studies of the mild steel electrode surfaces exposed to uninhibited and inhibited 0.5 M H₂SO₄ solutions for seven (7) days at 303K were taken by using a Jeol JSM – 7500F scanning electron microscope.

2.4 Gravimetric analysis

In gravimetric experiment, a previously weighed metal (mildsteel) coupon was completely immersed in 250ml of the test (in a close beaker). The beaker was inserted into a water bath maintained at a temperature of 303K. After every 24 hours, each sample was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100 g/L of zinc dust. The washed steel coupon was rinsed in acetone and dried in air before re- weighing. The difference in weight for a period of 168 hours was taken as the total weight loss. The effect of temperature on mild steel corrosion and corrosion inhibition was investigated by performing experiments in 0.5 M H₂SO₄ at 303, 313, 323 and 333K for 3 hours immersion period. All tests were run in triplicate and the data showed good reproducibility. From the weight loss results, the inhibition efficiency (%I) of the inhibitor was calculated using the formula (Okafor *et al.*, 2010).

$$\% I = (1 - W_1/W_2) \times 100 \quad 2$$

where W₁ and W₂ are the weight losses (g/l) of mild steel in the presence and absence of inhibitor (in 0.5 M H₂SO₄) solution, respectively. The degree of surface coverage (θ) was calculated using Equation (3):

$$\theta = 1 - W_1/W_2 \quad 3$$

The corrosion rates (CR) of mild steel in different concentrations of the acid and other media was determined using Equation (4):

$$CR(\text{gh}^{-1}\text{cm}^{-2}) = \Delta W/At \quad 4$$

where ΔW - weight loss (in grams), A -area of specimen (in cm²), and t - period of immersion (in hours).

2.5 Electrochemical measurements

Metal samples for electrochemical experiments were of dimensions 1.0mm x 1.0 mm. These were subsequently sealed with epoxy resin in such a way that only one square surface of area 1.0 cm² was left uncovered. The exposed surface was degreased in acetone, rinsed with distilled water and dried in warm air. Linear polarization studies were carried out in the potential -1000 to 2000 mV at a scan rate of 0.333 mV s⁻¹ at room temperature of 303K. Each test was run in triplicate to verify the reproducibility of the systems.

3. Results and discussion

3.1 Effect of concentration of acid/inhibitor

Figure 1 shows the variation of weight loss with time for the corrosion of mild steel in various concentrations of H₂SO₄. It is evident from the plot that weight losses of mild steel increases with increase in the concentration of H₂SO₄ and with increase in period of contact indicating that the rate of corrosion of mild steel increases with increasing concentration of H₂SO₄. It is also important to note that weight loss of mild steel decreases with increasing concentration of ethanol extract of *Boscia senegalensis* which indicates that ethanol extract of *Boscia senegalensis* is an adsorption inhibitor for the corrosion of mild steel. At higher temperature above the room temperature, the weight loss were found to be more higher than at room temperature and was also found to decrease with increase in concentration of inhibitors similar to those obtained at 303 K. However, the inhibition efficiency of ethanol extract of *Boscia senegalensis* decreases with increasing temperature. This also suggests that the adsorption of ethanol extract of B. Senegalensis on mild steel surface is consistent with the mechanism of physical adsorption. In order to further sustain the findings, the inhibition efficiencies of ethanol extract of *Boscia senegalensis* and the corrosion rates of mild steel in H₂SO₄ in the absence and presence of ethanol extract of *Boscia senegalensis* as an inhibitor. From the results obtained, it is evident that the corrosion rate of mild steel decreases with increasing concentrations of the extract while the inhibition efficiency increases with increasing concentration of the extract. Which implies that ethanol extract of the inhibitor retarded the rate of corrosion of mild steel in H₂SO₄.

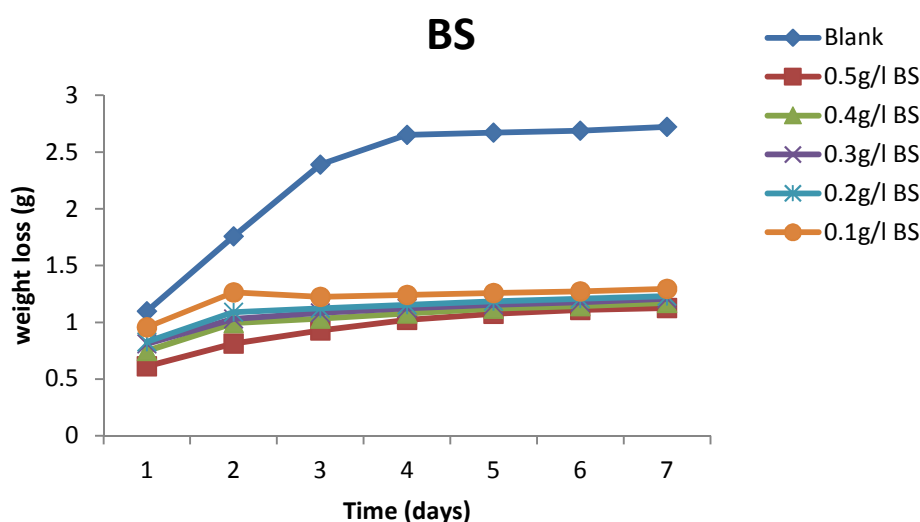


Fig. 1. Variation of weight loss of Mild Steel with time for the corrosion of Mild Steel in 0.5M H₂SO₄ containing various concentration of BS at 303K.

Table 1. Corrosion rates (CR) of mild steel and inhibition efficiencies (% I) of ethanol extract of B. senegalensis

C.(g/l)	CR x 10 ⁻³ (gh ⁻¹ cm ⁻²)				I%			
	333K	323K	313K	303K	333K	323K	313K	303K
Blank	37.79	30.18	19.98	13.84	-	-	-	-
0.1	34.31	26.60	17.28	8.07	9.20	11.87	13.51	41.67
0.2	33.83	25.48	14.14	6.08	10.48	15.57	29.22	56.08
0.3	32.14	21.94	11.13	4.59	14.95	27.31	44.29	66.84
0.4	31.22	20.90	9.41	3.51	17.36	30.76	52.93	74.67
0.5	29.57	20.67	8.57	2.73	21.76	31.51	57.10	80.29

3.2 Applicability of adsorption isotherms

The surface coverage (θ) values for different concentrations of the inhibitor in 0.5M H₂SO₄ have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of $\log(C/\theta)$ against $\log C$ (Figure 2) showed a straight line indicating that adsorption follows the Langmuir adsorption isotherm and a straight line was also found in the plot between $\log \theta$ versus $\log C$, this showed that the adsorption also obeys Freundlich adsorption isotherm (Figure 3). The weight loss data obtained were also tested in order adsorption isotherm and were also found fit, but the best fit adsorption isotherm for the adsorption of the inhibitor on mild steel was found to be Freundlich adsorption isotherm.

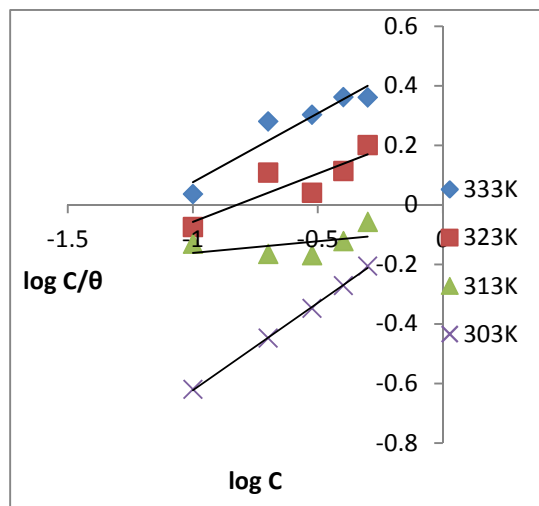


Fig. 2. Langmuir adsorption isotherm

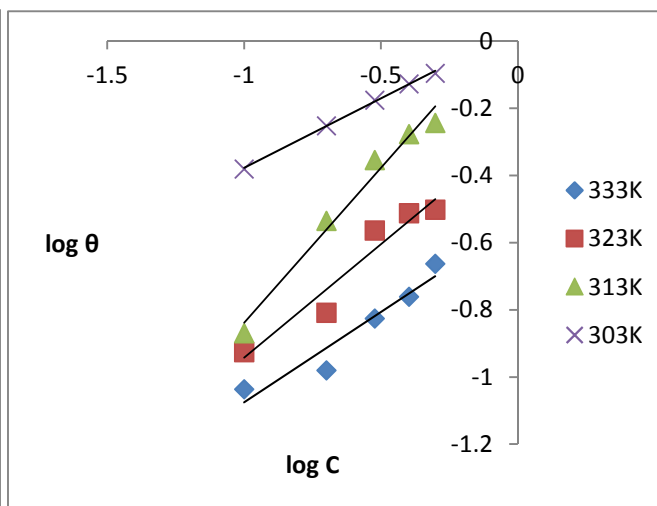


Fig. 3. Freundlich adsorption isotherm

It is also significant to note that the value of the adsorption equilibrium constant obtained from the intercept of each adsorption isotherm is related to the free energy of adsorption according to the equation.

$$\Delta G_{\text{ads}}^{\circ} = -2.303RT \log (55.5K_{\text{ads}}) \quad 5$$

The standard Gibbs' free energy were calculated for the two adsorption isotherms at the various temperature for the plant extracts are also presented in Table 2, from the results obtained, the free energies are found to be negatively less than the threshold value of -40kJmol^{-1} , required for the mechanism of chemical adsorption to take place. Therefore, the adsorption of the studied plant extracts on both aluminium and mild steel surface is spontaneous and is consistent with the mechanism of physical adsorption (Singh *et al.*, 2010 and Loto, 2011).

Table 2: Adsorption parameters for the adsorption of ethanol extract of *B. senegalensis* on the surface of mild steel in H_2SO_4

	Temperature (K)	Slope	ΔG_{ads} (KJ/mol)	R^2
Langmuir	333	0.463	-7.68	0.898
	323	0.325	-9.14	0.768
	313	0.078	-10.91	0.784
	303	0.587	-10.32	0.999
Freundlich	333	0.536	-7.68	0.922
	323	0.675	-9.14	0.934
	313	0.921	-10.91	0.976
	303	0.412	-10.32	0.998

3.3. Effect of temperature

The effect of temperature on the corrosion of mild steel in the absence and presence of various concentration of *B. senegalensis* was investigated using the Arrhenius and Arrhenius transition state equation as describe below: (Lebrini *et al.*, 2011).

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad 6$$

$$\log CR/T = \left\{ \log R/N_A h + \frac{\Delta S_a}{2.303R} \right\} - \frac{\Delta H_a}{2.303RT} \quad 7$$

where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, E_a is the activation energy (i.e the minimum energy needed before the corrosion reaction of the metal can proceed), R is the universal gas constant and T is the temperature of the system.

From equation 6, plot of log CR versus reciprocal of absolute temperature, $1/T$, as shown in Figure 3 gives a straight line with slope equal to $-E_a/2.303R$, from which the activation energy for the corrosion process can be calculated.

From equation 7, plot of log CR/T versus reciprocal of absolute temperature, $1/T$, as shown in Figure 4 gives a straight line with slope equal to $-\Delta H_a/2.303R$ and intercept of $\left\{ \log R/N_A h + \frac{\Delta S_a}{2.303R} \right\}$, from which the enthalpy and entropy of activation for the corrosion process can be calculated. Values of E_a , ΔS_a , and ΔH_a are presented in Table 3. Figure 3 and 4 also show a linear relationship between the corrosion rate and the temperature of the environment.

Values of the activation energy E_a extrapolated were found to be greater in inhibited than those obtained in blank indicating that the ethanol extract of *Boscia senegalensis* retarded the corrosion of mild steel in H_2SO_4 . It

is also found that the activation energy were lowered than the value of 80KJmol^{-1} required for chemical adsorption to take place, confirming that the adsorption of the ethanol extract of *Boscia senegalensis* occur through the mechanism of physical adsorption. The heat of adsorption (Q_{ads}) of the ethanol extract was also calculated using the standard equation and found to be negative, which indicate that the adsorption of the ethanol extract of *Boscia senegalensis* on the surface of the mild steel is exothermic. It is evident from Table 3 that the enthalpies of activation of the corrosion process to be positive which reflect endothermic nature of dissolution process. Moreover, the average difference value of ($E_a - \Delta H_a$) is 2.6433 which is approximately equal to the average value of RT (2.6438). Therefore, it is indicated that the corrosion process is a unimolecular reaction as it is characterized by the equation given below:

$$E_a - \Delta H_a = RT \quad 8$$

The entropy of activation in the presence and absence of the inhibitor also has negative values which indicate that the activated complex in the rate determining step represents an association rather than dissociation, meaning that a decrease in disordering took place on going from the reactant to the activated complex [40].

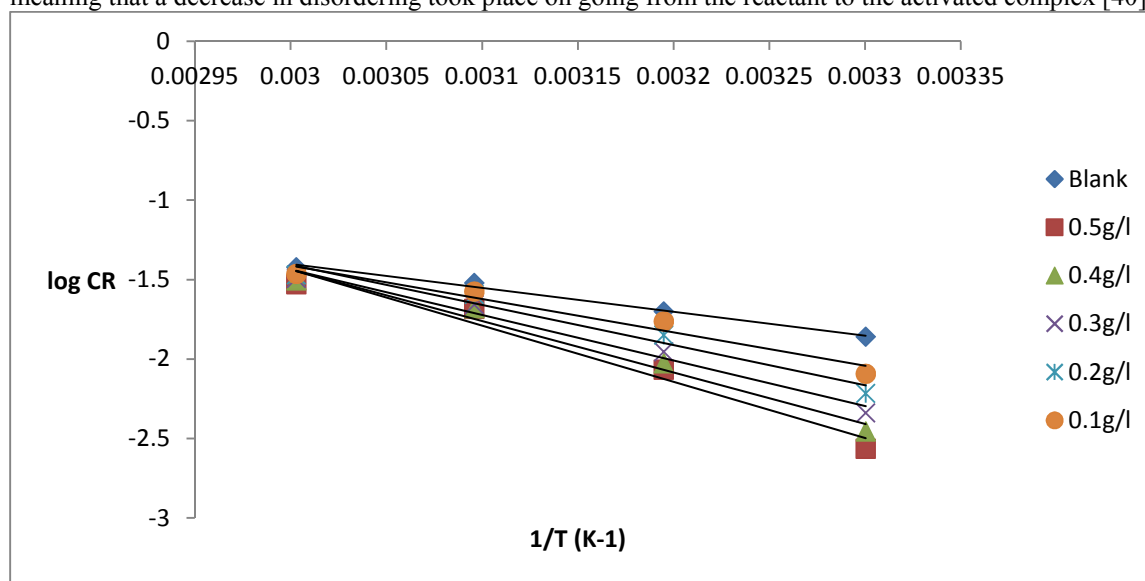


Figure 4. Plot of $\log CR$ against $1/T$ for mild steel in $0.5\text{ M H}_2\text{SO}_4$ solution in the absence and presence of various concentration of inhibitor.

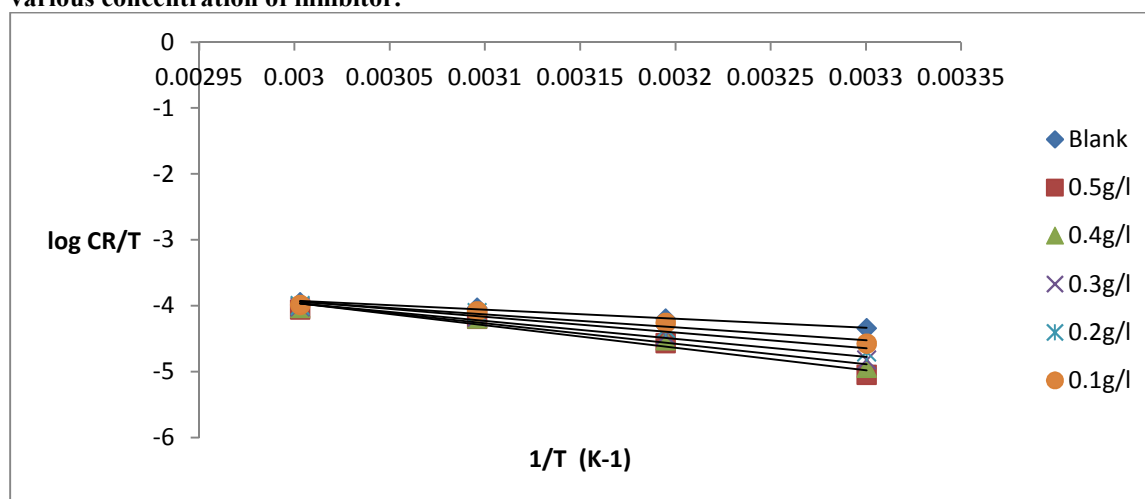


Figure 5. Plot of $\log CR/T$ against $1/T$ for mild steel in $0.5\text{ M H}_2\text{SO}_4$ solution in the absence and presence of various concentration of inhibitor.

Table 3: Activation energy parameters for the dissolution of mild steel in H₂SO₄ in the absence and presence of different concentration of *B. senegalensis*

Conc. (g/l)	E _a (KJ/mol)	ΔH _a (KJ/mol)	ΔS _a (KJ/molK ⁻¹)	(E _a - ΔH _a) (KJ/mol)
Blank	28.80	26.15	-0.194	2.65
0.1	40.29	37.64	-0.160	2.65
0.2	48.40	45.76	-0.136	2.64
0.3	54.91	52.27	-0.117	2.64
0.4	62.02	59.38	-0.095	2.64
0.5	67.74	65.10	-0.078	2.64

3.4. Linear polarization resistance

Linear polarization experiment was taken to understand the effect of *Boscia senegalensis* on both the cathodic and anodic dissolution of the mild steel. A typical polarization curves for mild steel in 0.5 M H₂SO₄ in the absence and presence of *Boscia senegalensis* is shown in Figure 6, and also parameters derived from the curves were also presented in Table 4. It can be observed that both cathodic and anodic reactions were suppressed with the addition of various concentration of *Boscia senegalensis* which indicate that the inhibitor affected the cathodic as well as the anodic partial reactions, shifting the corrosion potential slightly towards more positive values reducing the anodic and cathodic current densities and the corresponding corrosion current density. This indicate that the extracts functioned as a mixed-type inhibitor in the acid solution. From the value of the corrosion current densities in both the absence and presence of the inhibitor, the inhibition efficiencies were calculated using the equation given below:

$$IE_i \% = (1 - i_{inh}/i_{corr}) \times 100$$

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where i_{inh} and i_{corr} are the corrosion current densities in the absence and presence of inhibitors.

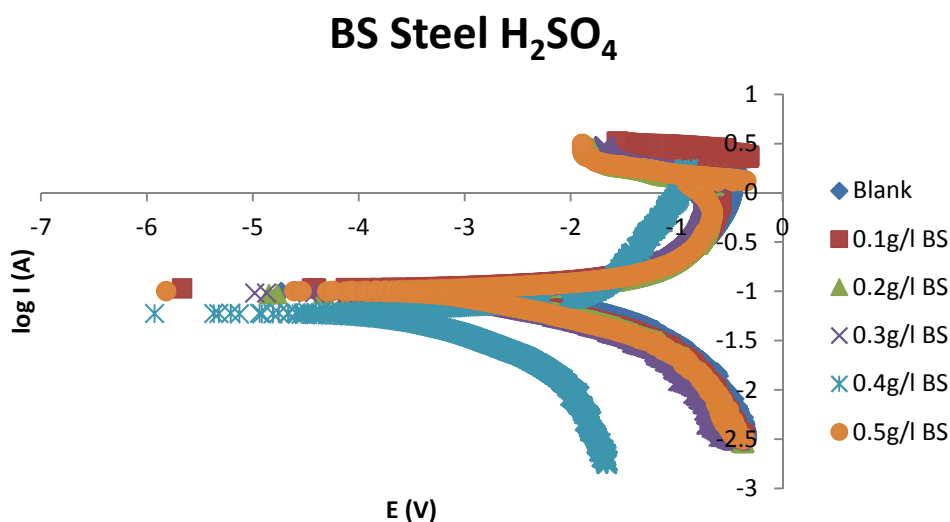


Fig. 6. Polarization curve for the corrosion of mild steel in 0.5 M H₂SO₄ in the presence and absence of various concentration of *B. senegalensis*.

Table 4: Polarization parameters for mild steel in 0.5 M H₂SO₄ in the presence and absence of *B. senegalensis*.

System	E _{corr} (mV vs SCE)	i _{corr} (μA/cm ²)	IE %
Blank	-1004.4	1642.0	-
0.1	-956.92	725.00	55.85
0.2	-945.32	557.00	66.08
0.3	-92.08	482.00	70.65
0.4	-928.56	361.24	78.02
0.5	-905.11	262.72	84.00

3.5. SEM Surface Analysis

Surface morphology of the mild steel specimens in uninhibited and inhibited acid solutions was carried out by SEM after immersion in the test solutions after 7 days at 303K. Figure 7 (a) and (b) shows the SEM images of the mild steel in the absence of inhibitor and presence of the inhibitor. A severely corroded surface morphology was observed after the immersion in the uninhibited system, due to the corrosive attack of the acid solution. Corrosion was relatively general with no evidence of localized attack. The corrosion product layer on the metal surface in uninhibited is clearly very loose and porous and would thus offer insignificant corrosion protection. With addition of *B. senegalensis*, the corrosion damage is visibly reduced, there is slight evidence of the adsorbate presence on the metal surface.

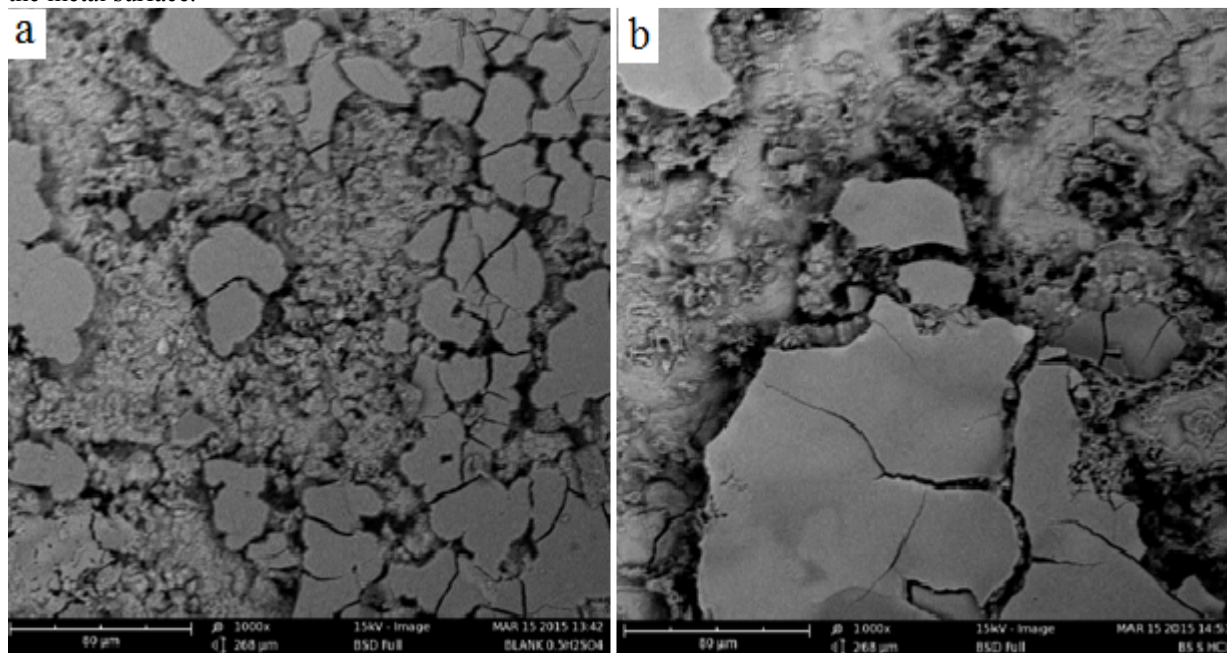


Fig. 8. SEM images of mild steel surface after 7 days immersion at 303K in 0.5 M H₂SO₄: a) without inhibitor b) with inhibitor.

3.6. Phytochemical constituent

Table 5 shows the phytochemical composition of ethanol extract of *Boscia senegalensis*. The results obtained, indicate that saponnin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid are present in ethanol extract of *Boscia senegalensis* hence the inhibition efficiency of ethanol extract of *Boscia senegalensis* may be attributed to the phytochemical constituent of the extract.

Table 5: Phytochemical composition of the ethanol extract of *Boscia senegalensis*

	Phytochemicals
Saponins	+++
Tanins	+++
Phlobatanins	++
Anthraquinone	+++
Cardiac glycoside	++
Flavanoid	++
Terpene	+++
Alkaloid	+++

Note ++ moderately present; +++ present in large amount

3.7. Conclusion

The following conclusion has been derived from the investigation:

- *Boscia senegalensis* was found to be an efficient natural corrosion inhibitor for mild steel in 0.5 M H₂SO₄ solution by using linear polarization and weight loss techniques.
- The results obtained from linear polarization and weight loss measurements are in good agreement.
- The corrosion inhibition efficiency of the extract increases with increasing of its concentration, while the corrosion rate was found to decrease with increase in concentration of inhibitor.
- The adsorption of *Boscia senegalensis* on the mild steel surface in 0.5 M H₂SO₄ solution obeys Freundlich

isotherm.

- The presence of *Boscia senegalensis* in 0.5 M H₂SO₄ solution increases the activation energy of corrosion process which indicates physical adsorption.

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