Investigation of Dalbergia sisso leaf extract as an effective green inhibitor for corrosion of mild steel in 0.5 M sulphuric acid medium.

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Abstract The effect of Dalbergia sisso leaf extract on the corrosion of mild steel in 0.5M sulphuric acid was investigated by Galvanostatic polarization measurement, electrochemical impedance spectroscopy and SEM methods. Results indicates that this indicator act as a mixed inhibitor. The corrosion rate of steel and the inhibition efficiency of the extract were calculated. The result obtained shows that the extract solution of plant serves as an effective inhibitor for the corrosion of mild steel in sulphuric acid media. The experimental results suggest that this plant extract is an efficient corrosion inhibitor and inhibitory efficiency increases with the increase in inhibitor concentration and it decreases with the increase in temperature.

Key words Polarization measurement, electrochemical impedance spectroscopy, inhibition efficiency, SEM

Introduction

Now days, the use of inhibitors is one of the best method for protection against metal corrosion especially in acidic solution. Mild steel is widely used for construction purpose in many chemical industries due to its mechanical properties. Many researchers had studied the corrosion of mild steel in acidic media by using many organic and inorganic compounds. Organic compounds contain nitrogen, oxygen and sulphur which is major absorption centres such type of compounds act as efficient inhibitors [Quraishi and Jamal (2002)], [Ahmed et al, (2010)]. But most of these inhibitors are toxic, expensive and hazardous to environment. Therefore, in last two decades development of nontoxic environmental friendly cheap and effective inhibitors become essential [Raja and Sethuraman (2008)]. The known hazardous effects of most synthetic inhibitors have now made the researcher to focus on the use of natural products. Several scientific studies have been carried out by number of researchers to investigate corrosion inhibition of various plants such as occimum virdis, Telferia occidentalis, Nauclea letifolia, Tinospora crispa on mild steel in acidic medium.

Recent research has shown that these green inhibitors exhibit good inhibition efficiency and serve as most effective eco-friendly corrosion inhibitors. The inhibition abilities of plant extracts depend upon the parts of the plant used [El-Etre (2006)]. Leaf extract and fruit extract of same plant have varying degree of inhibition abilities. Some inhibitors are effective in one medium may not be much effective in another medium [Saleh et al., (1983)].

The aim of present work is to investigate the corrosion of mild steel in 1 M H_2SO_4 using the extract of Dalbergia sisso leaves as corrosion inhibitor by using potentiodynamic polarization measurement, electrochemical impedance spectroscopy (EIS) and the morphology of inhibited mild steel surface was analyzed via scanning electron microscope (SEM). Through Temperature kinetic studies, different thermodynamic parameters can be calculated. These parameters explain the mode of adsorption of inhibitors on metal surface. Dalbergia sisso is commonly known as rosewood, hardy deciduous native to the Indian subcontinent and southern Iran.

2. Experimental

2.1. Preparation of Dalbergia sisso leaf extract:

Morus rubra leaves were dried in an oven and crushed. The powered leaves were refluxed with 0.5M sulphuric acid for three hours.

The extracted solution was then filtered and filterate used as stock solution. The testing solutions of different concentration were prepared from stock solution. The different concentration was 10%, 20%, 30%, 40%.

2.2. Specimen preparation: Mild steel specimens have 1.92% C, 0.165% Si, 0.60% Mn, 0.203% Cu, 0.034% S and 95.5% Fe encapsulated in an Araldite with exposed area of 1cm^2 was used as working electrode for potentiodynamic polarization measurement and EIS measurements. The surface area was abraded successively with 220, 400, 800 and 1000 grades of emery papers to obtain uniform surface degreased with acetone and washed with distilled water before each electrochemical experiment.

2.3. Electrochemical measurements

Electrochemical studies were carried out by using electrochemical work station impedance analyser model CHI 760D. A cell assembly usually contains three electrodes. Mild steel specimen as working electrode, platinum electrode as the counter electrode and saturated calomel electrode as the reference electrode. Before carrying out the electrochemical measurement, a stabilization period of 30 min was allowed to attain a stable value of open circuit potential (OCP). Potentiodynamic polarization curves were recorded at a scan rate of 0.01mVs^{-1} by adding -0.9 and +0.0V to the open circuit value. Electrochemical impedance spectroscopy measurements were carried out using alternating current (AC) signal with amplitude of 5mV at OCP in the frequency range from 10^5 Hz to 1Hz

2.4. Surface analysis

Surface of mild steel was abraded by emery papers of different grades to obtain uniform surface, degreased with acetone washed with distilled water before the experiment. Polished coupons were subjected to corrosion by dipping them in 0.5 M H_2SO_4 solution in the absence and presence of highest and lowest concentration of inhibitor for 24 hours. Then surface morphology was performed using Ziess scanning electron microscopy.

3. Result and discussion

3.1. Potentiodynamic Polarization

Potentiodynamic anodic and cathodic polarization curves for mild steel in presence and absence of inhibitor are shown in Fig 1. The respective corrosion current parameters including corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic slope (b_c), anodic slope (b_a) and percentage of inhibition efficiency calculated from table 1. Inhibition efficiency can be calculated as

IE% = (i^0_{corr} - i_{corr} / i^0_{corr}) × 100

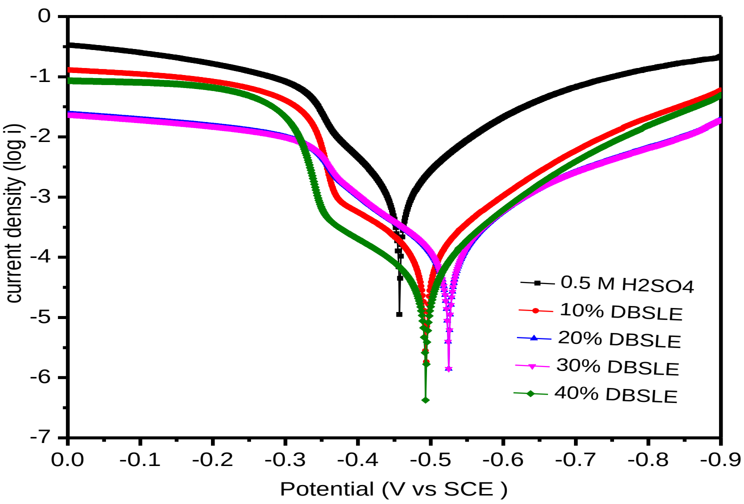
Where i^0_{corr} and i_{corr} are corrosion current density in absence and in presence of inhibitor

Table 1. Potentiodynamic polarization parameters for the corrosion of mild steel in 0.5 M H_2SO_4 having different concentrations of Dalbergia sisso leaf extract.

Temp.	conc.	$-E_{corr(mV)}$	$b_{c(Mv/dec)}$	$b_{a(mV/dec)}$	$I_{corr(mA/cm^2)}$	% IE
	40%	493	140	102	0.0547	94.6%
298K	30%	492	152	112	0.1121	89%
	20%	525	129	124	0.1326	87%
	10%	494	140	114	0.1593	84.3%
	0.5MH_2SO_4	457	114	61	1.017	-
	40%	507	155	106	0.1528	88%
308K	30%	464	115	102	0.1737	86.2%
	20%	495	163	116	0.3162	75%
	10%	513	172	121	0.3652	71%
	0.5MH_2SO_4	429	116	61	1.267	-
	40%	492	102	77	0.2892	85.4%
318K	30%	502	181	128	0.4294	78.3%
	20%	506	161	122	0.5308	73%
	10%	459	121	57	0.5855	70%
	0.5MH_2SO_4	474	144	66	1.984	-
	40%	523	200	112	0.4803	80.7%
328K	30%	518	165	125	0.7243	76%
	20%	520	198	118	0.8395	72%
	10%	497	137	109	1.075	64%
	0.5MH_2SO_4	470	133	63	3.009	

The corrosion rate of mild steel in 0.5 M H2SO4 with and without different concentrations of Dalbergia sisso leaf extracts was determined at 298-328K. It was evident from the Table. 1 that the corrosion current value (I_{corr}) was decreases with the increase in concentration of inhibitor. No definite trend was observed in the shift of E_{corr} values. Dalbergia sisso leaf exract suppressed both anodic and cathodic reactions through adsorption on the surface of mild steel results in decreased rate of corrosion [Chauhan and Gunasekaran, 2007]. With the increase in DBSLE concentration, inhibition efficiency was improved. At 10% IE was 84% and as the concentration increased to 40%, IE was 94.6%. Temperature influenced the corrosion rate in the presence of DBSE. The inhibition efficiency was decresed with the increase of temperature it occurs because of desorption of DBSE from the surface of mild steel [Bouklah et al., 2006] Inhibition efficiency decreased with increase in temperature. At 40% inhibition efficiency reduced from 94.6% at 298K to 80.7% at 328 K.

At a particular concentration, the decrease in corrosion current value is less at higher temperature thus inhibition efficiency also decreases. According to a literature report when corrosion potential is more than ± 85 mV with respect to that of the blank, the inhibitor can be considered distinctively as cathodic or anodic type. However, for DBSLE as inhibitor of corrosion for mild steel, the change in E_{corr} values is less than ± 85 mV suggesting that MRLE act as a mixed type of inhibitor (P. Muthukrishnan et al 2013). Both anodic and cathodic polarizations are influenced simultaneously, with a slightly more shift towards cathode



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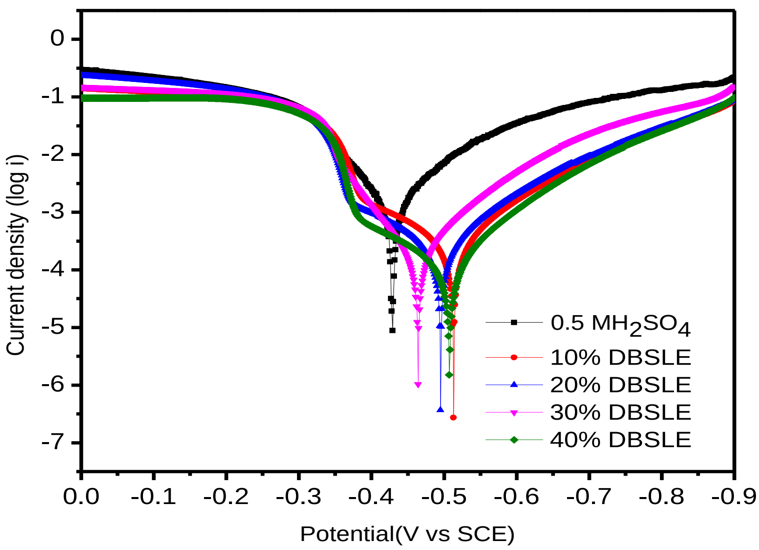

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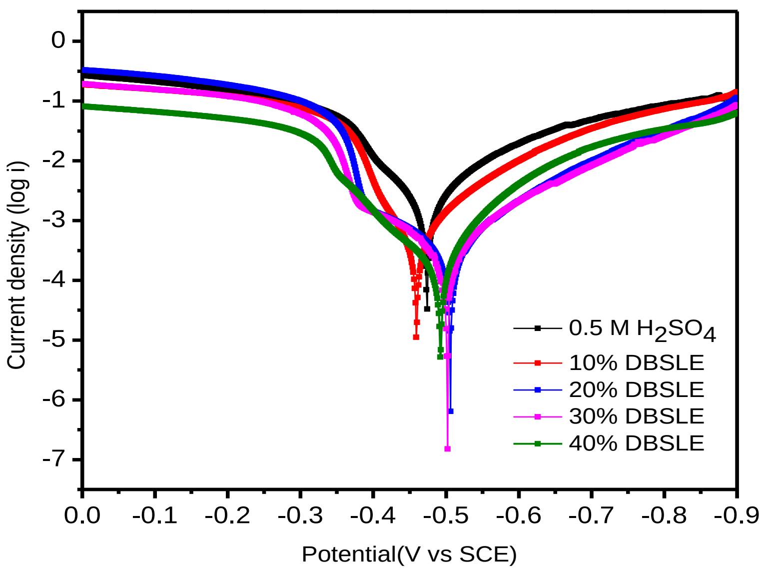

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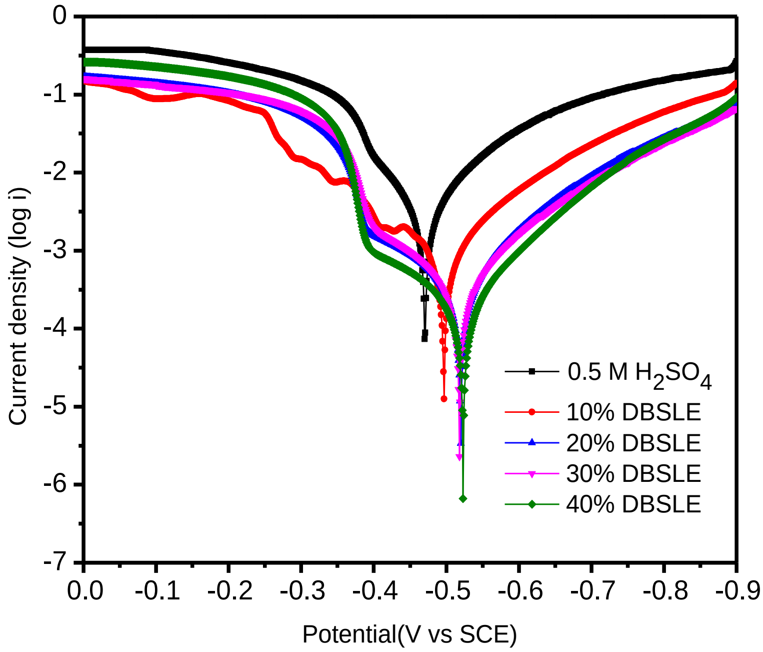


1 (d)

Figure 1 Polarization curves for mild steel in 0.5M H_2SO_4 with different concentrations of DBSLE (Dalbergia sisso leaf extract) at (a) 298K (b) 308K (c) 318K (d) 328K.

The change in the value of b_c and shift in the anodic Tafel slope (b_a) values suggest that DBSLE extract act as corrosion inhibitor suppressing both anodic and cathodic reactions by getting adsorbed on the mild steel surface. These results showed that DBSLE extract act as mixed type of inhibitor.

3.2. Electrochemical impedance spectroscopy

Impedance diagrams for mild steel in 0.5 M H_2SO_4 with and without different concentration of DBSLE are given in Fig. 2 and impedance parameters such as R_{ct} , C_{dl} and f_{max} obtained from electrochemical impedance measurements are shown in Table 2. Impedance diagrams show depressed semicircles; each spectrum consists of a capacitive loop in high frequency and an inductive in low frequency values. Diameters of capacitive loop increases with increase in inhibitor concentration which indicate that inhibitor film get strengthened. This capacitive loop indicates that the corrosion of mild steel is controlled by a charge transfer process [Khamis and Al-Andis, 2002)]. With the increase in concentration of inhibitor; charge transfer resistance increases and decreases the double layer capacitance value [Khaled and Hackerman, 2003]. This was mainly due to adsorption of DBSLE on the metal surface results in the formation of protective film on the electrode surface and decreased the extent of dissolution reaction [Bentiss, et al, 2004]. The charge-transfer resistances (R_{ct}) were calculated by the difference in impedance at the lower and higher frequencies by using following formula

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

Where R_{ct} and $R_{ct\,(inh)}$ are charge transfer resistance in absence and presence of inhibitor respectively. As the thickness of the protective layer increases, the inhibition efficiency also increases, since more inhibitor molecules will electrostatically adsorb on the electrode surface, resulting in a noticeable decrease in C_{dl} [Ibrahim and Habbab, 2011]. Double layer capacitance can be calculated by following relation

$$C_{dl} = 1 / 2\pi f_{max} R_{ct}$$

Where f_{max} is the frequency at which the imaginary component of the impedance is maximal and R_{ct} is charge transfer resistance. The inhibition efficiency calculated from EIS showed the same trend as those obtained from galvanostatic polarization measurement.

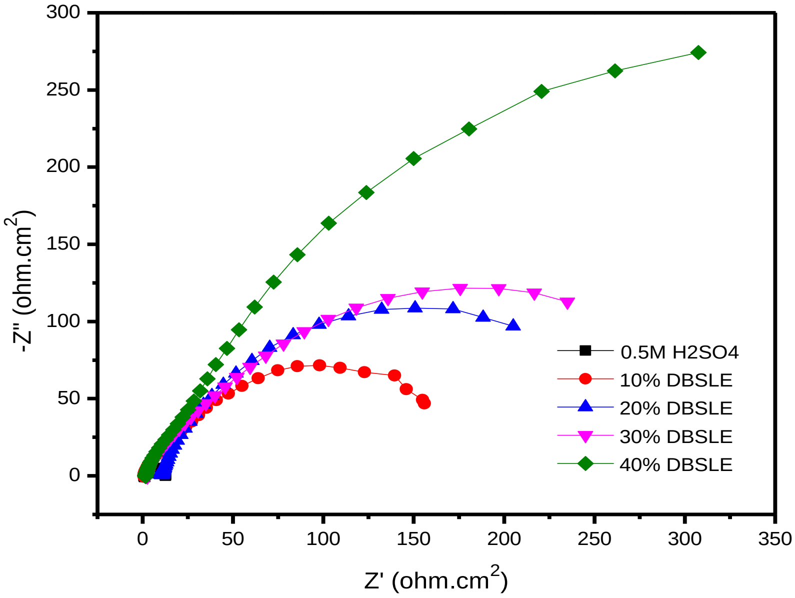


Figure 2a : Nyquist plots for mild steel in 0.5 M H_2SO_4 and in the presence of various concentrations of DBSLE at 298K

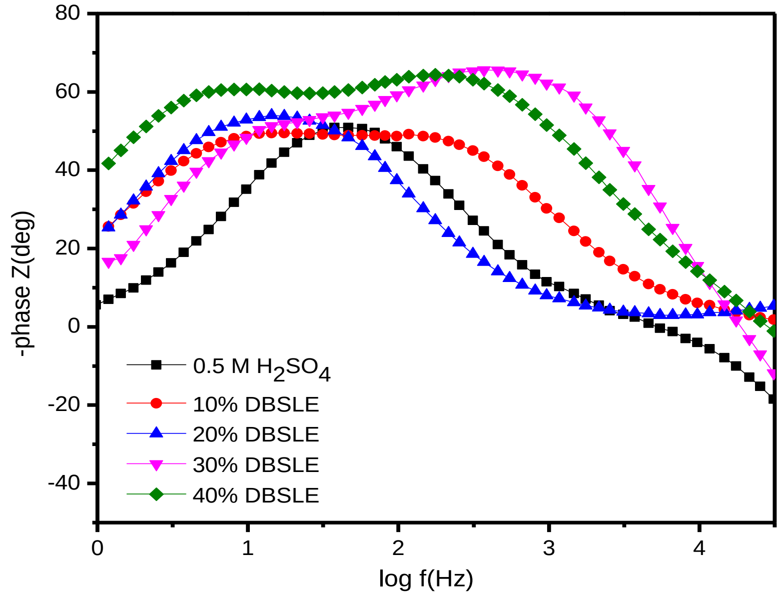


Figure 2b: Bode plot for mild steel in 0.5 M H_2SO_4 and in presence of MRLE at 298 K

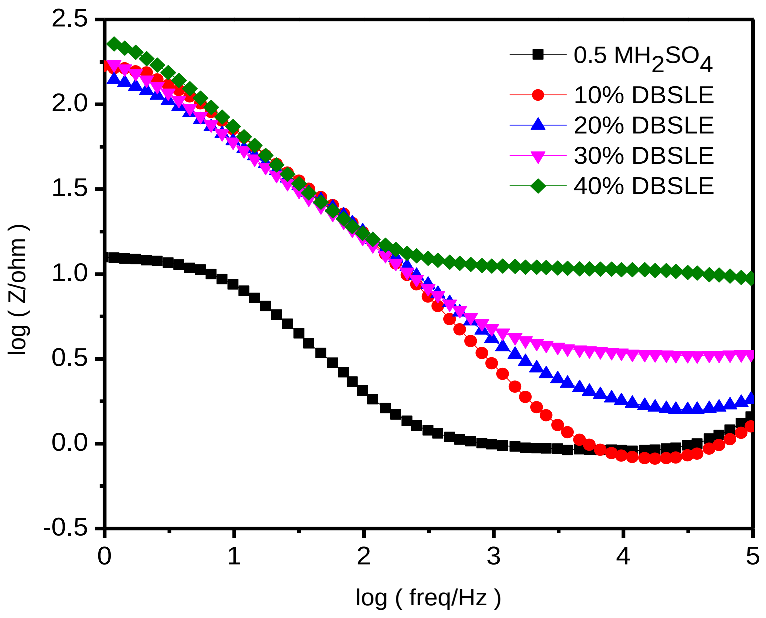


Figure 2c: bode plot for mild steel in 0.5 M H_2SO_4 and in presence of DBSLE at 298 K

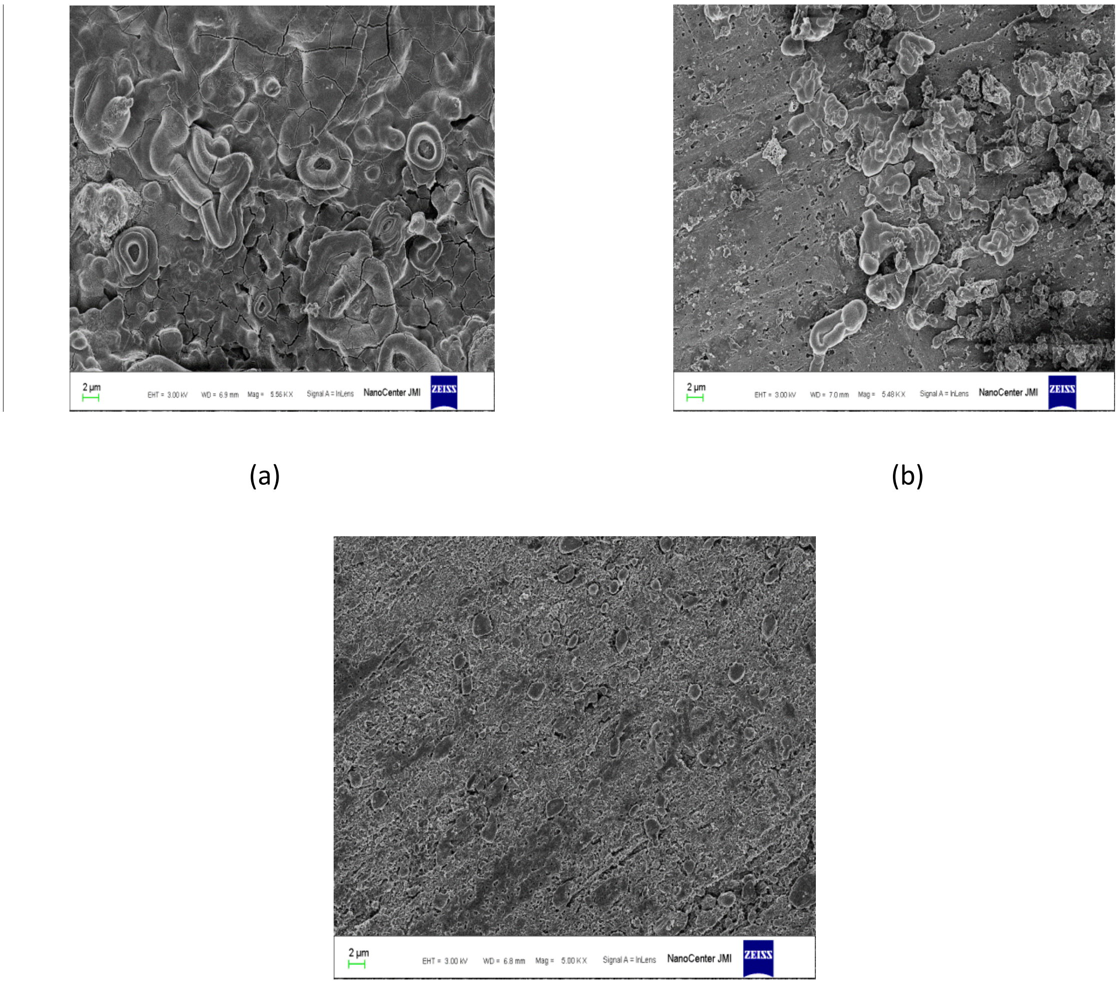
Table. 2: EIS data for mild steel in 0.5 M H_2SO_4 in presence and absence of different concentrations of inhibitor DBSLE.

Solution	conc.(v/v)%	R_{ct}	C_{dl}	F_{max}	%IE
H_2SO_4	0.5M	26.064		9.034	-
DBSLE	40%	535.609	1.032	288.015	95
	30%	283.41	5.154	109.011	90
	20%	205.350	9.702	79.925	87
	10%	187.006	11.99	71.008	86

The results from EIS parameters shown in Table 2. reveals that the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values decrease with increasing inhibitor concentration this leads to an increase of % $IE_{EIS.}$ Results obtained from EIS measurements are in good agreement with potentiodynamic measurements.

3.5 Surface characterization

From SEM surface morphology of mild steel in absence and presence of DBSLE can be seen clearly in Fig. 3(a–c). Fig. 3(a) shows the MS sample immersed in acid solution without inhibitor. In this image the MS surface is seems to be have some cracks and pits due to acid attack. The MS immersed in acid solution containing inhibitor are shown in Fig. (b, c). The inhibitor treated MS surfaces are smooth and protected from acid attack



(a) (b) (c)

Figure.3 SEM images of mild steel (a) in 0.5 M H_2SO_4 (b) In 10% DBSLE (c) 40% DBSLE

Conclusion

Dalbergia sisso leaf extract was found to be an effective inhibitor for mild steel corrosion in H_2SO_4. With increase in concentration of Dalbergia sisso leaf extract inhibition efficiency of the extract and with increase in temperature inhibition efficiency decreases. At the highest extract concentration, inhibition efficiency reaches to 94.6%. From polarization curve measurement, it was analyse that Dalbergia sisso leaf extract was a mixed type of inhibitor. From EIS plot it was concluded that the charge transfer resistance increases with increase in concentration of extract. Results obtained from polarization measurements and electron impedance spectroscopy is in good agreement with surface morphology.

Reference

1. Ahmed, I., Prasad, R., Quraishi, M.A., 2010, ‘ Graft co-polymer as corrosion inhibitor for mild steel in 15% Hcl’. Corros. Sci., 52 , 933–942.
2. Bentiss, F., Traisnel, M. Lagrene’e, M., ‘ Influence of 2,5-bis(4-imethylaminophenyl)-1,3,4-thiadiazole on corrosion inhibition of mild steel in acidic media’, J. Appl. Electrochem. 31 (2001) 41.
3. Chauhan, L: R., Gunasekaran,G., 2007, ‘Ecofriendly inhibitors for the corrosion inhibition of mild steel in phosphoric acid medium’, Corros. Sci., 49 , 1143.
4. El-Etre, A.Y., 2006, ‘Khillar Extract as inhibitor for acid corrosion of SX 316 steel’, Applied surface sci., 252 , 8521-8525
5. Sorkhabi, H.A., E. Asghari, E., 2008, ‘Effect of hydrodynamic conditions on the inhibition performance of l-methionine as a ‘‘green” inhibitor’, Electrochim. Acta 54 (2008) 162.
6. Ibrahim, T., Alayan, H., AL mowaqet, Y., 2012, ‘The effect of Thyme leaves extract on corrosion of mild steel in HCl’. Progress in organic coating 75, 456-462.
7. Khamis, E., Al-Andis, N., 2002. Mat-Wiss. U. Werkstofftech 9, 550.
8. Khaled,K.F., Hackerman, N., ‘ Investigation of the inhibitive effect of orthosubstituted anilines on corrosion of iron in 1 M HCl solutions’, Electrochim.Acta 48 (2003) 2715.
9. Quraishi, M.A., Jamal, D.,2002, ‘ Inhibition of mild steel corrosion in the presence of fatty acid triazoles’, J. Appl. Electrochem. 32 (2002) 425.
10. MuthuKrishnan, P., Jeyaprabha, B., Prakash, P., 2013, ‘Adsorption and corrosion inhibiting behavior of Lannea coromandelica leaf extract on mild steel corrosion’, Arabian Journal of chemistry.
11. Raja, P.B., Qureshi, A.K., Osman,H., Awang, K.,2013, ‘Neolamarkia cadamba alkaloids as ecofriendly corrosion inhibitors for mild steel in 1M Hcl media’, Corros sci.,69, 292- 301.
12. Raja, P.B., Sethuraman, M.G., 2008, ‘Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel’, Mateial letters, 62, 2977-2979.
13. Saleh,M.M., ‘ Inhibition of mild steel corrosion by hexadecylpyridinium bromide in 0.5 M H2SO4’, Mater. Chem. Phys. 98 (2006) 83.
14. Saleh, R.M., Ismail, A.A., Hosary, 1983, ‘Corrosion inhibition of mild steel in acidic media by using aqueous extract of few plant leaves’, Corros. Sci.23, 1239-1241.

15. Satapahty, A.K., Gunasekaran, G., Sahoo, S.C., Amit,K.,2009, ‘Corrosion inhibition by Justicia gendarussa plant extract in hydrochloric acid solution’, Corrs sci. 51, 2818-2856.
16. Sorkhabi, H.A., E. Asghari, E., 2008, ‘Effect of hydrodynamic conditions on the inhibition performance of l-methionine as a ‘‘green” inhibitor’, Electrochim. Acta 54 (2008).