Natural Non Toxic Green Inhibitors of Murraya Koenigii, Withania Somnifera and Glycyrrhiza Glabra Extracts for Mild Steel in 8% H_2SO_4

Akhil Saxena Dwarika Prasad*
Department of Chemistry, Lovely Professional University, Phagwara, Punjab, India

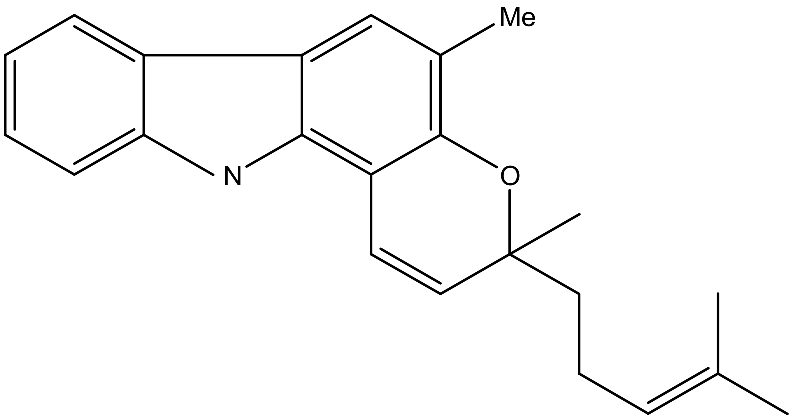
Abstract
By means of polarization measurements UV, IR and weight loss study, it has been detected that the extract of *Murraya koenigii, Withania somnifera* and *Glycyrrhiza glabra* leaves can act as corrosion inhibitor for the sake of mild steel in 8% H_2SO_4 solution. These plants show good inhibition efficiency at particular concentrations of the acid. It is observed that plants extract act as better inhibitor on increasing their concentration. Here we have focused on the corrosion inhibition action of different plant extracts in H_2SO_4 medium.
Keywords: Murraya koenigii, Withania somnifera, Glycyrrhiza glabra, Mild Steel, SEM.

1. Introduction

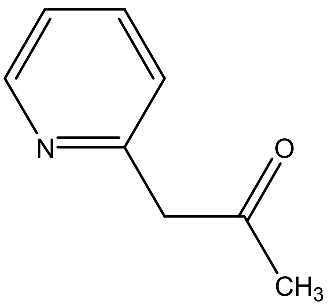
From last few decades corrosion inhibitor has been a colourable field of research. Acids are being used widely in the field of mild steel machinery in industries for different applications for e.g. cleaning, descaling, pickling etc [1]. To prevent the corrosion of mild steel by using plant extracts is one of the most enterprising methods. A number of organic inhibitors are dynamically used to prevent corrosion and it is the most provident method. The inhibition action of organic inhibitors relies on their adsorption capability on metal by replacing water molecules [2]. Organic compounds also show corrosion inhibition efficiency and there are several organic compounds which are notified to prevent corrosion [3-7]. But the problem with them is that they are extremely poisonous to both humanitarian as well as surroundings. Because of the poisonous effects of these organic inhibitors, natural non toxic inhibitors are the requirement of our environment [1]. Compounds which contain oxygen and nitrogen inhibit the corrosion of mild steel most effectually [8]. In green inhibitors secondary metabolize O and N are usually present and they are the active centers for adsorption [9-10].The adsorption of green inhibitors on the steel surface can be either in the form of physisorption or chemisorptions or it may also be as a combined effect of both [11].Therefore to overcome the toxic effect of commercial inhibitors, the development of natural non toxic inhibitors to prevent the metallic corrosion is necessary and seductive [12]. Extract of naturalistic products contain many compounds which are biodegradable in nature. In the present study we have used the extracts of Murraya *koenigii, Withania somnifera* and *Glycyrrhiza glabra* saturated with H_2SO_4 which play an effective role to inhibit corrosion of mild steel. These plant extracts consist of alkaloids for example Murraya *koenigii* consists of mahanimbine alkaloid, *Withania somnifera* consists of Isopelletierine alkaloid and *Glycyrrhiza glabra* consists of glabridin which are rich in heteroatoms hence we can use them to prevent corrosion. The inhibition effect of these plant extracts on the corrosion rate of mild steel in 8% H_2SO_4 was studied by using weight loss study, IR, UV and polarization measurements.

We see that green inhibitor of *Withania somnifera* has shown 90% efficiency at 300 ppm, *Murraya koenigii* 87% and *Glycyrrhiza glabra* shows 94% efficiency with 300 ppm at inhibitor concentration 8% H_2SO_4.

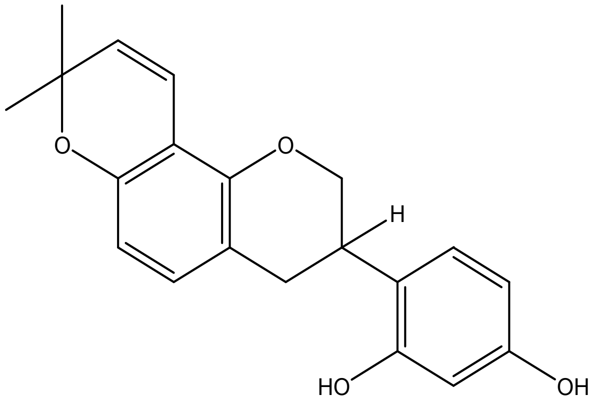
Fig.1. Chemical constituents of *Murraya koenigii* (a),*Withania somnifera* (b) and *Glycyrrhiza glabra*(c).



(a)- Mahanimbine



(b)- Isopelletierine



(c)-glabridin

2. Experimental

2.1. Preparation of plant extract

The very first we collected the plants mentioned above for our study and then dried and powered .The powder was soaked to 500 ml deionised water and then refluxed for 3 hours. In this manner we obtained the aqueous solution which was then filtered and concentrated to 100 ml with the help of soxhlet appratus.Then we can prepare the solutions of particular concentrations with the help of this concentrated solution.

2.2. Weight loss measurements

With the help of weight loss study we measure the loss in weight of mild steel strips when they are placed in saturated solution of H_2SO_4 with extract. For this purpose we take rectangular pieces of mild steel which composed of (wt %) Fe 97.60%, C 0.083%, Si 0.39%, Mn 0.43%, P 0.12%,Cr 0.45%, Ni 0.27% and Cu 0.43%[13]. These strips were then squeezed with fine grade emery paper (120, 600, 800, and 1000), washed with distilled water and dried. Then the mild steel strips were weighted accurately before inserting them into the saturated solution of H_2SO_4 with extract. The mild steel strips were then dipped into H_2SO_4 without extract and saturated with varied concentrations of extract. Then we left the set up for 3 hours and after the elapsed time, the mild steel strips were excluded, cleansed, drained and weighed. A difference in weight is noted between the mild steel strips dipped in H_2SO_4 solution without extract and with varied concentrations of extract. Here we have used 8% H_2SO_4 in the experiment. All the concentrations of inhibitors for weight loss are taken in mgL^{-1} by weight. The inhibition efficiency and surface coverage (θ) can be determined by using following equation:

$$\theta = \frac{w_0 - w_i}{w_0} \quad (1)$$

$$\eta(\%) = \frac{w_0 - w_i}{w_0} \times 100 \quad (2)$$

Where, w_i and w_0 are the weight loss values in presence and absence of inhibitor, respectively.

2.3. Electrochemical measurements

Electrochemical studies are conducted by using a Gamry interface Potentiostat/Galvanostate/ZRA03007.All techniques are useful. Polarization with Potentiostat measures current while on the other hand polarization with Galvanostate measures potential. The corrosion cell consists of three electrodes. We use a saturated calomel electrode in the form of reference electrode, a platinum foil in the form of counter electrode and mild steel is used in the form of a working electrode. Here we immerse the working electrode in the test solution and stabilize it for 30 minutes. With the help of such studies we obtain Tafel polarization curves which help us to get information about corrosion inhibition of mild steel. These slopes provide us the value of corrosion current densities (I_{corr}), we use this value in the following formula and find the inhibition efficiency.

$$\eta(\%) = \frac{I_{0corr} - I_{icorr}}{I_{0corr}} \times 100 \qquad (3)$$

Where I_{0corr} and I_{icorr} represent the corrosion current density values without and with inhibitor, respectively.

2.4. UV- Visible Spectroscopy: We subject the 8% H_2SO_4 solution saturated with extract before and after dipping the mild steel strips to UV- visible spectrophotometer. Here we obtained the UV- visible absorption spectra for various concentrations of extracts before and after dipping the mild steel strips. The spectra of extract before dipping the mild steel strip shows some smaller peaks which are not found in the spectra of extract after dipping the mild steel strip. It means that when we dip mild steel strip in the extract then some molecules adsorb on the mild steel surface, they forms a protective film on the surface and prevent the corrosion of mild steel.

2.5. IR Spectroscopy: The IR spectroscopy tells us about different types of functional groups, heteroatoms present in the extract.

2.6. Surface Analysis

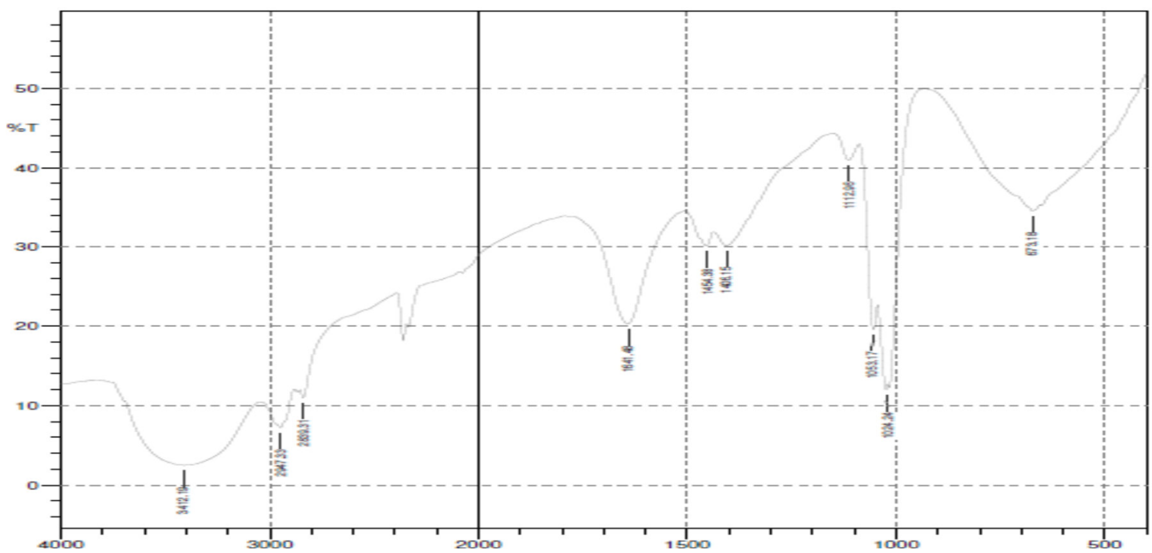
The SEM micrographs of mild steel samples that were immersed in 8% H_2SO_4 solution for 3 h in the absence and presence of extract. A rough surface can be seen for the mild steel immersed in H_2SO_4 without inhibitor which indicates the corrosion on mild steel surface in acidic medium. In the presence of inhibitor a smooth surface can be observed, which indicates that the mild steel surface is covered by inhibitor.

3. Results and discussion

3.1. *Murraya koenigii*

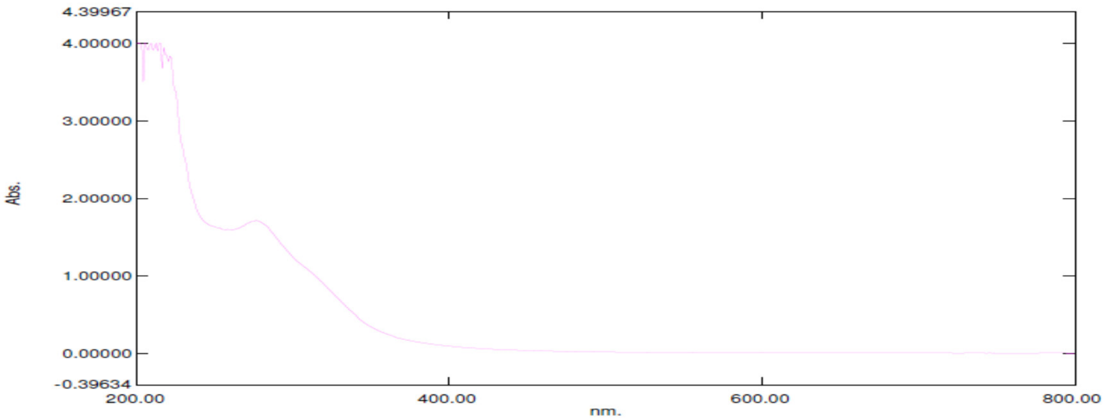
3.1.1. IR study

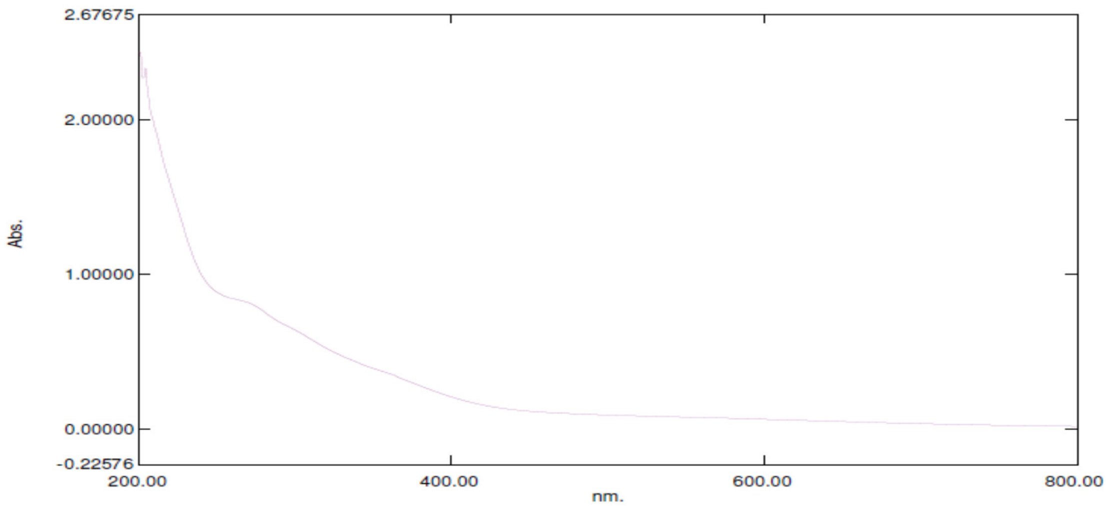
IR study tells about the functional groups present in the extract. The peak at 3412 cm^{-1} suggests O-H stretching of alcohol, peak at 1641 cm^{-1} suggests C=O stretching of amide. Further peak at 1024 cm^{-1} suggests C-O stretching of ethers.



3.1.2 UV Visible spectroscopy:

The UV spectra of *Murraya koenigii* extract saturated with 8% H_2SO_4 before and after dipping the mild steel strips are shown in the figure-





3.1.3. *Weight loss study*

For mild steel, the weight loss results in the absence and presence of different concentration of *Murraya koenigii* extract saturated with H_2SO_4 are summarized in Table 1. The table 1 clearly indicates that when concentrations of the Murraya koenigii extract increases, the inhibition efficiency also enhances. The *Murraya koenigii* extract gives maximum inhibition efficiency of 87 % at 300 ppm.*Murraya koenigii* consists of heteroatoms (O, N) which form the metal complex bond with the metal surface thereby reducing corrosion. Hence it proves that the *Murraya koenigii* extract can be treated effectively to prevent the corrosion of mild steel. Similar results were obtained by Quraishi et al. [1]. For *Murraya koenigii plant* extract he had observed 95% efficiency with 300ppm inhibitor concentration at 0.5 M (2.7%) H_2SO_4. However, we have observed inhibition efficiency of 87% with 300 ppm inhibitor concentration at 8% H_2SO_4 for *Murraya koenigii* extract. It means that when concentration of acid increases, inhibition efficiency of inhibitor decreases.

Table 1: Corrosion parameters for mild steel in 8% H_2SO_4 without and with different concentrations of *Murraya koenigii* extract.

Acid solution	Inhibitor concentration (ppm)	Weight loss ($mgcm^{-2}$)	η(%)	*Θ*
8%H_2SO_4	0	36.06	00.00	.0000
	30	16.56	54.07	.5407
	90	11.06	69.34	.6936
	180	09.20	74.48	.7448
	300	04.90	86.41	.8641

3.1.4. Polarization Measurements

Weight loss study is verified by polarization measurement. The polarization measurement for *Murraya koenigii* provides the values of corrosion current density (*I*corr) which has been shown in table 2.

Table 2. Potentiodynamic polarization parameters for the corrosion of mild steel in 8% H_2SO_4 without and with different concentrations of extract.

Con.(ppm)	E_{corr}(V)	I_{corr}(A)	$Beta_a$(V/decade)	$Beta_b$(V/decade)	CR (mpy)	E%
0	-0.44	0.0355	0.2742	0.7565	20687	-
30	-0.42	0.0159	0.1469	0.3335	9237	55
90	-0.41	0.0106	0.1337	0.3172	6173	70
180	-0.41	0.0087	0.1142	0.3014	5074	75
300	-0.75	0.0046	0.0842	0.2341	2703	87

We use these values in the following formula and will find inhibition efficiency.

$$\eta\ (\%) = \frac{I_{0\,corr} - I_{icorr}}{I_{0\,corr}} \times 100 \tag{4}$$

Where I_{0corr} and I_{icorr} represents the corrosion current density values without and with inhibitor, respectively. Figure 2 and Figure 3 represents the polarization curves of mild steel in 8% H_2SO_4 without and with various concentrations of *Murraya koenigii* extract.

Fig 2.Tafel polarization curve for mild steel in 8% H_2SO_4 without *Murraya koenigii* extract.

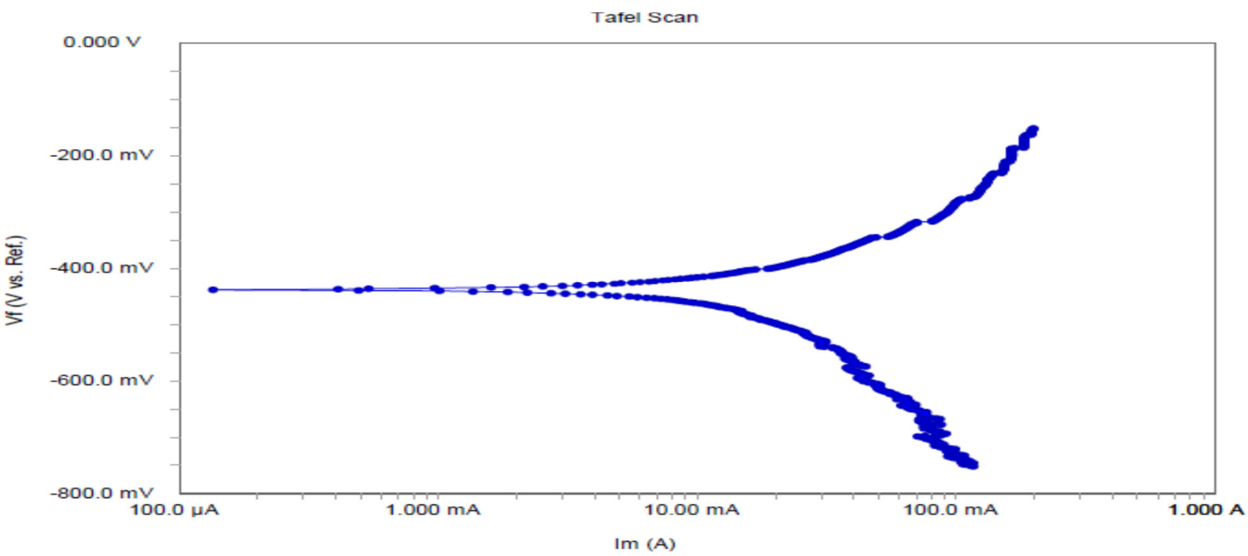
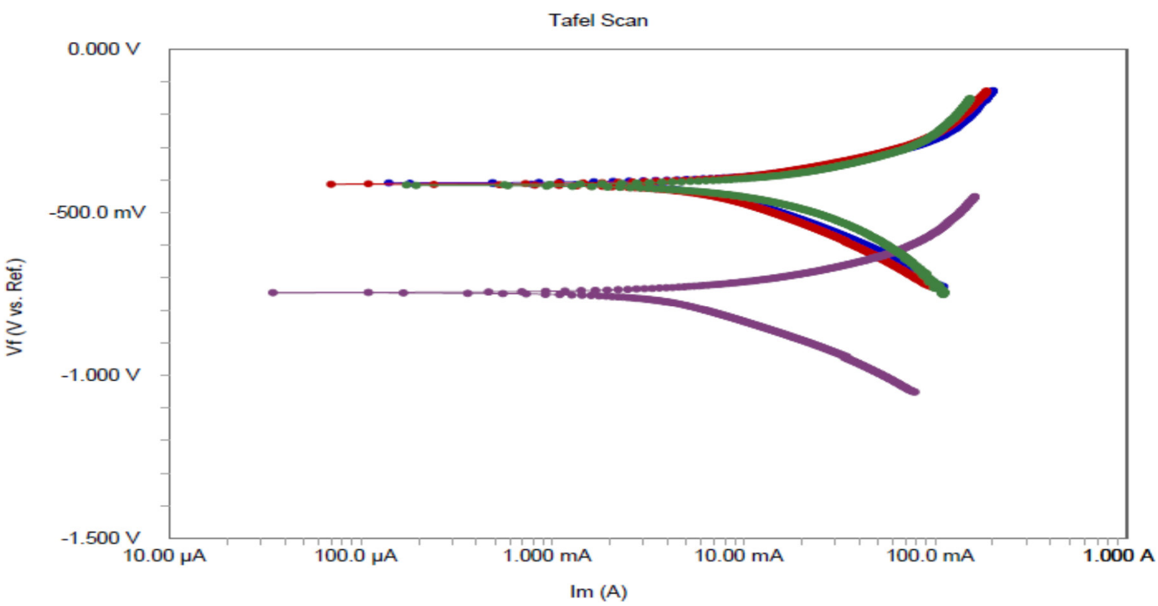
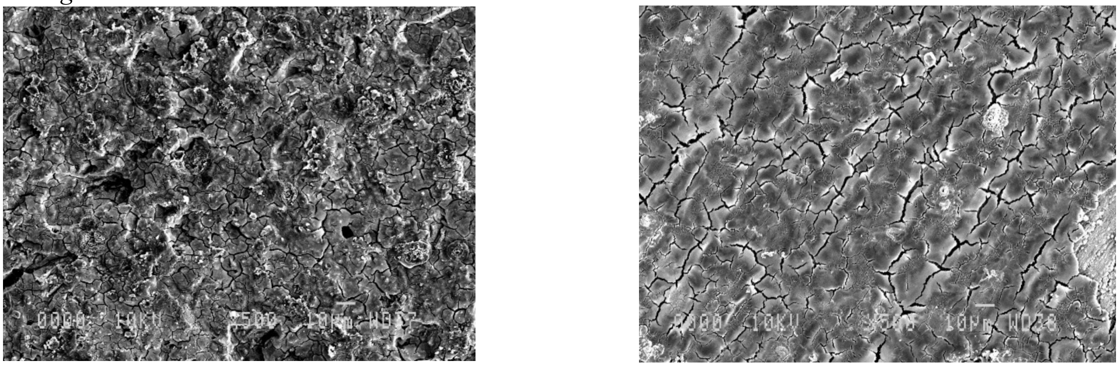


Fig 3. Tafel polarization curve for mild steel in 8% H_2SO_4 with different concentrations of *Murraya koenigii* extract.



3.1.5. Surface Analysis

The figure 4 shows the SEM micrographs of mild steel strips immersed in 8% H_2SO_4 without and with *Murraya koenigii* inhibitor.



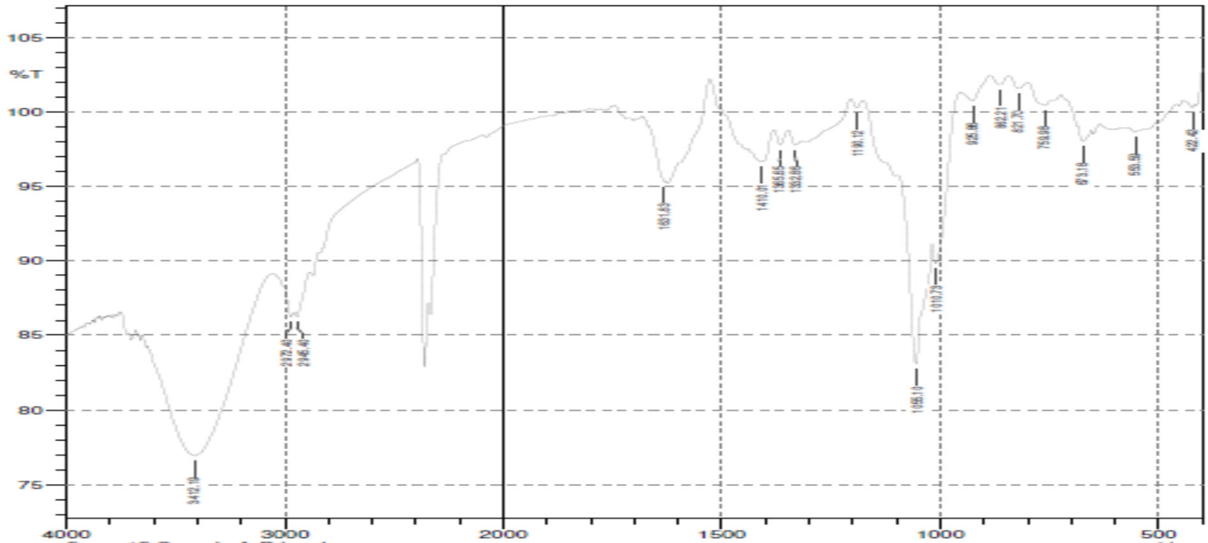
[a] **[b]**

Fig. 4 –SEM images of mild steel in 8% H_2SO_4 without [a] and with *Murraya koenigii* inhibitor [b].

3.2. Withania somnifera

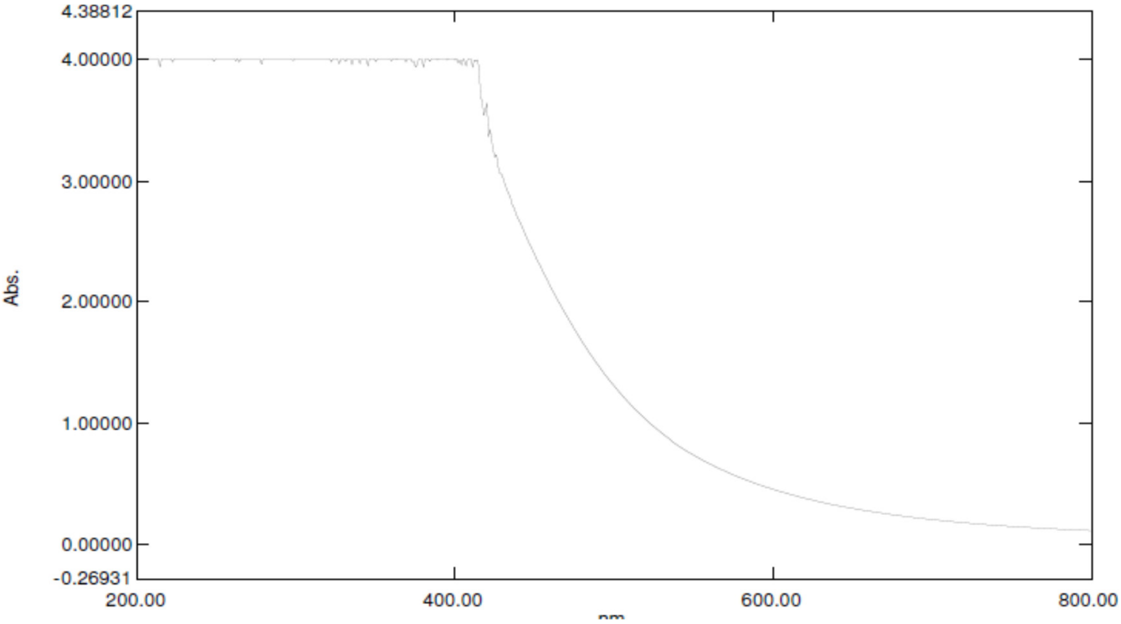
3.2.1. IR study:

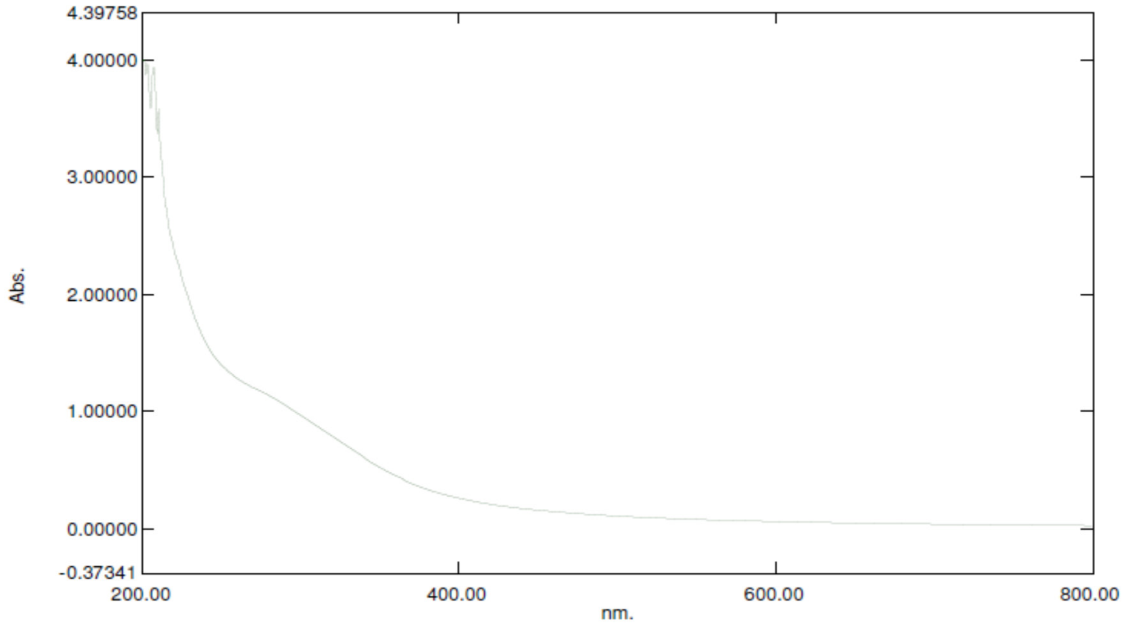
From IR spectra of *Withania somnifera, the* peak at 3412 cm^{-1} suggests aromatic O-H stretching. Further peak at 1631 cm^{-1} suggests C=O stretching of amide group. The peak at 1055 cm^{-1} suggests C-O stretching of alcohol.



3.2.2. UV Visible spectroscopy:

The UV spectra of acid solution saturated with *Withania somnifera* extract before and after dipping the mild steel strips are shown in the figure-





3.2.3. Weight loss measurements

The weight loss results for mild steel without and with different concentration of *Withania somnifera* extract in 8% H_2SO_4 are summarized in Table 3. The table 3 also indicates that when concentrations of the Withania somnifera extract increases, the inhibition efficiency also enhances. The *Withania somnifera* extract gives maximum inhibition efficiency of 91 % at 600 ppm. *Withania somnifera* consists of heteroatoms (O, N) which form the metal complex bond with the metal surface thereby reducing corrosion. Hence it proves that the *Withania somnifera* extract can be treated effectively to prevent the corrosion of mild steel. Therefore it is clear that *Murraya koenigii* extract shows 87% efficiency with 300 ppm inhibitor concentration at 8% H_2SO_4 while *Withania somnifera* extract shows 90% efficiency with 300 ppm inhibitor concentration at 8% H_2SO_4.

Table 3: Corrosion parameters for mild steel in 8% H_2SO_4 in absence and presence of different concentrations of *Withania somnifera* from weight loss measurements for 3 hours.

Acid solution	Inhibitor concentration (ppm)	Weight loss ($mgcm^{-2}$)	η(%)	Θ
8% H_2SO_4	0	36.06	00.00	.0000
	30	20.42	43.37	.4337
	90	18.20	49.53	.4953
	180	04.15	88.49	.8849
	300	03.45	90.43	.9043

3.2.4. Polarization Measurements

Weight loss study is verified by polarization measurement. The polarization measurement for *Withania somnifera* provides the values of corrosion current density (*I*corr) which has been shown in table 4.

Table 4. Potentiodynamic polarization parameters for the corrosion of mild steel in 8% H_2SO_4 without and with different concentrations of extract.

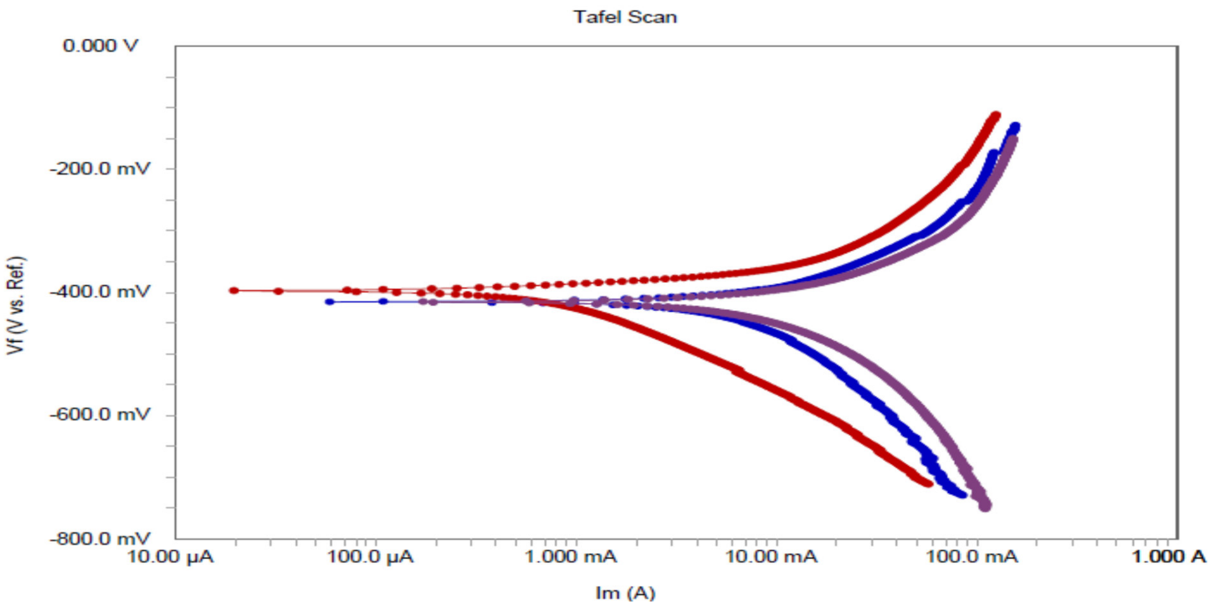
Con.(ppm)	E_{corr}(V)	I_{corr}(A)	$Beta_a$(V/decade)	$Beta_b$(V/decade)	CR (mpy)	E%
0	-0.44	0.0355	0.2742	0.7565	20687	-
90	-0.42	0.0126	0.1481	0.4345	7357	64
180	-0.43	0.0038	0.1062	0.2436	2212	89
300	-0.42	0.0033	0.0979	0.224	1924	91

We use these values in the following formula and will find inhibition efficiency.

$$\eta\ (\%) = \frac{I_{0\,corr} - I_{icorr}}{I_{0\,corr}} \times 100 \qquad (5)$$

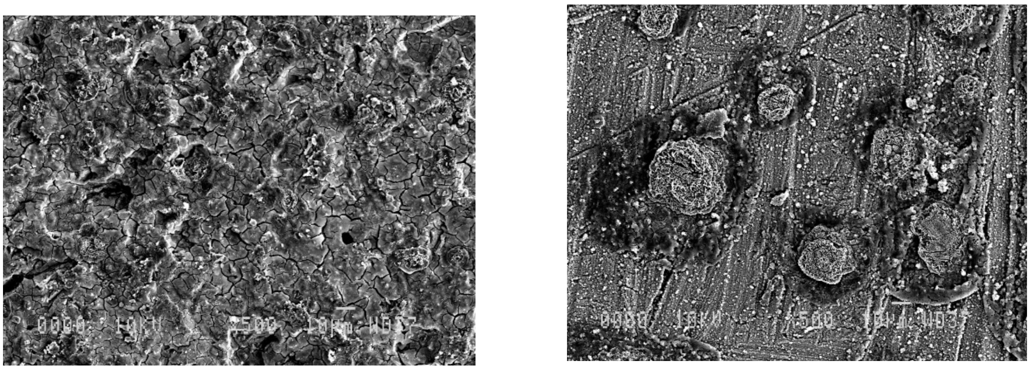
Where I_{0corr} and I_{icorr} represents the corrosion current density values without and with inhibitor, respectively. Figure 5 represents the polarization curves of mild steel in 8% H_2SO_4 without and with various concentrations of *Withania somnifera* extract.

Fig 5. Tafel polarization curves for mild steel in 8% H_2SO_4 with different concentrations of *Withania somnifera* extract in 8% H_2SO_4.



3.2.5. Surface Analysis

The figure 6 shows the SEM micrographs of mild steel strips immersed in 8% H_2SO_4 without and with *Withania somnifera* inhibitor.



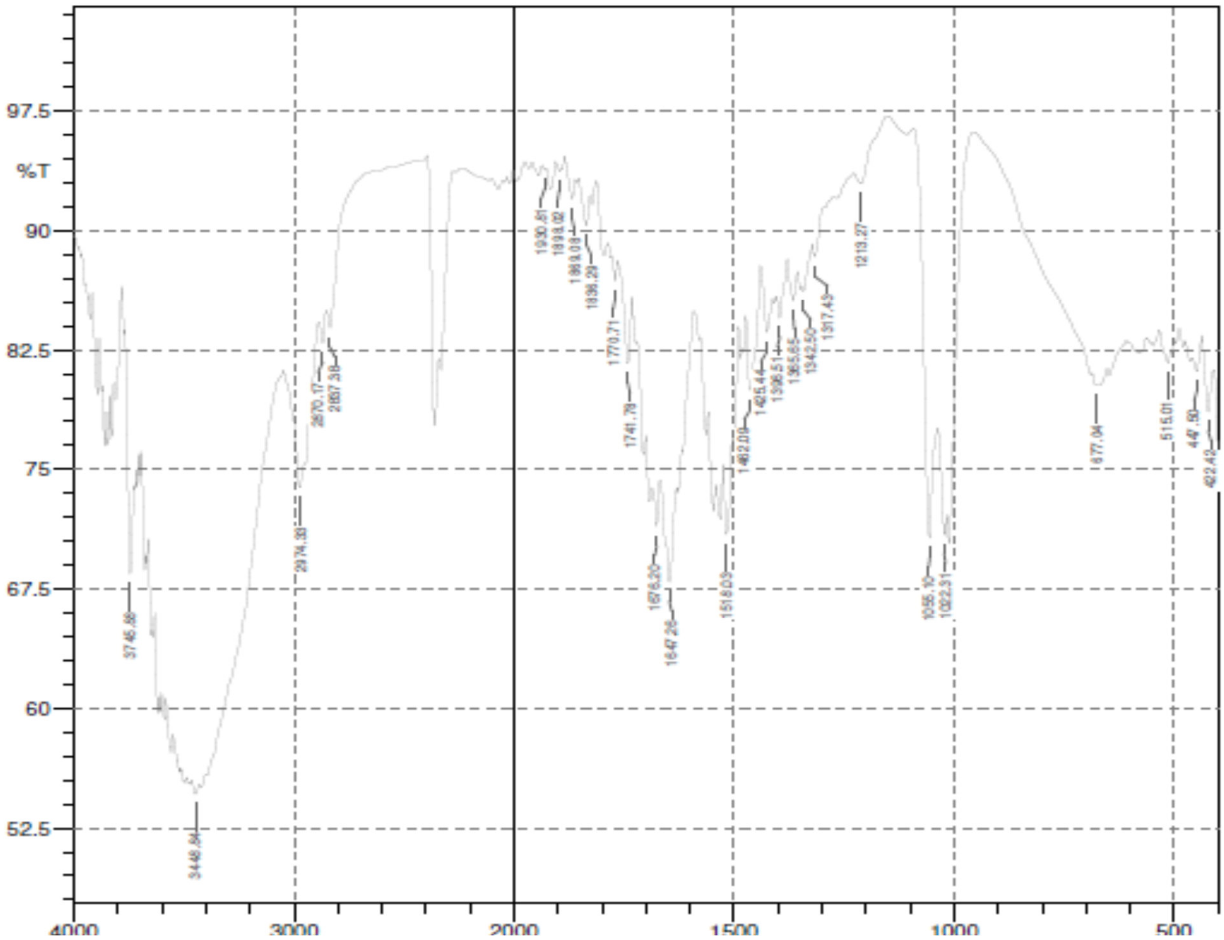
[a] **[b]**

Fig. 6- SEM images of mild steel in 8% H_2SO_4 without [a] and with *Withania somnifera* inhibitor [b].

3.3. Glycyrrhiza glabra

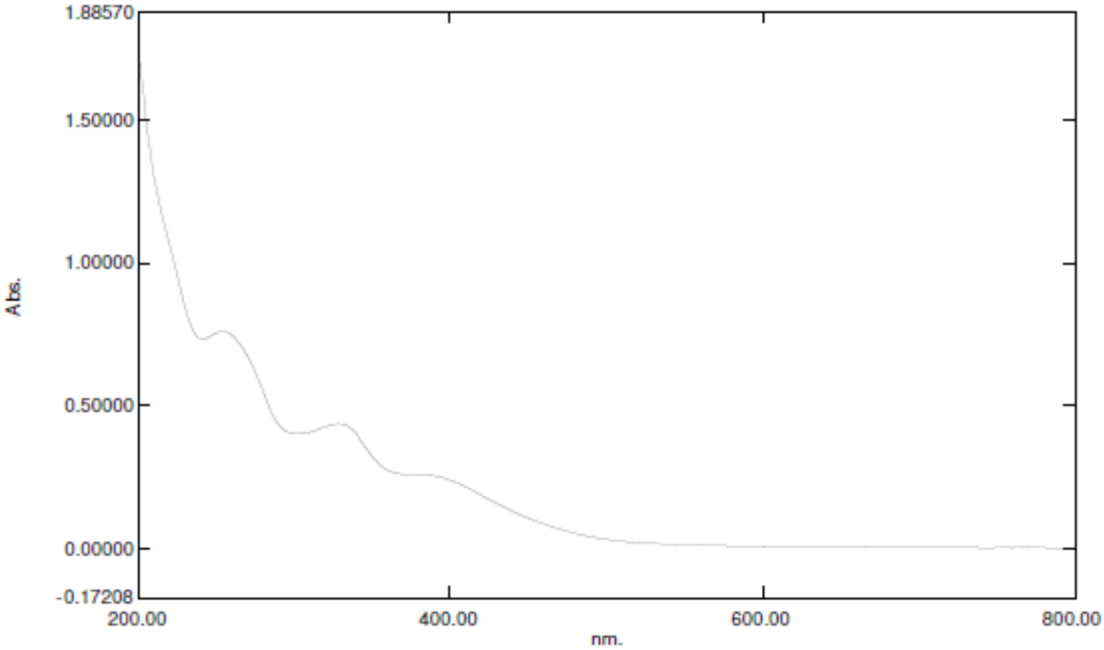
3.3.1. IR study

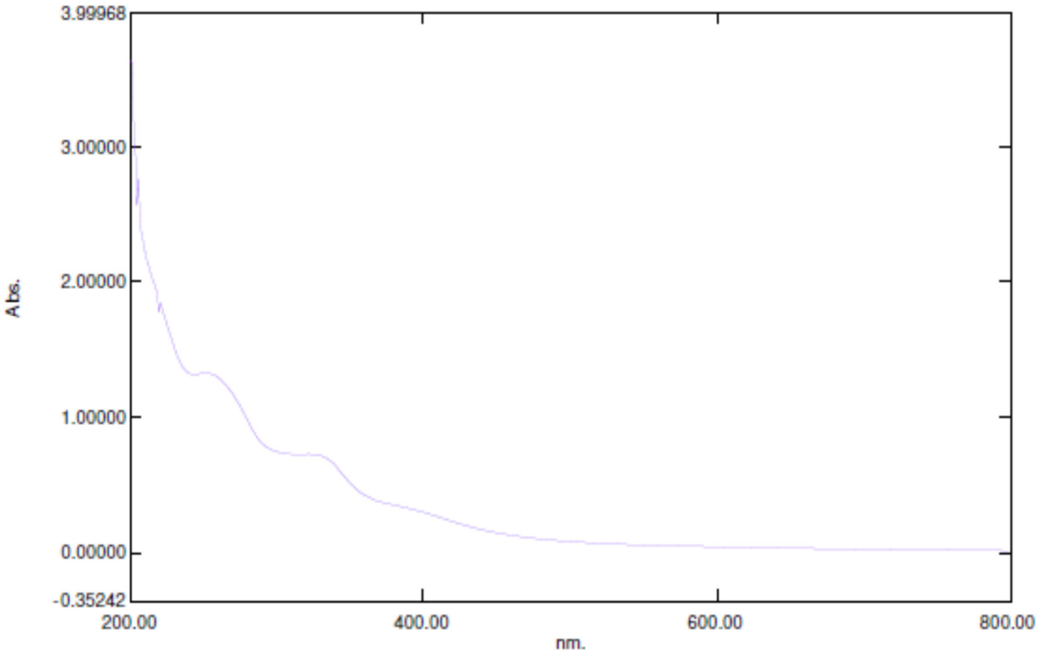
From the IR spectra of *Glycyrrhiza glabra* , the peak at 3448 cm^{-1} suggests N-H stretching of amide, the peak at 1647 cm^{-1} suggests C=O stretching of amide.



3.3.2. UV Visible spectroscopy:

The UV spectra of acid solution saturated with *Withania somnifera* extract before and after dipping the mild steel strips are shown in the figure-





3.3.3. Weight loss measurements

The weight loss results obtained for mild steel without and with different concentration of *Glycyrrhiza glabra* extract in 8% H_2SO_4 are summarized in Table 5. The table 5 also indicates that when the concentrations of the Glycyrrhiza glabra extract increases, the inhibition efficiency also increases. The *Glycyrrhiza glabra* extract shows maximum inhibition efficiency of 94% at 300 ppm. *Glycyrrhiza glabra* constituents consist of heteroatoms (O, N) which form the metal complex bond with the metal surface thereby reducing corrosion. Therefore it proves that the *Glycyrrhiza glabra* extract can be treated effectively to prevent the corrosion of mild steel. We have observed that *Murraya koenigii* extract shows 87% efficiency, *Withania somnifera* extract shows 90% efficiency and maximum inhibition efficiency of 94% is obtained for *Glycyrrhiza glabra* extract with 300 ppm inhibitor concentration at 8% H_2SO_4.

Table 5: Corrosion parameters for mild steel in 8% H_2SO_4 in absence and presence of different concentrations of *Glycyrrhiza glabra* from weight loss measurements for 3 hours.

Acid solution	Inhibitor concentration(mgL^{-1})	Weight loss (mgcm^{-2})	η(%)	θ
8% H_2SO_4	0	36.06	00.00	.0000
	30	07.45	79.34	.7934
	60	06.95	80.73	.8073
	90	05.14	85.74	.8574
	180	04.12	88.57	.8857
	300	02.25	93.76	.9376

3.3.4. Polarization Measurements

Weight loss study is verified by polarization measurement. The polarization measurement for *Glycyrrhiza glabra* provides the values of corrosion current density (*I*corr) which has been shown in table 6.

Table 6. Potentiodynamic polarization parameters for the corrosion of mild steel in 8% H_2SO_4 with and without different concentrations of extract

Con.(ppm)	E_{corr}(V)	I_{corr}(A)	Beta$_a$(V/decade)	Beta$_b$(V/decade)	CR (mpy)	E%
0	-0.44	0.0355	0.2742	0.7565	20687	-
30	-0.42	0.0071	0.117	0.3017	4139	80
180	-0.42	0.0038	0.0833	0.2173	2202	89
300	-0.50	0.0021	0.1047	0.1477	1222	94

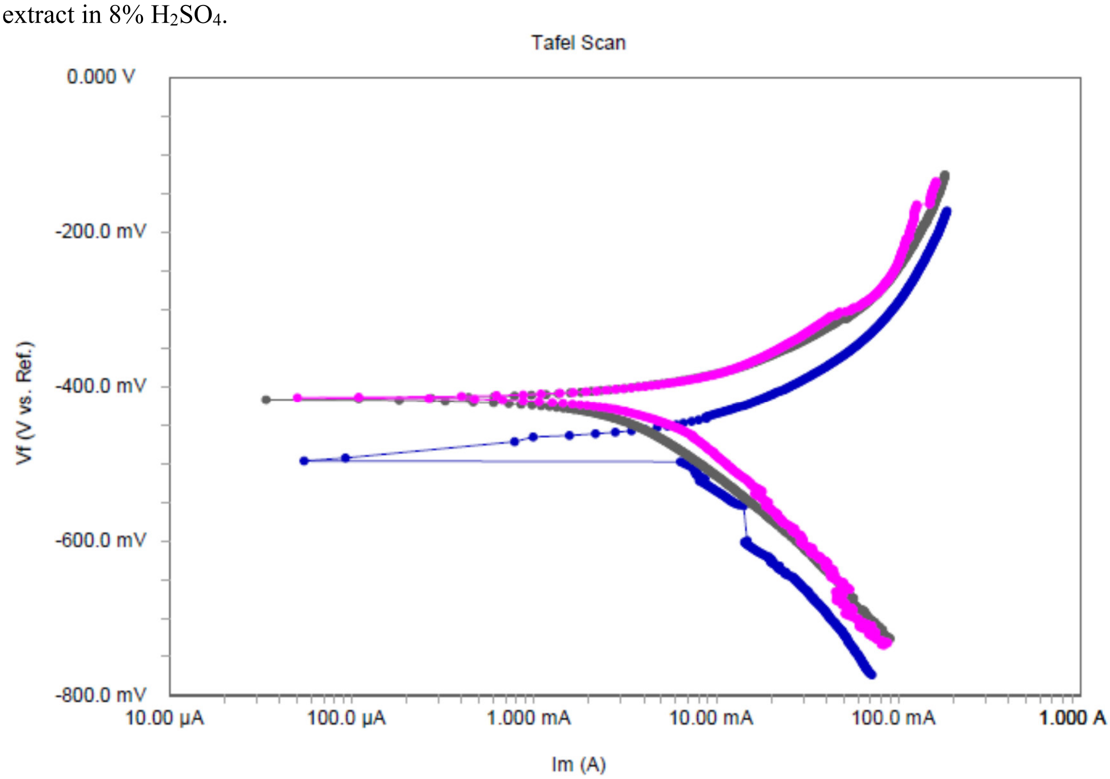
We use these values in the following formula and will find inhibition efficiency.

$$\eta\ (\%) = \frac{I_{0\,corr} - I_{icorr}}{I_{0\,corr}} \times 100 \qquad (6)$$

Where I_{0corr} and I_{icorr} represents the corrosion current density values without and with inhibitor, respectively.

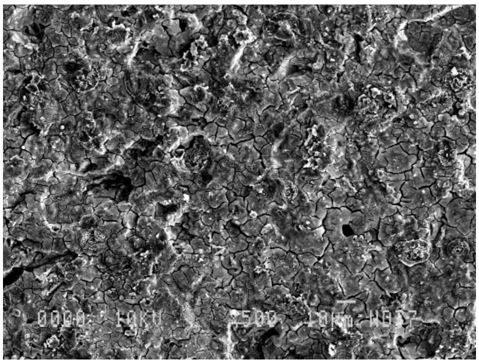
Figure 7 represents the polarization curves of mild steel in 8% H_2SO_4 without and with various concentrations of *Glycyrrhiza glabra* extract.

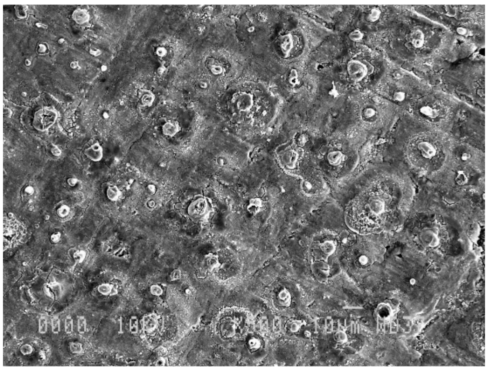
Fig 7. Tafel polarization curves for mild steel in 8% H_2SO_4 with different concentrations of *Glycyrrhiza glabra* extract in 8% H_2SO_4.



3.3.5. Surface Analysis

The figure 8 shows the SEM micrographs of mild steel strips immersed in 8% H_2SO_4 without and with *Glycyrrhiza glabra* inhibitor.



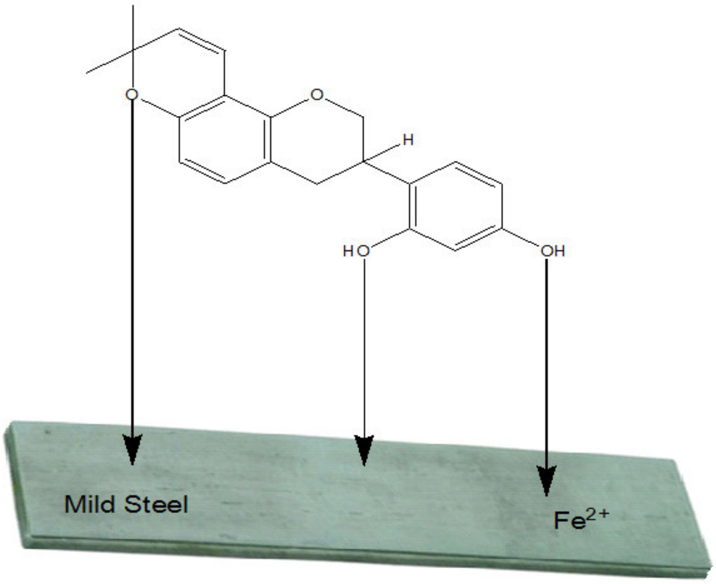


[a] **[b]**

Fig. 8- SEM images of mild steel in 8% H2SO4 without [a] and with *Glycyrrhiza glabra* inhibitor [b].

Mechanism of action

In the present study the plant extracts we are using to determine the corrosion inhibition action of plant extracts for mild steel, contain alkaloids which is explained above.These alkaloids are rich in heteroatoms like N, O, S. From the IR study of plant extracts it has been shown that they contain functional groups like hydroxyl group, amide group, carbonyl group etc. Hence the IR study also verifies the presence of heteroatoms N, O in the extract. These heteroatoms donate their lone pair of electron to the empty d-orbital of Fe. Similarly there is also the interaction between the Π electrons of C=O and empty d-orbital of Fe. In such a way the inhibitor adsorb on the mild steel surface and forms a protective thin film by the combination between inhibitor and mild steel surface. This protective film prevents the corrosion of mild steel.



Conclusion

In the present study we have considered the plant extracts of *Murraya koenigii, Withania somnifera* and *Glycyrrhiza glabra.* Here we have determined the corrosion inhibition rate of plant extracts for mild steel in 8% H_2SO_4. .The examined plant extract prevents the corrosion of mild steel in 8% H_2SO_4 by adsorbing on the mild steel surface. Enhancement of inhibition efficiency is observed on account of the concentration of inhibitors. Here we have observed 87% inhibition efficiency for *Murraya koenigii plant* extract, 90% inhibition efficiency for the plant extract of *Withania somnifera* and 94% for *Glycyrrhiza glabra* at 300 ppm inhibitor concentration with 8% H_2SO_4. Therefore it is clear that *Glycyrrhiza glabra* extract shows maximum inhibition efficiency of 94% with 300 ppm inhibitor concentration and 8% H_2SO_4 hence it can be a better corrosion inhibitor. Present study may be useful for all those areas where mild steel comes in contact with acidic medium or wherever mild steel corrosion occurs.

Acknowledgement

Author gratefully acknowledges Dr. R. Jayaganthan, Department of Metallurgical and Materials Engineering, IIT

Roorkee, Uttrakhand, India for provide lab facilitation of our study.

References

1. M. A. Quraishi, A. Singh, V. K. Singh, Mater. Chem. Phys. 122 (2010) 114-122.
2. A.S. Fouda, A.S.Ellithy, Corros. Sci. 51 (2009) 868.
3. M. A. Quraishi, R. Sardar, Corros. 58 (2002) 103.
4. H. M. Abd El-Lateef, L. I .Aliyeva, V.M .Abbasov, Adv. Appl. Sci. Res. 3 (2012) 1185.
5. M. Lebrini, M. Lagrenee, H.Vezin, L.Gengembre, F.Bentiss, Corros. Sci. 47 (2005) 485.
6. F.Bentiss, M. Bovanis, B. Mernari, M.Traisnel, M.Legrenee, Appl. Surf. Sci. 253 (2007) 3696.
7. G.Husnu, S. H.Ibrahim, Ind. Eng. Chem. Res. 51 (2012) 785.
8. D. K.Yadav, D. S.Chauhan, I.Ahamad, M. A.Quraishi, RSC Adv. 3 (2013) 632.
9. G.Ji, P.Dwivedi, S.Sundaram, R.Prakash, Ind. Eng. Chem. Res. 52 (2013) 10673.
10. L.Larabi. Y.Harek, O.Benali, S.Ghalem, Pros. Org. Coat. 54 (2005) 256.
11. J.Aljourani, K.Raeissi, M.A.Golozar, Corros. Sci. 51 (2009) 1836.
12. H.Ashassi-Sorkhabi, D.Seifzadeh, M. G.Hosseini, Corros. Sci. 50 (2008) 3363.
13. A.K. Singh, M.A. Quraishi, Corros. Sci. 52 (2010) 152.
14. A.Yurt, A Balaban., S.U.Kandemir, Mater. Chem. Phys. 85 (2004) 420.
15. G. K.Gomma, M.H.Wahdan, Mater. Chem. Phys. 39 (1994) 142.
16. M.A.Quraishi, R.Sardar, J. Appl. Electrochem. 33 (2003) 1163.