Green Approach to Corrosion Inhibition of Mild Steel in Sulphuric Acid Solution using Extract of Banana Leaves

Dakeshwar Kumar Verma* Fahmida Khan
Department of Chemistry, National Institute of Technology Raipur, Raipur, 492010 CG, India

Abstract
The inhibition of the corrosion of mild steel in sulphuric acid solution by the extract of *banana leaves* has been studied using weight loss, Fourier transform infrared spectra and scanning electron microscopy techniques. Inhibition was found to increase with increasing concentration of the leaves extract. Maximum inhibition efficiency observed 94.91% at optimum concentration of inhibitor. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the extract component on the mild steel surface obeys the Langmuir adsorption isotherm. The results obtained show that the extract of the leaves of banana could serve as an effective inhibitor of the corrosion of mild steel in sulphuric acid medium.
Keywords: Adsorption, Corrosion, Mild steel, Weight loss**,** Inhibition efficiency

1. INTRODUCTION

Mild steel is one of the most commonly used constructional materials in various industries due to its low cost, good tensile strength, and ready availability. Corrosion of metals in acidic solutions is the one of the severe problem in industrial cleaning and pre-treatment process such as acid pickling, and acid descaling. Hydrochloric acid, Sulphuric acid, and phosphoric acids are the extensively used acidic solutions for these applications [1-7]. Use of corrosion inhibitors is one of the most effective protection method for mild steel in various acidic solutions. Most of the corrosion inhibitors are heterocyclic organic compounds containing nitrogen, sulphur, oxygen and alkenes [4]. The dangerous effects of most synthetic organic corrosion inhibitors are the stimulus for the use of natural inhibitors [8]. Recently, natural plants extracts have become important as they are bearable, renewable and readily available. [9]. various researches have been reported using such natural plant extracts. A.M. Abder-Gaber [9] and co-workers reported the inhibitive action of extracts of *Chamoline*, *Black cumin, Halfabar*, and *Kidney bean* plants on the corrosion of steel in different concentrations of sulphuric acid. Taleb Ibrahim and Mehad Habbab [16] studied the inhibitive action of *eggplant peel* extract in the direction of the corrosion of mild steel in 2M HCl solution at different concentrations and temperatures. They indicated that the extract of the *eggplant peel* serves as an admirable corrosion inhibitor. Punita Mourya [19] and co-workers have investigated the extract of *Tagetes erecta* as a mild steel corrosion inhibitor in 0.5 M H_2SO_4 solution. The extreme corrosion inhibition efficiency 99.28% was reported for plant extract at 303 K. Various investigations showed that basic component of plant extracts are alkaloids, steroids, sugars, gallic acid, tannic acid and flavanoids etc. The presence of cellulose, tannins, and polyphenolic compounds have been reported to improve the protection of metal surface, thus decreasing metal corrosion [12-19].

The objective of the present work is to estimate the inhibitive action of *banana leaves* extracts as an inexpensive and ecological corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution.

2. EXPERIMENTAL

2.1. MATERIALS PREPARATION

Mild steel specimens containing composition (wt. %) of C = 0.23%, O = 1.99, Si = 0.58%, P = 0.02%, S = 0.01%, Cr = 0.03%, Ni = 0.03 and balance Fe were used for all the experiments. coupons were cut into 5 x 2 x 0.1 cm sizes and used for weight loss measurements and surface analysis. before the measurements, the surface of mild steel was abraded using different grades of emery paper. the metal surface was cleaned by washing with double distilled water and acetone respectively, than dried in desiccators before immersing in the corrosive medium [19]. for the corrosion study acid solution was prepared by dilution of AR grade H_2SO_4 with double distilled water.

2.2. INHIBITOR PREPARATION

Banana leaves were collected, wash with running tap water, dried in hot air oven, than weighed and grounded. Banana leaves powder was refluxed for 3 h in one litre of 0.5 MH_2SO_4 acid [11]. Then it was filtered and filtrate was made up to one litre using the same 0.5 M H_2SO_4 acid solution. This solution was taken as stock solution from which solutions of varying strengths were prepared and studied as mild steel corrosion inhibitor in acid solution [15].

2.3. WEIGHT LOSS MEASUREMENT

Weight loss measurement is the easiest way to find the total weight loss, corrosion rate (ρ), inhibition efficiency (*%I*), and degree of surface coverage (θ). For weight loss measurement, the specimens of 5 x 2 x 0.1 cm size were used. The polished mild steel coupons were weighed and suspended in the 100 ml beaker containing test solution in the presence and absence of inhibitor. After different immersion period the specimens were taken out and carefully washed with double distilled water and ethanol, then dried and weighted using metteler Toledo AL204 electronic balance, Accuracy in weighing up to 0.0001 gm.

2.4. SURFACE ANALYSIS

The surface morphology of mild steel specimens was examined using SEM and FTIR analysis. For these studies mild steel specimen first immersed in 100 ml beaker containing 0.5 M H_2SO_4 solution in the absence and presence of inhibitor. FT-IR spectra recorded by using Thermo Nicolet, AVATAR-370-FTIR (USA) over a range of 500-4000 cm^{-1} with a resolution of 4.000 cm^{-1}. Scanning electron microscope images obtained from *ZEISS EVO SEM 18* oxford model.

3. RESULTS AND DISCUSSION

3.1 WEIGHT LOSS MEASUREMENTS

Values of the inhibition efficiency (*%I*) corrosion rate (ρ) and degree of surface coverage (θ) with different concentrations of *banana leaves* extract for mild steel in 0.5 M H_2SO_4 solution shown in Table 1. The corrosion rate (ρ) was calculated from the equation given below [5]:

$$\rho = \Delta W / At \qquad \text{............ (1)}$$

Where ΔW is the weight loss in mg, A is the total area of metal specimen in cm^2, and t is the immersion time (24 h). Inhibition efficiency (*%I*) was calculated by using the relationship [8]:

$$\%I = \left(\frac{\rho1 - \rho2}{\rho1}\right) \times 100 \qquad \text{.............. (2)}$$

Where ρ1 and ρ2 are the corrosion rates of the mild steel specimens in the absence and presence of inhibitor, respectively.

Table 1: Weight loss result of mild steel in 0.5 M H_2SO_4 solution for 24 h immersion time in the presence and absence of different concentrations of inhibitor.

Time (h)	Conc. (*g l^{-1}*)	Corrosion rate ρ (*mg $cm^{-2}h^{-1}$*)	Inhibition efficiency (*%I*)
12	0.0	0.878	-
	0.5	0.119	86.64
	1.0	0.095	89.17
	1.5	0.066	92.48
	2.0	0.051	94.19
	2.5	0.046	94.76
24	0.0	1.198	-
	0.5	0.284	76.29
	1.0	0.159	86.72
	1.5	0.144	87.97
	2.0	0.112	90.65
	2.5	0.079	93.40
48	0.0	1.648	-
	0.5	0.221	86.48
	1.0	0.167	89.86
	1.5	0.154	90.65
	2.0	0.132	91.99
	2.5	0.087	94.72
72	0.0	1.887	-
	0.5	0.301	84.04
	1.0	0.212	88.76
	1.5	0.163	91.36
	2.0	0.110	94.17
	2.5	**0.096**	**94.91**

The values of corrosion rate (ρ), inhibition efficiency (*%I*), and surface coverage (θ) obtained with mild steel specimens in 0.5 M H_2SO_4 solution. These parameters were evaluated in the absence and presence of inhibitor. [2]. from the Table 1, it is evident that inhibition efficiency increases with increase inhibitor concentration. Fig. 1, shows the relationship between immersion time and surface coverage with various concentrations of inhibitors. From the Fig 1 it is evident that area of surface coverage increases as concentration of inhibitor increased.

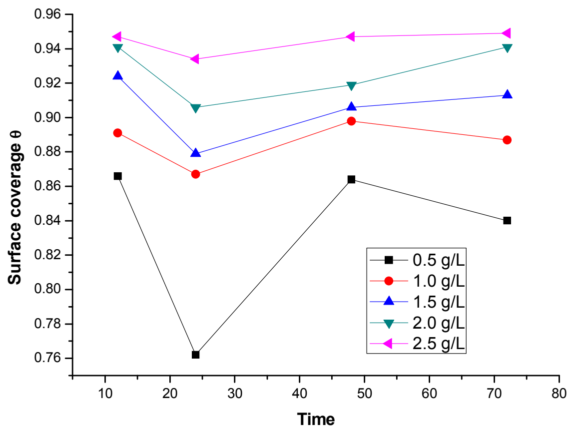

Fig. 1. The relationship between surface coverage and concentration at different immersion period.

3.2. ADSORPTION ISOTHERM

The adsorption of the inhibitor molecules on metal surface is influenced by the nature of the metal surface, distribution of the charge in the molecule, the chemical structure of the inhibitor, and the type of electrolyte [14]. The adsorption of main constituents of extract can be attributed to the presence of O, N, P and S atoms, p electrons, and aromatic rings. The degree of the surface coverage (θ) at different concentrations of inhibitors has been calculated for inhibition mechanism. These Calculated θ values were used to determine the adsorption isotherm best fits the surface coverage data. The correlation coefficient was used to determine the fitting of the experimental data to those isotherms [5]. Linear relationship between θ value and inhibitor concentration C must be found in order to obtain the adsorption isotherm [4]. Several adsorption isotherm models such as Temkin, Frumkin, Langmuir and Flory-Huggins were attempted to fit the θ values [4]. It was found that adsorption of this inhibitor followed the Langmuir adsorption. The Langmuir adsorption isotherm is given by [9]:

$$\frac{C}{\theta} = \frac{1}{\mathrm{Kads}} + C \qquad \text{…………… (3)}$$

Where θ is the surface coverage, K_{ads} is adsorptive equilibrium constant, and C is the equilibrium inhibitor concentration. The plot of C_{inh}/θ versus C_{inh} with slope around unity gives the best fitted straight line. Correlation coefficient (r^2) obtained from straight line equation, used to choose the adsorption isotherm that best fit experimental data. K_{ads} value can be calculated from the intercept of the straight lines C_{inh}/θ [21]. The most important thermodynamic adsorption parameters, adsorption free energy (ΔG_{ads}) was evaluated and value shows the physisorption mechanism on metal surface [1, 5]. The relationship between the adsorption constant, K, and the free energy of adsorption, ΔG_{ads} shown in equation given below [6, 21].

$$\Delta G_{ads} = -RT \ln (55.5\ K_{ads}) \qquad \text{……………… (4)}$$

Where R is gas constant, T is temperature, and K is the binding constant. The negative value of ΔG_{ads} (-16.23 kJ mol^{-1}) indicate the good interaction between the inhibitor molecules and the mild steel surface [10]. Generally, the standard free energy of adsorption values of -40 kJ mol^{-1} or more negative value involve charge transfer or sharing between inhibitor molecules and metals show the chemical adsorption those of -20 kJ mol^{-1} or less negative value are associated with physisorption. [1, 4, 10, 13].Therefore for present study the value of ΔG_{ads} (-16.23 kJ mol^{-1}) has been considered less negative value within the range of physical adsorption. [13].

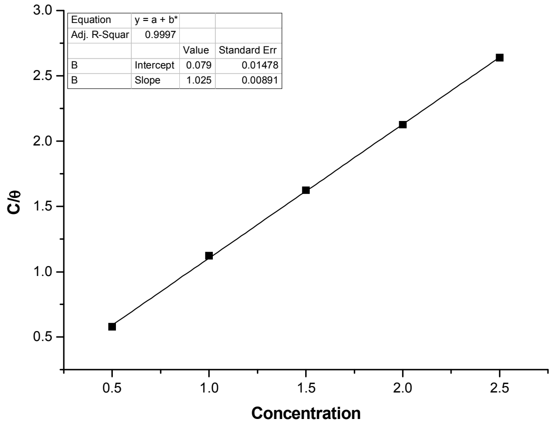

Fig. 2. Langmuir adsorption plot of *banana leaves* extract at different concentrations.

3.3. FT-IR ANALYSIS

Fig.3 shows the spectrum of inhibitor extract, the broad band at 3446.49 cm $^{-1}$ can be assigned because of stretching mode of a hydroxyl or N–H group. Absorption peak at 1639.08 cm^{-1} may be assigned stretching mode of carbonyl (C=O) group. Therefore, based on above results it is evidence that the extracted organic compounds are stable in 0.5 M H_2SO_4 [9, 22]. These groups contain non-bonding electrons which are main responsible for adsorption on mild steel surface.

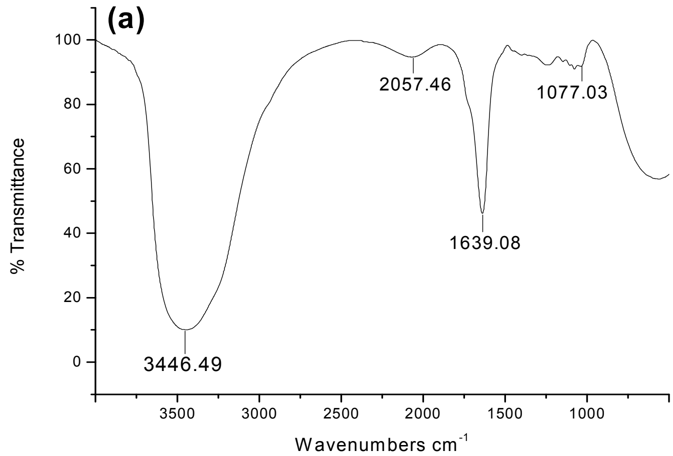

Fig. 3. FT-IR spectra of inhibitor extract

3.4. SEM ANALYSIS

SEM micrographs and the corresponding EDS spectra of the surface of the mild steel specimens in 0.5 M H_2SO_4 solution in the absence and presence of *banana leaves* extract are shown in Figs. 4 and 5. The SEM images of metal surface before and after exposing to acidic solution in the absence and presence of inhibitor for 24 h are shown in figure.4. It shows the abraded mild steel surface before immersion in corrosive solution and Fig.4b and Fig.4c shows the SEM images of mild steel surface that was immersed in 0.5 M H_2SO_4 solution in the absence and presence of inhibitor for 24 h, respectively. The SEM image of mild steel surface in Fig.4a shows the plane surface. Whereas from Fig.4b it is obviously seen that the metal surface was severely corroded due to presence of corrosive solution. However the appearance of mild steel surface is different after the addition of the inhibitor solution shown in Fig.4c. The uniform distribution of inhibitor on the high carbon steel surface prevent the further corrosion. Based on the corresponding EDS spectrum of Fig. 4a, it can be concluded that the mild steel surface corroded in aggressive media has areas with clearly high oxygen concentration compared to the surface in the presence of *banana leaves* extract.

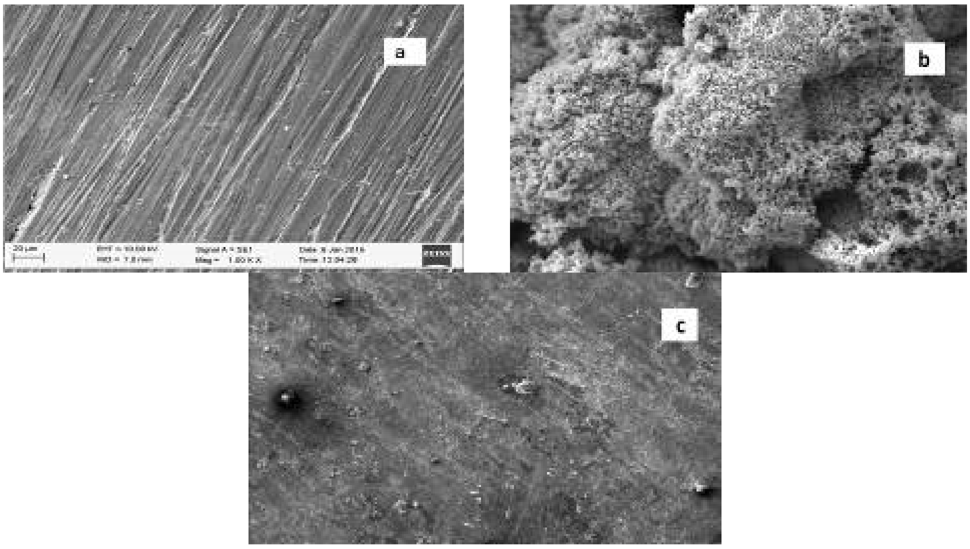

Fig. 4 SEM images of mild steel surfaces **a** polished mild steel **b** mild steel after immersion in 0.5 M H_2SO_4 **c** & **d** mild steel after immersion into inhibitor solution.

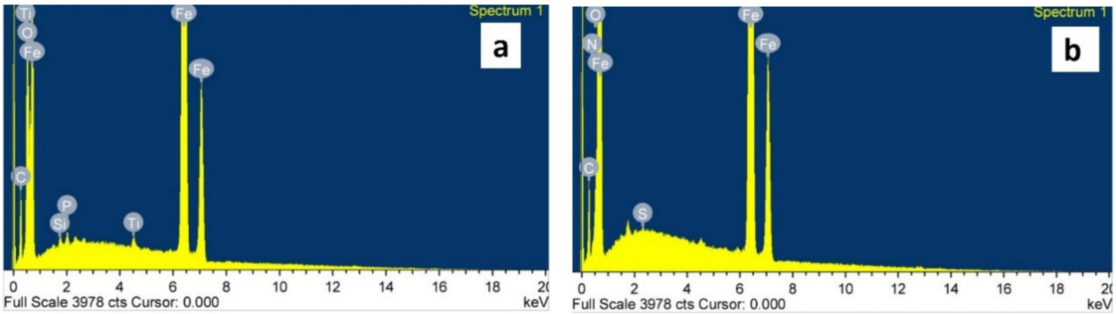

Fig. 5 EDS spectra mild steel surfaces **a** mild steel after immersion in 0.5 M H_2SO_4 and **b** mild steel after immersion into inhibitor solution.

CONCLUSION

Results of weight loss measurement show that *banana leaves* extract acts as a good mild steel corrosion inhibitor in 0.5 M H_2SO_4. The inhibition efficiency increases with the increase in inhibitor concentration. The maximum inhibition efficiency value of 94.91 was obtained for 2.5 g/l inhibitor concentration. The adsorption of *banana leaves* extract follows the Langmuir adsorption isotherm. Values of free energy of adsorption indicates that the adsorption of *banana leaves* extract on the mild steel surface involves the physical adsorption process. SEM analysis results show that inhibitor molecules form protective layer over the metal surface and prevent from the further corrosion. The result obtained from FTIR spectra provide the strong interaction between inhibitor molecules and mild steel surface.

REFERENCES

1. S. Saravanamoorthy, S.Velmathi (2013) Physiochemical interactions of chiral Schiff bases on high carbon steel surface: Corrosion inhibition in acidic media. Progress in Organic Coating. 76:1527-1535.
2. G. Moretti, F. Guidi, F. Fabris (2013) Corrosion inhibition of the mild steel in 0.5 M HCl by 2-butyl-hexahydropyrrolo [1, 2-b] [1, 2] oxazole. Corrosion Science. 76: 206-218.
3. B.P. Markhali, R. Naderi, M. Mahdavian, M. Sayebani, S.Y. Arman (2013) electrochemical impedance spectroscopy and electrochemical noise measurements as tools to evaluate corrosion inhibition of azole compounds on stainless steel in acidic media. Corrosion Science. 75:269-279.
4. Sh. Pournazari, M.H. Moayed, M. Rahimizadeh (2013) In situ inhibitor synthesis from admixture of benzaldehyde and benzene-1,2-diamine along with $FeCl_3$ catalyst as a new corrosion inhibitor for mild steel in 0.5 M sulphuric acid. Corrosion Science. 71:20-31.
5. Ime B. Obot, Eno E. Ebenso, Mwadham M. Kabanda (2013) Metronidazole as environmentally safe corrosion inhibitor for mild steel in 0.5 M HCl: Experimental and theoretical investigation. Journal of Environmental Chemical Engineering. 1: 431-439.
6. Yongming Tang, Fan Zhanga, Shengxiang Huc, Ziyi Cao, Zhenglei Wua, Wenheng Jing (2013) Novel

benzimidazole derivatives as corrosion inhibitors of mild steel in the acidic media. Part I: Gravimetric, electrochemical, SEM and XPS Studies. Corrosion Science. 74: 271- 282.
7. Sadeq Hooshmand Zaferani, Majid Sharifi, Davood Zaarei, Mohammad Reza Shishesaz (2013) Application of eco-friendly products as corrosion inhibitors for metals in acid pickling processes – A review. Journal of Environmental Chemical Engineering. 1: 652-657.
8. M. Prabakaran, K. Vadivu, S. Ramesh, V. Periasamy (2014) Enhanced corrosion resistance properties of mild steel in neutral aqueous solution by new ternary inhibitor system. J. Mater. Environ. Sci. 5:553-564.
9. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady, M. Saadawy (2006) Inhibitive action of some plant extracts on the corrosion of steel in acidic media. Corrosion Science. 48:2765-2779.
10. R. Solmaz (2014) Investigation of corrosion inhibition mechanism and stability of Vitamin B1 on mild steel in 0.5 M HCl solution.Corrosion Science. 81:75-84.
11. S. Kulandai Therese, V. G. Vasudha (2014) Studies on Mild Steel Corrosion Inhibition by Millingtonia Hortensis Extract in 1N Sulphuric Acid Medium. J. Environ. Nanotechnology. 3(1):09-15.
12. Kanchan Agrawal (2014) Fenugreek leaves and lemon peel as green corrosion inhibitor for mild steel in 1M HCl Medium. Journal of Materials Science & Surface Engineering .2014; 1 (2):44-48.
13. L. Y. S. Helen, A. A. Rahim, B. Saad, M. I. Saleh, P. Bothi Raja, Aquilaria Crassna Leaves Extracts – a Green Corrosion Inhibitor for Mild Steel in 1 M HCl Medium. Int. J. Electrochem. Sci. 9:830 – 846.
14. Niketan Patela, Anamika Rawatb, Smita Jauharia and Girish Mehta (2010) Inhibitive action of Bridelia retusa leaves extract on corrosion of mild steel in acidic media. European Journal of Chemistry. 1 (2):129-133.
15. A. U. Ezeoke, N.O. Obi-Egbedi, C. B. Adeosun, O. G. Adeyemi (2012) Synergistic Effect of Leaf Extracts of Cordia sebestena L. and Iodide Ions on the Corrosion Inhibition of Mild Steel in Sulphuric Acid. Int. J. Electrochem. Sci. 7:5339 – 5355.
16. Taleb Ibrahim, Mehad Habbab (2011) Corrosion Inhibition of Mild Steel in 2M HCl Using Aqueous Extract of Eggplant Peel . Int. J. Electrochem. Sci. 6:5357 – 5371.
17. Sudesh kumar, Surendra arora, Sanish sharma,Paresh arora and Suraj prakash mathur (2009) Synergistic effect of calotropis plant in controlling corrosion of mild steel in basic solution. J. chil. chem. soc.54 (1):83-88.
18. C.A. Loto, and A.P.I. Popoola (2012) Effect of Cola Acuminata and Camellia Sinensis Mixed Extracts on the Corrosion Inhibition of Mild Steel in 0.5M Sulphuric Acid. Int. J. Electrochem. Sci. 7: 2983-2996.
19. Punita Mourya, Sitashree Banerjee, M.M. Singh (2014) Corrosion inhibition of mild steel in acidic solution by Tagetes erecta (Marigold flower) extract as a green inhibitor. Corrosion Science. 85:352–363.
20. Tambi Ramde, Stefano Rossi (2014) Caterina Zanella, Inhibition of the Cu65/Zn35 brass corrosion by natural extract of Camellia sinensis. Applied Surface Science. 307:209–216.
21. A. Ostovari, S.M. Hoseinieh, M. Peikari, S.R. Shadizadeh, S.J. Hashemi (2009) Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone,Gallic acid, a-D-Glucose and Tannic acid). Corrosion Science. 51:1935–1949.
22. William kemp (2009) Organic Spectroscopy, third ed., Palgrave, New York, pp. 58-88.
23. M. Hazwan Hussain, M. Jain Kassim (2011) the corrosion inhibition and adsorption behaviour of Uncaria gambir extract on mild steel in 1M HCl. Materials Chemistry and Physics.125:461-468.