Sapium glandulosum leaf aqueous extract prevents mild steel corrosion in 1N HCl solition, a green corrosion inhibitor

[1]P.Sujatha, [2]B.Rajesh, [3]R.Govardhan
[1,2,3]Assistant Professor, Department of H & S, Brilliant Institute of Engineering and Technology, Hyderabad, India

ABSTRACT
The inhibiting effect of an aqueous extract of Sapium glandulosum (SG) plant leaves on the corrosion of mild steel in 1N HCl was investigated utilizing the weight loss technique and electrochemical measurements. Simulations were done to determine how well the extract prevented corrosion and how quickly mild steel corroded. The results showed that the extract may function as a potent mild steel corrosion inhibitor in 1N HCl media. Inhibition was demonstrated to increase with greater plant extract concentrations. According to FTIR measurements, the extract's organic moieties are what give the inhibitor its effective function. The inhibitor functions as a mixed type inhibitor, according to potentiodynamic polarization curves, and the medication's inhibitory potency can reach up to 95.22 percent can be obtained. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmedthe high performance of inhibitive effect of the plant extract. Surface coverage values were tested graphically for suitable adsorption.
Keywords: Mild Steel, EIS, SEM, Acid Corrosion, Polarization.

INTRODUCTION

Mild steel has been widely used in a range of chemical and related sectors to handle alkaline, acidic, and salt solutions. Chloride, sulphate, and nitrate ions are more aggressive in aqueous conditions and hasten corrosion. One way [1–5] to stop corrosion in mild steel is by using corrosion inhibitors. The use of some natural substances is encouraged by the documented hazards associated with the bulk of synthetic corrosion inhibitors. At the moment, environmentally friendly inhibitors are fashionable. Natural products are generally safe, biodegradable, and widely available [6–17]. Several researches [18–28] have examined the use of naturally occurring chemicals as corrosion inhibitors for different metals in diverse media. There are several chemical elements with anti-corrosion capabilities in the plant extracts. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

Experimental work

Experimental work mainly deals with the methodology adopted for the plant extraction aqueous and evaluation of corrosion inhibition of plant extract as green inhibitoron mild steel in 1N HCl medium.

Mild steel specimens

Weight loss and electrochemical experiments were conducted on mild steel specimensof dimensions 4cm X 2cm X 0.1cm and having the area of 1cm^2. The composition of mild steel is 0.03 C, 0.169 Mn, 0.015 Si, 0.031 P, 0.029 S, 0.09 Cr, 0.016 Mo, 0.030 Ni, 0.017 Cu
and remaining Fe.

Preparation of inhibitor Aqueous extract preparation

The leaves of the medicinal plant SG was taken and cut into small pieces and dried in room temperature and ground well into powder. 150 g of the powder from each was refluxed in 500 ml distilled water and kept overnight. The refluxed solution was then filtered carefully; thefiltrate volume was made up to 1000 ml using double distilled water and used as stock solution.Various concentrations of the plant extracts were prepared by dissolving the known quantity ofthe resultant powder in acid media. The concentrations of all additives were expressed in v/v. Thus the concentration (5, 10, 15, 20 v/v) was prepared by diluting 5 ml, 10 ml, 15 ml, 20 ml ofplant extract with 95 ml, 90 ml, 85 ml, 80 ml of HCl acid solution[24-26].

Reagents used

Analar grade hydrochloric acid was used and for the preparation of 1N HCl double distilled water was used.

FT-IR spectra

FT-IR spectroscopy allows us to examine the molecular structure and confirmation of biological macro molecules which produces an increase in the vibrational or rotational energy of atoms or groups within the molecules. FT-IR spectrum (KBr pellets) of the surface film of the mild steel specimen was recorded using Bruker alpha 8400 S spectrophotometer in the wave number range of 4000- 400 cm^{-1}.

Various methods used in corrosion inhibition process

Weight loss method

Weight loss analysis is one of the basic, easiest and frequently used method and classical way to determining the corrosion inhibition and corrosion rate of the mild steel. Coupons were completely immersed vertically in 250 ml of the test solution with and withoutinhibitor for 24 hours. The experiment was carried out at various immersion periods (1, 3, 5, 7, 12 hours and 3 days) and corrosion inhibition studies were also carried out at various temperature ranges at 303-323K. From the weight loss measurements, the corrosion rate and inhibition efficiency were calculated by using the following relationship:

$$CR\ (mmpy) = \frac{K \times \text{Weight loss}}{D \times A \times t\ (\text{in hours})} \qquad (1)$$

Where, K = 8.76×10^4 (constant), D is density in gm/cm^3 (7.86), W is weight loss in gramsand A is area in cm^2.

$$IE\ \% = \frac{W_0 - W_i}{W_0} \times 100 \qquad (2)$$

Where, W_0 and W_i are the weight loss with and without of the inhibitor.

Electrochemical studies

Electrochemical (Polarization and Impedance) measurements were obtained using CHI 660 E Electrochemical workstation. An electrochemical cell with a three electrode cell set up was used. Mild steel ($1cm^2$) was used as a working electrode, Pt electrode was used as counter electrode, and saturated calomel electrode was used as reference electrode. The working electrodewas polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers and washed with distilled water before usage. Prior to experiment the working electrode was immersed in the test solution for 20 minutes to reach open circuit potential (OCP). The anodic and cathodic polarization curves were obtained from -800 to -200 mV at a scan rate of $1mVs^{-1}$. The percentage inhibition efficiency wascalculated by using this equation:

$$IE\ \% = \frac{I_{Corr} - I^*_{Corr}}{I_{Corr}} \times 100 \qquad (3)$$

Where, I_{corr} and I_{*corr} are corrosion current without and with inhibitors.

Impedance spectroscopy is one of the most simple and consistent technique and also used to study the characterization of electrode (surface) behaviour in 1N HCl solution. AC signal with amplitude of 10mV at OCP in the frequency range from 100 KHz to 10 MHz. The impedance parameters were obtained from Nyquist plots. The double layer capacitance (C_{dl}) was determined using formula: are the charge resistance values for inhibited and uninhibited solution.

Surface Analysis

The mild steel specimens used for surface morphological examination were immersedin 100 ml of 1N HCl acid (blank solution) containing (optimum) various concentrations of green inhibitor for a period of one day. Then, they were removed, rinsed quickly with double distilled water, dried and examined for their surface morphology using scanning electron microscope.

Results and dissusion

Weight loss method:

The weight loss studies were done in 1N hydrochloric acid in the absence andpresence of various concentration of the plant extracts ranging from 05 to 20 v/v. Using the weight loss data, corrosion rate, inhibition efficiency, and the optimum concentration of the extract have been calculated. The corrosion parameters obtained in the weight loss method are in Table 1. It was observed from the table that the rise in concentration of ML leave extract, on the corrosion rate of mild steel in 1N HCl solution was decreased and the inhibition efficiency increased from 73.98% to 96.789% up to 20ppm. Beyond this concentration, corrosion inhibition efficiency was decreased from 96.789% to 95.49%, it indicates that 20 v/v is the optimum concentration to get maximum corrosion protection for mild steel in 1N HCl solution using SG leaves extract.

Table 1. Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at differentconcentration of inhibitor in 1N HCl medium.

Immersion Period: 1 day Inhibitor: Sapium glandulosum leaves extract

SI.NO	Concentrationof solution v/v	CR(mmpy)	IE%
1	Blank	1.8019	-
2	05	0.4231	72.18
3	10	0.1794	89.07
4	15	0.1210	92.76
5	20	0.0385	95.22

FTIR MEASURMENT

FTIR spectra have been used to analyze the protective film formed on metal surface. Lalitha et al. have confirmed that FTIR spectrometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitor adsorbed on the metal surface. Although various compounds present in the SG leaves extract which contributed in effective working inthe inhibitor, It is very difficult to identify each compound separately to know the group present in the SG leaves extracts.

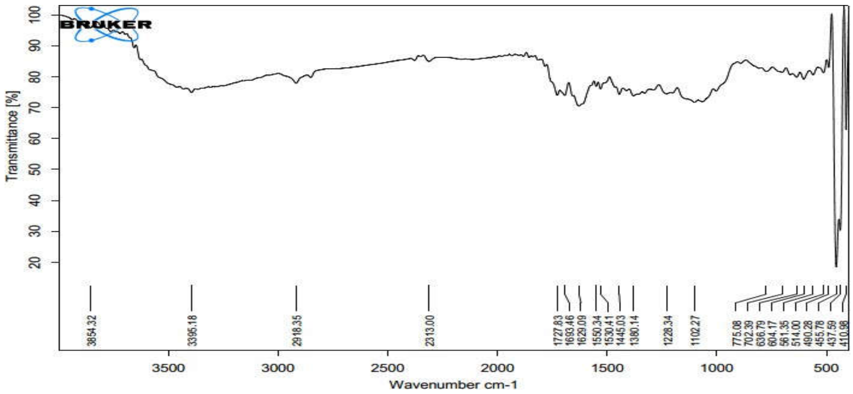

Fig. 1 FT-IR spectra of SG leaves extract

FTIR spectra of the SG leaves extract is shown in Fig. 1. It is observed from the figure, Broad peak obtained at 3395.18cm^{-1} can be assigned to N-H or O-H stretching. C-H stretching was observed at 2918.35 cm^{-1}. Other strong peak obtained at 1727.83 cm^{-1} correspond to C=O (may be aldehyde or ketone). Strong peaks obtained at 1693.46cm^{-1} and 1629.09cm^{-1} are due to C=C or C=N stretching or N-H bending vibration. Absorption band at 1445.03cm^{-1} can be assigned to C-H bending in CH_3 or O-H bending vibration. Peaks observed at 1380.14cm^{-1}, 1228.34cm^{-1} and 1102.27cm^{-1} are due to C-N and C-O stretching vibration. Few weak peaks can also observed at 1550.34cm^{-1}, 1530.41cm^{-1}, 1445.03cm^{-1} 1380.14cm^{-1}, 1228.34cm^{-1} which correspond to C=C stretching vibration of aromatic ring. On the basis of the result, it can be said that SG leaves extract contain Nitrogen and Oxygen (N-H, N=C=S, C=N, C-N, O-H, C=O, C-O) in various functional group and aromatic ring , which make this extract attractive for being used as inhibitor.

POTENTIODYNAMIC POLARIZATION MEASUREMENT

Potentiodynamic polarization studies were carried out in CHI-6O8D electrochemical workstation. A three electrode cell assembly was used as work station. The electrochemical parameter like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slopes (b_c), anodic Tafel slope (b_a) and percentage of inhibition efficiency for mild steel inthe absence and presence of various concentrations of SG extract in 1N HCl is given in Table 2 and their polarization curves are shown in Fig. 2. It is noted from the table that the addition of green inhibitor decreases the dissolution rate of mild steel in 1N HCl acid media. The corrosion current density values decreased considerably for green inhibitor in the acid media. However, the shift in the values of corrosion potential (E_{corr}) for SG leaves extract is not significant (Pandian et.al). This observation clearly showed that the inhibition of mild steel in the presence of the extract control both cathodic and anodic reactions and thus the inhibitoracts like mixed type inhibitors (30-34).

Table 2. Electrochemical parameters from polarization measurement, calculated values ofinhibition efficiency.

Conc.(v/v)	Ecorr/ (mV) vs. SCE	Icorr/ (mA/cm^2)	b_c (mV/decade)	b_a (mV/decade)	IE (%)
Blank	-471	5.220x10^{-3}	199	140	-
05	-469	3.293x10^{-3}	180	127	92.09
10	-466	3.398x10^{-3}	203	136	93.57

15	-469	$1.766x10^{-3}$	174	104	94.53
20	-474	$1.886x10^{-3}$	172	125	95.23

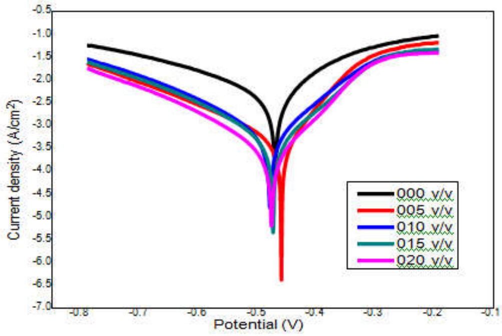

Figure-2. Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in theansence and presence of different concentration of inhibitor.

ELECTROCHEMICAL IMPEDANCE (EIS) METHOD

The surface resistances of blank and mild steel specimens with inhibitor in 1M HCl solutions were investigated using EIS techniques. The Nyquist plot of mild steel in 1 N HCl in the absence and the presence of various concentration of green inhibitor is shown in Fig.

The presence of a single semi circle in the blank and for different concentrations of the inhibitor systems corresponds to the single charge transfer mechanism during dissolution of mild steel, which is unaltered by the presence of inhibitor components.

The impedance parameters were calculated for mild steel in 1M HCl with andwithout inhibitors are given in Table 3. The charge transfer resistance (R_{ct}) value calculated for blank Mild steel exhibited 41.76Ωcm^2 and the double layer capacitance (C_{dl}) was 8.612μF/cm^2. When SG leaves extract is added, the R_{ct} value increases from 41.76Ωcm^2 and C_{dl} value decreases from 8.612μF/cm^2. The higher R_{ct} value obtained for higher inhibitor concentration suggests that a protective film is formed on the surface of the metal. The decreased in the C_{dl} values from the blank as the increased in the concentration of the inhibitor confirm the enhancement of the adsorption of the inhibitor on the metal surface. Thedecrease in C_{dl} is attributed to an increase in thickness of the electronic double layer due to adsorption (35-39). The adsorption is due to the electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface. All the electrochemical parameters clearly proposed that the corrosion control depends on the concentration of the inhibitor.

Table 3. Impedance parameter for mild steel in 1 N HCl acid solution in the absence andpresence of varied concentration of inhibitor.

SI.NO	Concentration (v/v)	R_{ct}(ohm cm^2)	Cdl (μF/cm^2)	IE (%)
1	Blank	7.58	1.173	-
2	05	12.93	0.502	5.85
3	10	16.26	0.499	16.85
4	15	19.96	0.219	36.17

5	20	22.45	0.198	57.02

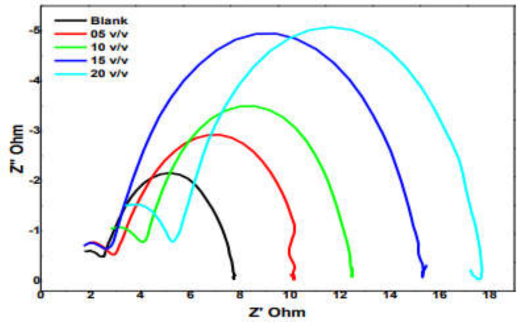

Figure-3. Nyguist plots for mild steel in 1N HCl acid solution without and with presence ofdifferent concentration of inhibitor.

3.5. Surface examination studies

Surface examination of mild steel specimen was made using JOEL scanning electron microscope (SEM) with the magnification of 3000 x. The mild steel specimens after immersion in 1N HCl solution in the presence of optimum concentration of the plant extracts for one day, at room temperature, were taken out, dried, and kept in desiccators. The SEM images of mild steel immersed in 1N HCl in the absence and presence of the inhibitor is shown in Fig.3. SEM studies revealed that the plants extract which is adsorbed on metal surface decreased the metal surface from corrosion attack. The specimen surface can be observed to be covered with thin layer of the inhibitor molecules, giving protection against corrosion (40-50).

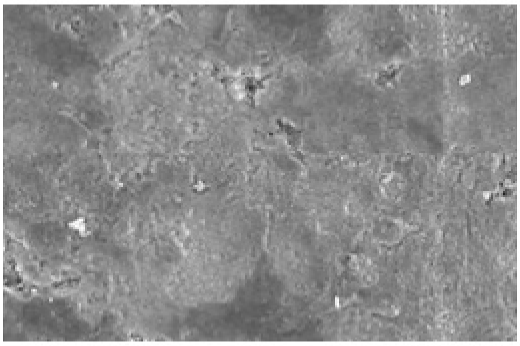

Fig. 3a

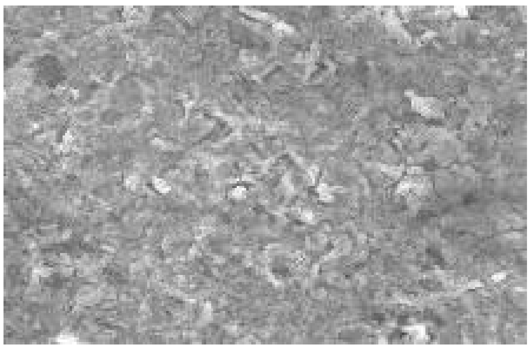

Fig. 3b

Conclusion

On mild steel in 1 N HCl acid, extract from Sapium glandulosum leaves efficiently inhibits corrosion. A easily available, affordable, nontoxic, and environmentally safe corrosion inhibitor is sapium glandulosum leaves extract. The Sapium glandulosum leaves extract revealed maximum efficiency of 99.80% stem at the optimal concentration of 20 v/v for a one-day soaking period at room temperature. Outcomes from electrochemical processes and non-electrochemical methods (such the weight loss method) are closely connected. The sapium glandulosum leaf extracts work as a mixed type inhibitor on the metal surface. When corrosion-inhibited mild steel samples were compared to unfettered samples, SEM examination showed that the surface morphology had improved.

References

[1] M. Ajmal, A.S. Mideen, M.A. Quraishi, 2-hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solutions, Corros. Sci. 36 (1994) 79–84.

[2] A.A. Hosary, R.M. Saleh, A.M.S. Eldin, Corrosion inhibition by naturally occurring substances—I. The effect of Hibiscus subdariffa (karkade) extract on the dissolution of Al and Zn, Corros. Sci. 12 (1972) 897–904.

[3] S.A. Verma, M.N. Mehta,‖Effect of acid extract of powered seeds of Eugenia Jambolans on corrosion of mild steel in HCl – study by DC polarization technigues,‖ Trans. Soc. Advan. Electrochem. Sci. Technol. 32 (1997) 89–93.

[4] I.B. Obot, S.A. Umoren, N.O. Obi-Egbedi,‖ corrosion inhibition and adsorption behavior for aluminuim by extract of aningeria robusta in HCl solution: synergistic effect of iodide ions‖ J. Mater. Environ. Sci. 2 (2011) 60–71.

[5] H. Al-Sehaibani, ―Evalution of Henna leaves as environmentally friendly corrosion inhibitor for metals,‖ Material wissenschaft und Werkstofftechnik, 31, (2000) 1060– 1063,.

[6] M. Lebrini, F. Robert, C. Roos,‖Inhibition effect of alkaloids extracts from Annona squamosal plant on the corrosion of C38 steel in normal hydrochloric acid medium,‖Int. J. Electrochem. Sci. 5 (2010) 1698–1712.

[7] C.A. Loto, A. I. Mohammed, Corros. Prevent. Control. 47, no. 2, pp. (2000) 5056–5063.

[8] G.D. Davis, DACCO SCI, Inc., Columbia, Md, USA, 2000.

[9] O.K. Abiola, J. Corros. Sci. Eng. 5 (2006) 10.

[10] A.O. James, E.O. Ekpe, Int. J. Pure Appl. Chem. 35 (2002) 10.

[11] M. Lebrini, F. Robert, C. Roos, Int. J. Electrochem. Sci. 6 (2011) 847–859.

[12] J. Bruneton, Pharmacognosie-Phytochimie, Plantes M´edicinales, revue et ugment´ e,Tec&Doc-Edition, M´ edicinales Internationales, Paris, France, 4th edition, 2009.

[13] E.E. Ebenso, N.O. Eddy, A.O. Odiongenyi, Afr. J. Pure Appl. Chem. 2 (2008) 107–115.

[14] I.M. Mejeha, A.A. Uroh, KB. Okeoma, G.A. Alozie, Afr. J. Pure Appl. Chem. 4 (2010)158–165.

[15] A.Y. El-Etre, Evaluation of Extracts of Henna Leaves as Environmentally Friendly Corrosion Inhibitors for Metals, Corros. Sci. 45 (2003) 2485–2495.

[16] A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, Inhibition of aluminum corrosionusing Opuntia extract, Corros. Sci. 47 (2005) 385–395.

[17] E.E. Oguzie, Studies on the inhibitive effect of Occimum viridis extract on the acidcorrosion of mild steel, Mater. Chem. Phys. 99 (2006) 441–446.

[18] G. Gunasekaran, L.R. Chauhan, Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium, Electrochimica Acta. 49 (2004) 4387–4395.

[19] K.O. Orubite, N.C. Oforka, Inhibition of the corrosion of mild steel in hydrochloric acidsolutions by the extracts of leaves of Nypa fruticans Wurmb, Mater. Lett. 58 (2004) 1768–1772.

[20] Y. Li, P. Zhao, Q. Liang, B. Hou, Berberine as a natural source inhibitor for mild steelin 1M H_2SO_4, Appl. Surf. Sci. 252 (2005) 1245–1253.

[21] M.A. Quraish, DK. Yadav, in Proceedings of the 14th National Congress on CorrosionControl, 2008.

[22] H.O. Edeoga, D.E. Okwu, B.O. Mbaebie, Phytochemical constituents of some Nigerian medicinal plants, Afr. J. Biotech. 4 (2005) 685-688.