INHIBITION STUDIES ON MILD STEEL USING *STACHYTARPHYTA JAMAINENSIS* LEAF EXTRACT

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ABSTRACT

The adsorption behaviour of *Stachytarphyta jamainensis* leaf extract on mild steel corrosion was studied using the Mass Loss method. The influence of temperature on the corrosion behaviour of mild steel in the temperature range of 303k to 333k was also examined. Increases in inhibitor concentration lead to higher inhibition efficiency, while increases in temperature lead to lower efficiency. The inhibitor follows the Langmuir isotherm among the many adsorption isotherms that have been studied thus far, including Temkin, Frumkin, Flory Huggins, and El-Awday. The corrosion process involved in evaluating the thermodynamic parameters such as Ea, ΔHads, ΔGads, and ΔSads. The activation and free energy of inhibitory processes shows the physical adsorption mechanism, Exothermic and spontaneous adsorption process. By using FTIR, EDX, and SEM, the corrosion products that formed on the surface of mild steel were examined. The data obtained using this method may also indicate that a thin coating is being formed on the metal surface to further prevents dissolution.

Keywords : Electrochemical, Non electrochemical studies, Mild steels, stachytarphyta Jamainensis leaf extract

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Introduction

Mild steel is one of the major materials for fabricating storage containers, construction materials and other industrial equipments, because it has weldable, cost effective, ductile and recyclable aspects. Despite the advantages, the unmitigated corrosion has the power to deplete the mechanical strength and ultimately causing permanent fracture in the structures. Barrier protection, galvanization and cathodic protection [1-6] methods have been enforced to defend and prohibit metal from corrosion. While in aggressive acidic environment is necessary to incorporate alternate corrosion prote ction techniques. Synthetic inhibitors are recurrently used to mitigate the metallic dissolution caused by the existence of diffused gases [7] in aqueous solution. Since these synthetic inhibitors exhibits toxic and carcinogenic properties, the search of nontoxic counterpart has been necessitated [8,9]. Thus, plant extracts with cost effective, sustainable, and eco-friendly attributes are a replacement for synthetic inhibitors. Plant extract comprises of hetero atoms through which they are adsorbed to metal surface which act as barrier between metal and environment [10-12]. Distinct plant parts inspected and proposed as active inhibitors for ferrous alloys in hydrochloric, sulphuric and phosphoric acid environments. Various leaf extracts from plants like Biden pilosa[7], henna[13], Date palm [14], Ocimum tenuiflorum [15] elephant grass[16] pogostemon Quadrifolius[17], Citrus aurantium[18], , Spirulina platensis[19], Gentiana olivieri[20], Tragacanth gum [21], Artemisia mesatlantica essential oil[22] have been analysed for its inhibition behavior in 1M HCl environment. Thus, in our present studies we mainly focus to utilize the cheap, sustainable and eco-friendly inhibitor using ***Stachytarphyta Jamainensis*** leaf extract on Mild steel in acid environment.

Materials and Methods

Specimen Preparation

Rectangular specimen of Mild steel was mechanically pressed, cut to form different coupons, each of dimension exactly 20cm2 (5x2x2cm2) with emery wheel of 80 and 120 and

then degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in desiccator for our present study.

Plant Extract Preparation

Stachytarpheta jamaicensis leaf (SJL) were collected from Western guards and kept under shadow, air-dried and powdered. This powder immersed in 95% ethanol at room temperature for 48 hr. The combined alcoholic extracts of leaf were concentrated under vacuum at 40°C until the excess of solvent were completely removed. These dried alcoholic extract pastes were used for corrosion inhibition activity.

Energy Dispersive X- ray spectroscopy (EDX)

By compositions of all elements presents on the surface of the specimen, before and after immersion were identified by EDX using the Oxford Instrument Model - INCA Penta xFET. The energy of an acceleration beam employed was 20 kV.

FT-IR

The composite scratched from the surface of the specimen and the plant extract was analysed using FTIR instrument and the samples were measured in the range of 400–4000 cm-1.

Scanning Electron Microscope (SEM)

Surface morphological examination of Mild steel specimen after immersion in acid solution containing optimum concentration of inhibitor and blank was performed by Model: Jeol – JSM 6390 scanning electron microscope (SEM).

Results and Discussion

Weight Loss Method

The variation of inhibition efficiency and the corrosion rate with change of concentration of inhibitor were presented in Table -1. It shows that the corrosion rate decreased with increase of inhibitor concentration for all immersion period of time. The decrease of corrosion rate and the increase of inhibition efficiency is usually attributed due to the adsorption of main inhibitor phyto constituents on the surface of mild steel which makes a barrier of mass and charge transfer and protect further attack of acid environment. The maximum inhibition efficiency up to 95% was noticed at a concentration level of 1000ppm in 1.0N Hydrochloric acid medium. The inhibitor efficiency increased with increase of immersion time, since it needs time relaxation to adsorb maximum on the metal surface to form a stable thin film.

TABLE: 1. Calculated values of corrosion rate and inhibition efficiency (%) with respect of different concentration on *Stachytarpheta jamaicensis* leaf on mild steel in 1.0 N Hcl.

Conc ppm	24 hrs			72 hrs			120hrs			360 hrs		
	CR (mm/y)	θ	%IE	CR (mm/y)	θ	%IE	CR (mm/y	θ	%IE	CR (mm/y	θ	%IE
0	15.59	-	-	5.85	-	-	3.51	-	-	1.92	-	-
10	6.32	0.594	59.46	3.54	0.393	39.33	2.49	0.291	29	1.49	0.224	22.49
50	5.81	0.627	62.74	3.02	0.483	48.34	2.04	0.418	41	1.30	0.320	32.04
100	3.34	0.785	78.53	0.16	0.687	68.74	1.34	0.617	61	1.18	0.389	38.69
500	1.85	0.880	88.07	0.14	0.735	73.50	0.53	0.849	84	0.51	0.732	73.27
1000	0.9	0.93	93.7	0.03	0.94	94.1	0.1	0.952	95	0.1	0.89	89.72

Note: CR-Corrosion Rate, θ-Surface Coverage, IE-Inhibition Efficiency

Effect of Temperature on CR and IE of Inhibitor on Mild Steel in 1.0 N HCl

Industrial cleaning process like pickling and acid cleaning, the choice of optimum temperature is of particular importance. It modifies the interaction between the mild steel surface and the acid media both in the presence and absence of inhibitor, thus the temperature has a great effect on the electrochemical corrosion. The corrosion rate increased with increase of temperature. It is generally assumed that in acid corrosion inhibition, the inhibitor adsorbs on the metal surface, resulting in a structural change of the double-layer and reduced the charge transfer reaction.

The observation of corrosion rate (CR) and the percentage of inhibition efficiency parameters are listed in Table- 2. The maximum efficiency was found to be 97.71 % at 303 K for the concentration of 1000ppm. This slight variation in efficiency with increase of temperature suggests that a stable thin film formation over the metal surface.

Table:2. Effect of temperature on the corrosion of mild steel in the presence of various concentration of SJL inhibitor in 1.0 N HCl

Concentration ppm	Corrosion rate (mm/Y)			Inhibition Efficiency (%)		
	303 K	313 K	333 K	303 K	313 K	333 K
0	0.484	0.503	0.754	-	-	-
10	0.149	0.254	0.605	69.20	49.46	19.73
50	0.079	0.231	0.266	83.65	54.06	64.74
100	0.066	0.081	0.244	86.31	83.74	67.40
500	0.020	0.067	0.195	95.81	86.57	74.05
1000	0.011	0.040	0.030	97.71	91.87	87.52

Adsorption studies

Inhibition of metal dissolution in acidic media involves adsorption of phytoconstituents at the metal–electrolytes interface. Adsorptions isotherm are very important to determine the reaction mechanism, the most frequently used isotherms are Langmuir, Frumkin, Temkin, Flory–Huggins, and El Awady. The data were tested graphically by fitting to various isotherms. The different parameters of K, R^2 and slope are derived from these various adsorption isotherms at temperature range from 303 to 333K are given in Table 3.

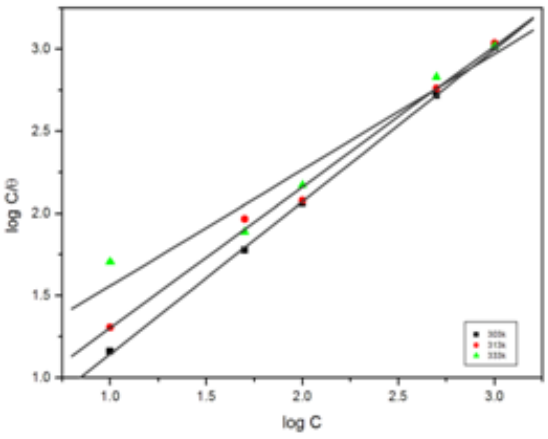


Figure 1. Langmuir, of SJL Inhibitor on mild steel in 1.0N HCl

Average regression co-efficient (R^2) values for Langmuir (0.990), Frumkin (0.967), El- Awady (0.947), Temkin (0.943), Freundlich (0.9213), Florry-Huggins (0.912). However, observed values relatively far from unity as compared with the values obtained with Langmuir adsorption isotherm, since R^2 value are almost close to unity, which clearly indicates that the weak correlation between the two variables (i.e. surface coverage, inhibitor concentration). It is concluded that the inhibitor obeys Langmuir adsorption isotherm.

Thermodynamic Parameters of Adsorption of the Inhibitor in 1.0 N HCl

Thermodynamic parameters (Ea, ΔH, ΔS, ΔG) play an important role to understanding the mechanism of inhibition process. The energy of activation (E_a) can be calculated from the Arrhenius equation (1) for mild steel dissolution in the presence and absence of inhibitor at temperatures range from 303–333 K. A plot of log (CR) obtained by weight loss measurement versus 1/T gave straight line as shown in fig (2).

$$\log (CR_2/CR_1) = \frac{-E_a}{2.303\ R}\ [\ ^1/_{T_1} - \ ^1/_{T_2}\ ] \quad (1)$$

The values of apparent activation energy (E_a) obtained from the slope ($-E_a/2.303R$) of the lines are given in Table -4. It is observed that the apparent activation energy (E_a) value increased from 12.97 kJ/mol to 58.24 kJ/mol in the presence of the inhibitor. This increase of activation energy in presence of inhibitor with raise in temperature is suggestive of strong chemical bonding between the inhibitor and the metal ions from its surface.

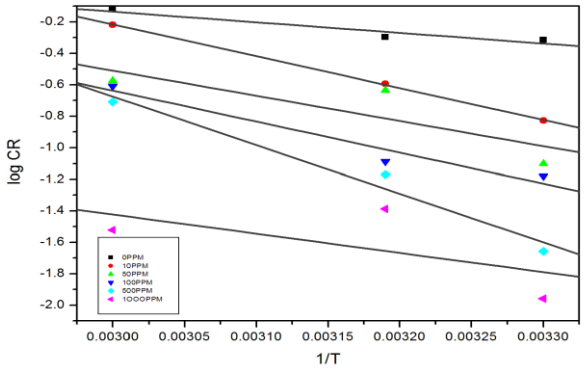


Figure 2. Arrhenius plot for mild steel corrosion 1.0 N HCl in the presence and absence of different concentration of SJL

Table 4. Activation parameters of SJL in 1.0N HCl on mild steel

Conc ppm	E_a KJ /mol	-ΔH KJ /mol	-ΔS J/mol K^{-1}
0	12.972	8.36	198.8
10	36.04	34.09	194.9
50	29.63	32.77	195.4
100	36.37	30.19	196.0
500	58.24	56.18	191.9
1000	22.09	29.28	196.8

Enthalpy change ΔH_{ads} and entropy change ΔS_{ads} were obtained from the Eyring transition state equation [2]. Straight lines were obtained from the Erying plots (Fig.3) with slope -ΔH/ 2.303R and intercept [log (R/Nh) +(ΔS/2.303R] from which ΔH and ΔS were calculated and listed out in Table -4.

$$CR = RT/Nh\ \exp(\Delta_S/R\ )\ exp(-\Delta_H/R\ ) \quad (2)$$

where: R is molar gas constant, T is absolute temperature, N is Avogadro's number, h is Planck constant.

It is also observed from Table - 4 values of both E_a with increase in concentration of inhibitor and the values of enthalphy (ΔH) shows the exothermic reaction taking place. The above data suggesting that the energy barrier is increased with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_a as the concentration of inhibitor becomes greater. Observed values of ΔS are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning that the decrease in disorder takes place on going from reactants to activated complex.

Free Energy of Activation

The equilibrium constant for the adsorption process from Langmuir is related to the standard free energy of adsorption by the expression:

$$\Delta G_{ads} = -2.303\ RT \log (55.5\ K) \qquad (3)$$

where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar. The standard free energy of adsorption, which can characterize the interaction of adsorption molecules and metal surface, was calculated by equation (3). The negative values (-16.568, -13.137, -11.385) ensure that the spontaneity of adsorption process and stability of the layer on the metal surface.

Characterization of Corrosion Products

EDX

Figs: 4(a-b) represents that the EDX spectra of the corrosion products on metal surface in the presence and absence of SJL extract in 1.0N Hydrochloric acid. The elemental spectrum in 4b clearly indicates the presence of the hetero atoms like Oxygen and micro alloying, when compared to 4a where only major metal alloys are visible. These hetro atom peaks clearly reveals the attachment of inhibitor molecules on the metal surface.

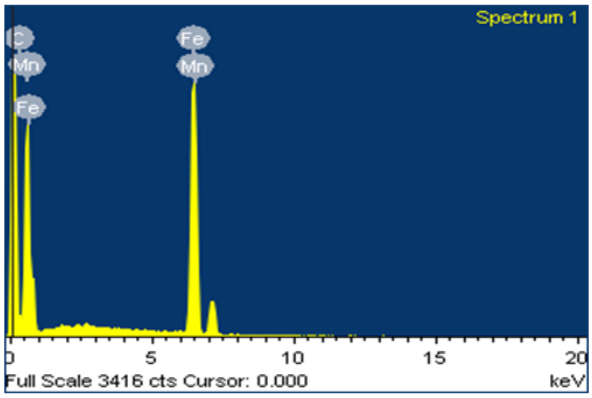


Figure 4. (a)EDX spectrum of the corrosion product on Mild steel surface in 1.0N HCl

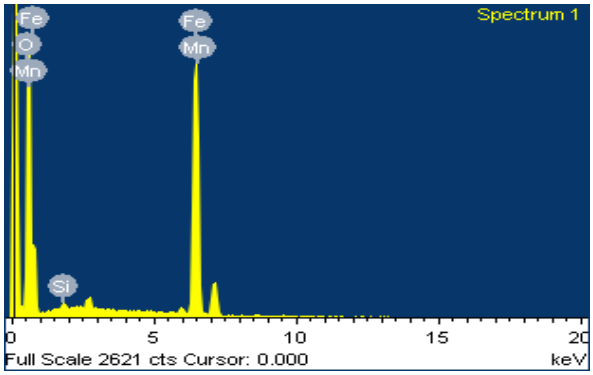


Figure 4(b). EDX spectrum of the corrosion product on Mild steel in the presence of SJL extract in 1.0N HCl

FTIR Analysis

The FT-IR spectra of plant extract and corrosion product obtained from Mild steel surface are shown in Figure 5. Spectra of SJL leaf extract exhibited peak at 3376, 2922, 2852, 1707, 1161 and 1027cm^{-1}. FTIR of film formed on the metal surface shows prominent peak at 3275,1621,1105,1028cm^{-1}. It is seen from the spectrum that the >OH stretching in SJL extract of frequency shifted from 3376cm^{-1} to 3275cm^{-1}. The peak at 1707cm^{-1} shifted to 1621cm^{-1} corresponding to >c=o stretching vibration. Also stretching in SJL extract of frequency shifted from 1161cm^{-1} to 1105cm^{-1}. The band shifted from 1027cm-1 to 1028cm-1 respectively. Some-functional groups were missing in the spectra of the corrosion product suggesting that the absorption of the inhibitor on the surface of the mild steel might have occurred through the missing bands.

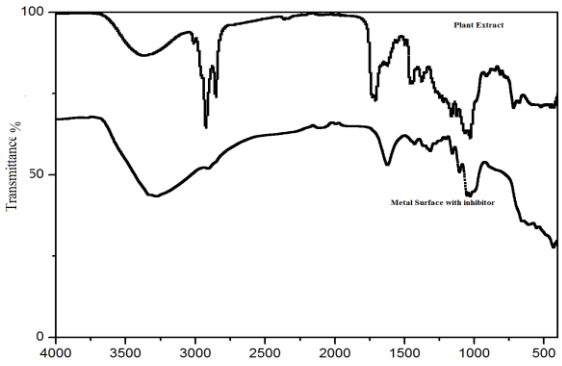
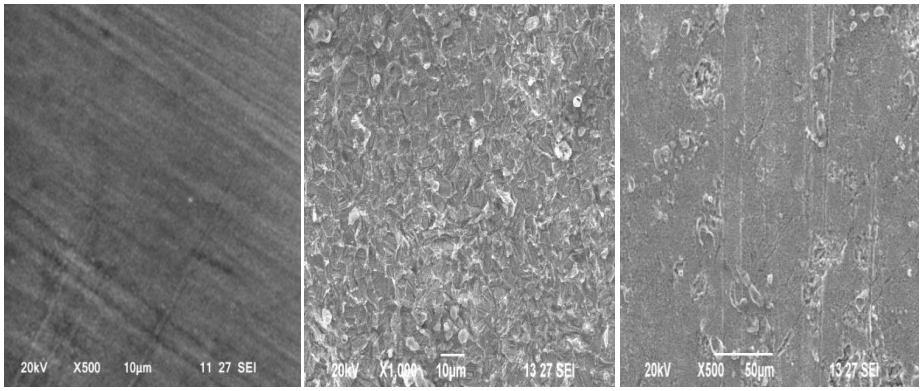


Figure 5. FTIR spectrum of SJL extract and after contact with Mild steel Surface

SEM Analysis

Image of the surface morphology of Mild Steel before and after immersion in 1.0NHCl in the presence and absence of SJL extract is represented in Figure 6(a-c). The surface morphology of Mild steel in the absence of inhibitor shows that the severe damage on the metal surface leads to pitting type of corrosion **(Figure 6b)**. However, in the presence of SJL extract, surface almost completely covered with film formation may confirm the further damage **(Figure 6c)** which could effectively safely guard the surface from corrosive environments.



(a) (b) (c)

Figure 6. (a-c) SEM image of the Polished Carbon Steel surface, Before and After immersed in 1.0N Hydrochloric acid with SJL extract respectively

Conclusion

Stachytarpheta jamaicensis leaf acts as an excellent inhibitor for the corrosion of Mild steel in 1N HCl solution. Inhibition efficiency increased with inhibitor concentration and attain maximum efficiency was found to be 95%. The adsorption of SJL extract on Mild steel follows the Langmuir adsorption isotherm. Since the average regression co-efficient values is almost close to unity (R^2=0.99). The values of apparent activation energy increased (12.97-22.09 KJ/mol) with the increase of inhibitor concentration. The observation of higher inhibition efficiency with the increase of temperature and the activation energy suggests the strong chemical bond formation. Enthalpy of activation reflects the endothermic nature of dissolution process. Entropy of activation decreased (198.8-196.8 KJ/mol) with increase of inhibitor concentration; hence inhibitor molecule orderly adsorbed onto the steel surface. Negative sign of the Gibb's free energy of adsorption indicate that the adsorption process is spontaneous. The corrosion composite analyzed by the EDX and FTIR. Images of SEM clearly revealed that the formation of the strong protective thin film formed on the surface.

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