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Inhibiting effect of fruits extract of Santalum Album on corrosion of mild steel in Hydrochloric Acid solution

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Abstract: *The inhibitive effect of Santalum Album (SA) fruits extracts on the corrosion of mild steel in aqueous solution of 1N HCl was investigated by weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy techniques (EIS) at room temperature. Potentiodynamic polarization curves indicated that the studies plant extracts acts as mixed type inhibitor. EIS measurements showed that the corrosion process was under activation control. The inhibition efficiency increase with increase inhibitor concentration of fruits extract at room temperature. The inhibitive effect of the santalum album fruits could be attributed to the presence of some compound in the plant which is adsorbed on the surface of the mild steel. Characterization of SA fruits extract was carried out using FTIR spectroscopy. The SEM morphology of the absorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract. Surface coverage values were tested graphically for suitable adsorption isotherm.*

Keywords:*Mild Steel; Corrosion Inhibition; Weight Loss Method; Electrochemical Techniques; Scanning Electron Microscopy (SEM).*

I. Introduction

Corrosion can be defined as the deterioration of a metal due to its reaction with its environment. Corrosion of iron or steel occurs due to the reaction of Fe with reactive species such as oxygen and water. Corrosion product or rust is formed and gradually appears on the surface of steel or low alloyed steel when they are exposed to humid air at high temperature or even at room temperature. Generally, iron surface turns rusty in the presence of oxygen gas and water. A region of the metal's surface serves as an anode, where oxidation occurs. Then, the electrons given up by iron reduce atmospheric oxygen to water at the cathode which is another region of the same metal's surface (1). Acidic solutions are used in many industrial areas. The most important applications are acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing (2). The use of inhibitor is one of the most practical methods for protection against corrosion and prevention of unexpected metal dissolution and acid consumption, especially in acid solution. Different organic and inorganic compounds have been studied as inhibitors to protect metals from corrosive attack. The efficiency of this organic corrosion inhibitor is related to the presence of polar function with S, O and N atoms in the molecule, heterocyclic compounds and pi electron (3-6). Such compounds can adsorb onto the metal surface and block the active surface sites, thus reducing the corrosion rate. Although many synthetic compound show good anticorrosive activity, most of them are highly toxic to both human beings and the environment and they are often expensive and non – biodegradable (4-13). Thus, the use of natural products as corrosion inhibitors has become a key area of research because plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that are biodegradable in nature and can be extracted by simple procedures with low cost (14-21). The extracts of their leaves, peels, seeds, fruits and roots (22-31) have been reported as effective corrosion inhibitors in different aggressive environments. The natural products extracted from leaves have been widely studied as corrosion inhibitors. A large number of scientific studies have been devoted to the inhibitive action of some plant extracts on the corrosion of mild steel in acidic media, showing that these extracts could serve as good corrosion inhibitor. In this study, the medicinal plants fruits have been selected to study the inhibition effect on the corrosion of mild steel in 1N HCl media.

II. Materials and Methods

2.1 Preparation of mild steel specimen

Mild steel strips were mechanically cut into strips of size 4 cm x 2 cm x 0.1cm containing the composition of (C- 0.030%, Mn- 0.169%, Si- 0.015%, P- 0.031%, S - 0.029%, Cr- 0.029%, Ni- 0.030%, Mb- 0.016%, and Cu- 0.017%) and the remainder Fe and provided with a hole of uniform diameter to facilitate suspension of the strips in the test solution for weight loss method. For electrochemical studies, mild steel strips of the same composition but with an exposed area of $1cm^2$ were used. Mild steel strips were polished by using emery paper of (400, 600, 800, 1000, and 1200) grade, subsequently degreased with acetone and finally washed with deionized water, and stored in the desiccators. Accurate weight of the metal was taken using four digital electronic balances model (Shimadzu ay220).

2.2 Preparation of the plant extract

The medicinal plants of Santalum album fruits were taken and cut into small pieces, and dried in room temperature and ground well in to powder. 10g of the powder was refluxed in 200 ml distilled water kept and overnight. The refluxed solution was then filtered carefully, the filtrate volume was made up to 500ml using double distilled water which is the stock solution, and the concentration of the stock solution is expressed in term of ppm. From the stock solution, 5 - 25 ppm concentration of the extract was prepared using 1N hydrochloric acid. Similar kind of preparation has been reported in studies using aqueous plant extract in the recent years (32).

2.3 Weight loss method

Mild steel specimens were immersed in 200ml of 1N HCl solution of various concentration of the inhibitor in the absence and presence of mild steel for 24 hours. The weights of the specimens before and after immersion containing were determined using four digit model (Shimadzu ay220).

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

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

Where, K = $8.76\text{x}10^4$ (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.

The inhibition efficiency (%) was calculated using equation (2) respectively,

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

Where, W_0 and $W_i$are the weight loss in the absence and presence of the inhibitor

2.4 FTIR Measurements

FTIR spectra were recorded in a Bruker ALPHA 8400S spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

2.5 Potentiodynamic polarization methods

Potentiodynamic polarization measurements were carried out using CHI 660 E electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential, and Tafel slope. Experiment were carried out in a conventional three electrode cell assembly with mild steel specimen of $1cm^2$ area which was exposed and the rest being covered with red lacquer, as working electrode and a rectangular Pt foil as the counter electrode, and asaturated calomel electrode was used as the reference electrode. A time interval of 15 minutes was given for each experiment to attain the steady state open circuit potential. The polarization was carried from a cathodic potential of -800 mV (vs. SCE) to an anodic potential of -200 mV (vs. SCE) at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential, and corrosion current were calculated. The inhibitor efficiency was calculated using the formula:

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

Where I_{corr} and I^*_{corr} are corrosion current in the absence and presence of inhibitors.

2.6 Electrochemical impedance method

The electrochemical AC- impedance measurements were also performed using CHI660 E electrochemical analyzer. Experiments were carried out in a conventional three electrode cell assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude of 10 mV was superimposed on the steady state open circuit potential. The real part (Z') and the imaginary part (Z") were measured at various frequencies in the range of 100 KHz to 10 MHz. A plot of Z' versus Z" was made. From the plot, the charge transfer resistance (R_{ct}) was calculated, and the double layer capacitance (C_{dl}) was then calculated using formula:

$$C_{dl} = 1/2\pi f_{max} Rct \qquad (4)$$

Where R_{ct} is charge transfer resistance, and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentration of inhibitor.

$$\text{IE\%} = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \text{X100} \qquad (5)$$

Where R_{ct} and R^0_{ct} are the charge resistance values in the inhibited and uninhibited solution respectively.

2.7 Phytochemical analysis

Phytochemical screening were performed to assess the qualitative chemical composition of the different samples of fruits extract using commonly employed precipitation and coloration reactions to identify the major secondary metabolites like alkaloids, flavonoids, glycosides, proteins, phenolic compounds, saponins, starch, steroids, tannins and terpenoids.

2.8 Scanning Electron Microscopy

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of mild steel were examined using (JEOL) computer controlled scanning electron microscope.

2.9 Effect of immersion time

The prepared mild steel coupons were immersed in 100 ml of the test solution without and with the SA fruit extract of various concentrations for 1h, 3 h, 5 h, 7 h and 12 h at room temperature. The weight of the coupons before and after immersion was determined. Inhibition efficiency of the mild steel was calculated.

2.10 Effect of temperature

The polished and pre – weighed specimens were suspended in 100 ml of the test solution without and with the addition of various concentration of the SA fruits extract for 1h in the temperature range of 303 – 333K using water thermostats. The specimens were removed from the test solution after 1 h and washed with distilled water, dried and weighed. The inhibition efficiency was calculated from the weight loss.

III. Results and Discussion

3.1 Weight loss Methods

Weight loss method was done for mild steel in 1 N HCl with various concentrations of Santalum album fruits extract ranging from 5 to 25 ppm, and the corresponding values of inhibition efficiency and corrosion rate are given in TABLE 1. It was observed from the table that the corrosion rate decreased and thus the inhibition efficiency increases with increasing concentration of Santalum album fruitsextract (5 - 25 ppm). The maximum inhibition efficiency of about 86.14 % was achieved at 20 ppm of SA fruits extract. This result indicated that SA fruits extract could act as an excellent corrosion inhibitor.

Table 1: Data from Weight Loss Method for MS corroding in 1 N HCl solutions at various concentrations of SA fruits extract.

Conc.ofSAfruitsExtract(ppm)	Corrosion Rate(mmpy)	Inhibition Efficiency (%)
0	0.2440	*
5	0.0611	70.50
10	0.0480	72.98
15	0.0475	78.85
20	0.0327	86.14
25	0.0337	83.96

3.2 FTIR Measurement

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 SA fruits extract which contributed in effective working in the inhibitor, it is very difficult to identify each compound separately to know the group present in the SA fruits extracts.

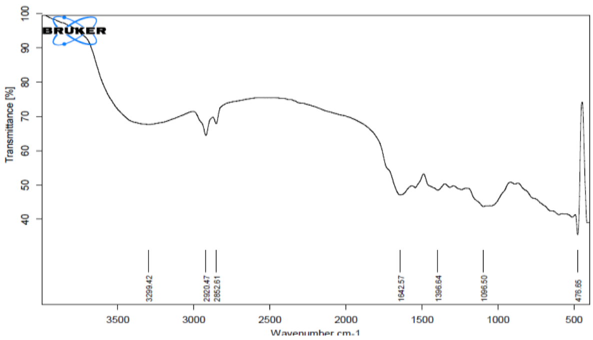

Figure .1 FTIR spectra of SA fruits extract.

FTIR spectra of the SA fruits extract is shown in Fig. 2. It was observed from the figure, Broad peak obtained at 3919cm^{-1} can be assigned to O-H stretching. N-H stretching was observed at 3421 cm^{-1}. Absorption band at 2919 cm^{-1} and 2850 cm^{-1} can be assigned to C-H stretching vibration. Medium absorption band at 2375 cm^{-1} and 2312cm^{-1} are observed due to CN (nitrile) or alkyine stretching vibration. Other strong peak obtained at 1870 cm^{-1} corresponds to C=O (may be aldehyde or ketone). Strong peaks obtained at 1651cm^{-1} and 1561cm^{-1} are due to N-O stretching or N-H bending vibration. Absorption band at 1458cm^{-1} can be assigned to C-H bending in CH_3 or O-H bending vibration. Peaks observed at 1399cm^{-1}, 1239cm^{-1} and 1046cm^{-1} are due to C-N and C-O stretching vibration. Few weak peaks can also observed at 1542cm^{-1}, 1530.41cm^{-1}, which correspond to C=C stretching vibration of aromatic ring. On the basis of the result, it can be said that SA fruits extract contain Nitrogen and Oxygen (N-H, 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.

3.3 Potentiodynamic Polarization Methods

The potentiodynamic polarization curves for mild steel in 1 N HCl with and without inhibitor (extract) are shown in Fig.2. It is evident from the figure that the anodic and cathodic curves for mild steel inhibited with extract were shifted towards positive potential region compared to the blank metal immersed in 1 N HCl. The corrosion parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}), obtained from Tafel plots are given in TABLE 2. From the TABLE, it is observed that the I_{corr}values are found to decrease with increase in the inhibitor concentrations, ranging from 5 to 25 ppm.

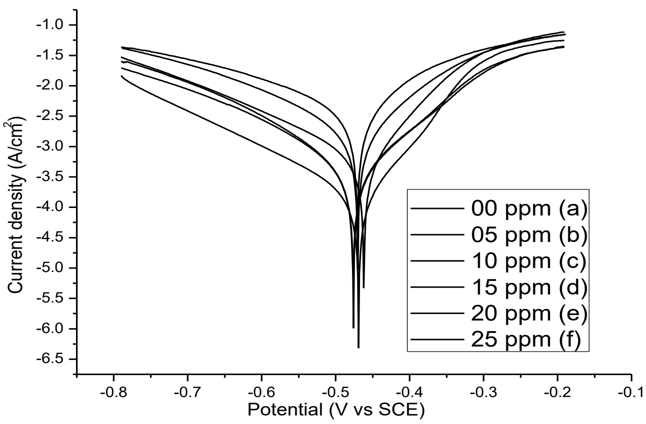

Figure 2.potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of SA fruits extracts.

Table. 2 Potentiodynamic polarization parameter for mild steel in 1N HCl solution containing various concentrations of SA fruits extract

Conc. ppm	**E_{corr} (mV/ SCE)**	**I_{corr}/ (mA/cm^2)**	**b_c (mV/dec.)**	**b_a(mV/dec.)**	**IE (%)**
Blank	-0.471	3.972	110.44	105.57	*
05	-0.466	2.102	096.50	096.46	48.08
10	-0.472	1.794	097.53	097.81	53.33
15	-0.481	1.672	097.62	101.17	59.80
20	-0. 490	1.434	098.15	104.75	64.10
25	-0.486	1.541	097.51	104.31	62.29

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 SA fruits extract is not significant (34). 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 inhibitor acts like mixed type inhibitors.

3.4 Electrochemical Impedance Studies

The surface resistances of blank and mild steel specimens with inhibitor in 1N HCl solutions were investigated using EIS techniques. The Nyquist plot of mild steel in 1N HCl in the absence and the presence of various concentration of green inhibitor is shown in Fig. 3. 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 1N HCl with and without inhibitors are given in TABLE 3.

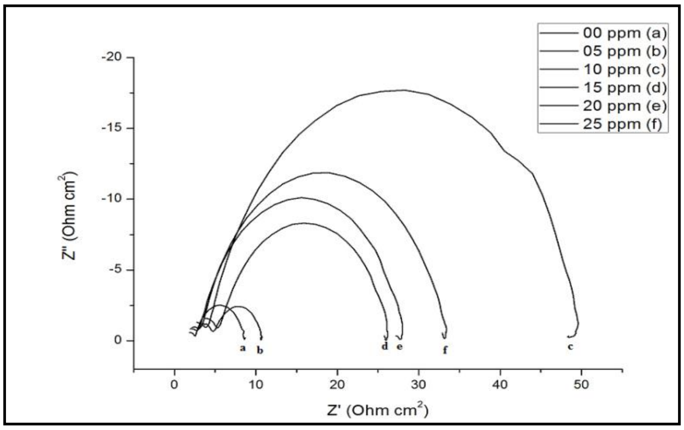

Figure 3. Nyquist plots of mild steel immersed in 1N HCl in absence and presence ofdifferent concentrations of SA fruits extract

As noticed in Fig. 3, the obtained impedance diagrams are almost in a semi-circular appearance, indicating that the charge transfer process mainly controls the corrosion of mild steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from roughness or interfacial phenomena. In fact, the presence of SA fruits extract enhanced the values of R_{ct} in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitorand the decrease in values of C_{dl}follows the order similar to that obtained for I_{corr} in this study. The decrease in C_{dl} shows that the adsorption of this inhibitor takes place on the metal surface in acidic solution.

Table 3 The electrochemical parameters (EIS) for mild steel corrosion rate in 1N HCl solution for different concentrations of SA fruits extract

Conc. of SAfruits (ppm)	**C_{dl} (μF cm^{-2})**	**R_{ct} (Ω cm^2)**	**IE (%)**
blank	9.857×10^{-3}	6.787	-
5	0.1842×10^{-4}	49.226	85.21
10	0.9663×10^{-4}	86.235	93.12
15	0.5867×10^{-5}	26.948	74.81
20	0.8530×10^{-5}	22.306	74.05
25	0.9374×10^{-5}	21.471	68.38

Moreover, the increase in the value of R_{ct} with the inhibitor concentration leads to the increase in inhibitor efficiency. The maximum R_{ct} value of 86.23 and minimum C_{dl} value of 0.966 are obtained at an optimum concentration of 10 ppm with maximum inhibition efficiency of 93.12 %.

3.5 Phytochemical analysis

Phytochemical screening was carried out on the aqueous extracts freshly prepared to the common phytochemical methods described by Harborne(35). The finding of the phytochemical screening of the aerial parts aqueous extract are shown in TABLE 4.

Table 4. Phytochemical screening test of SA fruits

Phytochemical test	**Aqueous extract**
Alkaloids	-
Carbohydrates	-
Diterpens	+
Saponins	+
Phytosterols	-
Tannins	+
Flavanoids	+
Phenol	+
Glycosides	-
Amino acids	+
anthocyanine	+

(+).. Presence (-)... Absence

3.6 Scanning electron microscopy

Surface examination of the mild steel specimens was made using JEOL scanning electron microscope (SEM). The mild steel specimens after immersion in 1N HCl solution for 24 hours at room temperature in the absence and presence of optimum concentration of the SA fruits extract were taken out, dried and kept in a desiccator. The SEM image of mild steel immersed in 1N HCl in the absence and presence of the optimum concentration of the plant extract are shown in Fig .4(a) and 4(b). The protective film formed on the surface of the mild steel was confirmed by SEM studies. From the SEM image, it was found that more grains were found for mild steel immersed in 1N HCl solution in the absence of the inhibitor. Whereas no grain were found in the SEM image of mild steel immersed in 1N HCl solution in the presence of the plant extract Fig.4(b). The metal surface is almost free from corrosion due to formation of insoluble complex on the surface of the metal. In the presence of inhibitor, the surface is covered by a thin layer of inhibitor which effectively controls the dissolution of mild steel (37).

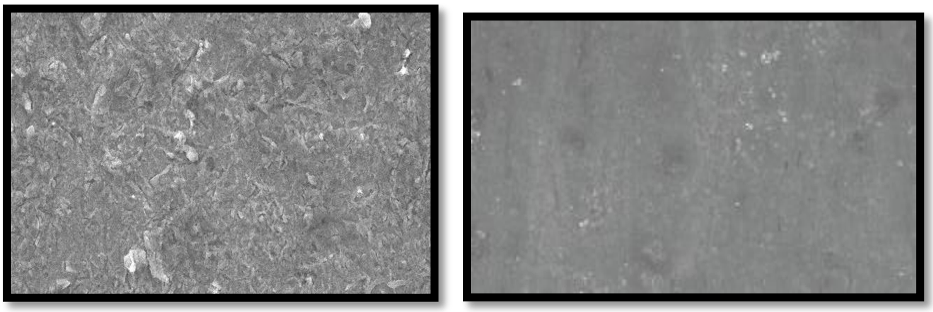

Figure 4.SEM image of the surface of the mild steel after immersion for 24 hours in 1N HCl solution absence (4a) and in the presence (4b) of optimum concentration of the SA fruits extract.

3.7 Effect of immersion time

The variation of inhibition efficiency for different concentration of fruits extract of SA was listed in the TABLE 5. Maximum inhibition efficiency for 1N HCl was found to be 98.21% at 24 h with 25 ppm concentration of the inhibitor respectively. This behavior may be attributed to the increase of the surface coverage by the extract, which retards the corrosion of mild steel.

Table 5. Inhibition efficiency as a various immersion time

Conc. of SAfruits (ppm)	**IE (%)**				
	1h	**3h**	**5h**	**7h**	**24h**
5	56.27	56.15	70.14	73.00	74.30
10	58.89	62.39	78.22	78.36	79.12
15	69.12	72.97	83.14	83.75	87.53
20	74.56	80.16	84.65	84.07	98.21
25	82.30	79.64	86.90	90.43	96.12

3.8. Effect of temperature

The effect of temperature on the corrosion inhibition properties of SA fruits extract was studied by exposing the mild steel to 1 N HCl containing 5, 10, 15, 20, 25 ppm of the SA fruits extract in the temperature range of 303-323K. The data in TABLE 6 Indicate that the fruits extract is effective as inhibitor for mild steel in 1N HClupto 303K and increase thereafter. The inhibition showed a maximum of 98.21 % at 303K for SA fruits extract in 1N HCl.

Table 6.IE at various Temperature

Conc. of SA fruits extracts (ppm)	**IE (%)**		
	303K	313K	323K
5	40.10	34.90	22.00
10	44.50	37.57	37.09
15	52.90	50.62	49.86
20	98.21	57.89	55.66
25	86.08	60.43	59.33

3.9. Adsorption isotherms

The results of weight loss study (Table 6) showed that the percentage of IE increases with increase in the concentration of inhibitor. This suggests that the corrosion inhibitive activity is mainly due to adsorption of various components of plant species on to the MS surface, particularly adsorption of the basic constituents like alkaloids, flavonoids, polyphenols, hydrolysis products of proteins, amine compounds which are present in the plant extract may be the reason for anticorrosion activity of the analyzed plant species. In the case of *SA fruits*increase of temperature increases the IE but in most of the cases as the temperature increases, the IE decreases. It suggests that the inhibition occurred through chemisorption of phytoconstituents on the MS surface. The increase of temperature decreases the hydrogen evolution overvoltage that leads to the spurt in the cathodic reaction. On the other hand increase of temperature accelerates the chemisorption of the inhibitor on the metal surface. When the latter effect is predominant the final result is an increase of the inhibiting effect, which was observed in most investigated plants.

Weight loss data are quite useful in determining inhibitor adsorption characteristics. Such data are applied in construction of adsorption isotherms which give detailed information on adsorption mechanism. Well known isotherm Temkin isotherm (given below) was tested for all the data. For Temkin isotherm, surface coverage (θ) was plotted against Ln C (Fig. 5). A straight line was obtained for all the plants indicating that the green inhibitors follow Temkin isotherms.

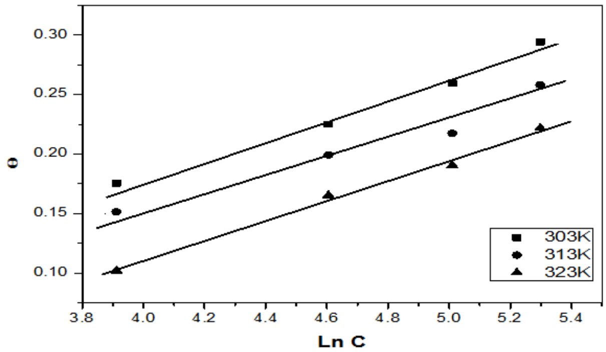

Figure.5 Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of the extract.

3.10 Mechanism of inhibition

The probable mechanism of inhibition can be explained on the basis of adsorption process and the structure of the constituents present in the SA fruits extracts. Inhibitor functions by adsorption or hydrogen bonding to the metal. This depends on the chemical composition and structure of the inhibitor, the nature of metal surface, and the properties of the medium. Structural and electronic parameters like functional group, steric and electronic effects may also be responsible for inhibition efficiency of any inhibitor, which was the adsorption mechanism. The compounds have to block the active corrosion sites on the metal surface and hence the adsorption occurs by the bonding of the free electron of inhibitor with the metal. The SA fruit extracts may constitute organic compounds containing (i) lone pair of electron present on a hetro atom (eg. N, S, P, O) (ii) pi –bonds (iii) triple bonds (eg. Cyano groups) and (iv) heterocyclic compounds such as pyridine ring, pyrrole, imidazole etc. Phytochemical analysis of SA fruits extract showed the presence of alkaloids, flavonoids, saponins, tannins, glycosides and steroids [38]. These compounds possess hetro atoms such as – O and – N which strengthen their adsorptive property over mild steel surface. The inhibiting influence of these molecules may be attributed to their adsorption through the –NH, C=O, OH, COOH etc. groups and also may be due to presence of pi electrons in the rings. These organic molecules get physisorbed on the metal surface forming a protective film and hence the anti – corrosive behaviour.

IV. Conclusion

The results obtained show that SA fruits extract is a good corrosion inhibitor for mild steel under acidic condition. The maximum inhibition efficiency was 93.12 %. Good agreement between the inhibition efficiencies calculated using different techniques was obtained. The adsorption of the green inhibitor onto the mild steel surface was characterized by the decrease in (i) the cathodic and anodic current densities observed in the potentiodynamic polarization curves carried out in the presence of SA fruits extract, (ii) the polarization resistance in the solution containing the inhibitor, (iii) the double layer capacitance computed from electrochemical impedance spectroscopy experiments. It was also found that inhibitor worked as a mixed type inhibitor retarding both anodic and cathodic reactions. Surface images of the mild steel surface clearly showed that SA fruits extract inhibited corrosion of mild steel by getting adsorbed on the metal surface.

References

[1]. A.P. Srikanth, A. Lavanya, S. Nanjundan, and N. Rajendran, Appl. Surf. Sci., 253, (2006), 1810.
[2]. A.S. Fouda,A.A. Al-Sarawyand E.E. El-Katori*desalination,201*, (2006) 1.
[3]. O. Benali, L. Larabi,M. Traisnel,L. Gengembre, Y. Harek*Appl.Surf.Sci.253*,(2007), 6130.

[4]. S. Merah,L. Larabi, O.Y. Benali, L. Harek, *Pigm.Resin.Technol. 37(5)*,(2008), 291.
[5]. O. Benali, L. Larabi, Y. Harek, *J.Appl.Electrochem.39*,(2009), 769.
[6]. O. Benali, L. Larabi, Y. Harek, *J.Saud.Chem.Soc.,14 (2)*,(2010),231.
[7]. A.Y. El-Etre, *Corrosion science*, *43*,(2001), 1031.
[8]. A.Y. El-Etre, *Material Chemistry and Physics 42,* (2000),731.
[9]. M. Saleh, A.A. Ismail, A.G. El Hosary, *Corrosion sci., 23*,(1983), 1239.
[10]. E.A. Noor, *International Journal of Electrochemical Science 2*,(2007), 996.
[11]. G.O. Avwiri, F.O. Igbo, *Material Lett., 57,* (2003), 3705.
[12]. S.A. Umoren, *Cellulose 15,* (2003), 751.
[13]. S.A. Umoren, I.B. Obot, N.O. Obi-Egbedi,*J. Material Sci., 44,* (2009), 274.
[14]. S.A. Umoren, I.B. Obot, E.E. Ebenso, *E-J. Chemi., 5,* (2008), 355.
[15]. P.B. Raja, M.G. Sethuraman, *Matter.Lett., 62,* (2008), 2977.
[16]. D. Shuduan, Li Xianghong, *Corros.Sci., 55*, (2012), 407.
[17]. O.K. Abiola, A.O. James, *Corros.Sci., 52*,(2010), 661.
[18]. G. Ji, S.K. Shukla, P. Dwivwdi, S. Sunadarm, R. Prakash, *Int.J.Electrochem. Sci., 7*,(2012) 9933.
[19]. G. Ji, S.K. Shukla, P. Dwivwdi, S. Sunadarm, R. Prakash, *Int.J.Electrochem. Sci., 7*, (2012) 12146.
[20]. E.E. Oguzie, *Corros.Sci., 50*, 2008,2993.
[21]. A. Lecante, F. Robert, P.A. Blandinieres, C. Roos, *Current Appl.Phy., 11*,(2011), 714.
[22]. A.Y. El-Eltre, *Corros.Sci, 45*,(2003),2485.
[23]. M. Sangeetha, S. Rajendran, T.S. Muthumegala, A. Krishnaveni, *ZastitaMaterijala*, *52,* (2011) 3.
[24]. P.R. Vijayalakshmi, R. Rajalakshmi, S. Subhashini, *Port. Electrochimacta 29(1)*, (2011), 9.
[25]. N. Lahhit, A. Bouyanzer, J.M. Desjobert, *Port Electrochimacta 29(2)*, (2011), 9.
[26]. K.P. Viondkumar, N.S. Narayanan pillai, N.S. Rexin, G. Thusnavis, *Port.Electrochimacta 28(6)*, (2010), 373.
[27]. A. Bouyanzer, B. Hammouti, L. Majidi, *PortElectrochimacta 28(3)*,(2010),165.
[28]. A.O. Odiongenyi, S.A. Odoemelam, N.O. Eddy, *Port.ElectrochimicaActa, 27(1)*, (2009), 33.
[29]. I.B. Obot, N.O. Obi-Egbedi, *Port. ElectrochimicaActa, 27(4)*,(2009),517.
[30]. O.K. Aboia, A.O. James, *Corros. Sci.52(2)*,(2010), 661.
[31]. JanainaCardozo da Rocha, Jose Antonio da Cunha PoncianoGomes, Eliane DElia, *Corros. Sci.52(7)*, 2341,2010.
[32]. M. Ferry,C.W. Mohd Noor, F. Gaspersz, M. Manuputty, *J. engineering, computers & applied sci, 2*,(2013),3.
[33]. A. Lalitha, S. Ramesh, S. Rajeshwari, *Electrochim.Acta, 51*,(2005), 47.
[34]. K. Lakshmi prabha, S. Rajam, B.R. Venkatraman, *J.Der.ChemicaSinica, 3*, (2012), 114.
[35]. J.B. Harborne, Phytochemical Methods. *A guide to modern techniques of plant analysis*, Chapman and Hall, London (1998).
[36]. Biswapriya B.Misra, SatyahariDey, *Journal of Pharmacognosy and Phytochemistry, 1,* (2012) 3.
[37]. Benita Sherine, A. Jamal abdul Nasser, S. Rajendran, *Int.J.Eng.Sci.Technol., 2*,(2010), 341.
[38]. K. Vishalakshi, P.R. Sivakumar, A.P Srikanth, IOSR Journal of Applied Chemistry, 9, (2016), 50.