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CORROSION INHIBITION OF MILD STEEL IN ACID MEDIUM USING *CANNA INDICA* AS GREEN CORROSION INHIBITOR

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ABSTRACT

The corrosion inhibition of mild steel in 1M HCl by *Canna Indica* flower extract (CIFE) has been studied by mass loss method and electrochemical techniques (potentiodynamic polarization and electrochemical impedance spectroscopy). The results showed that increase in concentration of CIFE decreases the rate of mild steel dissolution which indicates the inhibitive behaviour of CIFE in acid medium. Electrochemical impedance spectroscopy (EIS) results showed that corrosion inhibition of mild steel occurred mainly by charge transfer process. The potentiodynamic polarization results revealed that the acid extracts of CIFE act as mixed type inhibitor. SEM studies provide strong evidence for the protection of mild steel surface by CIFE inhibitor.

Keywords: Corrosion, Mild steel, *Canna Indica* flower extract (CIFE), Acid medium, SEM.

INTRODUCTION

Corrosion of metals is a serious environmental problem and it has given much attention in the oil and gas industries. Because, in several industrial processes such as acid cleaning and etching, acid solutions are used for the removal of rust and scale and the metal surfaces are often made to come in contact with the acids. This causes corrosion of metals. Mild steel is employed widely in most of the industries due to its low cost and high availability. Although there are various options to control corrosion, the use of inhibitors is one of the best methods for protecting metals against corrosion[1]. Acid inhibitors are essentially used in metal finishing industries, acidizing of oil wells, cleaning of boilers and heat exchangers[2].

Most of the corrosion inhibitors are synthetic chemicals which are expensive and very hazardous to environments. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors[3]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds[4]. The use of plant extracts as corrosion inhibitor has become important because they are environmentally acceptable, readily available and renewable source for a wide range of green inhibitors. The use of natural products such as leaves and seeds as corrosion inhibitors have been widely reported by many researchers[5-18]. Our research group has also successfully investigated some natural products as corrosion inhibitor[19-28]. In continuation of our previous work, the present study is focussed to investigate the inhibitive effect of acid extract of *Canna indica* flower for the corrosion of mild steel in1M HCl by mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods.

Canna indica is an erect perennial herb widely cultivated throughout India for its beautiful foliage and flowers. *Canna indica L.* is commonly known as Indian shot or Canna lily. Several varieties are common all over India and are grown in gardens. It is extensively used in constructed wetland for removal of organic pollutants, nitrogen, phosphorous and heavy metals [29, 30]. The flowers are red or yellow and showy. Flowers contain lutein, ß–carotene, violxanthin. Anthocyanins and methylated anthocyanidin glycosides were also isolated from *Canna indica* flowers [31-32].

EXPERIMENTAL

Rectangular size specimens of Mild Steel (MS) with dimension 1×5 cm^2 strips and 2 mm thickness, containing a small hole near the upper edge were employed for mass loss study. The strips were mechanically polished, degreased, washed in double distilled water, dried, and stored in a dessicator and were used for the entire immersion studies. A cylindrical mild steel rod of the same composition embedded in a Teflon rod with an exposed area of 1×1 cm^2 was used for electrochemical polarization studies and AC impedance measurements. Analar grade HCl and double distilled water were used to prepare the 1M HCl.

Preparation of plant extract

The *Canna Indica (CI)* flowers were collected from the nearby locality and shade dried**.** 25 g of the dried flowers were refluxed with 500 mL of 1M HCl for 3 hours and the content was kept overnight. The cooled extract was filtered and made up to 500 mL (5% extract). Phytochemical screening of the *Canna Indica* flower extract was carried out using standard procedure[33].

Canna Indica flower (CI) specimen was authenticated in Botanical Survey of India (BSI/SRC/5/23/2015/Tech/527) and a voucher specimen has been deposited in our university for further reference.

Mass loss studies

The cleaned and pre weighed MS specimens were suspended in triplicate in 100 mL test solutions without and with inhibitor at different concentrations for a predetermined period. After the exposure the specimens were washed with de-ionised water, dried and weighed. From the initial and final masses of the specimen, the mass loss was calculated as per ASTM G1-2 procedure[34, 35].

$$\text{Corrosion Rate (mpy)} = \frac{K \times W}{DAT}$$

K = Constant-3.45*10^{-6} (mpy), W = Mass loss in grams; D = Density of mild steel in mg / cm^3; A = Area of the specimen in cm^2; T = Exposure time in hours.

From the mass loss, corrosion rate, inhibition efficiency and surface coverage were determined using the following relationship.

$$\text{Inhibitor Efficiency (\%)} = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \text{ x } 100$$

$$\text{Surface Coverage } (\theta) = \frac{W_o - W}{W_o}$$

Where CR_{blank} and CR_{inh} are the corrosion rates of mild steel in the absence and presence of inhibitor in acid medium and W_o and W are the mass loss of mild steel without and with inhibitor respectively.

The experiments were performed for various parameters such as:

- Concentration variation (0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%)
- Different time intervals (½ h, 1 h, 3 h, 6 h, 12 h and 24 h)
- Effect of Temperature (303 K, 313 K, 323 K, 333 K, 343 K and 353 K)

Electrochemical measurements

Potentiodynamic measurement

Electrochemical measurements were carried out using Biologic model v1023 operated with EC lab software in a conventional three electrode glass cell with MS specimen as a working electrode. Pt electrode and calomel electrode served as auxiliary and reference electrodes respectively. Potentiodynamic polarization studies were carried out from a cathodic potential of -0.1V to an anodic potential of -1V with respect to corrosion potential, at sweep rate of 2mV/sec. Both anodic and cathodic polarization curves were recorded in the absence and presence of various concentrations of CIF extract.

From the polarization curves, Tafel slopes, corrosion potentials and corrosion current densities were calculated. The inhibition efficiency was calculated using the formula

$$\text{Inhibition efficiency (\%)} = \frac{I_{corr(blank)} - I_{corr(inh)}}{I_{corr(blank)}} \text{ x } 100$$

$I_{corr\ (blank)}$ and $I_{corr\ (inh)}$ are corrosion current densities in the absence and presence of the inhibitor respectively.

I.E from LPR technique is based on the equation,

$$\text{Inhibition efficiency (\%)} = \frac{R_{p(inh)} - R_{p(blank)}}{R_{p(inh)}} \text{ x } 100$$

$R_{p\ (inhi)}$ and $R_{p\ (blank)}$ are linear polarization resistance in the presence and absence of the inhibitor respectively.

Impedance Spectroscopy

The electrochemical impedance measuremnets were carried out in the same setup used for potentiodynamic polarization studies described above. In this method an AC signal of 5 – 10 mV amplitude and a frequency 10 KHz to 10MHz is applied to the system. Impedance data were derived from their Nyquist representations. From the data, the R_{ct} and C_{dl} are obtained.

The I.E can be calculated using the equation,

$$\text{Inhibition efficiency (\%)} = \frac{R_{ct(inh)} - R_{ct(blank)}}{R_{ct(inh)}} \text{ x } 100$$

$R_{ct(inh)}$ and $R_{ct(blank)}$ are charge transfer resistance in the presence and absence of the inhibitor respectively.

With the help of the double layer capacitance C_{dl}, θ can be calculated using the equation,

$$\text{Surface Coverage } (\theta) = \frac{C_{dl(blank)} - C_{dl(inh)}}{C_{dl(blank)}}$$

$C_{dl\ (blank)}$ and $C_{dl\ (inh)}$ are the double layer capacitance in the absence and presence of the inhibitor respectively.

Surface analytical technique

Scanning electron microscope

The surface morphologies of mild steel specimens after exposure to 1 M HCl solution in the absence and presence of CIFE extract for 3h were examined by SEM using a JEOL MODEL JSM 6390 SEM instrument.

RESULTS AND DISCUSSION

Mass loss measurements

Effect of concentration

Values of corrosion rate and inhibition efficiencies are given in Table-1. It is clear from the table that corrosion rate decreases more and more with the increase in concentration of CIF extract. Further inspection of Table 1 reveals that inhibition efficiency increases with an increase in concentration of CIF extract. This indicates that more inhibitor molecules are adsorbed on mild steel surface at high concentration, leading to the formation of protective film[36].

Table-1: Inhibition efficiency of mild steel in1M HCl in presence and absence of CIFE

	1/2 h		1h		3h		6h		12h		24h	
Conc(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)
Blank	1032	-	1273	-	1482	-	1734	-	1762	-	1232	-
0.1	189	81.72	663	47.91	394	73.42	295	82.97	280	84.11	312	74.64
0.2	154	85.09	643	49.47	362	75.58	155	91.05	143	91.86	204	83.46
0.3	141	86.34	643	49.47	350	76.41	139	91.99	131	92.58	168	86.36

0.4	121	88.32	583	54.17	342	76.91	93	94.65	107	93.90	161	86.96
0.5	99	90.43	530	58.33	318	78.57	84	95.13	106	93.96	146	88.12
0.6	99	90.43	488	61.68	315	78.73	82	95.29	86	95.13	129	89.49
0.7	94	90.86	458	64.06	283	80.89	79	95.45	84	95.22	116	90.59

It has been pointed out that the increase in inhibition efficiency with increase in extract concentration is an indication of an increase in the number of components of the extract adsorbed over the mild steel surface blocking the active sites, in which direct acid attacks proceed and protect the metal from corrosion. It is concluded that greater the surface coverage the greater is the inhibition efficiency. This is good agreement with the results of several investigators.[37, 38]

Effect of immersion time

The results obtained for the variation of inhibition efficiency with different exposure time for mild steel specimens immersed in 1M HCl with and without the various concentrations of CIF extract are presented in Table-1. The inhibition efficiency was found to increase with time suggesting the formation of persistent film on the metal surface. Initially IE decreased with increase in immersion time from 1/2 to 1 h in the presence of inhibitor. The decrease in inhibition efficiency with time may be attributed to increase in cathodic reaction or increase in ferrous ion concentration[39]**.** Maximum inhibition efficiency of 95.45% was obtained at 6h of immersion period. The variation of inhibition efficiency with immersion time is shown in Figure-1.

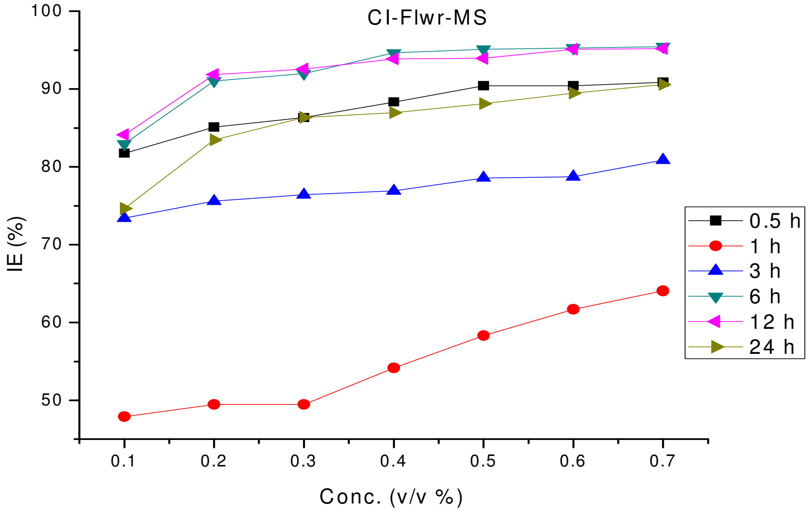

Fig.-1: Effect of concentration of the inhibitor on mild steel in 1M HCl at room temperature.

Effect of Temperature

Temperature has more pronounced effect on the rate of corrosion of metals. The corrosion rates and the inhibition efficiencies calculated in the presence of CIFE on mild steel corrosion in 1 M HCl at each experimental temperature (303 K, 313 K, 323 K, 333 K, 343 K and 353 K) are listed in Table-2. As observed from the table, a remarkable decrease in mild steel corrosion rate was obtained in the presence of CIFE extract compared with the ones in the blank solution at each temperature under study.

Further, the inhibition efficiencies are observed to decrease with increasing temperature. This is mainly because of the fact that the adsorbed film is unstable and easily damaged at high temperature[40]. The decrease of inhibition efficiency with respect to temperature is due to desorption of inhibitor molecules from mild steel surface at elevated temperatures. Similar results were reported earlier[41].

The variation of inhibition efficiency with temperature is shown in Figure- 2. It can be seen from the figure, the percentage of inhibition efficiency of CIFE extract on mild steel was reduced with raise in temperature.

Table-2: Inhibition efficiency of mild steel in1M HCl in presence and absence of CIFE at different temperatures

	303K		313K		323K		333K		343K		353K	
Conc(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)
Blank	1032	-	2791	-	6613	-	8342	-	17090	-	19362	-
0.1	189	81.72	522	81.31	1442	78.19	2854	65.79	7012	58.97	7491	61.31
0.2	154	85.09	485	82.61	1188	82.03	1850	77.82	5495	67.85	4751	75.46
0.3	141	86.34	389	86.05	983	85.14	1768	78.81	4079	76.13	4641	76.03
0.4	121	88.32	385	86.19	912	86.21	1636	80.39	3743	78.1	4327	77.65
0.5	99	90.43	294	89.48	839	87.31	1232	85.23	3498	79.53	3321	82.85
0.6	99	90.43	268	90.38	811	87.73	1200	85.62	2921	82.91	2989	84.56
0.7	94	90.86	238	91.48	762	88.47	1088	86.96	2302	86.53	2957	84.73

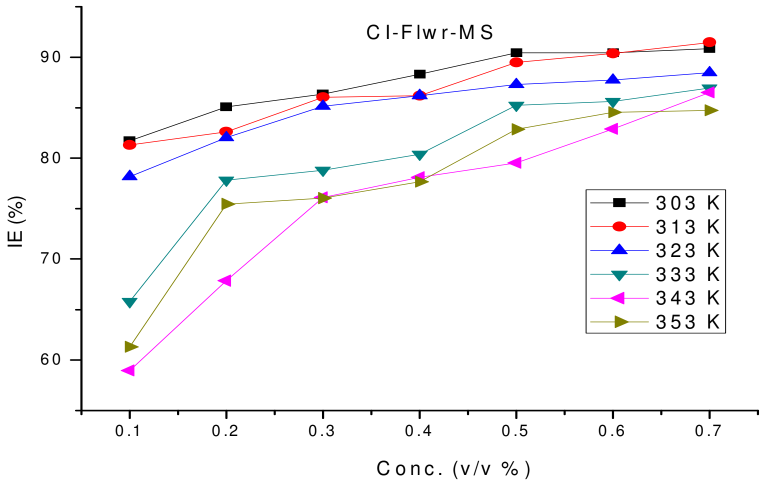

Fig.-2: Effect of concentration of the inhibitor on mild steel in 1M HCl at higher temperature.

Electrochemical Measurements

Potentiodynamic Polarization Measurements

Polarization experiments are carried out potentiodynamically in unstirred 1M HCl solution in the absence and presence of different concentration of CIFE. The electrochemical parameters, namely, corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c), and percentage inhibition efficiency (IE), determined from the polarization curves are summarized in Table-3.

It can be seen from the table that the corrosion current density (I_{corr}) decreased noticeably with increase in CIFE concentration and also the corrosion potential (E_{corr}) of mild steel shifts toward less negative direction which suggests that CIFE behaves as a good corrosion inhibitor for mild steel in 1 M HCl solution. An inhibitor can be classified as an anodic or cathodic type when the change in E_{corr} value is larger than 85 mV[42].

But in the present study, change in E_{corr} is less than 85 mV and CIFE acts as a mixed type inhibitor. It is apparent from the table that the value of Rp increased with increasing concentration of inhibitor. The increase in Rp values is attributed to the formation of an insulating protective film at the metal/solution interface.

Figure-3 shows that the Potentiodynamic polarisation curve for CIFE in 1M HCl without and with various concentration of CIFE at room temperature. The close examination of polarization curves shown in Figure reveals that the addition of CIFE to 1 M HCl affects both the anodic and cathodic parts of the curve. This indicates that the addition of extract to acid solution reduces the anodic dissolution of metal and also impedes the cathodic hydrogen evolution reaction[43].

Table-3: Electrochemical polarization parameters for MS in 1M HCl solution in the absence and presence of various concentrations of CIFE extract

Conc (%)	Tafel polarisation parameters					Linear polarisation resistance parameters	
	$-E_{corr}$ mV/ SCE	I_{corr} µA/cm^2	b_a mV/dec	b_c mV/dec	IE (%)	R_p Ohm/cm^2	IE (%)
Blank	416	1007	90	171	-	17.3	-
0.1	432	743	104	135	26.22	20.4	15.20
0.2	424	652	111	88	35.22	22.9	24.45
0.3	493	414	100	188	58.92	30.1	42.52
0.4	431	400	79	89	60.28	52.5	67.05
0.5	462	369	128	138	63.37	62.6	72.36
0.6	471	223	73	209	77.84	68.6	74.78
0.7	431	166	70	89	83.47	100	82.70

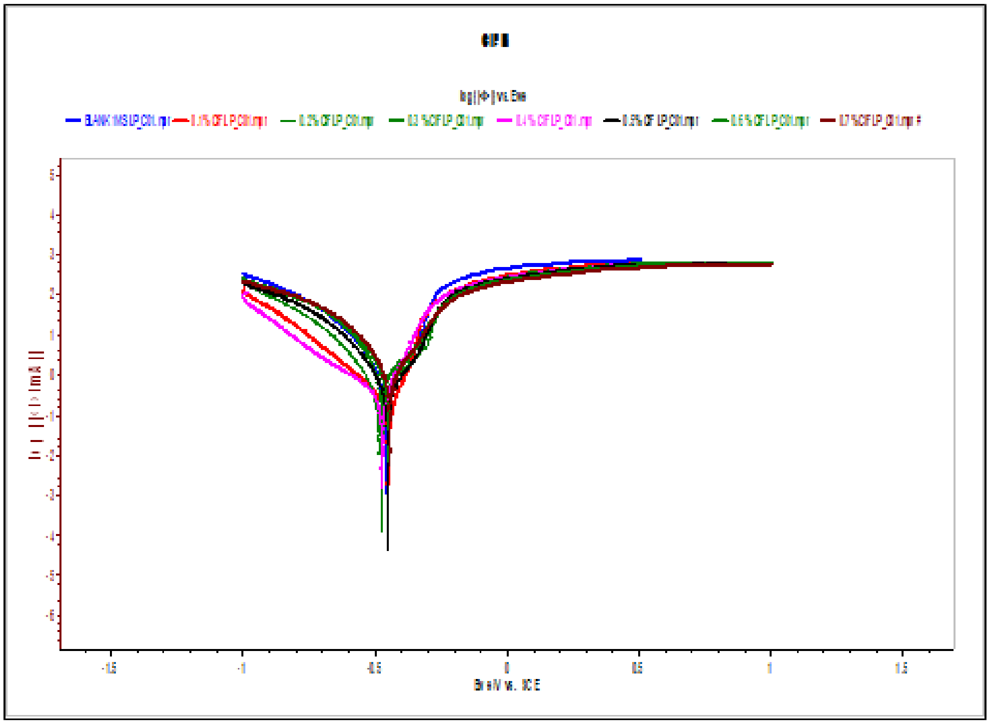

Fig.-3: Electrochemical polarization curves for Mild Steel in 1M HCl solution in the absence and Presence of various concentrations of CIFE extract

Electrochemical Impedance Spectroscopy

Nyquist plots of mild steel in 1M HCl in the absence and presence of various concentrations of CIFE are given in Figure 4, where it can be observed that the diameter of the semicircle increases with increasing concentration of CIFE. This fact revealed that impedance of mild steel against corrosion was increased in accordance with the CIFE amount in acid solutions.

Figure 4 illustrates that the impedance spectra are not perfect semicircles, which reflected deviation of the electrode (mild steel) from ideal capacitive behaviour. This type of deviation (depressed capacitive loops) is often shown by the systems due to surface heterogeneity and irregularity, which may be the result of surface roughness, distribution of the active sites, or adsorption of the inhibitor molecules[44, 45].

The constant phase element (CPE) has been used in the place of capacitor to compensate the non-homogeneity of the surface that causes a greater depression in Nyquist semicircle diagram[46]. Nyquist impedance plots were analysed by fitting the experimental data to a simple circuit model shown in Figure 5. In this circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance, and CPE is a constant phase element that has been considered to compensate for ideal capacitive behaviour and surface inhomogeneity (n).

The impedance function of a CPE is defined by the mathematical expression given below:

$$Z_{CPE} = Y_o^{-1} (i\omega)^{-n}$$

The double layer capacitance (C_{dl}) derived from the CPE are also presented, using the following equation

$$C_{dl} = (Y_o\, Rct^{\,n-1})^{1/n}$$

where Y_o is the CPE constant ,ω is the sine wave modulation angular frequency, i^2 =-1 is the imaginary number, n=α/ (π/2) in which α is the phase angle of CPE and n is the CPE exponent ($0 \leq n \leq 1$) which measures the deviation from the ideal capacitive behaviour and it represents the surface irregularity.

The impedance parameters, namely charge-transfer resistance (R_{ct}), solution resistance (R_s), the constant phase element (Y_o) related to the capacity of the double layer and the exponent (n), relevant to the capacitive semicircle of the mild steel in1M HCl in presence of CIFE extract are listed in Table-4.

Table-4: Impedance parameters for the corrosion of MS in 1M HCl in the absence and presence of various concentrations of CIFE

CIFE-MS									
Conc (%)	Rs	y0	n	Rct	IE	f max	Cdl	theta	τ
Blank	1.593	48532.66	0.45	3.281	-	20.6	2360	-	0.0077
0.1	1.292	44628.83	0.47	3.568	8.04	19.7	2271	0.04	0.0081
0.2	1.581	42565	0.49	3.741	12.30	21.0	2024	0.14	0.0076
0.3	1.354	35527.82	0.54	4.482	26.80	18.1	1968	0.17	0.0088
0.4	1.574	30353.73	0.59	5.246	37.46	18.1	1679	0.29	0.0088
0.5	1.508	27896.93	0.61	5.708	42.52	17.0	1638	0.31	0.0093
0.6	1.438	24225.72	0.64	6.573	50.08	28.4	852.6	0.64	0.0056
0.7	1.339	10781.02	0.82	14.77	77.79	18.5	583.4	0.75	0.0086

It can be seen from the table that the presence of CIFE enhances the values of R_{ct} and reduces the C_{dl} values. Increase in R_{ct} value with increase in concentration of the inhibitor might be due to blocking of the active sites by the film formed by the inhibitor at the surface of the metal. The decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the electric double layer[47–50]. This suggests that CIFE molecules function by adsorption at the metal/solution interface. Thus, the decrease in C_{dl} values and the increase in R_{ct} values and, consequently, increase in inhibition efficiency might be due to the gradual replacement of water molecules by the adsorption of the CIFE molecules on the metal surface, decreasing the extent of the dissolution reaction[51,52].

After analyzing the impedance results in Table-4, it is obvious that the exponent (n), increases with the concentration of CIFE and reaches a maximum value at 0.7%. The lower n value for uninhibited solution (n=0.45) indicates a high surface inhomogeneity resulting from surface metal roughening and/or formation of corrosion products on the surface. The values of n lies between 0.47 and 0.82 in the case of inhibited solutions. Addition of inhibitor increases n value indicating reduction of surface inhomogeneity occurs which is due to the adsorption of investigated inhibitors on the most active adsorption sites at the mild steel surface. Experimentally determined values of n for the corroding metal electrode lies around 0.9[53] which can also be seen from Table 4 in the present case.

When the plant extract concentration is increased to 0.7% in 1M HCl, the interface (τ) parameter changes while the capacitance (C_{dl}) value decreases signifying that the charge and discharge rates to the metal–solution interface is greatly decreased. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of investigated inhibitors on the mild steel surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the surface[54]. In conclusion, the results of the electrochemical studies were in good agreement with the results of gravimetric studies with slight deviations. This is due to the difference in immersion period of MS in the aggressive media[55].

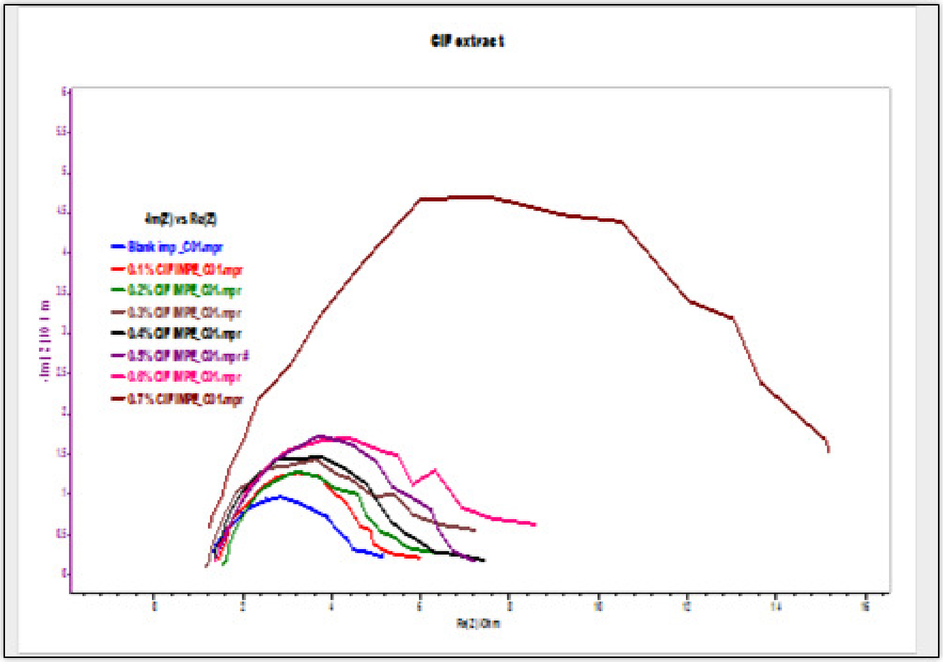

Fig. - 4: Nyquist plot for MS in 1M HCl in the absence and presence of various concentrations of CIFE extract

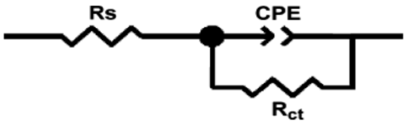

Fig.-5

Table-5: Screening of Preliminary Phytochemicals of Canna indica L. flower

Phytochemical constituents	Result
Alkaloids	+
Amino acids	-
Carbohydrates	+
Cholesterols	+
Flavonoids .	+
Glycosides	+
Phlobatinins	+
Proteins	+

Saponins	+
Steroids	+
Terpenoids	+
Coumarine	-
Phenolic compounds	-

(+) = indicate presence (-) = indicate absence

Scanning electron micrograph (SEM)

The surface morphology of mild steel immersed in the corrosion solution for 3h in the absence and presence of 0.7% concentration of CIFE is shown in Figure-6 and 7. It can be observed that the mild steel surface was strongly damaged as a result of the attack of the corrosive solution in the absence of inhibitor. Examination of Figure 6b reveals that the metal surface immersed in the inhibitor solution was in better condition, having smooth surfaces compared with the surface of the sample immersed in 1 M HCl alone. This improvement in surface morphology is due to the formation of a good protective film of inhibitor on the mild steel surface, which was responsible for the inhibition of corrosion.

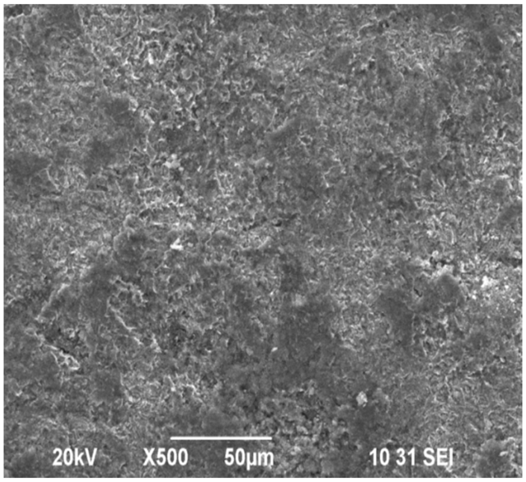

Fig.-6: MS in Blank

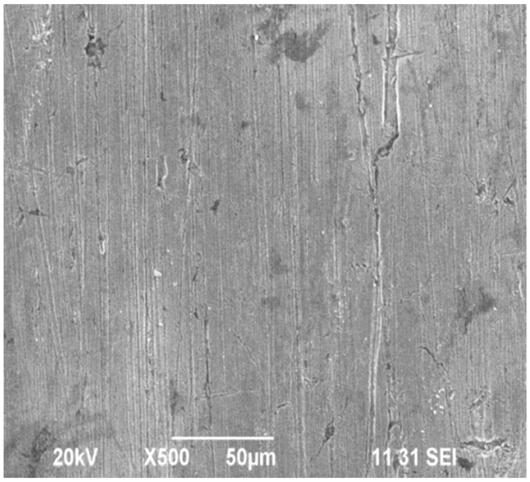

Fig.-7: MS in the presence of HRFE

Mechanism

Phytochemical screening of *Canna Indica* flower extract (CIFE) was carried out using standard procedure [33]and listed in the table 5.

The main constituents of the extract are alkaloids, Glycosides, Saponins, Terpene, Carbohydrate, Steroid, Protein, Cholesterol, Flavonoid, Phylobatinin and Tannin[56] and these organic compounds contains fused benzene rings and O heteroatom in the rings.

Generally the first stage in the corrosion inhibition mechanism is the adsorption of inhibitor molecules on the mild steel surface. The process of adsorption is influenced by the type of the aggressive electrolyte, the chemical structure of the inhibitor molecules, and the nature and charge of the metal. The charge on the metal surface is due to the electric field generated at the metal/electrolyte interface[57]. CIFE may adsorb on the mild steel surface by (i) electrostatic interaction of the inhibitor molecules with already adsorbed chloride ions (physisorption), (ii) vacant d-orbitals of metal surface atoms and unshared electron pairs of hetero atoms (chemisorption), or (iii) interaction of vacant the d-orbital of the inhibitor molecule with the d-electron of the metal surface(retro-donation).

In HCl medium CIFE molecules may adsorb through protonated heteroatoms (N, O, and S) and already adsorbed Cl^- ions on the mild steel surface. Initially the protonated forms of CIFE in acid medium compete with H^+ ions for electrons on the mild steel surface. After the evolution of H_2 gas from 1M HCl, the cationic form of inhibitor returns to its neutral form and hetero atoms with lone pair electrons promote adsorption. The high electron density on the mild steel surface renders more negative charge to it. In order to relieve the surface from the high negative charge, the electron from the d-orbital of Fe may be transferred to the vacant π*-orbital (antibonding) of the inhibitor molecules and in turn strengthen their adsorption on the mild steel surface. The presence of Cl^- in the solution should be mentioned. They are characterized with strong absorbability on the metal surface which brings about a negative charge favouring the adsorption of cation type inhibitors [58].

These studies showed that the larger the substance is adsorbed, the more effectively it protects surface. In the current investigation CIFE works out to be a good inhibitor for mild steel corrosion.

CONCLUSIONS

The present study shows *Canna Indica* flower extract acts as an effective inhibitor for mild steel corrosion in 1M HCl. The inhibition efficiency increased with increase in inhibitor concentration but decreased with increase in temperature. The inhibiting effect of the studied extract could be attributed to the presence of phytochemical constituents present in the extract which is adsorbed on the surface of the mild steel. Tafel polarization measurements indicate the extracts behave as mixed type inhibitor. SEM studies confirm that the surface is smoother in the presence of the extract.Therefore, the plant extract can be considered as an eco-friendly and effective green corrosion inhibitor for mild steel in acid medium.

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