J. Mater. Environ. Sci. 3 (4) (2012) 698-705 *Singh et al.*
ISSN : 2028-2508
CODEN: JMESCN

Hibiscus cannabinus extract as a potential green inhibitor for corrosion of mild steel in 0.5 M H_2SO_4 solution

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Received 25 March 2012, Revised 27 April 2012, Accepted 27 April 2012
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Abstract
The inhibitory effect of extract of *Hibiscus cannabinus* on corrosion of mild steel in aqueous 0.5 M H_2SO_4 was investigated by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of *Hibiscus cannabinus* extract on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in concentration of the extract and decreases with rise in temperature. Potentiodynamic Polarization measurement indicates that *Hibiscus cannabinus* acts as a mixed-type inhibitor. The increase in activation energy of corrosion process in the presence of the extract indicates that the extract retards the rate of corrosion of mild steel in 0.5 M H_2SO_4 solution. The nature of adsorption of the extract on mild steel surface is found to obey Langmuir adsorption isotherm. EIS measurement result is also correlated with the result of polarization. SEM study confirmed the adsorption of inhibitor molecules on mild steel surface.

Keywords: Mild steel; Acid corrosion; SEM; EIS; Hibiscus cannabinus; Corrosion inhibition.

1. Introduction
The study of corrosion inhibition of mild steel using inhibitor in acidic media is one of the challenging tasks in the current research due to its potential applications in industries such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes [1-4]. The ability of a compound to serve as inhibitor is dependent on its ability to form a compact barrier film and/or nature of adsorption on metal surface. The majority of well-known inhibitors are organic compounds containing heteroatoms, such as O, N, S and multiple bonds [5]. Although many synthetic compounds show good anticorrosive properties, most of them are highly toxic to both human beings and environments [6]. The known hazardous effect of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmental friendly inhibitors like natural products as corrosion inhibitors [7]. The natural product extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable source of materials [8-9]. The use of these natural products such as extracted compounds from the leaves, flowers, seeds and roots as corrosion inhibitors have been widely reported by several authors [10-17].
The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used for inhibition of corrosion of mild steel in acidic medium. An attempt has been made to ascertain their corrosion inhibition properties. Therefore, in this present work, the aqueous extract of *Hibiscus cannabinus* in 0.5M H_2SO_4 was tested by using weight loss, potentiodynamic polarization and electrochemical impedance techniques. SEM study was also used to study the surface morphologies. *Hibiscus cannabinus* is a member of the Malvaceae family that is related to cotton and okra. *Hibiscus cannabinus* faber has been used

in paper, pulp, twines, burlap, animal bedding, ropes and fishing nets [18]. *Hibiscus cannabinus* are also used in India as folk medicine [19]. However, literature search reveals that no study has been done on the inhibitive effects of *Hibiscus cannabinus* extract on acidic corrosion of mild steel.

2. Experiments

2.1 Preparation of extract of Hibiscus cannabinus

Double distilled water and analytical reagents-grade H_2SO_4 (E Merk, India, AR Grade) were used for preparing the solutions. The leaves and stems of the seed of *Hibiscus cannabinus* was dried for 6 hours in an oven at 70^oC and ground into powder and 10 grams of the powder of *Hibiscus cannabinus* was refluxed in 100 ml double distilled water for 1 hour. The extract of the plant was prepared by evaporating the filtrate. The required concentrations of solution were prepared by using the residues in aqueous solution of 0.5 M H_2SO_4.

2.2 Weight loss method

Mild steel coupons having percent composition of C (0.18), Si (0.19), Mn (0.51), P (0.044), S (0.057), Cr (0.14), Ni (0.09), Mo (0.02), Cu (0.06), V (less than 0.01) and remaining Fe (Chemical analysis: % by weight by Equipment, IS:228 &ICP-OES) were used. The rectangular specimens with dimension of (1 x 4 x 1) cm were used in weight loss experiments. The specimens were abraded into smooth surface successively by using the emery papers of 150, 180, 320, 400, 600 and 1000 grade. The smooth uniform surface were degreased with acetone and washed with distilled water before the experiment. Weight loss of mild steel coupons immersed in 100 ml of the electrolyte with and without the extract was determined after 4 hours at 298 K. The percentage inhibition efficiency (I%) was calculated from the following equation:

$$I\% = \frac{W_o - W_i}{W_o} \times 100 \quad (1)$$

Where Wo and Wi are weight losses of mild steel in absence and presence of the extract.

2.3 Electrochemical measurements

An electrochemical cell assembly of three electrodes was used for potentiodynamic polarization and electrochemical impedance measurements, in which working electrode was mild steel, Calomel electrode (SCE) was the reference electrode and a Platinum wire was the counter electrode. The working electrode was coated thoroughly with epoxy resin keeping surface area of 1 cm^2 for the study. The surface of the mild steel was abraded into uniform surface with the help of grinding machine by using 150, 320, 400, 600 and finally 1000 grade emery papers. The uniform smooth surface were degreased with acetone and washed with distilled water before the experiment. The measurements were done by using computer controlled electrochemical workstation of CHI 760c model. Before each polarization and EIS measurement, the working electrode was introduced into the test solution and kept for 4 hours to attain the open circuit potential (OCP). Polarization measurements were made under thermostatic conditions at 298, 308, 318 and 328K and the measurements were carried out in the range of potential from -1.2 to 2 V with scan rate of 0.01(V/s). The percentage inhibition efficiency (I%) from the polarization measurement was calculated using the following equation [20]:

$$I\% = \frac{i^o_{corr} - i^i_{corr}}{i^o_{corr}} \times 100 \quad (2)$$

Where i^o_{corr} and i^i_{corr} are the corrosion current density values without and with the extract.

Electrochemical Impedance measurement was carried out at 298K and the measurement of the response of the electrochemical system to a.c. excitation with a frequency ranging from 10,0000 to 0.1 Hz and peak to peak a.c. amplitude of 0.005 V with quiet time of 2 seconds was done. The percentage inhibition efficiency (I%) from the electrochemical impedance measurement was calculated using the following equation [21]:

$$I\% = \frac{R_{ct(i)} - R_{ct(a)}}{R_{ct(i)}} \times 100 \quad (3)$$

where $R_{ct(i)}$ and $R_{ct(a)}$ are the values of charge transfer resistance in presence and absence of the extract respectively.

2.4 Surface analysis

The test coupons of the size 1x1 cm^2 were exposed in 100 ml of 0.5 M H_2SO_4 solutions in absence and presence of 1 grams and 3 grams of the plant extracts for 5 hours at 298 K and then washed with distilled water. After drying the specimens, they were examined by Scanning electron microscope (SEM) model Leo 435 VP with an Oxford Inca energy dispersion spectrometer system.

3. Results and discussions

3.1. Weight loss method

The percentage of inhibition efficiency (I%) obtained at different concentrations of *Hibiscus cannabinus* extract at 298 K are summarized in the table 1. It is indicated that inhibition efficiency of the extract on corrosion of mild steel increases with increase in concentration.

Table1. Corrosion parameters for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different *Hibiscus cannabinus* extract concentrations from Weight Loss method

Temperature (K)	Solution	(Conc.), g/L	I%
298	0.5 M H_2SO_4	0.0	-
		1.0	73.4
		2.0	87.5
		3.0	92.6

3.2 Potentiodynamic Polarization measurement

Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solutions in the absence and presence of various concentrations of *Hibiscus cannabinus* extract at 298 K are shown in figure 1. The extrapolation of Tafel straight line allows the calculation of the corrosion current density (i_{corr}). The values of i_{corr}, the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) and the percentage of inhibition efficiency (I%) are given in the table 2.

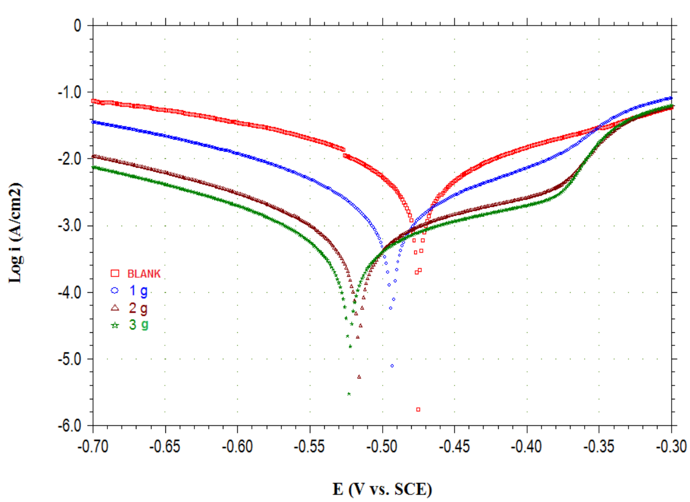


Figure1. Potentiodynamic polarization curves for mild steel in 0.5 MH_2SO_4 solution in absence and presence of different concentrations of *Hibiscus cannabinus* extract at 298 K.

ISSN : 2028-2508
CODEN: JMESCN

Inspections of the data of the figure 1 infer that, at a given temperature, the addition of the extract of *Hibiscus cannabinus* to the acid solution increases both the anodic and cathodic overpotentials, decreases the corrosion current density (i_{corr}). The change in cathodic and anodic Tafel slopes (β_c and β_a) shown in the table 2 indicates that adsorption of extract on mild steel modify the mechanism of the anodic dissolution as well as cathodic hydrogen evolution. From figure 1, it is cleared that both cathodic and anodic reactions are inhibited but the cathodic reaction (Hydrogen evolution reaction) is seem to be slightly more inhibited. From table 2, it is also cleared that the inhibition increases with increase in concentration and there is no definite trend in the shift of E_{corr} values in presence of various concentration of extract in 0.5 M H_2SO_4 solutions. This result indicates that *Hibiscus cannabinus* may be classified as a mixed type of inhibitor in 0.5 M H_2SO_4 solution [22].

3.3. Effect of temperature

The effect of temperature on inhibition is summarized in the table 2. It shows that an increase in temperature decreases the inhibition efficiency. This can be explained on the fact that an increase in temperature usually accelerates corrosive processes, particularly in media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal. The activation energies (E_a) for the corrosion process in absence and presence of inhibitor are evaluated from Arrhenius equation [22]:

$$\mathbf{k = A\ e^{(-Ea/RT)}} \quad (4)$$

where A is the pre-exponential factor, T is absolute temperature , R the gas constant and k is the rate constant of metal dissolution reaction which is directly related to corrosion current density. Therefore, the equation can be rewritten as [23]:

$$\mathbf{i_{corr} = A\ e^{(-Ea/RT)}} \quad (5)$$

where i_{corr} is the corrosion current density. The activation energy of the corrosion reaction in the presence and absence of the inhibitor can be determined by plotting log i_{corr} against 1/T which gives a straight line with a slope permitting the determination of E_a as shown in figure 2. The values of the activation energies are given in table 3.

Table 2. Electrochemical parameters for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of different *Hibiscus cannabinus* extract concentrations.

Temperature (K)	Solution	(Conc.), g/L	$-E_{corr}$ (mV vs.SCE)	β_c (mV/Dec)	β_a (mV/Dec)	i_{corr}(mA/cm^2)	I%	θ
298	0.5 M H_2SO_4	0.0	475	54	61	8.11	-	-
		1.0	493	70	83	1.98	75.6	0.756
		2.0	516	70	50	0.94	88.4	0.884
		3.0	523	69	49	0.69	91.5	0.915
308	0.5 M H_2SO_4	0.0	475	53	59	14.99	-	-
		1.0	494	60	56	6.45	56.9	0.569
		2.0	493	60	66	5.77	61.5	0.615
		3.0	508	64	65	2.72	81.8	0.818
318	0.5 M H_2SO_4	0.0	481	48	51	16.39	-	-
		1.0	490	55	56	9.45	42.3	0.423
		2.0	478	60	61	7.46	54.5	0.545
		3.0	497	51	50	4.65	71.6	0.716
328	0.5 M H_2SO_4	0.0	500	49	50	19.98	-	-
		1.0	475	51	55	13.19	33.9	0.339
		2.0	480	54	46	10.52	47.3	0.473
		3.0	478	60	61	7.45	62.7	0.627

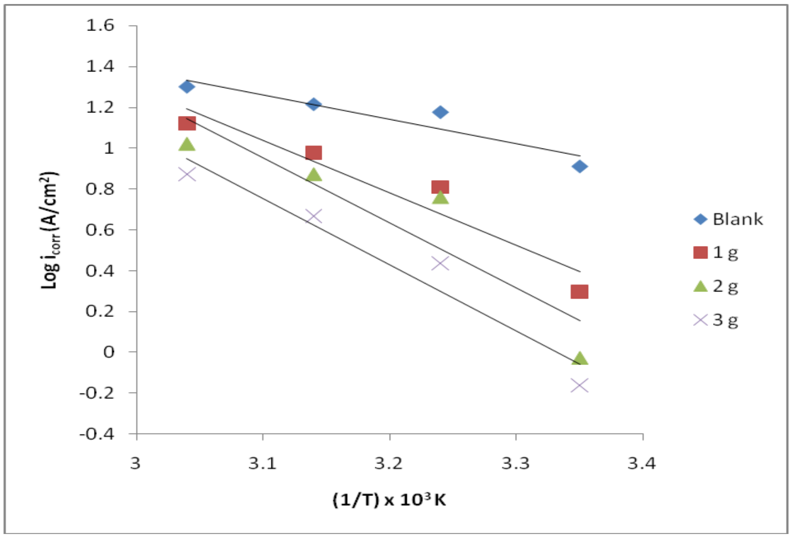


Figure 2. Arrhenius plots of log i_{corr} versus 1/T for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of different concentrations of *Hibiscus cannabinus* extract.

The values of activation energies (E_a) increase in presence of the extract which suggested that the inhibitors reduce corrosion processes by creating a physical barrier to charge and mass transfer through adsorption process [24].

Table 3: Calculated values of activation energy (E_a) for various concentrations of *Hibiscus cannabinus* extract during mild steel corrosion in 0.5 M H_2SO_4 solution

Solution	Concentration (g/l)	E_a (k J/mol)	R^2
0.5 M H_2SO_4	0.0	22.72	0.876
	1.0	49.28	0.980
	2.0	61.25	0.978
	3.0	62.29	0. 974

3.4. Adsorption isotherms.

Basic information on the interaction between the inhibitor and mild steel surface can be provided by the adsorption isotherms. For this purpose, the values of surface coverage (θ) at different concentrations of *Hibiscus cannabinus* extract in acid media in the temperature range (298-328 K) have been used to explain the best isotherm to determine the adsorption process. The value of the surface coverage (θ) was calculated using the relationship [25-26]:

$$\theta = [I\%] /100 \qquad (6)$$

Attempts were made to fit these Θ values to various isotherm including Langmuir, Temkin, Frumkin, El-Awady, Freundlich, and Flory-Huggins etc.

The best fit was obtained with Langmuir isotherm as suggested by the plot between C/θ and C (as shown in figure 3) and the linear correlation coefficient of the fitted data was close to 1, indicating that the adsorption of the inhibitor molecules obey the Langmuir's adsorption isotherm as expressed as [27]:

$$[C/\theta] = C + [1/K_{ads}] \qquad (7)$$

Where C is the inhibitor concentration and K_{ads} is the equilibrium constant for adsorption/desorption process of the inhibitor molecules on the metal surface. K_{ads} values were calculated from the intercept of the plot for adsorption process.

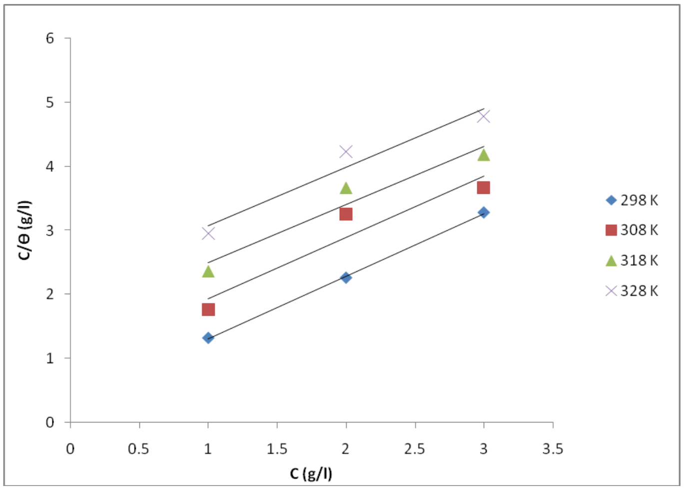


Figure 3. Langmuir adsorption isotherm for adsorption of *Hibiscus cannabinus* extract on the surface of mild steel in 0.5 M H_2SO_4.

3.5. EIS Measurements

EIS technique was applied to investigate the electrode/electrolyte interface and corrosion processes that occur on mild steel surface in presence and absence of *Hibiscus cannabinus* extract. To ensure complete characterization of the interface and surface processes, EIS measurements were made at OCP in a wide frequency range at 298 K. Figure 4 shows Nyquist plots for mild steel electrode immersed in 0.5 M H_2SO_4 solution at 298 K in absence and presence of various concentrations of *Hibiscus cannabinus* extract at the respective open circuit potential. It is cleared from the figure 4 that the diameter of the semicircle increases with the increase in inhibitor concentration in the electrolyte, indicating an increase in corrosion resistance of the material [28].

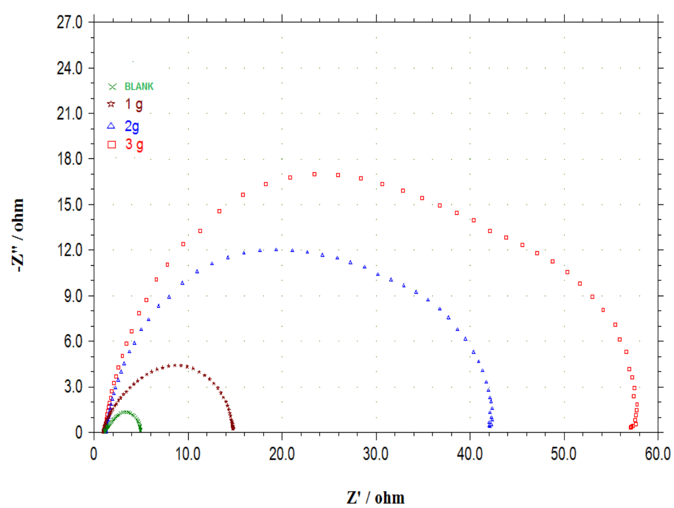


Figure 4. Nyquist plots (EIS) of mild steel immersed in 0.5 M H_2SO_4 in absence and presence of different concentrations of *Hibiscus cannabinus* extract at 298 K.

The value of electrochemical double layer capacitance (C_{dl}) was calculated at the frequency, f_{max} using the following equation [29]:

$$\mathbf{C_{dl} = 1/2\pi f_{max} R_{ct}} \tag{8}$$

where f_{max} is the frequency at which the imaginary component of the impedance is maximal.

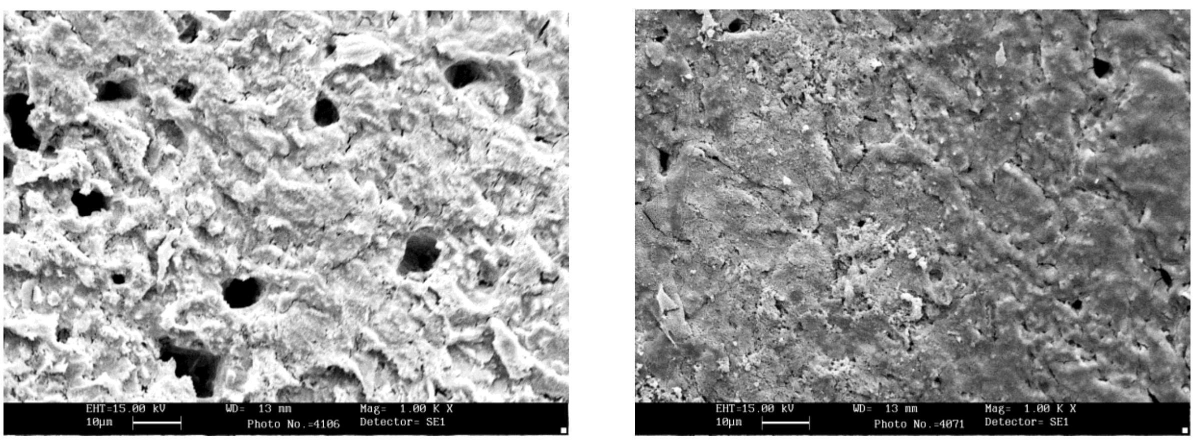
The impedance data listed in the table 4 indicate that the values of both R_{ct} and I% are found to increase by increasing the inhibitor concentration, while the values of C_{dl} are found to decrease. This behavior can be attributed to a decrease in dielectric constant and/ or an increase in the thickness of the electric double layer, suggesting that the inhibitor molecules act by adsorption mechanism at mild steel/acid interface [30].

Table 4: Electrochemical impedance parameters for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of different *Hibiscus cannabinus* extract concentrations.

Temperature (K)	Solution	(Conc.), g/L	C_{dl} (F cm^{-2})	R_{ct} (Ω cm^2)	I%
298	0.5 M H_2SO_4	0.0	$105 x 10^{-3}$	4.1	-
		1.0	60.86×10^{-3}	15.39	73.4
		2.0	7.59×10^{-3}	46.62	91.2
		3.0	3.58×10^{-3}	67.32	93.9

3.6. Scanning electron microscopy

SEM micrograms of the polished surface of mild steel exposed for 5 hours in 0.5 M H_2SO_4 solutions in absence and presence of 3 grams of *Hibiscus cannabinus* extract were shown in figure 5 (a)-(b). In the comparison of the SEM micrograms in absence and presence of the extract, there was a rough surface on mild steel in absence of the extract. There was a smooth surface with deposited extract on it in presence of the extract [31]. This result supplements the results of electrochemical techniques and confirms that the extract inhibited corrosion of mild steel through adsorption of the inhibitor on metal surface.



(a) (b)

Figure 5. Scanning electron microgram of polished mild steel (1000 x) after exposure to (a) 0.5 M H_2SO_4 (b) 0.5 M H_2SO_4 containing 3 grams of *Hibiscus cannabinus* extract.

Conclusions

1. The inhibition efficiency of *Hibiscus cannabinus* on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in concentration of extract and decreases with rise in temperature. Potentiodynamic Polarization measurement show that it acts as mixed type inhibitor
2. The increase in the values of activation energy of corrosion process in presence of the extract indicates that *Hibiscus cannabinus* extract retards the rate of corrosion of mild steel in 0.5 M H_2SO_4 solution. Adsorption of inhibitor molecules of extract on mild steel surface is found to obey Langmuir adsorption isotherm.
3. EIS measurement reveals that charge transfer resistance increases with increase in concentration of the extract, indicating that the inhibition increases with increase in concentrations.
4. SEM study confirm that the inhibition of corrosion of mild steel is through adsorption of the extract on surface of metal and this study also supplements the results of electrochemical techniques.

Acknowledgement
Authors are very thankful to University Grants Commission, India for financial support for this research work.

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