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A green Approach:A corrosion inhibition of mild steel by adhatoda vasica plant extract in 0.5 M H_2SO_4

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Abstract

The extract of adhatoda vasica in aqueous 0.5 M H_2SO_4 was systematically investigated to ascertain its inhibitory effect on corrosion of mild steel and its mechanism of the inhibition by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of adhatoda vasica on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in its concentration and decreases with rise in temperature. Potentiodynamic Polarization measurement show that adhatoda vasica acts as mixed type inhibitor. The increase in activation energies of corrosion process in presence of the extract indicates that adhatoa vasica extract retarded 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 was in conformity with Langmuir isotherm. The result of EIS was correlating with the result of polarization measurement. Scanning electron microscopy (SEM) study confirmed that the inhibition of corrosion of mild steel is through adsorption of the extract molecules on surface of metal.

Keywords: Mild steel; EIS; SEM; Acid Corrosion; Acid inhibition.

1. Introduction

Mild steel has been the most widely used alloy for structural and industrial applications since the beginning of industrial revolution. The use of acid media in the study of corrosion of mild steel has become important because of its industrial applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes [1-3]. The refining of crude oil were carried out in a variety of corrosive conditions and in such, the corrosion of equipments are generally caused by a strong acid through attacking on equipment surface. And in many of structural and industrial applications of mild steel, they are also exposed to corrosive environments and they are susceptible to different types of corrosion. Therefore, the use of corrosion inhibitors to prevent metal dissolution will be inevitable. The use of inhibitors is found to be one of the most practical methods for protection against corrosion, especially in acidic media [4]. The majority of well-known inhibitors are organic compounds containing heteroatoms, such as O, N, S and multiple bonds [5]. Most of these organic compounds are not only expensive but also toxic to both human beings and environments [6] and therefore, their use as corrosion inhibitors are limited. Thus, efforts have been made to develop cost-effective and non-toxic corrosion inhibitors. The plant extracts are considered as an incredibly rich source of environmentally acceptable corrosion inhibitors. 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 [7-9]. Several authors have reported the use of the natural products as the potential corrosion inhibitors for various metals and alloys under different environments [10-19].

In the present work, an attempt was made to find a naturally occurring, cheap and environmentally safe substance that can be employed for inhibiting the corrosion of mild steel in acidic medium. In this present work, Adhatoda vasica with the common name ‘vasaka’ was taken for the study, which is a shrub widespread throughout the tropical regions of Southeast Asia, including India [20]. The fresh leaves and flowers of adhatoda vasica were collected from Kakching village, Thoubal district, Manipur (India) and an attempt has been made to ascertain its corrosion inhibition properties and its mechanism of inhibition. The aqueous extract of its leaves and flowers in 0.5 M sulphuric acid was tested by using weight loss, potentiodynamic polarization and electrochemical impedance techniques. SEM study was also used to study the surface morphologies. The extract of adhatoda vasica leaves has also been found to use as an herbal remedy for allergen-induced bronchial obstruction, asthma, tuberculosis and in the Naga tribes of north-easthern part of India, the leaf decoction of adhatoda vasica, locally called ‘sorukni, have a long history of traditional medicine use, where it is used to get rid of intestinal worm infections [21]. The chemical examination of adhatoda vasica revealed to contain alkaloids, glycosides, phenolic components and sterols in which the major constituents identified are the two alkaloids: vasicine ($C_{11}H_{12}N_2O$) and vasicinone ($C_{11}H_{10}N_2O_2$). The structures of the molecules are shown in fig. 1.

(a) (b)

Figure1: The structure of (a) Vasicine molecule ($C_{11}H_{12}N_2O$) and (b) Vasicinone molecule ($C_{11}H_{10}N_2O_2$)

2. Materials and methods

2.1 Mild steel used

Mild steel coupons of 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 specimens were abraded into the uniform surface successively using the emery papers of 150, 180, 320, 400, 600 and 1000 grade. The surface were then degreased with acetone and washed with double distilled water before the experiment.

2.2 Preparation of extract of adhatoda vasica

Double distilled water and analytical reagents-grade H_2SO_4 (E Merk, India, AR Grade) were used for preparing solutions. Adhatoda vasica was dried for 6 hours in an oven at 70^{o}C and grinding to powdery form and 10 grams of the powder of adhatoda vasica 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.

2.3 Weight loss method

The rectangular specimens with dimension of (1 x 4 x 1) cm were used in weight loss experiments. Weight loss of mild steel coupons immersed in 100 ml of the electrolyte with and without the extract of plant was determined after 4 hours at 298 K. The percentage inhibition efficiency (I%) was calculated from the following equation:

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

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

2.4 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 was the reference electrode and Platinum wire was counter electrode. The working electrode was coated thoroughly with epoxy resin keeping surface area of 1 cm^2 for the study. The surface were then 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 298K, 308K, 318K and 328K and the measurements were carried out in the range of potential from -1.2 to 2 V with scan rate (V/s) of 0.01. The range of potential from -0.3 to -0.7 V was chosen for Tafel plot. The percentage inhibition efficiency (I%) from the polarization measurement was calculated using the following equation [22]:

$$I\% = \frac{i^{o}_{corr} - i^{i}_{corr}}{i^{o}_{corr}} \times 100 \qquad (2)$$

Where i^{o}_{corr} and i^{i}_{corr} are the corrosion current density values without and with the extract, respectively.

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 was done. The percentage inhibition efficiency (I%) from the electrochemical impedance measurement was calculated using the following equation [23]:

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

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

2.5 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 for surface analysis by Scanning electron microscope (SEM) model Leo 435 VP with an Oxford Inca energy dispersion spectrometer system.

3. Results and discussion

3.1. Weight loss method

The percentage of inhibition efficiency (I%) of the extract from weight loss method at different concentrations of adhatoda vasica at 298 K are summarized in the table 1. It is indicated that inhibition efficiency of the extract increases with increase in its concentration.

Table 1: The corrosion parameters for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different adhatoda vasica extract concentrations.

Temperature (K)	Solution	Conc.(g/L)	I%
298	0.5 M H_2SO_4	0.0	-
		1.0	92.5
		2.0	95.4
		3.0	98.8

3.2 Potentiodynamic Polarization measurement

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

The analysis of the data of the figure 2 reveals that, at a given temperature, the addition of the extract of adhatoda vasica 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 Adhatoda vasica extract modify the mechanism of the anodic dissolution as well as cathodic hydrogen evolution. From figure 2, it is clear that both cathodic and anodic reactions are inhibited and the inhibition increases as the inhibitor concentration increases in acidic media. As the anode is more polarized, the process of metal dissolution is more inhibited. From table 2, it is also clear that there is no definite trend in the shift of E_{corr} values, in presence of various concentration of the extract in 0.5 M H_2SO_4 solutions, indicating the mixed type of inhibitor in 0.5 M H_2SO_4 solutions.

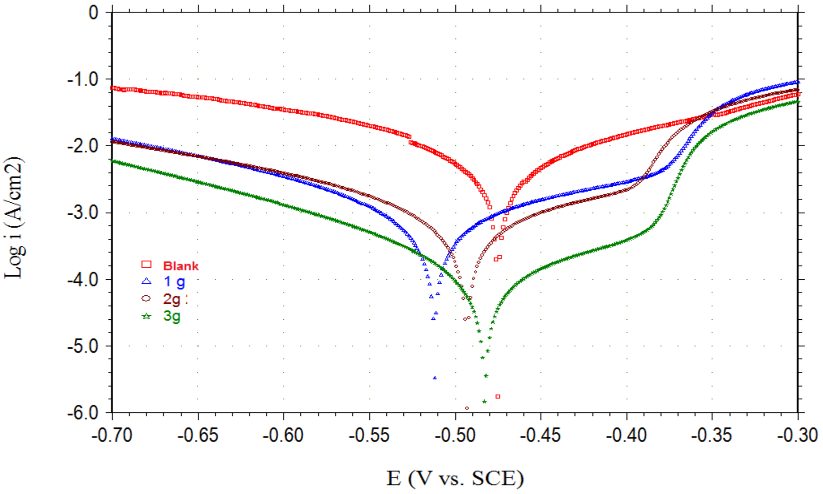


Figure2: Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentrations of Adhatoda vasica extract at 298 K**.**

3.3. Effect of temperature

The effect of temperature range from 298K to 328K on inhibition efficiency is summarized in the table 2. It shows that an increase in temperature decreases the inhibition efficiency of the extract. This can be explained on the fact that an increase in temperature usually assists corrosion processes, particularly in media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal.

Table2: The electrochemical parameters for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of different adhatoda vasica extract concentrations.

Temp (K)	Solution	(Conc.), g/L	$-E_{corr}$ (mVvs.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	512	69	54	1.01	87.5	0.875
		2.0	493	64	149	0.53	93.5	0.935
		3.0	483	82	216	0.07	99.1	0.991
308	0.5 M H_2SO_4	0.0	475	53	59	14.99	-	-
		1.0	518	57	45	2.94	80.4	0.804
		2.0	486	58	142	1.77	88.2	0.882
		3.0	491	72	138	0.18	98.7	0.987
318	0.5 M H_2SO_4	0.0	481	48	51	16.39	-	-
		1.0	516	57	46	4.50	72.5	0.725
		2.0	479	70	63	2.88	82.4	0.824
		3.0	498	58	103	1.55	90.5	0.905
328	0.5 M H_2SO_4	0.0	500	49	50	19.98	-	-
		1.0	480	54	46	10.52	47.3	0.473
		2.0	513	54	45	9.70	51.5	0.515
		3.0	468	57	54	5.50	72.5	0.725

The activation energies (E_a) for the corrosion process in absence and presence of the extract are evaluated from Arrhenius equation [24]:

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

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 [25]:

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

where i_{corr} is the corrosion current density. The activation energy of corrosion reaction in presence and absence of the extract 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 3. The values of activation energies are given in table 3.

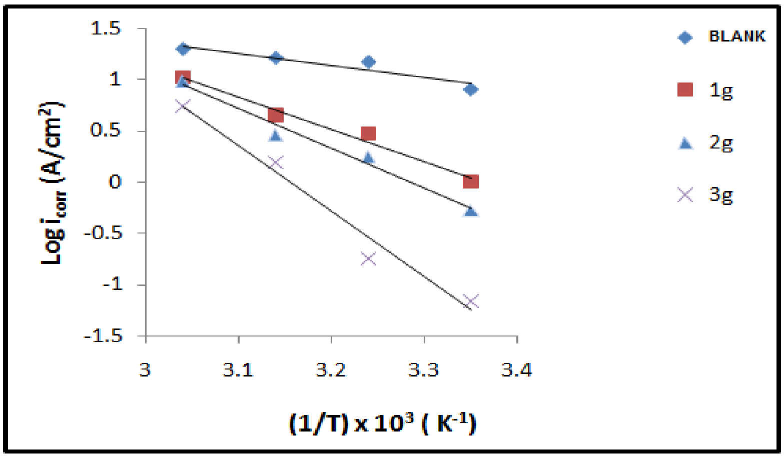


Figure 3: Arrhenius plots of log i_{corr} versus 1/T for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of different concentrations of Adhatoda vasica extract

The increasing values of activation energies (E_a) in presence of the extract at all the studied concentration in 0.5 M H_2SO_4 suggested that there is a reduction in corrosion rate [26].

Table 3: Calculated values of activation energies (E_a) for various concentrations of adhatoda vasica extract during mild steel corrosion in 0.5 M H_2SO_4 solutions

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	60.33	0.980
	2.0	74.33	0.978
	3.0	122.67	0. 974

3.4. Adsorption isotherms

Basic information on the interaction between the inhibitor and mild steel surface are investigated by the adsorption isotherms. For this purpose, the values of surface coverage (θ) at different concentrations of adhatoda vasica 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 [27]:

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

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 4) 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 [28]:

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

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.

The adsorption equilibrium constant, $K_{ads,}$ is related to the standard free energy (ΔG^o_{ads}) by the following equation [29]:

$$K_{ads} = [1/55] \exp [-\Delta G^{o}_{ads}/RT] \qquad (8)$$

where the value 55.5 in the above equation is the molar concentration of water in solution in mol/L and the negative sign of ΔG^{o}_{ads} indicated that adsorption of the extract was spontaneous process [30]. The adsorption of the extract can be presented as a substitution adsorption process between the organic molecules in aqueous solution (Org_{aq}) and the water molecules (H_2O_{ads}) on the metallic surface [30]:

$$Org_{aq} + Y.\ H_2O_{ads} \longleftrightarrow Org_{ads} + Y.\ H_2O_{aq} \qquad (9)$$

where Y is the number of water molecules displaced by one molecule of the extract and Y is assumed to be independent of coverage or charge on the electrode.

Since the adsorption of the extract on the metal surface is in conformity with Langmuir isotherm, there is no interactive or repulsive force between the adsorbed molecules on metal surface [31].

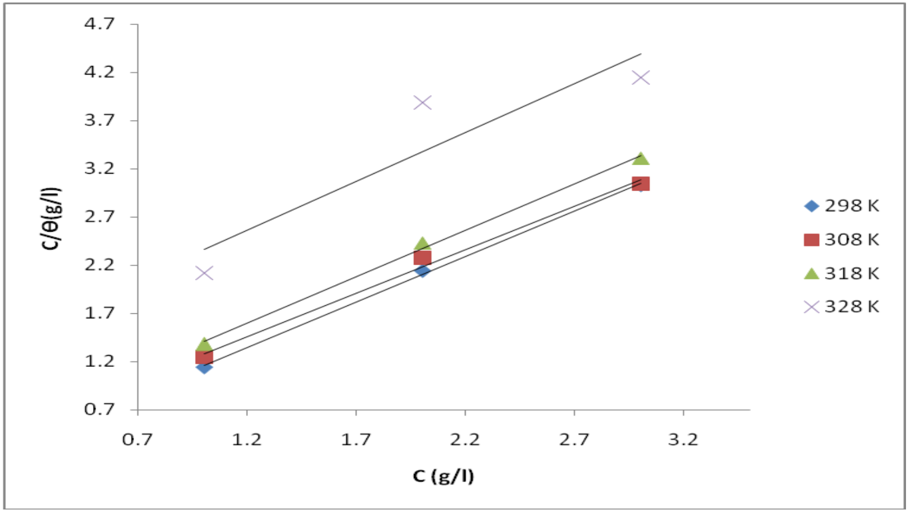


Figure 4: Langmuir adsorption isotherm for adsorption of Adhatoda vasica extrac in 0.5 M H_2SO_4 on surface of mild steel.

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 adhatoda vasica 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 5 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 the extract. It is clear from the figure 6 that the diameter of the semicircle increases with the increase in concentration of the extract, indicating an increase in corrosion resistance of the metal.

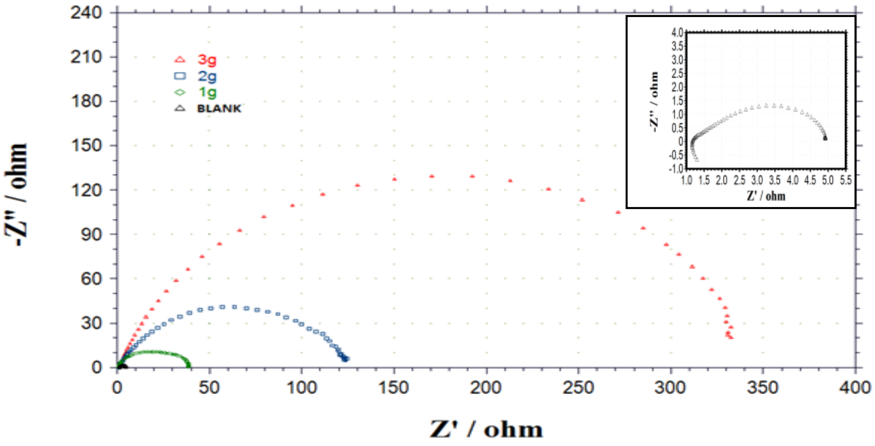


Figure 5: Nyquist plots (EIS) of mild steel immersed in 0.5 M H_2SO_4 in absence and presence of different concentrations of Adhatoda vasica extract at 298 K.

The value of electrochemical double layer capacitance (C_{dl}) was calculated at the frequency, f_{max} using the following equation [32]:

$$C_{dl} = 1/2\pi f_{max} R_{ct} \qquad (10)$$

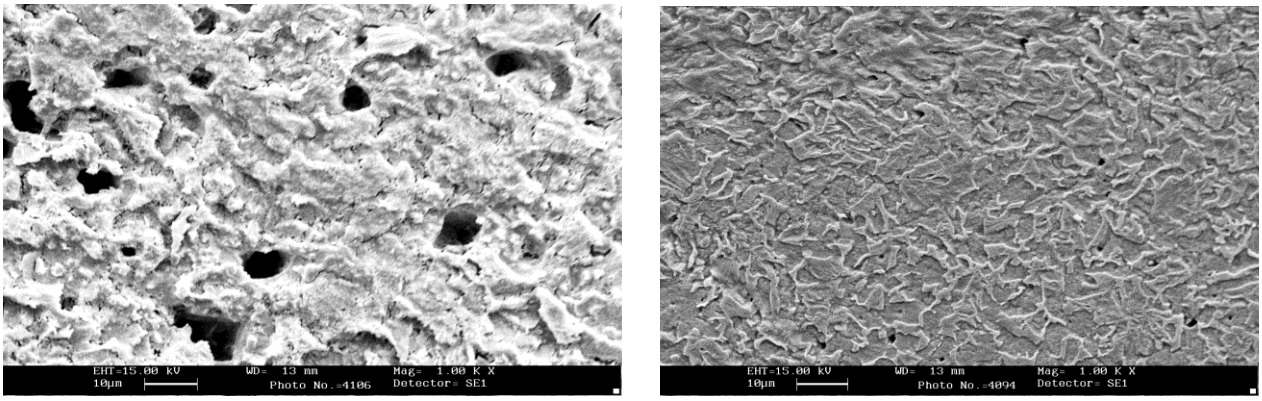
where f_{max} is the frequency at which the imaginary component of the impedance is maximal.
The impedance data listed in the table 4 indicate that the values of both R_{ct} and I% are found to increase with increase in concentration of the extract, while the values of C_{dl} are found to decrease. This behaviour can be attributed to a decrease in dielectric constant and/ or an increase in thickness of the electric double layer, suggesting that the extract molecules act by adsorption mechanism at mild steel/acid interface [33].

Table 4: The electrochemical impedance parameters for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of different adhatoda vasica 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	105×10^{-3}	4.1	-
		1.0	9.38×10^{-3}	46.7	91.2
		2.0	2.54×10^{-3}	136.8	97.3
		3.0	1.46×10^{-3}	351.8	98.9

3.6. Scanning electron microscopy

SEM micrograms of 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 adhatoda vasica extract were shown in figure 6 (a)-(b). In comparison of 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 [34]. This result supplements the results of electrochemical techniques and confirms that the extract of adhatoda vasica inhibited corrosion of mild steel through adsorption of the inhibitor molecules on metal surface.



(a) (b)

Figure 6: Scanning electron microgram of polished mild steel (1000 x) after exposed to (a) 0.5 M H_2SO_4 (b) 0.5 M H_2SO_4 containing 3 grams of Adhatoda vasica extract.

4. Conclusions

(i). The inhibition efficiency of adhatoda vasica extract on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in concentration of adhatoda vasica extract and decreases with rise in temperature. Potentiodynamic Polarization measurement show that adhatoda vasica acts as mixed type inhibitor.
(ii). The increase in activation energies of corrosion process in presence of the extract indicates that adhatoa vasica extract retards the rate of corrosion of mild steel in 0.5 M H_2SO_4 solution. The nature of adsorption of the extract molecules on mild steel surface is found to obey Langmuir adsorption isotherm.
(iii). EIS measurement reveals that charge transfer resistance increases with increase in concentration of the extract, indicating that the inhibition increases with increase in concentration. This result is correlating with the result of polarization measurement.
(iv). SEM study confirm that the inhibition of corrosion of mild steel is through adsorption of the extract on surface of metal and these studies also supplement the results of electrochemical techniques.

Acknowledgements

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