

## ***Argemone mexicana* Leaf Extract for Inhibition of Mild Steel Corrosion in Sulfuric Acid Solutions**

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Inhibition potential of *Argemone mexicana* leaf extract (AMLE) for corrosion inhibition of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been determined by weight loss, Tafel polarization and electrochemical impedance spectroscopy techniques. It is found from the results of weight loss method that inhibition efficiency of AMLE increases in concentration dependent manner which is also supported by the results of electrochemical techniques. Maximum inhibition efficiency of 87% has been achieved using 600 mg L<sup>-1</sup> of inhibitor. Adsorption behavior of AMLE has been studied and it is found to be described most suitably by Langmuir isotherm. Organic moieties present in extract are found responsible for effective performance of inhibitor which is well supported by optical microscopy and FTIR studies.

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**Keywords:** Mild steel; Corrosion inhibition; *Argemone mexicana*; leaf extract; optical microscopy, Adsorption.

### **1. INTRODUCTION**

Metals and alloys are most useful materials which are employed for construction work, pipe lines, parts of machines and in many other industries. Among all the metals iron and alloys has most promising features for being used in engineering applications due to its remarkable mechanical properties, effective cost and high strength [1]. Normally metals exist in unstable form and try to get stability reacting with the environment. These types of interactions depend upon aggressiveness of the

medium and reactivity of the material. In many industries (especially chemical industry) mineral acids are frequently used in various applications which cause loss of functional properties of the metals, in form of corrosion, due to violent reaction of acid with metals [2]. Many methods are being used by peoples for prevention of metals and alloys from corrosion but use of inhibitors [3-9] is one of the most efficient methods which give effective solution of corrosion problem. Efficiency of inhibitors depends upon its molecular structure, electron density, distribution of charges, aromaticity and its molecular size [10-12]. In many cases organic inhibitors (chemically synthesized) were found very efficient [13-15] but its toxicity and synthesis cost motivated people to develop environment friendly and cheap inhibitors [16-19]. Now a days many scientists are working on plants extract which are not only efficient but also non toxic and cheap inhibitors [20-27].

In this work we report *Argemone mexicana* plant extract, Papaveraceae family, for corrosion inhibition of mild steel in sulfuric acid solution. This plant is famous as Svarnakshiri and used in Indian ayurvedic system since ancient time. Aqueous extract of this plant contain organic compounds as proteins, amino acids, tannins, phenolic compounds, saponins and flavonoids [28] which are very effective for mild steel in acidic medium. Reasons for selecting this plant for corrosion study are low cost, easy availability and presence of effective organic moieties which fulfill requirements of efficient inhibitor.

Corrosion inhibition efficiency of AMLE for corrosion of mild steel has been investigated by conventional weight loss method, Tafel polarization and electrochemical impedance spectroscopy studies. Effect of inhibitor on surface morphology of mild steel is also monitored by optical microscope. Further FTIR study is done to know the functional groups present in the AMLE which play an important role for effective inhibition.

## 2. MATERIALS AND EXPERIMENTAL METHODS

### 2.1 Preparation of Plant Extract

Aqueous extract of *Argemone mexicana* leaves was prepared according to the method described in Dash et. al [28]. Plant leaves (100 gm) of *Argemone mexicana* were collected from the field and washed thoroughly under running tap water. It was dried on tissue paper for two days at room temperature. Further it was crushed in the grinder properly and 100 mL of distilled water was added to make solution. This prepared solution was kept for 48 hours with constant stirring. After giving time for extraction, solution was centrifuged and residue obtained was dried in vacuum oven at 40° C for full night. Stock solution was prepared by dissolving 1 g of dried residue in 10 ml of distilled water and used for the study.

### 2.2 Test specimens

Mild steel strips of dimensions  $1 \times 5 \times 0.02 \text{ cm}^3$  and  $1 \times 1 \times 0.02 \text{ cm}^3$  were used for study of corrosion effect using weight loss method and electrochemical measurements respectively. Test

specimens for the study were prepared by abrading the surface with emery paper of grade 1/0 to 6/0 successively. After this process cleaning of the samples was performed using AR grade acetone.

### 2.3 Corrosive Solution

GR grade H<sub>2</sub>SO<sub>4</sub> (98%) was used as corrosive medium to investigate inhibition efficiency of AMLE for mild steel corrosion. Required concentration of acid was obtained by dilution with distilled water.

### 2.4 Techniques Employed

#### 2.4.1 Weight Loss Method

Weight loss method is very simple and reliable technique to determine inhibition efficiency of inhibitor. For taking observations prepared mild steel specimens were immersed for 5 h in 100 mL of acid with various concentrations of AMLE. For achieving accurate results, three sets for each concentration of inhibitor were used. After optimized immersion time, samples were drawn out and cleaned with distilled water followed by drying in vacuum oven for half an hour. Weight loss in exposure period was recorded and inhibition efficiency was determined using following equation at each inhibitor concentration-

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

Effect of inhibitor on mild steel corrosion is greatly influenced by surface coverage parameter  $\theta$  which is directly related with adsorption behavior of inhibitor for mild steel surface. It was obtained by following relation-

$$\theta = \frac{W_o - W_i}{W_o} \quad (2)$$

Where  $W_o$  and  $W_i$  are weight of samples immersed in acid without and with inhibitor respectively.

Corrosion rate values for each concentration of extract were computed from following equation-

$$Cr = \frac{87.6W}{td} \quad (3)$$

Where  $W$  is weight loss cm<sup>-2</sup> of sample at particular inhibitor concentration,  $t$  is immersion time in hour and  $d$  is density of materials used (for mild steel  $d = 7.86$  g cm<sup>-3</sup>)

#### 2.4.2 Electrochemical Measurements

Electrochemical study provides kinetic parameters involved in corrosion process which vary with inhibitor concentrations and clearly reflect the effect of inhibitor on corrosion. For the study a three electrode cell assembly was used to conduct experiments which include mild steel specimen (Surface area-1×1×0.2 cm<sup>3</sup>) as working electrode, platinum foil as counter electrode and Ag-AgCl as

reference electrode. All the measurements were recorded with the help of CH instruments USA (CHI 7041 C) and analyzed by software provide with this instrument. All the electrochemical experiments were conducted on mild steel specimens (exposure area- 1 cm<sup>2</sup>) using 100 mL of acid at room temperature.

For polarization test potential was applied from -0.25 V vs Ag-AgCl to + 0.25 V vs Ag-AgCl with respect to open circuit potential of the system at a scan rate of 0.5 mV s<sup>-1</sup>. Corrosion current density ( $I_{\text{corr}}$ ) and equilibrium corrosion potential ( $E_{\text{corr}}$ ) for each concentration of inhibitor was obtained with the help of CHI 7041 C software. Inhibition efficiency was determined using  $I_{\text{corr}}$  values by following relation-

$$\mu_p (\%) = \frac{I_{\text{corr}}^o - I_{\text{corr}}^i}{I_{\text{corr}}^o} \times 100 \quad (4)$$

Where  $I_{\text{corr}}^o$  and  $I_{\text{corr}}^i$  is corrosion current densities in case of uninhibited and inhibited samples.

Impedance spectroscopy test was carried out in the frequency range from 100 kHz to 10 mHz using signal of 5 mV amplitude. Prior to measurements, system was left to achieve constant ocp for better results and mild steel was allowed to corrode in H<sub>2</sub>SO<sub>4</sub>. Inhibition efficiency by this method was obtained using formula reported below-

$$\mu_{R_t} (\%) = \frac{R_t^i - R_t^o}{R_t^i} \times 100 \quad (5)$$

Where  $R_t^i$  and  $R_t^o$  are charge transfer resistances obtained for inhibited and uninhibited samples respectively.

## 2.5 Optical Microscopy

To capture the morphology of mild steel surface at various concentrations of inhibitor optical microscope (Leica DFC 295) was employed. This test was performed on mild steel specimen of 1 cm<sup>2</sup> effective area and surface morphology was recorded after 3 hours immersion in acid. To study the effect of AMLE on mild steel corrosion, surface morphology at optimum inhibitor concentration only was obtained and compared with the surface morphology of mild steel and uninhibited samples.

## 2.6 FTIR Spectroscopy

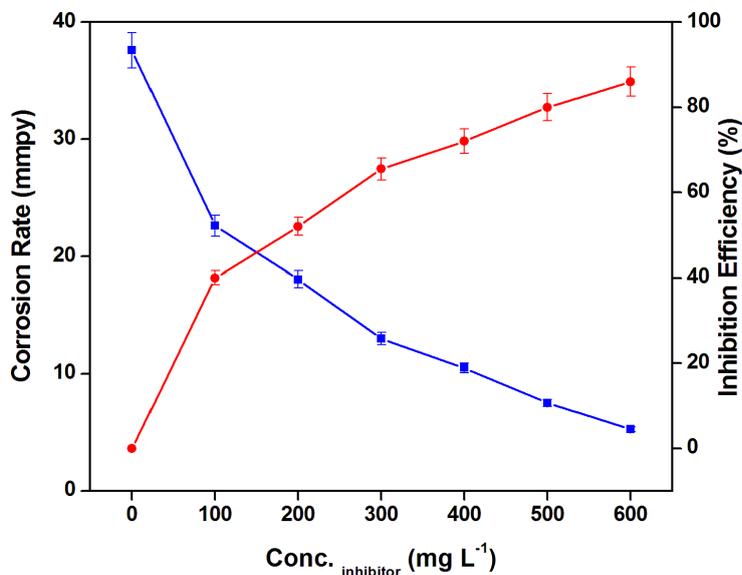
Presence of functional groups in the extract was analyzed by Thermo scientific (Nicolet 6700) FT-IR instrument. Small amount of extract (liquid) was analyzed by the instrument with the help of attachments provided with it for characterization of liquid materials. There were many peaks present in the spectra obtained by this method which were characterized by comparison with the standard peaks position of functional groups.

# 3. RESULTS AND DISCUSSION

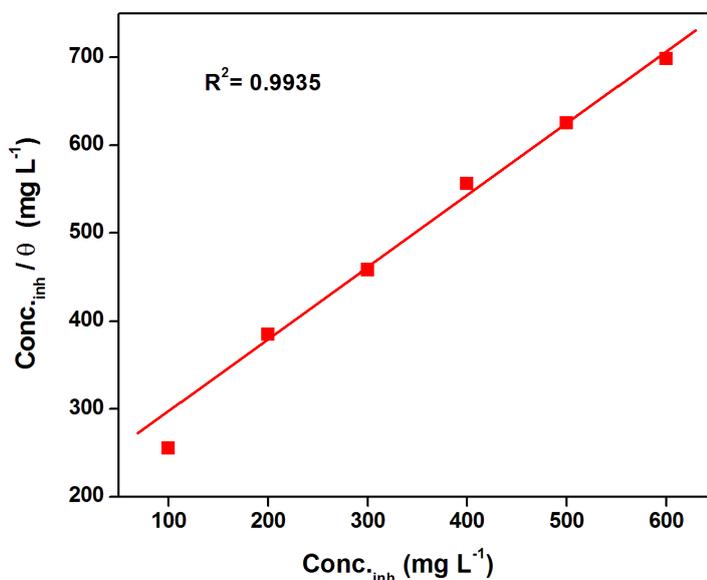
## 3.1 Weight Loss Method

From the investigation of the results obtained by this method it was found that mild steel corroded in sulfuric acid very easily whereas remarkable improvement in corrosion resistance of mild

steel was acknowledged in presence of *Argemone mexicana* extract. Initially corrosion rate was very high (37.60 mmpy) which was noticed to decrease with increasing inhibitor concentration and found minimum for 600 mg L<sup>-1</sup> AMLE concentration. On the other side, maximum inhibition efficiency of 86 % (C<sub>r</sub>=5.26 mmpy) was obtained at same inhibitor concentration (Figure 1).



**Figure 1.** Corrosion rate and inhibition efficiency at various concentrations of inhibitor in 0.5 M sulfuric acid at 26±1° C for 5h.



**Figure 2.** Langmuir adsorption isotherm for mild steel in 0.5 M sulfuric acid containing different concentrations of *Argemone mexicana* leaf extract.

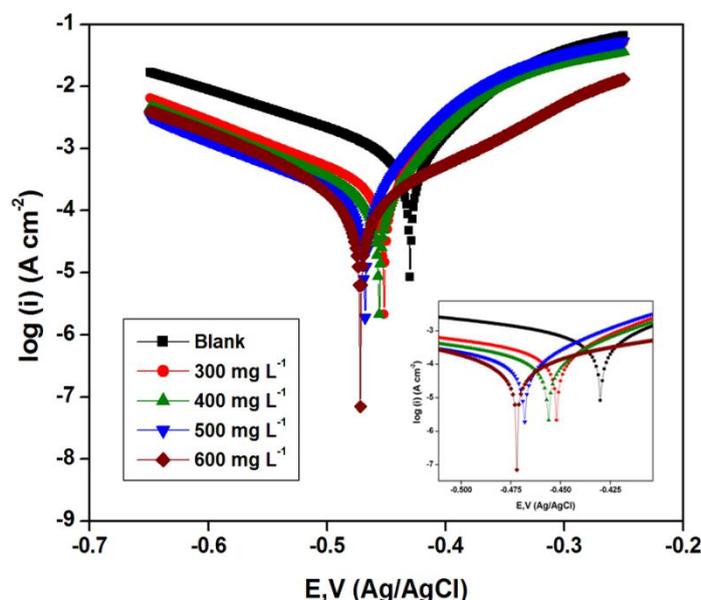
It was worth noting that increase in inhibition efficiency was achieved due to blockage of the active sites on mild steel surface by adsorbed inhibitor molecules. We tried to fit surface coverage data for many adsorption isotherms i.e. Langmuir, Temkin, Frumkin etc. but we found Langmuir isotherm most suitable (higher regression coefficient) to describe adsorption behavior of AMLE (Figure 2).

According to Langmuir isotherm model concentration of inhibitor  $C$  can be related with surface coverage  $\theta$  by following formula [29]:

$$\frac{C}{\theta} = \frac{1}{K} + c \quad (6)$$

Where  $K$  is parameter showing degree of interaction between inhibitor and steel.

### 3.2 Polarization Curves



**Figure 3.** Polarization curve plot for mild steel in 0.5 M sulfuric acid with different concentrations of AMLE . Inset: Zoom view of polarization curves.

Figure 3 shows polarization curves obtained for mild steel in 0.5 M  $H_2SO_4$  with various concentrations of inhibitor. It was found that presence of inhibitor shifted corrosion potential towards cathodic direction which can be clearly observed in figure shown in inset. Polarization curves are parallel in the cathodic region (Figure 3) which suggested that evolution of hydrogen (reduction reaction at cathode) was not much influenced by increasing inhibitor concentration. Change in anodic Tafel curves can be clearly observed from Figure 3 which showed that inhibition was achieved mainly due to reduced mild steel dissolution in acid.

Details of the results are listed in Table 1. From inspection of the data it was noticed that  $E_{corr}$  values were shifting in presence of AMLE. Maximum shift, with respect to blank solution, was obtained as 42 mV for 600 mg  $L^{-1}$  inhibitor concentration which indicated that both anodic and cathodic reactions were suppressed by addition of inhibitor [30,31]. It was observed that corrosion rate (proportional to  $I_{corr}$ ) was reduced with increasing AMLE concentration. Initially corrosion current was

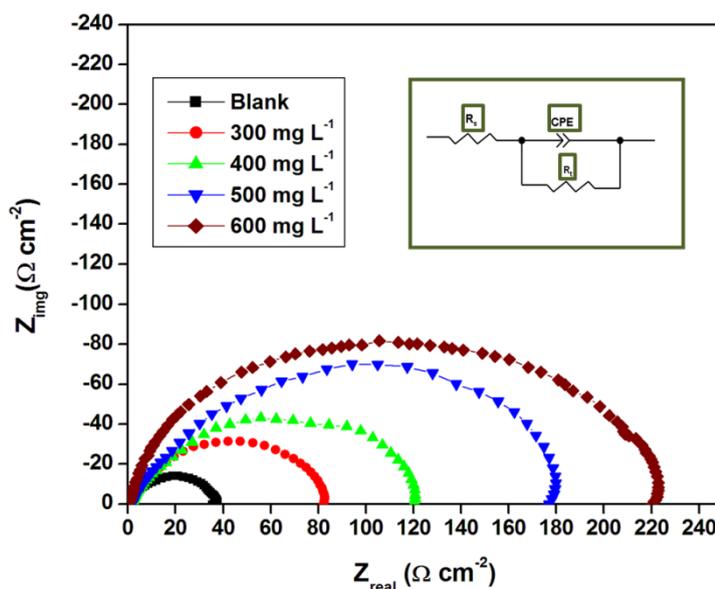
1138  $\mu\text{A cm}^{-2}$  which was effectively reduced (145  $\mu\text{A cm}^{-2}$ ) at maximum inhibitor concentration used in the study. The influence of inhibitor was also reflected from changing values of  $b_a$  and  $b_c$  although no specific pattern was noticed in slope values which supported mixed type inhibition. Maximum inhibition efficiency (87%) was acknowledged at 600  $\text{mg L}^{-1}$  inhibitor concentration.

**Table 1.** Parameters obtained from polarization curves at different concentration of inhibitor for 0.5 M sulfuric acid.

Concentration ( $\text{mg L}^{-1}$ )	-E <sub>corr</sub> (mV, Ag-AgCl)	I <sub>corr</sub> ( $\mu\text{A cm}^{-2}$ )	$b_a$ (mV dec <sup>-1</sup> )	$b_c$ (mV dec <sup>-1</sup> )	$\mu_p$ %
Blank	430	1138	93	62	-
300	452	450	90	76	60
400	456	304	94	75	73
500	468	250	102	73	78
600	472	145	96	79	87

### 3.3 Impedance Spectroscopy

Results of the electrochemical impedance spectroscopy are shown in Figure 4. Plots obtained at every concentration followed same pattern and found in the shape of semicircles having depressed centre under x axis.



**Figure 4.** Nyquist plot for mild steel in 0.5 M sulfuric acid with different concentrations of AMLE . Inset: Electrochemical equivalent circuit.

From investigation of Nyquist plots it was found that diameters of the depressed semicircles were increased with amount of inhibitor used which indicated increased corrosion resistance of mild steel against acid. This type of behavior is commonly seen in the case of metal-acid interaction due to roughness and heterogeneity of the electrode surface [32-34]. An equivalent circuit is used (Figure 4 inset) to explain the corrosion inhibition process which is frequently used for iron-acid interface model. In this circuit  $R_s$  is used for solution resistance,  $R_t$  for charge transfer resistance and CPE for constant phase element. Impedance value of CPE depends upon surface factor  $n$ , magnitude of CPE  $Y$  and angular frequency  $\omega$  used for the study [35].

Addition of inhibitor affects the surface property of electrode and it can be effectively monitored by change in values of double layer capacitance  $C_{dl}$  at the acid-metal interface.  $C_{dl}$  values at different concentrations were calculated using formula given below [36]:

$$C_{dl} = (Y_0 \cdot R_t^{1-n})^{1/n} \quad (7)$$

Usually inhibitor retard the corrosion of metals and alloys by getting adsorbed on the electrode surface, forming a layer, due to which  $C_{dl}$  is affected and it can be monitored according to following relationship:

$$C_{dl} = \epsilon^0 \epsilon \frac{A}{t} \quad (8)$$

where  $\epsilon$  is dielectric constant of medium,  $\epsilon^0$  is dielectric constant of space,  $A$  is the area of the electrode surface and  $t$  is thickness of the layer formed at metal-acid interface.

**Table 2.** Nyquist plots obtained for mild steel in 0.5 M sulfuric acid with different concentration of inhibitor.

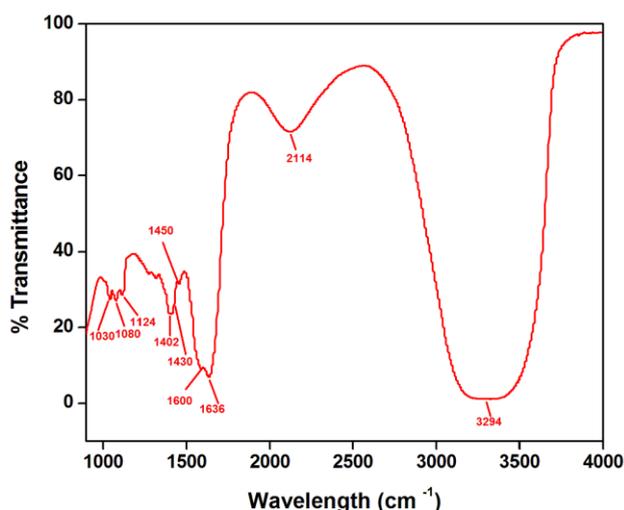
Concentration (mg L <sup>-1</sup> )	$R_s$ ( $\Omega$ cm <sup>2</sup> )	$R_t$ ( $\Omega$ cm <sup>2</sup> )	$n$	$Y_0$ ( $10^{-6}\Omega^{-1}\text{cm}^{-2}$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	$\mu_{Rt}$ %
Blank	1.25	37	0.808	198	61	-
300	1.32	83	0.810	154	55	56
400	1.28	120	0.815	132	51	70
500	1.70	180	0.820	113	48	80
600	1.82	220	0.824	89	39	84

We fitted data according to the circuit described above and results are shown in Table 2. From the inspection of data listed in Table 4 it was observed that values of charge transfer resistance were increased with increasing amount of AMLE. In sulfuric acid alone resistance ( $R_t$ ) was  $37 \Omega \text{ cm}^2$  which was increased up to  $220 \Omega \text{ cm}^2$  in presence of  $600 \text{ mg L}^{-1}$  AMLE. Further it was found that value of  $n$  increased, accompanying decrease in  $C_{dl}$  values, with concentration of inhibitor used. It suggested that surface roughness of mild steel decreased in presence of inhibitor due to adsorbed inhibitor molecules on mild steel surface and corrosion of mild steel in acid was inhibited because of increased thickness of film formed at metal-acid interface (Equation 8).

Maximum inhibition efficiency of 84% was achieved at 600 mg L<sup>-1</sup> AMLE concentration which was very close to the results of weight loss and Tafel polarization test. On the basis of the results obtained by this method it can be concluded that addition of inhibitor in corrosive solution retarded corrosion rate of mild steel due to increased charge transfer resistance accompanying decreased double layer capacitance.

### 3.4 Characterization of Extract

There were many compounds present in the AMLE which contributed in effective working of the inhibitor. It is very difficult to identify each compound separately although efforts have been made to know groups present in the AMLE.



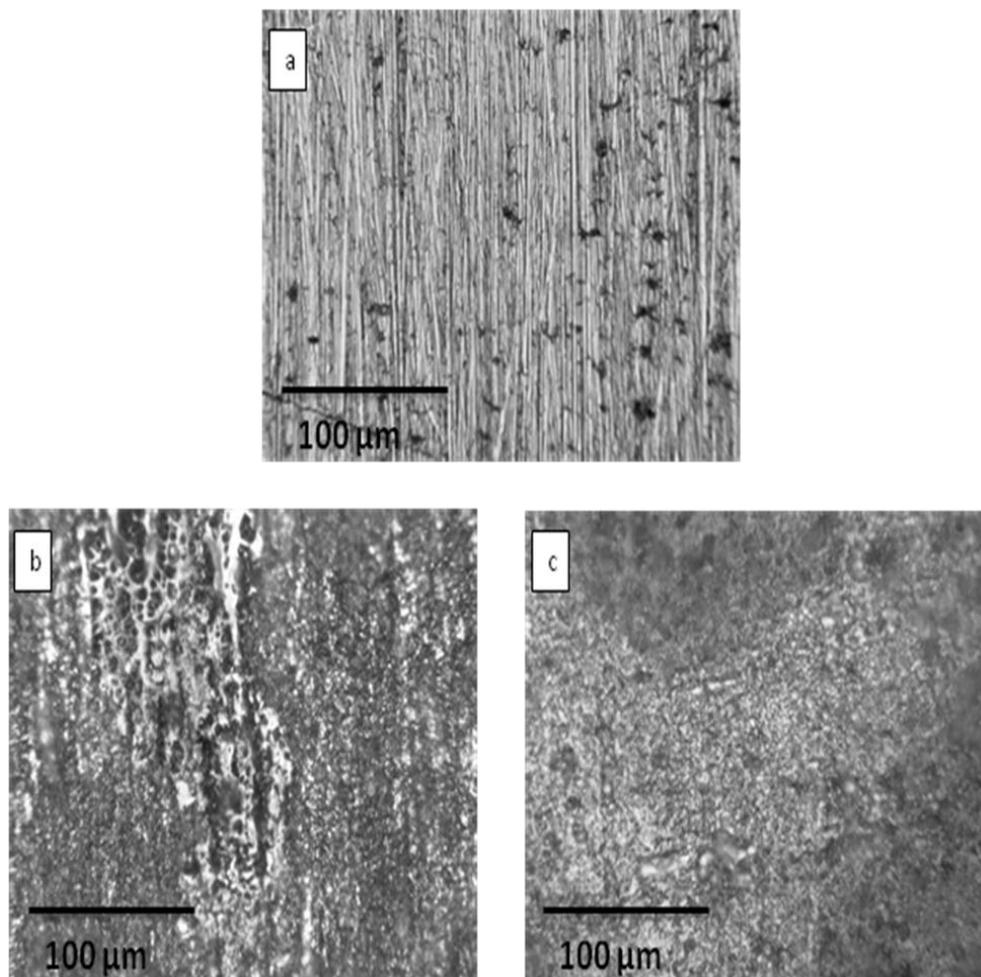
**Figure 5.** FT-IR spectra of aqueous leaf extract of *Argemone mexicana*

Figure 5 shows FT-IR spectra of the *Argemone mexicana* leaf extract (aqueous). Broad peak obtained at 3294 cm<sup>-1</sup> can be assigned to N-H or O-H stretching vibration. Absorption band at 2114 cm<sup>-1</sup> is related with N=C=S stretching vibration. Strong peak obtained at 1636 cm<sup>-1</sup> correspond to C=C or C=N stretching or N-H bending vibration. Absorption band at 1402 cm<sup>-1</sup> can be assigned to C-H bending in -CH<sub>3</sub> or O-H bending vibration. Peaks obtained at 1030 cm<sup>-1</sup>, 1080 cm<sup>-1</sup>, and 1124 cm<sup>-1</sup> are observed due to C-N and C-O stretching vibration. Few weak peaks can also be observed at 1430 cm<sup>-1</sup>, 1450 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> which correspond to C=C stretching vibrations of aromatic rings. On the basis of results it can be said that AMLE contain nitrogen and oxygen (N-H, N=C=S, C=N, C-N, O-H, C=O, C-O) in various functional groups and aromatic rings, which make this extract attractive for being used as inhibitor.

### 3.5 Surface Morphology

Figure 6a shows surface morphology of mild steel test coupon before immersion in H<sub>2</sub>SO<sub>4</sub> solution. Some scratches can be noticed on the surface, which are the results of grinding of the mild

steel surface with emery paper. Further Test coupon was immersed in 0.5 M  $\text{H}_2\text{SO}_4$  solution for 3 hours and surface morphology was captured (Figure 6b). Sulfuric acid interacted with mild steel aggressively and drastic change in surface morphology of mild steel was observed in comparison to morphology of test sample (Figure 6a). In contrast, a smooth and pits free surface can be seen in Figure 6c reflecting retarded mild steel corrosion in presence of inhibitor. On the basis of photomicrographs obtained for mild steel, it can be concluded that AMLE inhibited mild steel dissolution in acid by covering the surface area with protective film which was found absent in case of acid interaction with steel.



**Figure 6.** Photomicrograph obtained by optical microscope for Surface morphology of mild steel (a) abraded by emery paper (b) corroded in 0.5 M  $\text{H}_2\text{SO}_4$  and (c) in 0.5 M  $\text{H}_2\text{SO}_4$  with 600  $\text{mg L}^{-1}$  inhibitor concentration.

### 3.6 Corrosion Inhibition

Corrosion of iron in acid solutions involves mainly two reactions-Anodic reaction i.e. dissolution of iron in acid and Cathodic reaction i.e. evolution of hydrogen. Thus inhibition efficiency of the inhibitor depends upon the ability to retard these reactions.

AMLE is a mixture of various organic compounds [28] and contain nitrogen and oxygen in several functional groups present in the extract (FT-IR). These organic compounds (Saponins, Tannins, Flavonoids, amino acids etc) may exist in the corrosive solution either in protonated form or neutral form. It is well recognized fact that iron carries positive charge in the acid solution [37] which is extreme adverse condition for adsorption of protonated species on iron surface.  $\text{SO}_4^{2-}$  ions, getting specifically adsorbed on surface, increases adsorption of protonated moieties over steel surface acting like a bridge between protonated moieties and positively charged iron (Physical adsorption). Organic moieties may also adsorb on the mild steel surface chemically via electron sharing between inhibitor (N,O hetero atoms,  $\pi$  bonds from aromatic rings) and iron.

From the results of techniques used it was revealed that adsorption of inhibitor molecules over steel surface could be accounted for inhibitive performance of AMLE. Probably organic moieties present in AMLE formed some complex compounds, reacting with iron, which were stable in sulfuric acid environment. These compounds were adsorbed on the surface of mild steel forming a protective film at metal acid interface. This film acted like a barrier for acid solution and protected mild steel from further being corroded. This concept of inhibition was well supported by surface images (Figure 6c) and results of weight loss and electrochemical techniques. On the basis of facts discussed above it can be stated that AMLE inhibited acid corrosion of mild steel through adsorption of its effective constituents on mild steel surface.

#### 4. CONCLUSIONS

It was found that AMLE inhibited mild steel corrosion in sulfuric acid solutions effectively with maximum inhibition efficiency of 87% at  $600 \text{ mg L}^{-1}$  inhibitor concentration. Results of weight loss and electrochemical techniques indicated that blockage of the active sites on the surface was the reason of increased resistance of mild steel against corrosion. It was also found that inhibitor worked as a mixed type inhibitor retarding both anodic and cathodic reactions. Adsorption behavior of AMLE was studied and it was found to obey Langmuir isotherm model. Surface images of the mild steel surface clearly showed that AMLE inhibited corrosion of mild steel by getting adsorbed on the metal surface.

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