A Comparative Study of Inhibition Efficiency of Eco friendly Inhibitors *Aloe Barbedensis Miller* and *Aegle Marmelos* on the Corrosion of Mild Steel in 1M H_2SO_4

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Abstract

Corrosion inhibition of mild steel using extract from plant sources have been widely studied in different media. The aggressive nature of the acid solutions necessitates the use of inhibitors to reduce the corrosive damage on metals and alloys. Low-cost, environmental friendly and practical benefits of plant extracts make them the preferred choice for corrosion protection. A comparative study of the inhibitory effect of plant extracts *Aloe Barbedensis Miller* and *Aegle marmelos*, on the corrosion of mild steel in 1M H_2SO_4 medium is investigated by weight loss method, Gasometric measurement and Electrochemical methods (Potentiodynamic polarization,Ac impedance). On comparison, maximum inhibition efficiency is found to be 88% at 800 ppm in *Aloe Barbedensis Miller*. Gasometric studies reveals that the evolution of Hydrogen decreases as increase in the concentration of the inhibitor. Polarization method indicates these plant extracts behaves as a Cathodic-type inhibitor. The impedance method reveals that charge-transfer process mainly controls the corrosion of mild steel. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts.

Keywords: Mild steel, Aloe Barbedensis Miller, Aegle marmelos, Gasometric method ,AC impedance.

1.Introduction

Mild steel is a structural material widely used in automobiles, pipes and in most of the chemical industries. Mild steel suffers from severe corrosion in aggressive medium of acids and pickling processes. Though many synthetic compounds have shown good anticorrosive activity, most of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. Such inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system viz., kidney, liver, or to disturb a biochemical process or to disturb an enzyme system at some site in the body. The toxicity may manifest either during the synthesis of the compound or during its applications. Although the most effective and efficient organic inhibitors are compounds that have π bonds, the biological toxicity of these products, especially organic phosphate, is documented specifically about their environmental harmful characteristics. From the standpoint of safety, the development of non-toxic and effective inhibitors is considered more important and desirable, nowadays, which are also called eco-friendly or green corrosion inhibitors [1-10]. Aloe Vera is an important medicinal plant which belongs to the family of Liliacea. A more recent review concludes that the cumulative evidence supports the use of *Aloe barbadensis miller for* the healing of first to second degree burns.Internal intake of *Aloe barbadensis miller* has been linked with improved blood glucose levels in diabetes, and with lower blood lipids in hyper lipidaemic patients, also with acute hepatitis (liver disease).Aegle marmelos plants leaf, fruit and bark are widely used for many diseases. According to the verse in Agathiyar Gunavakadam, leaf, flower, and fruit are used for venereal diseases, ulcers and azoospermia.All parts of Aegle marmelos are medicinally useful like, leaves, fruit pulp,flower, stem bark, root bark, (Chopra et al ., 1956, 1968;

Kirtikar and Basu, 1986; Anonymous, 1986; 1968). Root and stem bark are used as antipyretic. Decoction of the root, root- bark and sometimes the stem-bark is useful in intermittent fever, also in hypochondriacs, melancholia and palpitation of the heart (Nadkarani, 1927). In this study, ethanolic extracts of two medicinal plants,namely, *Aloe barbadensis miller and Aegle marmelos* have been selected to study the inhibition effect on the corrosion of mild steel in 1M H_2SO_4.

2. Materials and Methods

2.1Qualitative Phytochemical Analysis

The Bioactive compounds were analysed by the qualitative tests for the solvent extracts. It was screened for alkaloids, flavonoids, saponins, phenolic compounds, tannins, steroids,terpenoids, alkaloids, carbohydrates, proteins, anthraquinone, polyphenol and glycosides by using standard procedures[11, 12, 13].

2.2 Weight loss measurements

The pretreated specimens' initial weights were noted and were immersed in the experimental solution with the help of glass hooks. The experimental solution used was 1 M H_2SO_4 in the absence and presence of various concentrations of the two inhibitors. After two hours, the specimens were taken out, washed thoroughly with distilled water, and dried completely, and their final weights were noted. From the initial and final weights of the specimen, the loss in weight was calculated and tabulated. From the weight loss, the Corrosion rate (mpy), Inhibition efficiency (%), and Surface coverage (θ) of plant extracts were calculated using the formula.

Corrosion Rate =87.6 × W (mpy) /A × T × D

Corrosion Inhibition Efficiency

(IE) = $100[1-(W_2/W_1)]$ %

2.3 Gasometric Experiments

Gasometric technique is based on the principle that corrosion reactions in aqueous media is characterised by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion [14]. The rate of evolution of the gas (RV_H) is determined from the slope of the graph of volume of gas evolved (V) versus time (t),

$RV_H=\Delta V/\Delta T$

and the inhibitor surface coverage (θ) and efficiencies (η%) determined using below equation equations

$$\Theta = \frac{RV_{H(blank)} - RV_{H(inhibitor)}}{RV_{H(blank)}}$$

$$\eta\% = \frac{RV_{H(blank)} - RV_{H(inhibitor)}}{RV_{H(blank)}} \times 100\%$$

where RV_{Hblank} and RV_{Hinh} are the rate of hydrogen evolution in the absence and presence of the inhibiting molecules, respectively.

2.4 Electrochemical Impedance Spectroscopy

Electrochemical measurements were run using a Potentiostat/galvanostat (Electrochemical system Model Vertex.100mA.D) and a personal computer was used. IVIUM software was used for Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization (PDP) analysis. The EIS measurements were carried out using AC signals of amplitude 10 m V peaks-to-peaks at the open circuit potential in the frequency range of 10 MHz to 1Hz.The charge transfer Resistance (R_{ct})values have been calculated from the difference in the impedance at low and high frequencies.The capacitances of the double layer (C_{dl}) values are estimated from the frequency (f) at which the imaginary component of the impedance (-Z") is maximum and the double layer capacitance (C_{dl}) was calculated by using following equation:Obtained from the equation:

$$C_{dl} = ½ \times 3.14 \times R_{ct} \times f_{max}$$

2.5 Potentiodynamic Polarization

After impedance spectrum was obtained, the potentiodynamic current potential curves was recorded immediately by changing the electrode potential automatically taken from OCP value with scan rate of 5 m V /S [3].Tafel lines extrapolation method was used for detecting I_{corr} and E_{corr} values for the studied systems.

2.6 Scanning Electron Microscope

Surface morphological study of the uninhibited and inhibited mild steel samples were sent to SEM analysis[4][5].

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3.Results and Discussion

3.1Phytochemical Screening :

Table 3.1 : The phytochemical screening of *Aloe Barbadensis Miller* and *Aegle Marmelos* bark extract was done with ethanol.

Name of the phytochemicals	*Aloe Barbadensis miller*	*Aegles Marmellos*
Tannin	+	-
Saponin	+	+
Flavonoids	+	+
Steroids	-	+
Terpenoids	+	-
Triterpenoids	+	-
Alkaloids	-	-
Carbohydrates	-	-
Protein	+	-
Glucoside	+	-

Table 3.2: Corrosion rate of mild steel in 1M H_2SO_4

	Aloe Barbadensis miller			*Aegle Marmelos*		
Conc. (ppm)	**C.R (mpy)**	**Ɵ**	**% I.E**	**C.R (mpy)**	**Ɵ**	**% I.E**
Blank	118	-	-	53.7	-	-
400	62	0.38	38	-	-	-
500	50	0.58	58	31.8	0.45	45
600	42	0.65	65	27.9	0.48	48
700	31	0.74	74	24.1	0.55	55
800	19	0.84	84	20.3	0.62	62
900	-	-	-	16.4	0.71	71

CR-Corrosion Rate,Ɵ –Surface Coverage
ABM-Aloe Barbedensis Miller
AM-Aegle Marmelos

3.2Mass loss Measurements

3.2.1Effect of Inhibitor Concentration

The mass loss method of monitoring corrosion rate is useful because of its simple application and reliability[31].Inhibition efficiency of mild steel with different concentration of *Aloe Barbadensis Miller* and *Aegle Marmelos* bark extract in 1M H_2SO_4 at room temperature are presented in Table 3.2.From the table, it is clear that the corrosion rate decreases with an increase in inhibitor concentration. *Aloe Barbadensis Miller* shows the maximum Inhibition Efficiency of 84% at 800ppm and *Aegle Marmelos* shows the maximum Inhibition efficiency of 71% at 900ppm. The results show that ABM and AM effectively restrains the acid corrosion of mild steel in the acid environments.

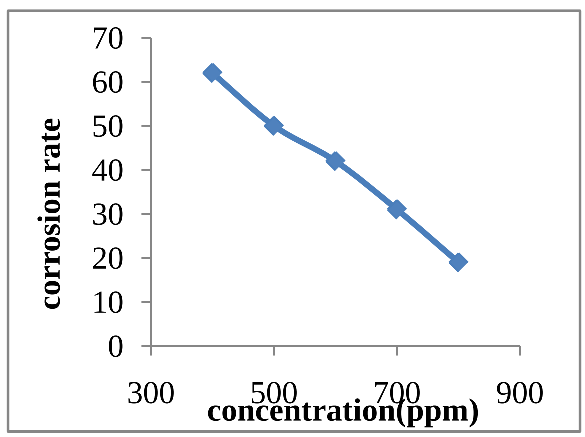

Fig3.2a.Corroion rate of *Aloe Barbadensis miller* at different concentration.

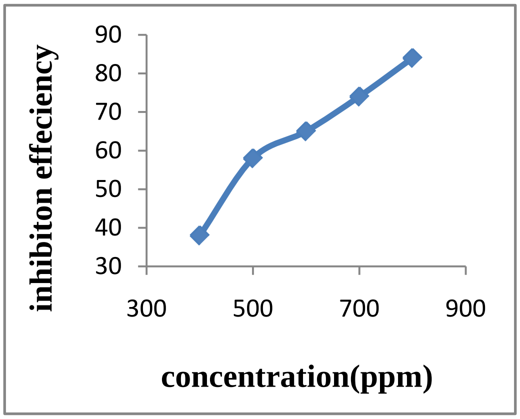

Fig 3.2a:Inhibion efficiency of *Aloe Barbadensis miller* at different concentration.

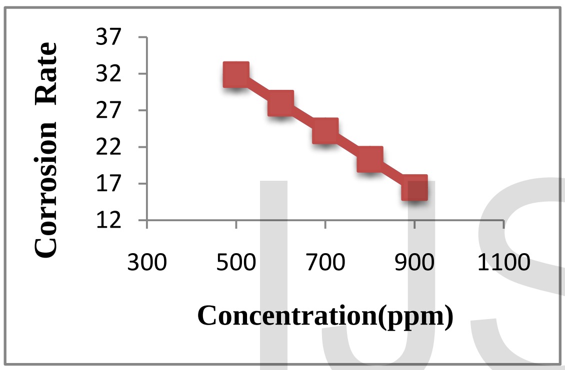

Fig 3.2b: Corrosion rate of *Aegles Marmelos* at different concentration.

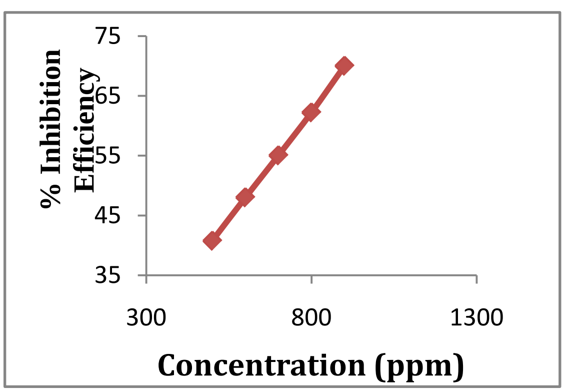

Fig3.2b.Inhibition efficiency of *Aegle Marmelos* at different concentration.

3.3Gasometric Measurments

The rate of Hydrogen gas evolution in various concentration of *Aloe Barbadensis Miller* and *Aegle Marmelos* for mild steel in 1M H_2SO_4 are displayed in Table.3.3a & 3.3b and also in Fig 3.3a and 3.3b.The inhibition efficiency and surface coverage values are increased as the concentration of inhibitor increases. The maximum inhibition efficiency was found to be 88.75%. at 800 ppm for ABM and 78 % at 900ppm for AM inhibitor. The rate of gas evolution is equivalent to the rate of corrosion. During corrosion reaction therate of anodic reaction is equal to the rate of cathodic reaction, because all electrons released in the anodic half reactions are used up in the cathodic half reaction. Hence the rate at which gas is evolved at the cathode is the measure of the corrosion of the mild steel specimen.FromFig.3.3a &3.3b,It is seen that the volume of hydrogen gas evolved is found to be reduced on addition of different concentration of ABM and AM inhibitor at different intervals of time. This indicates that inhibit the corrosion of mild steel in 1M H_2SO_4.

Table 3.3a:Evolution of Hydrogen gas using gasometry technique for *Aloe Barbadensis Miller*

Conc (ppm)	Time (mins)	H_2 Evolution	ΔV/ΔT	Surface Coverage (Θ)	% I.E
Blank	15	13.3	0.88	-	-
400	30	10.65	0.710	20	0.20
500	45	8.1	0.540	39.12	0.39
600	60	6.39	0.420	58	0.52
700	75	4.65	0.310	65	0.65
800	90	3	0.200	77.45	0.77
900	105	1.5	0.099	88.75	0.89

Table3.3b:Evolution of Hydrogen gas using gasometry technique for *AegleMarmelos*

Conc (ppm)	Time (min s)	H_2 Evolution	ΔV/ΔT	(Θ)	% I.E
Blank	15	13	0.86	-	-
500	45	11	0.74	13.95	0.14
600	60	9.1	0.61	29.10	0.29
700	75	7	0.46	46.51	0.46
800	90	4.9	0.33	62	0.62
900	105	2.8	0.19	78	0.78

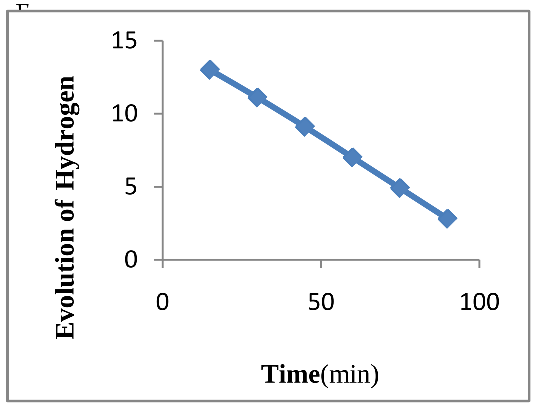

Fig.3b : Evolution of Hydrogen gas at different time intervals of *Aegle Marmelos*

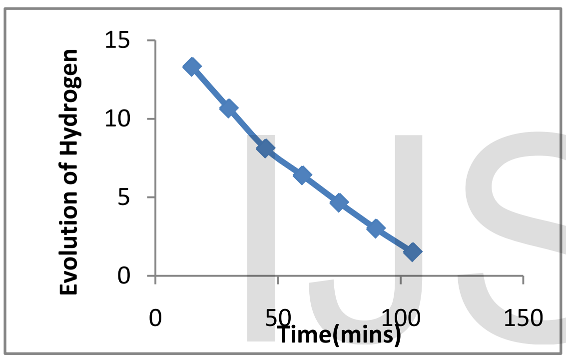

Figure 3.3a: Evolution of Hydrogen gas at different time intervals of*Aloe Barbadensis miller*.

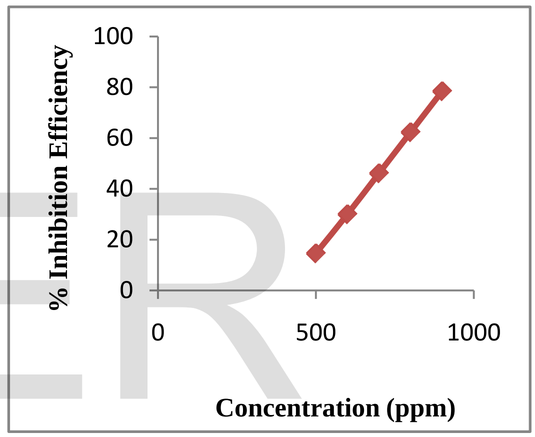

Fig 3.3b:Inhibtion efficiency of *Aegle Marmelos*

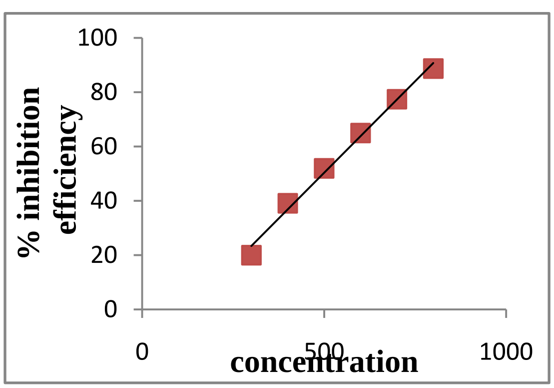

Fig 3.3a. Inhibition efficiency of *Aloe Barbadensis miller*

3.4 Elecrochemical Impedance Spectroscopy

Impedance measurements were studied to Evaluate the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), through these parameters, the inhibition efficiency was calculated. Figure 3.4a& 3.4bshows the impedance diagrams for mild steel in 1M H_2SO_4at optimum concentration of ABM and AM, the impedance parameters derived from these investigations are given in Table 3.4.As noticed from Figure 3.4a &3.4b, the obtained impedance diagrams are almost in a semicircular appearance, indicating

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that the charge-transfer process mainly controls the corrosion of mild steel. In the presence of the plant extracts, the values of R_{ct} have enhanced and the values of double-layer capacitance are also brought down to the maximum extent. The decrease in C_{dl} shows that the adsorption of the inhibitors takes place on the metal surface in acidic solution. For *Aloe Barbedensis Miller* extract, the maximum R_{ct} value of 63.37 Ω cm²and minimum C_{dl} value of 2.083X10^{-7}μF/cm²are obtained at an optimum concentration of800ppm.Likewise for *AegleMarmelos* extract, the maximum R_{ct}value of 31.87Ωcm² and minimum C_{dl} value of 9.876×10^{-9}μF/cm² are obtained at an optimum concentration of 900ppm.

Table3.4a&b:EIS Parameters of ABM & AM in 1M H_2SO_4

	Aloe Barbadensis miller		
System	**R_s Ω**	**R_{ct} Ω cm^2**	**C_{dl} F cm^{-2}**
Blank	10.55	11.37	6.597X 10^{-5}
Inhibitor	45.44	63.37	2.083X10^{-7}
	Aegle Marmelos		
System	**R_s Ω**	**R_{ct} Ω cm^2**	**C_{dl} F cm^{-2}**
Blank	14.92	5.428	1.238X 10^{-7}
Inhibitor	6.352	31.87	9.876X10^{-9}

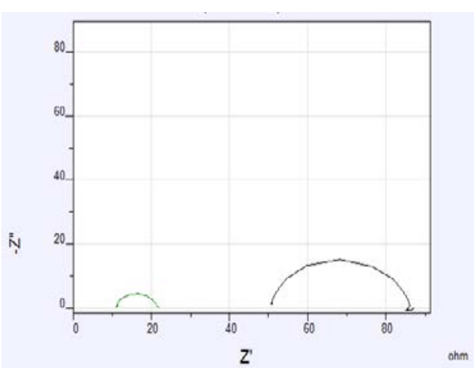


Fig 3.4a.Nyquist plot in absence and presence of optimum concentration of *Aloe Barbadensis.*

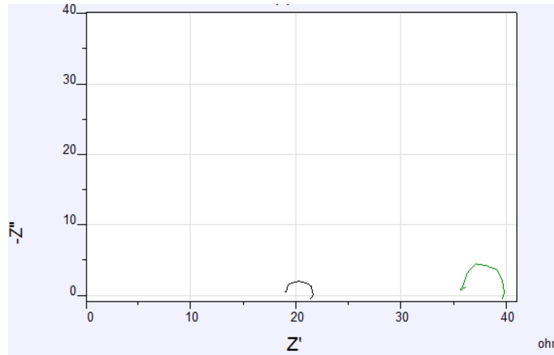


Fig.3.4bNyquist plot in absence and presence of optimum concentration of *Aegles Marmelos*.

3.5 Linear Polarization Measurement:

The inhibition behaviour of *ABM &AM* in 1 M H_2SO_4 in the presence and absence of the inhibitor at optimum concentration are calculated by linear polarization Parameters and are given in Table.3.6.The efficiency found by linear polarization shows good agreement with efficiency obtained from Tafel and EIS data.in the presence and absence of the inhibitor at optimum concentration are calculated by linear polarization Parameters and are given in Table.3.6The efficiency found by linear polarization shows good agreement with efficiency obtained from Tafel and EIS data.

3.6 Potentiodynamic Polarization Measurements

The potentiodynamic polarization behaviour of mild steel in 1M Sulphuric acid in the absence and in the presence of *Aloe Barbedensis Miller* and *Aegle marmelos* is shown as Tafel plot in fig.3.6.The various electrochemical potentiodynamic parameters such as corrosion potential(E_{corr}),corrosion current density (I_{corr}),anodic and cathodic slope (β_a and β_c) are calculated from Tafel plots and the values are listed in Table.3.6. The decrease in the corrosion current on the addition of the inhibitor indicates that both extracts functions as an inhibitor and reduces the corrosion of mild steel in acidic medium. The shift in the E_{corr} value to a more negative value indicates that the inhibitor functions as cathodic inhibitor. In both the cases the cathodic slope is found to change from 146 mV/dec to 130 mV/dec and 102mV/dec to 116mV/dec and the anodic slope is found to change from 502mV/dec to 519 mV/dec and 302 mV/dec to 350mV/dec respectively.This shows that the inhibitor controls both the anodic and cathodic reactions but predominantly behaves as cathodic inhibitor[15].

Table 3.6. The potentiodynamic polarization and linear polarization parameters of ABM & AB

	Aloe Barbadensis miller				
System	**E_{corr} m V /SCE**	**I_{corr} µA cm^{-2}**	**β_a m V /dec**	**β_c**	**R_p**
Blank	-547	441	502	146	15.0
Inhibitor	-565	107	519	130	67.4
	Aegle Marmelos				
System	E_{corr} m V /SCE	I_{corr} µA cm^{-2}	β_a m V /dec	β_c	R_p
Blank	-532	488	302	102	118
Inhibitor	-540	452	350	116	157

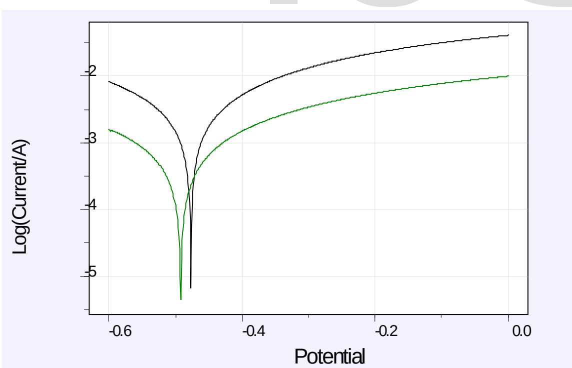


Fig3.6a: Tafel polarization curves for corrosion product of mild steel in 1M H_2S0_4 in the absence and presence of *Aloe Barbadensis Miller*.

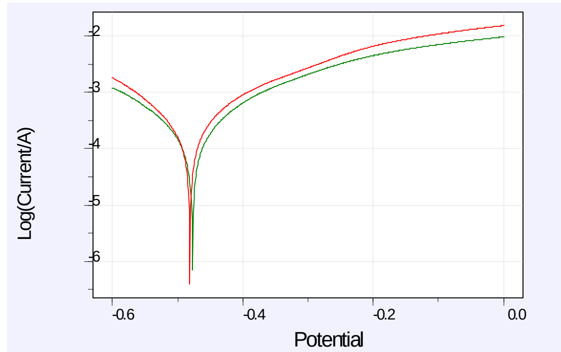
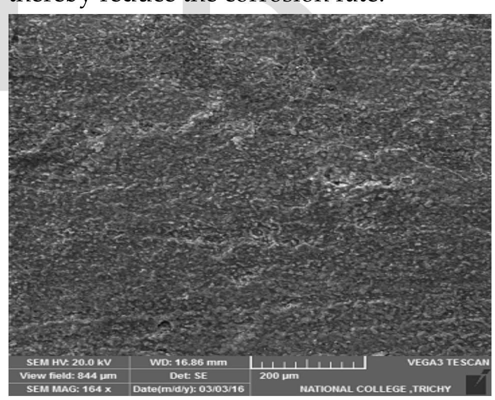


Fig 3.6b: Tafel polarization curves for corrosion product of mild steel in 1M H_2SO_4 in the absence and presence of *Aegle Marmelos*.

3.7 SEM Analysis

The SEM mages were recorded to establish the interaction of inhibitor molecule with metal surface .Figure 3.7.represents the SEM images of (a) mild steel immersed in 1M H_2SO_4, (b)&(c) mild steel immersed in the presence of ABM & AM in 1 MH_2SO_4.Result shows that the phytochemical constituents present in the inhibitors form a protective layer of the mild steel specimen and thereby reduce the corrosion rate.



(a)

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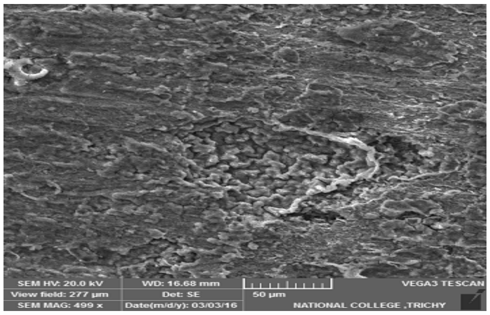
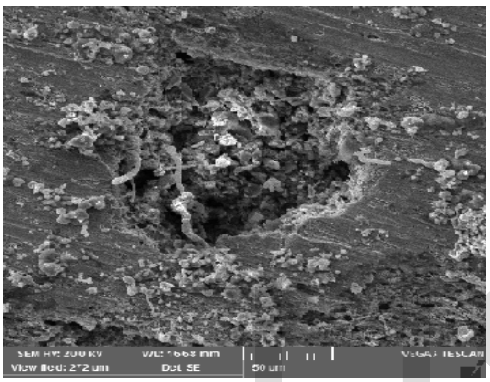


(b)



(c)

4.Conclusion

The leaf extracts of *Aloe Barbedensis miller* and *Aegle marmelos* act as good and efficient inhibitors for corrosion of mild steel in 1M Sulphuric acid. Potentiodynamic polarization studies revealed that the extracts act as cathodic type inhibitor. The Nyquist diagrams obtained in impedance method revealed that charge-transfer process mainly controls the corrosion of mild steel. The mechanism involved in this study is the phytochemical constituents in the plant extracts that have adsorbed on the mild steel surface forming a protective thin film layer preventing the discharge of H^+ ions and dissolution of metal ions and has prevented the small corrosion on the surface of the metal. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts. Gasometry study reveals the amount of hydrogen evolution. From the decrease in the evolution of H_2,it can be concluded that the efficiency of the inhibitor increases with concentration.Results obtained in weight loss method were very much in good agreement with the electrochemical methods and gasometric method in the order*Aloe Barbedensis miller*> *Aeglemarmelos* .Among the two plant extracts studied, the maximuminhibition efficiency was found in *Aloe Barbedensis miller*which showed 84% inhibition efficiency at 800 ppm.

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