Centella asiatica extracts as green corrosion inhibitor for mild steel in 0.5 M sulphuric acid medium

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ABSTRACT

The leaf extracts of centella asiatica(CE) was tested as green corrosioninhibitor for mild steel in 0.5 M H_2SO_4 by using gravimetric, polarization and electrochemical impedance spectroscopy (EIS) measurements. The data obtained from all the three methods are in good agreement with each other. Results indicate that leaf extracts of CE is a good green corrosion inhibitor for mild steel corrosion in 0.5 M H_2SO_4 solution. The inhibition efficiency was found to increase with increase in CE extracts concentration. A maximum inhibition efficiency of 95.08% was observed for 1200 ppm at 303K. Polarization measurements showed that the CE extracts acts as mixed type of inhibitor.Temperature studies revealed a decrease in inhibition efficiency with increase in temperature which suggests physisrption mechanism. The adsorption characteristics of CEextracts of on mild steel surface obeys Langmuir isotherm. Both kinetic and thermodynamics adsorption parameters were calculated and discussed,and SEM was used to analyse the surface adsorbed film.

Key words: Mild steel, Gravimetric, Polarization, Electrochemical impedance, SEM
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INTRODUCTION

Mild steel is extensively used in many industries such as automobiles, pipes and chemical industries. However, the metal corrodes when it comes in contact with acid solutions during process called acid cleaning or pickling [1, 2]. Sulphuric acid is widely used as a pickling acid for iron and its alloys to remove undesirable corrosion products. These problems can be resolved by introducing appropriate inhibitor to the medium.Organic compounds containing nitrogen and sulphur are usually employed as corrosion inhibitors for iron and steel in acidic solutions due their rapid action [3-10]. Extracts of naturally occurring products contain mixtures of compounds having oxygen, sulphur and nitrogen are eco-friendly, cheap, renewableand ecologically anticorrosion substances [11, 12]. The successful uses of naturally occurring substances to inhibit the corrosion of metals in various environments have been reported by several researchers [13-23].

Centella asiatica belongs to the family, apiaceae. The herb is known as Brahmi in unani medicine, Mandookaparani in ayurvedia and is valued in Indian system of medicine for improving memory,nervine disorder and skin diseases [24]. It is reported to contain triterpene acids(asiatic, terminolic, centic, centillic, centoic acid), alkaloids (hydrocotylin), volatile fatty oils (glycerides of palmitic, stearic, lignoceric, oleic, linoleic and linolenic acids), glycosides (asiaticoside A, asiaticoside B, madecassoside, centellic acid)and flavonoids (3-glucosylquercetin, 3-glucosylkaempferol and 7-glucosylkaempferol) [25-27].However,*CE* has not beenexploited as corrosion inhibitor for mild steel in sulphuric acid medium. In view of its phytochemical investigation, the present paper reporting for the first time the inhibitive performance of *CE* extract as an eco-friendly corrosion inhibitor for mild steel in sulphuric acid medium by using gravimetric, polarisation and electrochemical impedance spectroscopy (EIS) methods.

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MATERIALS AND METHODS

1.1. Materials

Corrosion tests were performed on mild steel having the following composition (in wt %) 0.016 P, 0.322 Si, 0.01 Al, 0.062 Cr, 0.05 Mn, 0.09 C, 0.05 Sand the remainder iron. Prior to gravimetric and electrochemical measurements, the surface of the specimens was polished under running tap water using SiC emery paper (grade 220-600), rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for 5 s, dried and immersed in acetone for 5 s, and dried with clean tissue paper. Finally, the specimens were kept in desiccators until use. At the end of the test, the specimens were carefully washed with acetone and benzene, dried, and then weighed.

Fresh *Centella asiatica* leaves were collected in and around Mysore city, India, cleaned with water and then dried in an oven at 70 ^{0}C and ground to powder. The 10 g of the powder sample was refluxed in 250 mL ethyl alcohol for 5 h. The refluxed solution was filtered and the filtered liquor was evaporated to 100 mL dark green residue, and extracted with separating funnel. The solution was evaporated and the dark green solid residue obtained after complete drying was preserved in a desiccator. The residue so obtained was used in preparing different concentrations of the extracts in 0.5 M H_2SO_4 solution.

2.2. GravimetricMeasurements

Pre-weighed mild steel coupons with a dimension of $2 \times 2 \times 0.3$ cm were immersed in 200 ml 0.5 M $H_2SO_4$with and without the addition of different concentrations of *CE* extracts in an aerated condition. After 6 h of immersion, the specimens were taken out, washed, dried and weighed accurately. Experiments were carried out in triplicate. The average weight loss of the three parallel specimens was obtained. Relative weight losses of the coupons were used to calculate the percent inhibition efficiency (η%). Then the tests were repeated with different concentrations of *CE* at varying temperatures.

From the weight loss, the corrosion rate (mg cm^{-2} h^{-1}), inhibition efficiency (η %), and surface coverage (θ) of plant extracts was calculated using the formula,

$$C_R = \frac{\Delta W}{St} \qquad\qquad (1)$$

$$\eta\% = \frac{(C_R)_a - (C_R)_p}{(C_R)_a} \times 100 \qquad\qquad (2)$$

Where ΔW is the weight loss (mg), tis the immersion time (h), S is the surface area of the specimen in (cm^2), $(C_R)_a$and $(C_R)_p$ are corrosion rate in the absence and presence of *CE* extract respectively.

2.3. Electrochemical Measurements

Polarization and Electrochemical impedance spectroscopy (EIS) experiments were carried out using a CHI660D electrochemical workstation. A conventional three-electrode cell consisting of a saturated calomel reference electrode, a platinum auxiliary electrode and the working electrode with 1cm^2 exposed areas were used. The specimens were pre-treated similarly as done in the gravimetric measurements. The electrochemical tests were performed using various *CE* extracts concentrations ranging from 0 to 1200 ppm at 30 ^{0}C using a thermostatically controlled water bath (Weiber, India) under aerated condition. Potentiodynamic polarization measurements were performed in the potential range from -900 to +500 mV with a scan rate of 0.4 mV s^{-1}.

Inhibition efficiency can be calculated from the electrochemical measurements by the following equation:

$$\eta\% = \frac{(I_{cor})_a - (I_{cor})_p}{(I_{cor})_a} \times 100 \qquad\qquad (3)$$

where $(I_{cor})_a$ and $(I_{cor})_p$are the corrosion current density in the absence and presence of inhibitor, respectively. The corrosion potential (E_{cor}) and corrosion current density (I_{cor}) were calculated by extrapolation of anodic and cathodic Tafel slopes.

The electrochemical AC-impedance measurements were also performed using a CHI660D electrochemical workstation. Experiments were carried out in a conventional three-electrode cell assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude of 10mV was superimposed on the steady open circuit potential. The real part (Z_{re}) and the imaginary part (Z_{im}) were measured at various frequencies in the range of 100 KHz to 10MHz. The experiments were carried out in the absence and presence of different concentrations of the inhibitor. The percentage of inhibition efficiency was calculated using following equation:

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$$\eta\% = \frac{(R_{ct})_a - (R_{ct})_p}{(R_{ct})_a} \times 100 \qquad\qquad (4)$$

where $(R_{ct})_a$ and $(R_{ct})_p$ are the charge transfer resistance in the absence and presence of inhibitors.

2.4. Scanning Electron Microscopy

The SEM analysis was performed using a JSM-5800 electron microscope with the working voltage of 20 kV and the working distance 24 mm. In SEM macrographs, the specimens were exposed to the 0.5 M sulphuric acid in the absence and presence of inhibitors under optimum conditions after a desired period of immersion. The SEM images were taken for polished mild steel specimen and specimen immersed in solution without and with inhibitors.

RESULTS AND DISCUSSION

1.2. Effect of Temperature

To assess the effect of temperature on corrosion and corrosion inhibition process, gravimetric experiments were performed at different temperatures (30 - 60 °C) in the absence and presence of various concentrations of the inhibitor during 6 h of immersion. The results are given in Table 1.

Table 1: C_R and $\eta\%$ obtained from weight loss measurements of mild steel in 0.5 M H$_2$SO$_4$ containing various concentrations of *CE* extract at different temperatures

C ppm	Temperature							
	30 °C		40 °C		50 °C		60 °C	
	C_R mg cm^{-2}h^{-1}	$\eta\%$	C_R mg cm^{-2}h^{-1}	$\eta\%$	C_R mg cm^{-2}h^{-1}	$\eta\%$	C_R mg cm^{-2}h^{-1}	$\eta\%$
0	1.991	-	4.158	-	7.713	-	15.403	-
200	0.311	84.38	0.961	78.73	2.192	71.58	6.621	57.01
400	0.251	87.39	0.822	81.81	2.011	73.93	6.312	59.02
600	0.209	89.50	0.741	83.60	1.905	75.30	5.532	64.08
800	0.159	92.01	0.571	87.36	1.693	78.05	4.949	67.87
1000	0.098	95.08	0.442	90.22	1.365	82.30	4.843	68.56
1200	0.061	96.94	0.333	92.63	1.143	85.18	4.655	69.78

From the Table 1, it is clear that, the C_R increases with increasing the temperature in the absence of the inhibitor. However, this increase seems slightly in presence of the *CE* extracts (Fig.1).
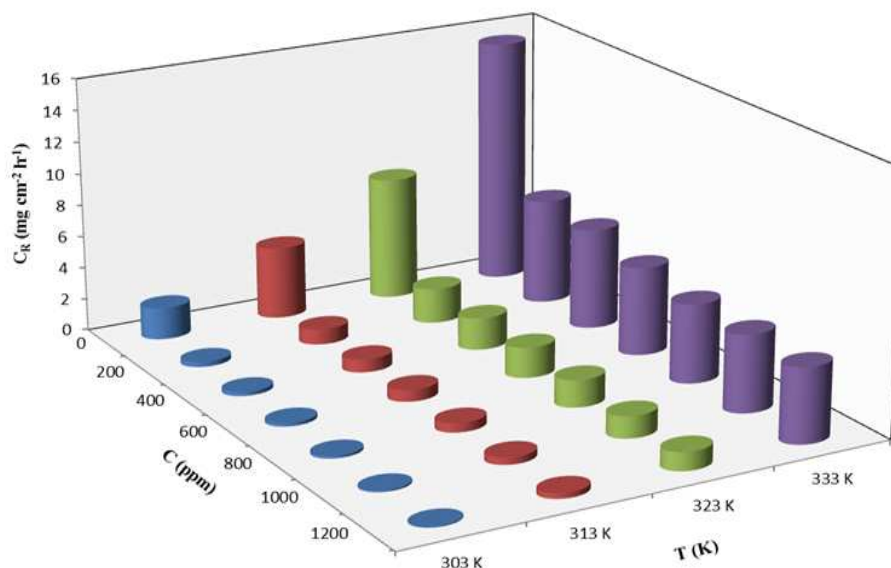

Fig. 1. Variation of C$_R$ of mild steel as a function of temperature and concentration of *CE* extracts.

The relationship between the corrosion rate (C_R) of mild steel and temperature (T) can be expressed by the Arrhenius equation,

$$C_R = k \exp\left(-\frac{E_a^*}{RT}\right) \qquad\qquad (5)$$

where E_a* is the activation energy, k is the pre-exponential constant, R is the universal gas constant and T is the absolute temperature. Using Eq. (5), and from aplot of the log C_R versus 1/T (Fig. 2), the values of E_a* and k at various concentrations of *CE* extracts were computed from slopes and intercepts, respectively and the values are given in Table 2.

Table 2: Activation parameters for mild steel in 0.5 M H₂SO₄ in the absence and presence ofdifferent concentrations of *CE* extract

C ppm	E_a^* kJ mol⁻¹	ΔH^* kJ mol⁻¹	$\Delta H = E_a^* - RT$ kJ mol⁻¹	ΔS^* J mol⁻¹K⁻¹
0	56.01	53.37	53.16	-62.90
200	84.04	81.37	81.16	-44.39
400	88.83	86.18	85.98	-44.17
600	90.63	88.00	87.78	-43.67
800	96.12	93.47	93.27	-42.48
1000	106.84	104.20	103.99	-42.19
1200	117.83	115.20	114.98	-41.06

The activation energy increases with increase in the concentration of the inhibitor. Generally, the inhibitive additives cause a rise in activation energy value when compared to the blank solution. The change of the values of the apparent activation energies may be due to the modification of the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [28] and could be often interpreted as an indication for the formation of an adsorbed film on metal surface [29,30].
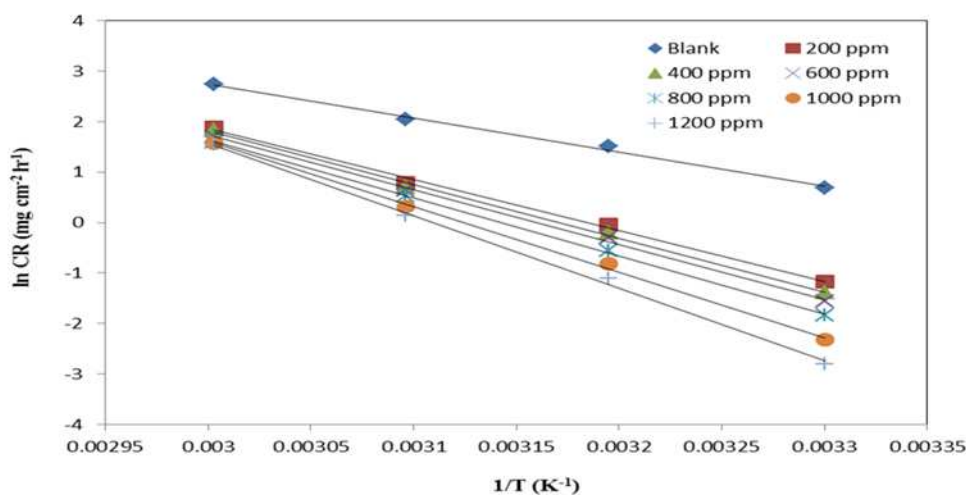

Fig. 2. Arrhenius plots for mild steel immersed in 0.5 M H₂SO₄ solution in the absence and presence of different concentration of *CE* extracts.

The values of enthalpy and entropy of activation can be calculated from the alternative form of Arrhenius equation as follows:

$$C_R = \frac{RT}{Nh} exp\left(\frac{\Delta S_a^*}{R}\right) exp \left(\frac{-\Delta H_a^*}{RT}\right)$$ (6)

where h is Planks constant, N is Avogadro's number, ΔS_a^* is the entropy of activation, $\Delta H_a^*$is the enthalpy of activation. Plots of log (C_R / T) versus 1/ T gave straight lines (Fig. 3) with a slope of $(-\Delta H_a^*/ 2.303R)$ and an intercept of [log (R/Nh) + ΔS_a^* / 2.303R] from which the values of $\Delta H_a^*$and ΔS_a^* were calculated and are listed in Table 2. The ΔH_a^*values obtained from the slope of Eq. (6) and those values calculated from the equation, $\Delta H_a^* = E_a^* - RT$ are in good agreement with each other.

The positive values of ΔH_a^* both in the absence and presence of inhibitor reflect the endothermic nature of mild steel dissolution process[31]. The negative values of ΔS_a^*obtained indicate that the activated complex in the rate determining step represents an association rather than dissociation, means that decrease in the disorder of the system due to the adsorption of inhibitor molecule on to the metal surface [32].This reveals the formation of an ordered stable layer of inhibitor on the steel surface [33].
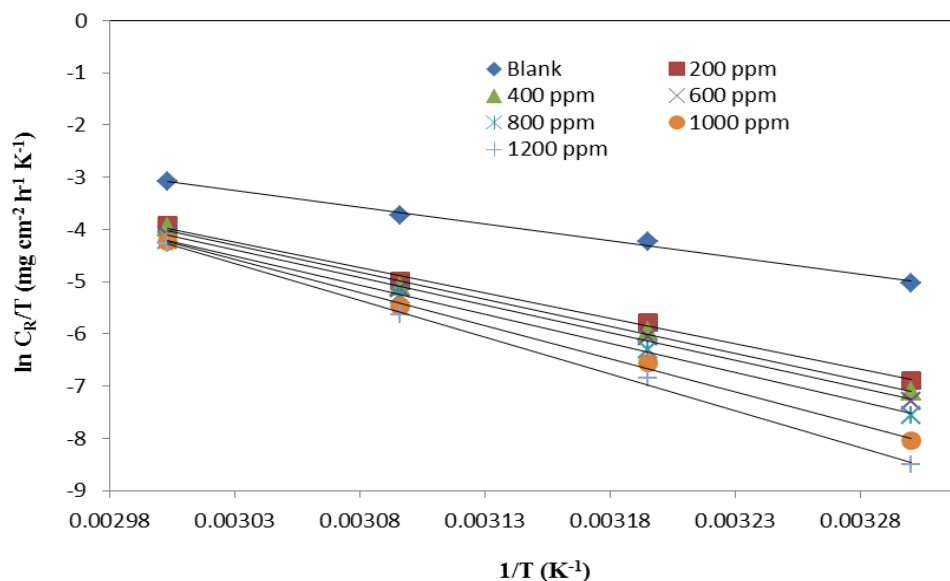
Fig. 3. Alternative Arrhenius plots for mild steel immersed in 0.5 M H₂SO₄ solution in the absence and presence of different concentration of *CE* extracts.

1.3. Adsorption Isotherm

The interaction between the inhibitors and steel surface can be provided by the adsorption isotherm. During corrosion inhibition of mild steel, the nature of inhibitor on the corroding surface has been deduced in terms of adsorption behaviour of inhibitors.

Many attempts were made to find the best isotherm which describes this study. Langmuir adsorption isotherm was found to be the best description for adsorption *CE* extract on mild steel. According to this isotherm, θ is related to the inhibitor concentration, *C*, and adsorption equilibrium constant K_{ads}, via:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + c \qquad\qquad\qquad (7)$$

The plot of *C/θ* versus *C* gave a straight line (Fig. 4) with a slope close to unity confirming that the adsorption of *CE* extracts on mild steel surface in sulphuric acid obeys the Langmuir adsorption isotherm. According to Langmuir adsorption isotherm there is no interaction between the adsorbed inhibitor molecules, and the energy of adsorption is independent on the degree of surface coverage (θ). Langmuir isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site occupies one adsorbed species.

Table 3: Thermodynamic parameters for adsorption of *CE* leaves extract on mild steel in 0.5 M H₂SO₄ solutions at different temperatures from Langmuir adsorption isotherm

Temperature (K)	R^2	K_{ads} (L mol⁻¹)	ΔH_{ads} (kJ mol⁻¹)	ΔH_{ads} (kJ mol⁻¹)	ΔS_{ads} (J mol⁻¹ K⁻¹)	$\Delta G = \Delta H_{ads} - T\Delta S_{ads}$
303	0.999	18.02	-17.40			-17.41
313	0.999	14.20	-17.36	-19.24[a]	-6.04[a]	-17.35
323	0.995	11.36	-17.31	-19.26[b]	-6.10[b]	-17.29
333	0.998	9.03	-17.21			-17.23

[a] *values obtained from Eq. (10)*   [b] *values obtained from Eq. (11)*

The equilibrium adsorption constant, K_{ads} is related to the standard Gibb's free energy of adsorption (ΔG_{ads}) with the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left[\frac{-\Delta G_{ads}}{RT}\right] \qquad\qquad (8)$$

Where 55.5 is the concentration of water in solution (mol L⁻¹), R is the universal gas constant and *T* is the absolute temperature. The enthalpy and entropy of adsorption *(ΔH_{ads} and ΔS_{ads})* can be calculated using the equations (9) and (10).

$$\ln K_{ads} = \ln\left(\frac{1}{55.5}\right) - \frac{\Delta G_{ads}}{RT} \qquad\qquad (9)$$

$$\ln K_{ads} = \ln\frac{1}{55.5} - \frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \qquad\qquad (10)$$

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Using Eq. (10), the values of ΔH_{ads} and ΔS_{ads} were evaluated from the slope and intercept of the plot of $\ln K_{ads}$ versus $1/T$ (Fig. 5). The values of ΔG_{ads}, ΔH_{ads} and ΔS_{ads} are listed in Table 3.
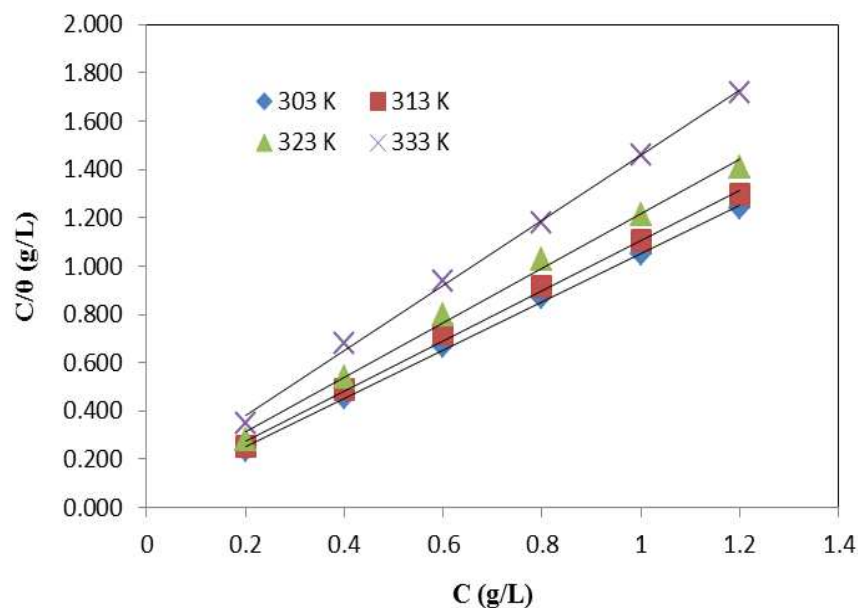
Fig. 4.Langmuir adsorption isotherm plot for the adsorption of various concentrations of *CE* extracts onthe surface of mild steel in 0.5 M H₂SO₄ solution.
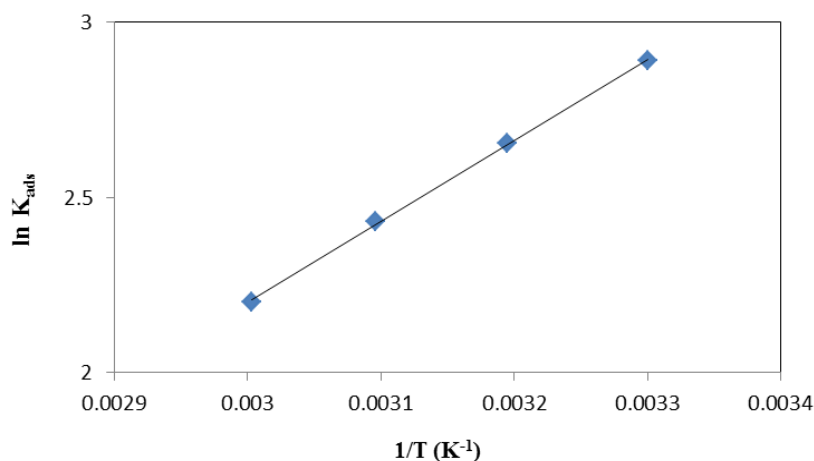
Fig. 5.Plot of lnK_ads versus 1/T.

The negative values of standard free energy of adsorption ΔG_{ads} confirm the spontaneity of adsorption process [34, 35] and stability of the adsorbed layer on the steel surface. Itis seen that the calculated ΔG_{ads} values, is ranging from about -17.21 to -17.40 kJ mol^{-1}, indicating that the adsorption mechanism of the *CE* extract on mild steel surface in 0.5 M H₂SO₄ solution as physisorption [36].

The values of ΔH_{ads} and ΔS_{ads} can also be calculated by using following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (11)$$

Using Eq. (11),the plot of ΔG_{ads} versus T gives a straight line with a slope of **-** ΔS_{ads} and intercept of ΔH_{ads}. The values obtained are correlated with those obtained from Eq. (10).
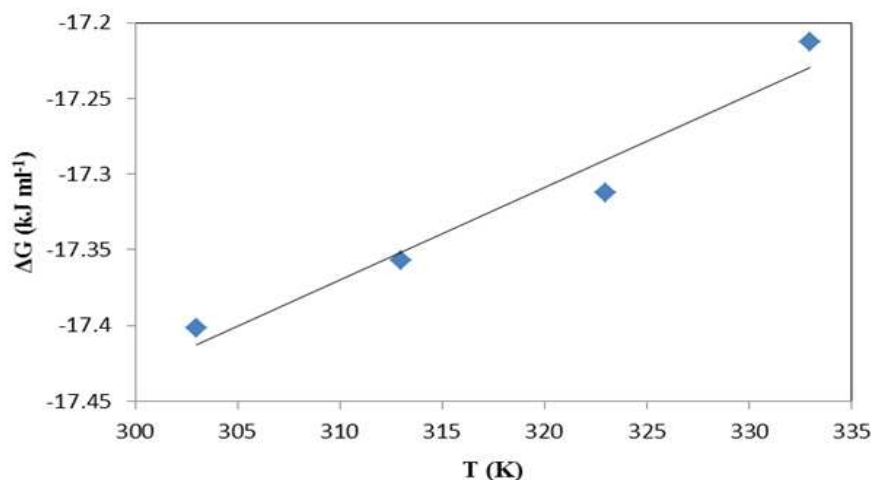
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Fig. 6.Plot of ΔGads versus absolute temperature.

The negative values of *ΔHads* mean that the dissolution process is an exothermic phenomenon [37]. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [38]whereas endothermic process corresponds to chemisorption [39]. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of *ΔHads.* For physisorption process,the value of *ΔHads*is lower than 40 kJ mol^{-1} while the heat of adsorption for chemisorption process is approaches to 100 kJ mol^{-1}[40]. In the present study, the heat of adsorption is -19.24 kJmol^{-1} postulates that a physisorption is more favoured. The negative values of ΔS_{ads} implies that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [41].

3.3. Polarization Study

Potentiodynamic polarization curves obtained for mild steel in 0.5M sulphuric acid at various concentrations of *CE* extracts ranging from 200 ppm to 1200ppm are shown inFig.7.It can be observed that the addition of *CE* extracts at all the studied concentrations decreased the anodic and cathodic current densities and resulted in significant decline in the I$_{cor}$. This indicates that *CE* extracts shifted to smaller I$_{cor}$ values in both anodic and cathodic branches of the curves, thus, acting as a mixed-type inhibitor [42] and the decrease is more pronounced with the increase in the inhibitor concentration. By comparing polarization curves in the absence and in the presence of various concentrations of *CE* extracts, it is observed that, increase in concentration of the inhibitor shift the corrosion potential (E$_{cor}$) in the positive direction and reduces both anodic and cathodic process [43].
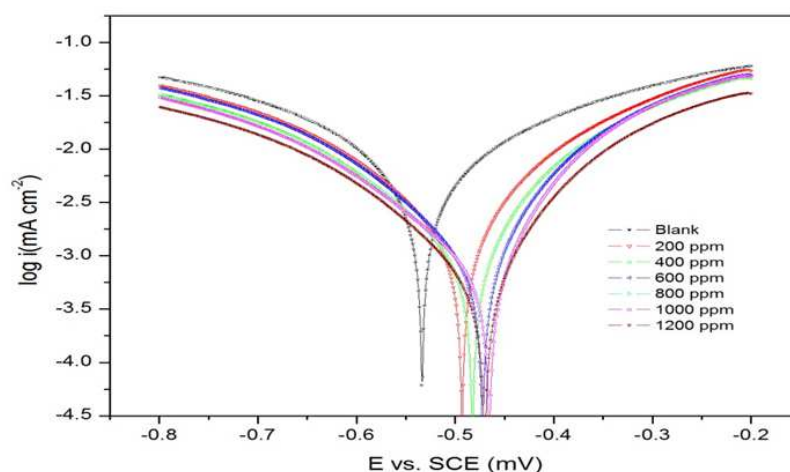

Fig. 7. Potentiodynamic polarization curves for mild steel in 0.5 M H$_2$SO$_4$ solution in the absence and presence of different concentration of *CE* extracts at 30 ºC.

Table4: E_{cor}, I_{cor},R_{ct}**and**η**% obtained from polarization and impedance measurements for mild steel in 0.5 M H_2SO_4 containing various concentrations of *CE*extract at 30 ^{0}C**

C ppm	EIS		Polarization		
	R_{ct} Ω cm^2	η%	E_{cor} mV	I_{cor} mA cm^{-2}	η%
0	34.3	-	-549	3.954	-
200	185	81.46	-487	0.781	80.25
400	310	88.94	-481	0.509	87.13
600	425	91.93	-475	0.365	90.77
800	550	93.76	-471	0.235	94.06
1000	590	94.19	-468	0.217	94.51
1200	695	95.06	-470	0.152	96.16

3.4. Electrochemical Impedance Study

The effect of the inhibitors concentration on the impedance behaviour of mild steel in 0.5 M H_2SO_4solution has been studied and the results are given in Fig. 8.The impedance spectra show a single semicircle and as the concentration of inhibitor increases diameter of the semicircle increases. It is evident from the results that *CE* extracts inhibited the corrosion of mild steel in 0.5 M H_2SO_4 at all the concentrations used, and the *η%* increased continuously with increasing concentration at 30 ºC, and the maximum *η%* of 95.06was observed at 1200 ppm of *CE* leaves extracts(Table 4). The results indicate that the R_{ct} significantly increases with increase in concentration of inhibitor and C_{dl} tends to decreases. This decrease in C_{dl} may probably due to decrease in local dielectric constant and/or an increase in the thickness of a protective layer at electrode surface which enhances the corrosion resistance of the mild steel [44]. The increase in R_{ct} values is attributed to the formation of protective film at the metal-solution interface [45-46]. These observations suggest that *CE* leaves extracts function by adsorption at the metal surface thereby causing decrease in C_{dl} values and increase in R_{ct} values.
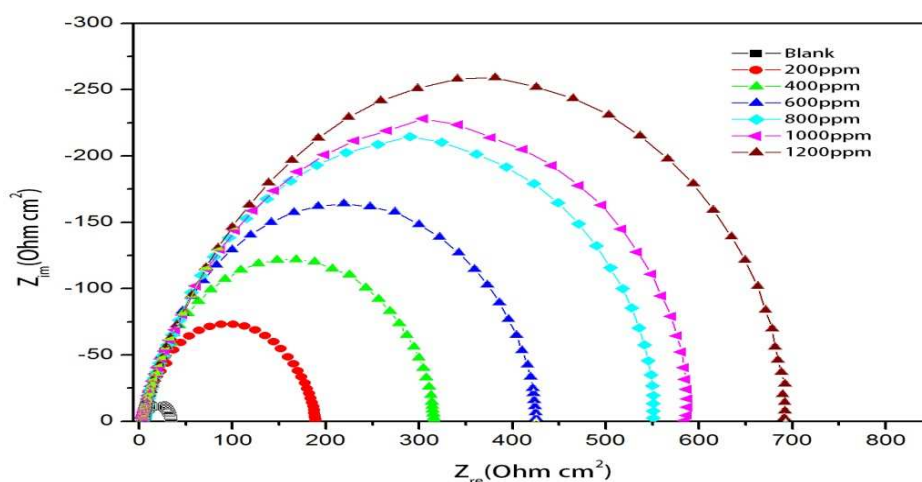

Fig. 8. Electrochemical impedance diagrams for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of different concentration of *CE* extracts at 30 ºC.

3.5. Scanning Electron Microscopy

The protective layer that formed on the metal surface was characterized by SEM analysis. Morphologies of mild steel in the absence and presence of optimum concentration of *CE* extracts at 30 ºCare shown in Figs. 9a -9c. It can be seen from Fig. 9athat the mild steel samples before immersion seem smooth. Inspection of Fig. 9b reveals that the mild steel surface after immersion in uninhibited 0.5 M sulphuric acid for 6 h shows an aggressive attack of the sulphuric acid on the steel surface. The corrosion products appear very uneven and lepidoteral-like morphology, and the surface layer is rather rough. In contrast, in the presence of 1200 ppm *CE* extract (Fig. 9c) there is an adsorbed film on mild steel surface exposed to 0.5 M sulphuric acid solution containing *CE* extract, which do not exist in the Fig. 9b. In accordance, it might be concluded that the adsorption film can efficiently inhibit the corrosion of steel.
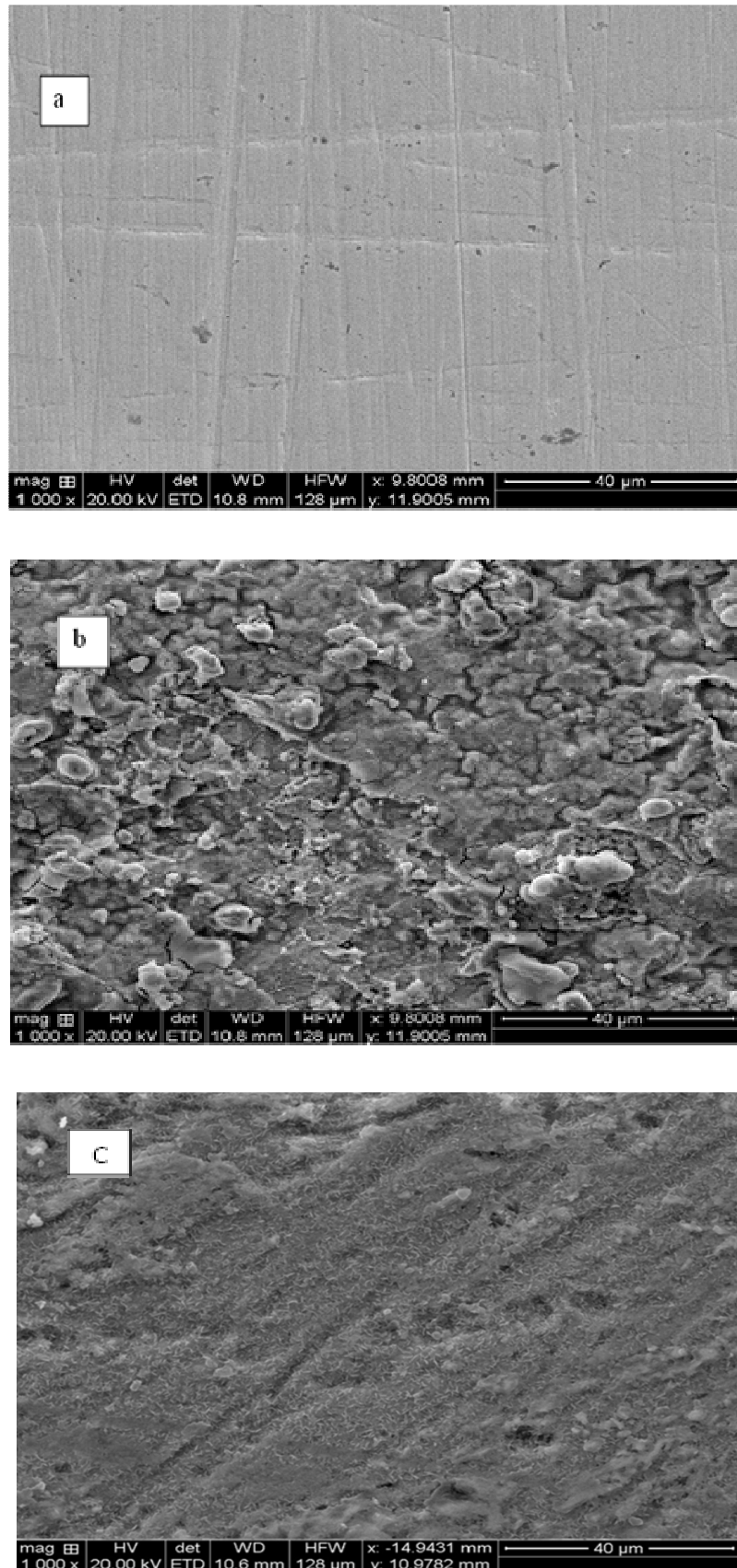
Fig. 9. SEM images of Mild steel in 0.5M H₂SO₄ after 6 h immersion at 30°C (a) before immersion (polished) (b) without inhibitor (blank) (c) with 1200 ppm *CE* extracts.

CONCLUSION

➢ *CE* extracts is a good inhibitor for the mild steel corrosion in 0.5 M H_2SO_4 solution showing 97% inhibition efficiency at 1200 ppm concentration. The results obtained from three different techniques viz., gravimetric, polarization and EIS were in good agreement with each other.

➢ Tafel polarization curves show that the *CE* extracts acted as mixed-type inhibitor.

➢ Electrochemical impedance measurements indicated that corrosion inhibition occurred by adsorption process.

➢ The adsorption of *CE* extracts at mild steel-acid solution interface obeyed the Langmuir adsorption isotherm model.

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