Non-Electrochemical Study of Mild Steel Corrosion Inhibition in Sulphuric Acid Solution by Using the Cuscuta Reflexa Extract

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Abstract

The anticorrosive effect of *Cuscuta reflexa Roxb. e*xtract (CRRE) on the mild steel corrosion in 0.5 M H_2SO_4 employing weight loss measurements. Weight loss measurement shows that inhibitor exhibited the best inhibition efficiency of 92.58 at optimum concentration. The inhibition action of inhibitor is discussed in view of blocking the metal electrode surface by mean of adsorption of the indicator molecules following the Langmuir adsorption isotherm. Scanning electron microscopy (SEM) displays that the inhibitor formed protective film over the mild steel surface. Weight loss measurement as well as SEM, indicate that CRRE can efficiently protect the mild steel from corrosion in 0.5 M H_2SO_4.

Keywords: Adsorption · Corrosion inhibition · Mild steel · CRRE

1. Introduction

In acidic media the study of mild steel corrosion inhibition has become important because of its increased industrial applications involving descaling, pickling, chemical cleaning, and acid oil-well acidizing. The study of mild steel corrosion inhibition involving green inhibitors in acidic media such as HCl and/or H_2SO_4 is one of the challenging topic of recent research. Application of green inhibitors is the most efficient and useful technique to control the corrosion process [1-3]. Organic compounds are widely used as corrosion inhibitors in acidic media. Although these organic inhibitors shows high inhibition efficiency, but their uses are limited because of their toxicity and cost of application [4, 5]. Most of the well-known organic inhibitors contain nitrogen, oxygen, sulphur and phosphorus elements and pi-electrons. The formation of protective layer on metal surface is due to adsorption of inhibitor molecules. The adsorbed inhibitor film protect the metals from corrosive attack by blocks the active sites present on metal surface. Various researches suggest that the adsorption of these inhibitor molecules on metal surface depends on the physico-chemical properties of the donor atoms. Usually adsorption takes place due to interaction of unoccupied d-orbitals of the metal with non-bonded electrons and/or pi-electrons of inhibitors [21-34]. Among the corrosion inhibitors, plant extracts possess the abundant phytochemical components of significant potential as cheap, inoffensive and renewable source of a wide range of organic molecules. The extracts of *Artemisia pallens* [6], *Glycine max* [7], *Coconut coir* [8], *Bamboo leaves* [9] *Mentha rotundifolia* [10], *Camellia sinensis* [11], *Musa paradisiac* [14] *Calotropis Gigantiea* [15] *Alstonia angustifolia var. latifolia* [17] and *black pepper* [19] have been reported as good mild steel corrosion inhibitors in acidic media (HCl, H_2SO_4). From these studies it is concluded that the inhibition performance of plant extract is usually attributed to the presence of complex organic molecules. Alkaloids, carbohydrates, tannins, proteins, amino acids, and nitrogen bases are mainly present in composition of plant extract as complex organic species. These complex organic compounds contain polar functional groups containing O, N, S, P as well as pi-bonds in their structure. These groups are the major adsorption centers on the metal surface.

Cuscuta reflexa Roxb. is a leafless coiling stem parasite having pale white flowers. The plant is found distributed throughout India as a condensed yellow wiry mass on trees and plants. The chemical constituents identified in *Cuscuta reflexa* plant are; Quercetin, Cuscutine, Cuscutamide, Amarbelin, Kaempferol and Reflexin [35]. *Cuscuta reflexa* plant is also well known for its medicinal uses such as anticancer, antibacterial etc. [36, 37]. Inhibition action of CRRE on corrosion behaviour of mid steel in 0.5 M H_2SO_4 has been investigated through weight loss techniques. Mild steel surfaces are examined with scanning electron microscope (SEM). The aim of this study is to evaluate the inhibitive effect of CRRE as a green corrosion inhibitor of mild steel in 0.5 M H_2SO_4.

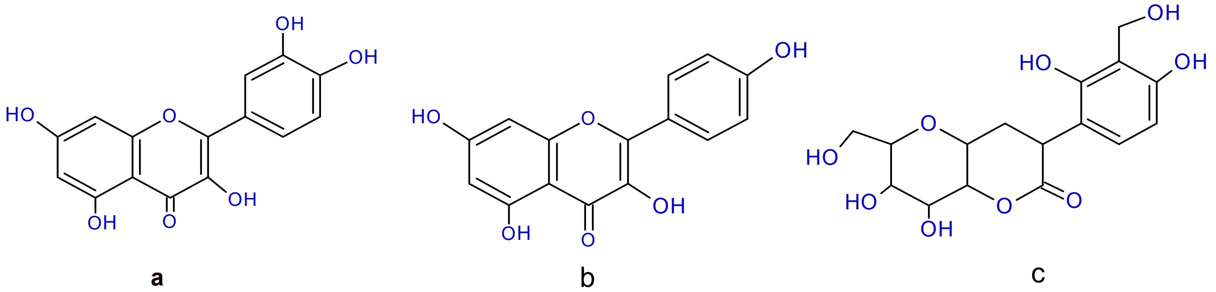


Fig. 1 The chemical structure of (a) Quercetin, (b) Kaempferol and (c) Cuscutin

2. Experimental

2.1 Electrode preparation

Mild steel of following composition were used for the gravimetric and electrochemical analysis:

Medium	Composition (wt %)						
	Fe	**C**	**O**	**P**	**S**	**Cr**	**Mn**
Mild steel (MS)	98.30	0.21	0.29	0.02	0.03	0.61	0.54

The surface of mild steel specimens (size 5cm x 2cm x 0.1 cm) were abraded using different grade of emery grit papers (600-1200 grits) before the measurement. The mild steel was cleaned by washing with millipore water and acetone respectively, then kept in dried desiccator before immersing in the corrosive medium.

2.2 Electrolytic solution

For the corrosion study corrosive solution, 0.5 M H_2SO_4 was prepared by dilution of analytical grade H_2SO_4 (Merck) of predetermined normality with purified water obtained from Elix essential 10 millipore water purifier. 1.0 - 3.0 g L^{-1} concentration range of the CRRE was used for each experiment.

2.3 Preparation of inhibitor

Fresh *Cuscuta reflexa roxb.* was collected and washed with millipore water for elimination of dust and soil, than shade dried for few days. This dried *Cuscuta reflexa roxb.* was powdered into small pieces and 500g of the powdered was extracted in boiled millipore water for 4h. The extracted solution then filtered using whatmann filter paper and concentrated until the water from the extract evaporates using rotary evaporator at 40°C. Finally the high viscous dark brown liquid was obtained which is used to study the corrosion inhibition property on mild steel. This brown liquid was used to prepare the required concentrations of inhibitor solution.

2.4 Weight loss measurements

Weight loss studies were carried out to study the effect of addition of different concentrations of CRRE on the mild steel corrosion in 0.5 M H_2SO_4 at temperature range 298-328K. The test specimens were weighed and suspended in 100 ml electrolytic solution for 24 h in the absence and presence of various concentration of inhibitor at studied temperatures. After immersion time the mild steel specimens were picked out, cleaned with millipore water, and dried in hot air oven for 5 minutes. The specimens were weighed using METTLER TOLEDO electronic balance (sensitivity up to 0.0001gm). The corrosion rate (ρ) in mg cm^{-2} h^{-1} of CRRE were calculated from the following equation [7]:

$$\rho = \frac{\Delta W}{At} \qquad (3)$$

Where ΔW is the weight loss in mg, A is the total area of metal specimen in cm^2, and t is the immersion time (24 h). Inhibition efficiency (*%I*) of CRRE was calculated from the following equation:

$$\%I = \left(\frac{\rho^1-\rho^2}{\rho^1}\right) \times 100 \qquad (4)$$

Where ρ^1 and ρ^2 are the corrosion rates of the test specimens in the absence and presence of inhibitor, respectively.

2.5 SEM analysis

The surface morphology of mild steel specimens were examined using SEM analysis. SEM micrographs were taken to establish the protective film formed on the mild steel surface. Also the changes in morphology of the mild steel surface in the absence and presence of mild steel surface were studied using SEM. Scanning electron microscope ZEISS EVO SEM 18 model 20mm Detector Oxford used for SEM analysis.

3. Result and Discussion

3.1 Weight loss measurements

The weight loss measurements of inhibition efficiency (I %) and corrosion rate (ρ) is the useful because of the easiness of method. The inhibition efficiency and corrosion rate values for mild steel in 0.5 M H_2SO_4 solution at studied temperature (298-328K) in the absence and presence of CRRE are given in Table 1. It is revealed that inhibition efficiency of metal increases with the increase of CRRE. The maximum inhibition efficiency value of 92.58% obtained at the optimum concentration of inhibitor at 308 K. The decrease in corrosion is noticeable with increase in CRRE concentration, whereas high corrosion rate values observed with the rise in temperature for the 0.5 M H_2SO_4 solution. The presence of CRRE extract leads to increase the inhibition efficiency and decrease the corrosion rate as well. The inhibition efficiency increases because the extant of adsorption and the consequential coverage by the CRRE components on the mild steel surface increases as the inhibition concentration increased [2]. Fig. 2 and 3 shows the difference of the values of weight loss and surface coverage (θ) with concentration at the studied temperature. Variation of weight loss (g) with temperature show in Fig. 2 for corrosion of mild steel in 0.5 M H_2SO_4 in the presence and absence of different concentration of CRRE. It is seen that weight loss of mild steel increases as temperature increased.

Table 1 Corrosion parameters obtained from weight loss measurements of mild steel in 0.5 M H_2SO_4 at studied temperature in the absence and presence of different concentration of CRRE.

Temperature (K)	Concentration (g L^{-1})	Corrosion Rate ρ (mg cm^{-2} h^{-1})	Inhibition efficiency (% I)
298	0.0	0.653	-
	1.0	0.121	81.47
	1.5	0.106	83.76
	2.0	0.120	81.62
	2.5	0.103	84.22
	3.0	0.083	87.27
308	0.0	1.820	-
	1.0	0.580	68.13
	1.5	0.354	80.54
	2.0	0.298	83.62
	2.5	0.193	89.39
	3.0	0.135	92.58
318	0.0	3.252	-
	1.0	1.633	49.78
	1.5	1.046	67.83
	2.0	0.719	77.89
	2.5	0.575	82.31
	3.0	0.460	85.85
328	0.0	4.899	-
	1.0	3.139	35.91
	1.5	1.774	63.78
	2.0	1.421	70.99
	2.5	1.277	73.93
	3.0	0.952	80.56

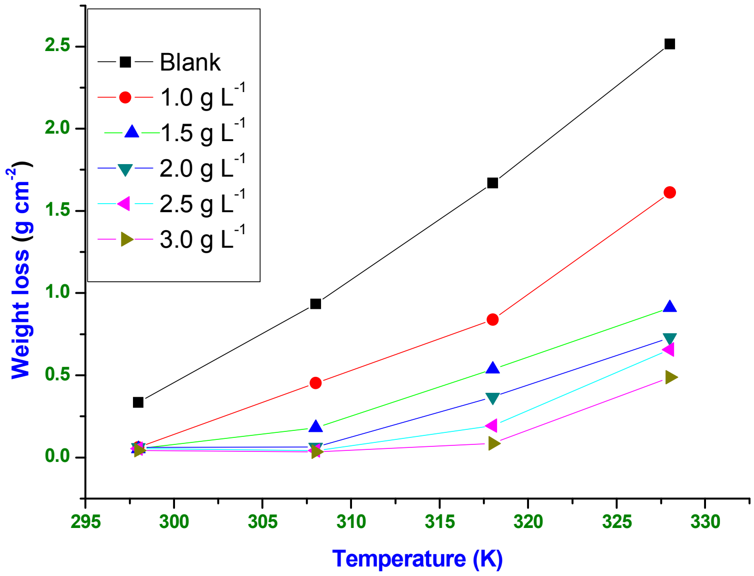


Fig. 2 Plot of weight loss against temperature for mild steel in 0.5 M H_2SO_4 at different concentrations.

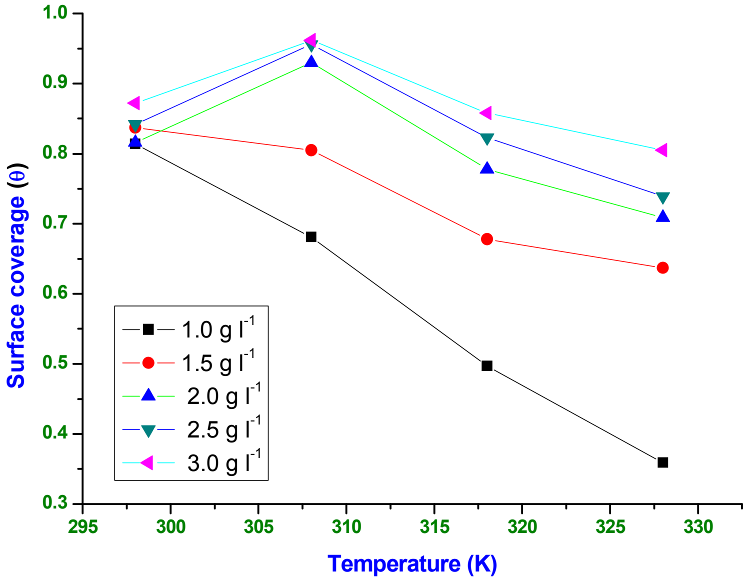


Fig. 3 Plot of surface coverage against temperature for mild steel in 0.5 M H_2SO_4 with different concentration of CRRE.

3.2 Adsorption and thermodynamic consideration

The values of surface coverage (θ) at different concentrations of CRRE in 0.5 M H_2SO_4 solution have been used to elucidate the best isotherm to determine the adsorption process at 308 K temperature. Attempt were made to fit θ values to various isotherm including Langmuir, Frumkin, and Temkin with a clarified relationship between C/θ, and inhibitor concentration (C). The Langmuir adsorption isotherm fits the data well in the 0.5 M H_2SO_4 solution at 308 K temperature. The correlation coefficient was used to determine the fitting of the experimental data to this isotherm. The isotherm is characterized by the following given mathematical model [13]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (6)$$

Where K_{ads} is adsorptive equilibrium constant, θ is the surface coverage, and C is the equilibrium inhibitor concentration. Binding constant value indicate the binding ability of the CRRE to the metal surface. Greater Kads value indicates the high binding ability of CRRE on mild steel surface. The relationship between the surface coverage (C/θ) by the adsorbed molecule and concentration of inhibitor (C) shown in Fig. 4. It represent the Langmuir adsorption isotherm for the CRRE at 308 K with slope of unity. From the intercept of the line, K_{ads} value can be obtained and related to the free energy of adsorption (Gads) from the following equation [16]:

$$\Delta G_{ads} = -RT \ln (55.5\ K_{ads}) \qquad (7)$$

Where K is the binding constant, R is gas constant, and T is temperature.

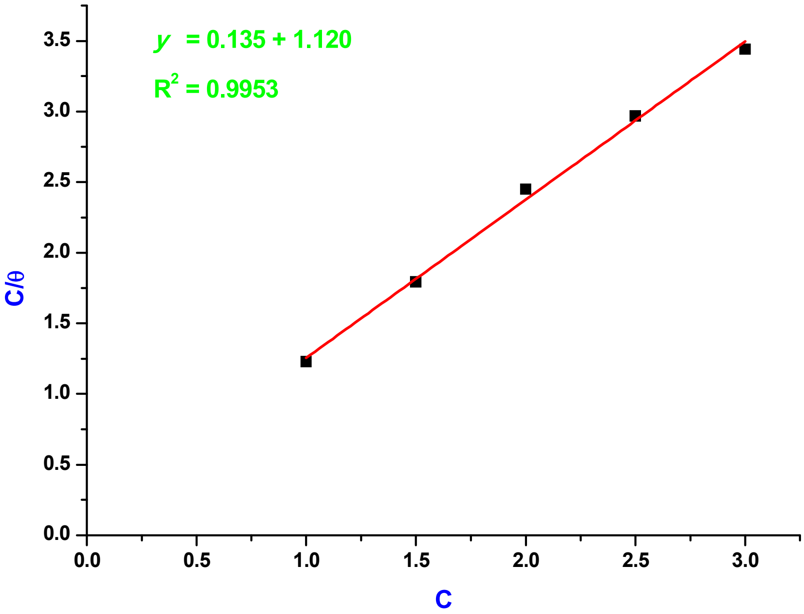


Fig. 4 Linear fitting of CRRE to Langmuir adsorption isotherm with different concentration at 308 K.

The adsorption equilibrium constant (K_{ads}) value was obtained from the linear regression of Langmuir adsorption isotherm. The calculated free energy of adsorption value was found to be ΔG_{ads} -16.574 kJ mol $^{-1}$ (Table 2) at 308 K temperature. Generally, values of ΔG_{ads} around -40 kJ mol^{-1} or higher are associated with chemisorption as a result of the sharing or transfer of electron from inhibitor to the metal surface to form a co-ordinate bond while those up to -20 kJ mol^{-1} are associated with physisorption [3]. The obtained ΔG_{ads} value for CRRE was -16.574 kJ mol $^{-1}$, which lie near the value of -20 kJ mol^{-1} anticipate for physical adsorption.

Table 2 Thermodynamic parameters for the adsorption of CRRE on mild steel in 0.5 M H_2SO_4 at 308 K.

T (K)	R^2	K_{ads} (L mol $^{-1}$)	ΔG_{ads} (kJ mol $^{-1}$)
308	0.998	14.49	-16.574

3.3 Effect of temperatures

In order to study the effect of temperature on the inhibition activity of CRRE on mild steel in 0.5 M H_2SO_4, weight loss measurements were carried out at the studied temperatures. Measurement were taken in the absence and presence of inhibitor at different concentration (1-3 g L^{-1}). An alternative formulation of Arrhenius equation is [7]:

$$\log \rho = \log A - \left(\frac{Ea}{2.303RT}\right) \qquad (8)$$

Where Ea is the apparent activation energy, ρ is the corrosion rate, R is the gas constant, T is the absolute temperature and A is the constant. Activation energy (Ea) of mild steel were calculated from the slope of log ρ versus $1/T$ (K) plots in 0.5 M H_2SO_4 solution at studied temperatures (Fig. 5). Corresponding values of activation energy are summarized in Table 3.Values of activation energy in the presence of different concentration of inhibitor (1-3 g L^{-1}) are higher than that for the uninhibited one, indicating a strong inhibitive action for the CRRE by increasing the energy barrier for the corrosion process [28]. The entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) for the mild steel corrosion in 0.5 M H_2SO_4 solution were obtained by applying the transition-state equation:

$$log\left(\frac{\rho}{T}\right) = \left[\left(log\ \left(\frac{R}{Nh}\right)\right) + \left(\frac{\Delta S^*}{2.303}\right)\right] - \frac{\Delta H^*}{2.303RT} \qquad (9)$$

Where ΔH^* is the enthalpy of activation, ΔS^* is the entropy of activation, h is the plank constant, and N is the Avogadro's number. The transition state plot of log ρ/T against $1/T$ (K) presented in Fig. 6. Values of enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were calculated from straight lines of transition state plots and listed in Table 3. The straight lines were obtained with an intercept of log (R/Nh) + ($\Delta S^*/2.303$), and a slope of -$\Delta H^*/2.303R$.

From examination of Table 3, it is apparent that values of enthalpy of activation and entropy of activation are higher in the presence of CRRE than values in blank solution. It implies that the energy barrier for corrosive reactions were lower in blank solution and higher in the presence of CRRE. Moreover positive value of enthalpy of activation (Δ*H**) exposed that corrosion reaction were endothermic in nature. It revealed that in the presence of CRRE the metal dissolution in acid solution was more difficult than in acid solution alone [5].

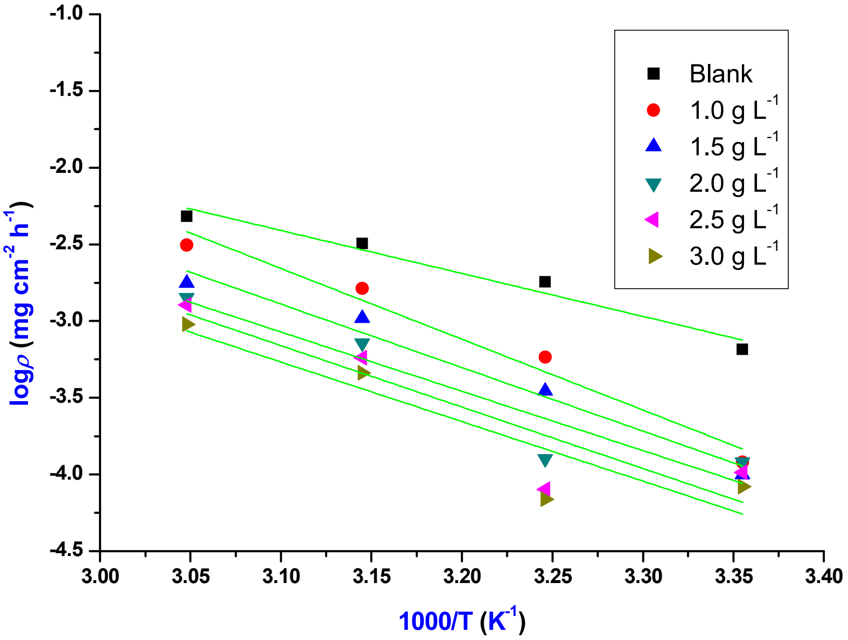


Fig. 5 Arrhenius plot for mild steel corrosion rates in 0.5 M H_2SO_4 in the absence and presence of different concentrations of inhibitor at studied temperature.

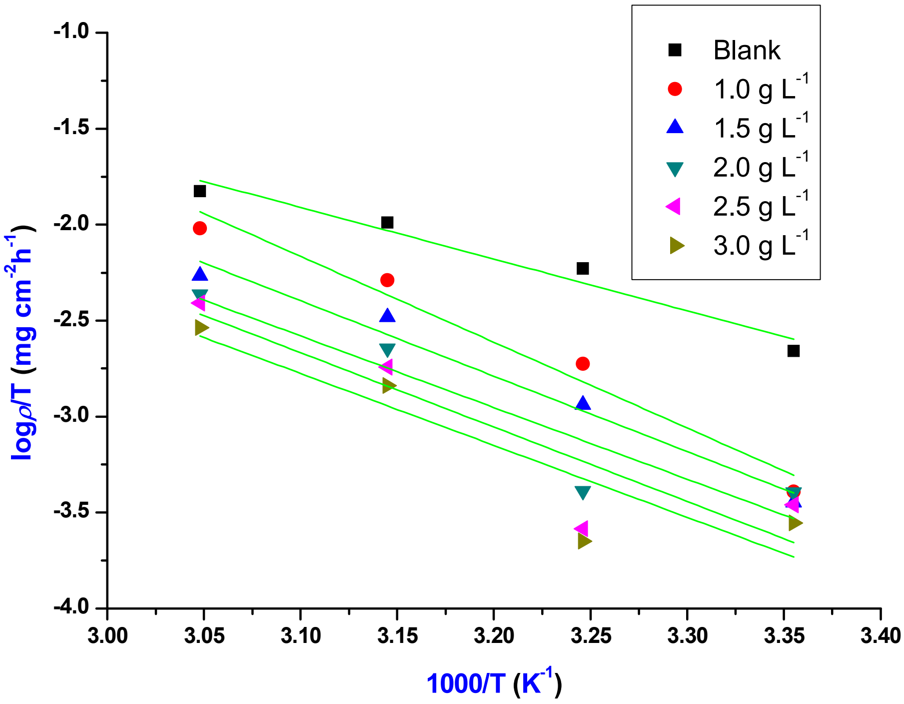


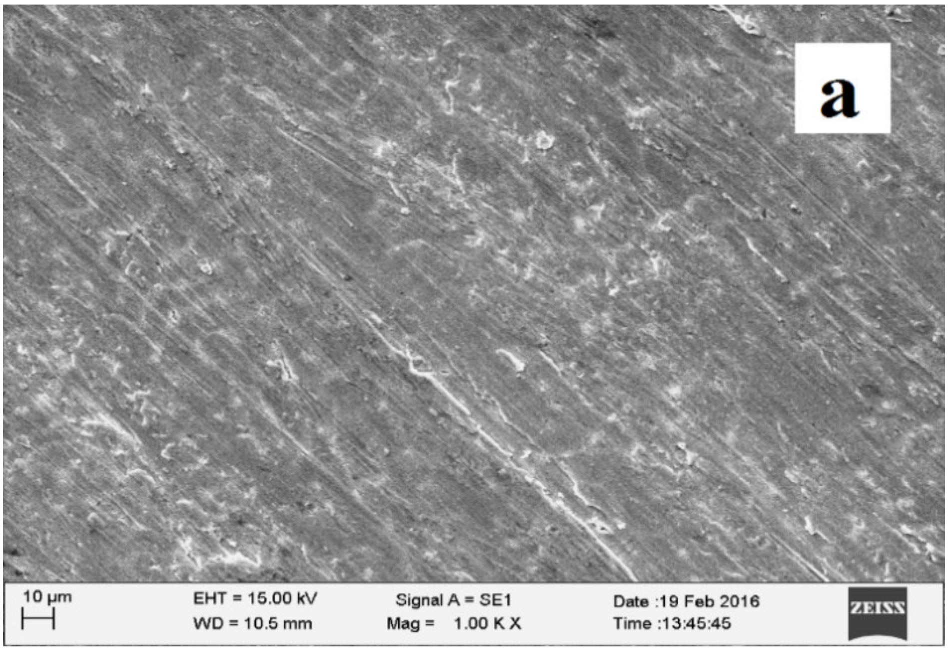
Fig. 6 Transition state plot for mild steel corrosion rates in 0.5 M H_2SO_4 in the absence and presence of different concentrations of inhibitor at studied temperatures.

Table 3 Activation parameters *E*a, Δ*H** and Δ*S** of the dissolution of mild steel in 0.5 M H_2SO_4 in the absence and presence of different concentration of CRRE.

Conc. (g L^{-1})	*A* (g cm^{-2} h^{-1})	*E*a (kJ mol^{-1})	Δ*H** (kJ mol^{-1})	Δ*S** (kJ mol^{-1})
0.0	1.90×10^4	53.67	51.58	-8.922
1.0	4.46×10^8	88.26	85.58	3.182
1.5	8.83×10^6	79.26	75.25	-1.225
2.0	8.25×10^5	74.02	71.47	-3.055
2.5	1.80×10^6	76.68	74.25	-2.218
3.0	5.91×10^5	74.29	71.80	-3.383

3.4 SEM Analysis

The SEM images of polished mild steel surface and the surface of mild steel immersed in 0.5 M H_2SO_4 solution shown in Fig. 7a and b respectively. Fig. 7a show the uncorroded, and homogeneous polished mild steel surface. However Fig. 7b represents that the whole surface is severely corroded exposed for 24 h in 0.5 M H_2SO_4 solution. Fig. 7c shows a formation of protective film by the CRRE components on the mild steel surface which may be responsible for the inhibition of corrosion.



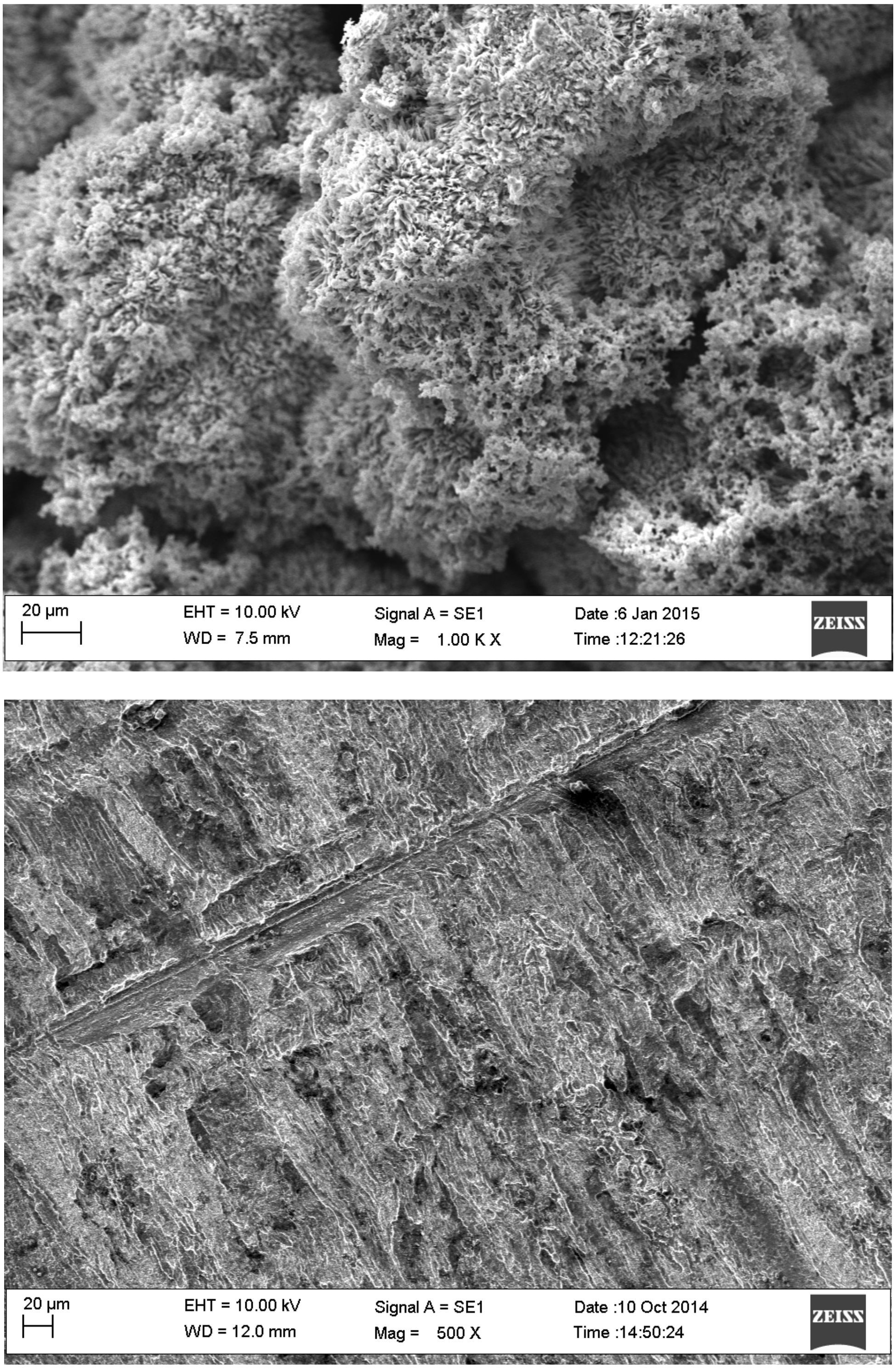


Fig. 7 SEM images of (a) mild steel, (b) mild steel in 0.5 M H_2SO_4, and (c) mild steel in presence of CRRE.

4. Conclusions

The weight loss measurements studies show that the CRRE is good corrosion inhibitor for mild steel in 0.5 M H_2SO_4. *Cuscuta reflexa roxb.* extract (CRRE) decreases the mild steel corrosion in 0.5 M H_2SO_4 solutions as the concentrations of CRRE increased. The adsorption of CRRE components on the mild steel surface was found to obey Langmuir adsorption isotherm at 308 K in 0.5 M H_2SO_4 solution. Thermodynamic parameters shows that the inhibitor constituents were adsorbed on the mild steel surface by physisorption mechanism. SEM displays the enhancement on the surface morphology after being added with the CRRE. Overall, the CRRE acts as a good mild steel corrosion inhibitor in 0.5 M H_2SO_4 solution.

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