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Electrochemical Study of Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution by the Extract of Cuscuta Reflexa

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Abstract

The extract of *Cuscuta reflexa Roxb.* (CRRE) evaluated as effective corrosion inhibitor for mild steel in 1 M HCl. The inhibition action of CRRE has been investigated by using polarisation and electrochemical impedance spectroscopy. Electrochemical measurement shows the maximum inhibition efficiency of (91.28%) for optimum concentration of inhibitor at 25^0C. Polarization studies showed that inhibitors acts as a mixed type inhibitor. Scanning electron microscopy (SEM) studies shows that the inhibitor formed protective film over the mild steel surface. Potentiodynamic polarization, electrochemical impedance, and SEM studies, indicate that CRRE can effectively protect the mild steel from corrosion in 1 M HCl.

Keywords: Adsorption · Corrosion inhibition · Mild steel · CRRE

1. Introduction

Corrosion is a process which plays an important role in the field of safety and economics**.** Mild steel (MS) is useful for the industrial acid cleaning, acid pickling, acid descaling and oil well acidizing applications and in many industries due to its excellent mechanical properties and low cost. The study of corrosion inhibition of mild steel 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 effective 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 efficacy, but their uses are limited because of their toxicity and cost of application [4, 5]. Most of the well-known organic inhibitors contain oxygen, nitrogen, phosphorus and sulphur elements and π-electrons. The adsorbed inhibitor molecules film protect the metals from corrosive attack by blocks the active sites present on mild steel surface. Various researches suggest that the adsorption of these inhibitor molecules on metal surface depends on the physico-chemical properties of the donor atoms. Generally 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).

The chemical constituents identified in *Cuscuta reflexa* plant are; Cuscutine, Quercetin, Cuscutamide, Kaempferol, Amarbelin and Reflexin [35]. *Cuscuta reflexa* plant is also well known for its medicinal uses such as antibacterial, anticancer etc. [36, 37]. Inhibition action of CRRE on corrosion behaviour of mid steel in 1M HCl has been investigated through potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Mild steel surfaces are examined with scanning electron microscope-energy dispersion spectroscopy (SEM-EDS). The aim of present investigation is to evaluate the inhibitive effect of CRRE as a green corrosion inhibitor of mild steel in 1M HCl.

2. Experimental

2.1 Electrode preparation

The chemical compositions (wt %) of mild steel used was as follows:

Medium	Composition (wt %)						
	Fe	**C**	**O**	**P**	**S**	**Cr**	**Mn**
Mild steel (MS)	98.32	0.22	0.28	0.03	0.04	0.56	0.57

The surface of mild steel specimens (1 cm^2) were rubbed using different grade of emery grit papers (400-1200) 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 solutions.

2.2 Electrolytic solution

Corrosive solution was prepared by dilution of analytical grade HCl (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 than shade dried for 5 days. This dried *Cuscuta reflexa roxb.* was powdered into small pieces and 400g of the powdered was extracted in boiled millipore water for 3h. The extracted solution then filtered using and concentrated until the water from the extract evaporates using rotary evaporator at 35°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 SEM analysis

The surface morphology of mild steel specimens were examined using SEM-EDS 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 Potentiodynamic polarization measurements

The potentiodynamic polarization behaviour of mild steel in 1 M HCl in the absence and presence of different concentration of CRRE is shown in Fig. 1. Various Potentiodynamic polarization parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c), and anodic Tafel slope (b_a) were calculated and values are given in Table 1. Inhibition efficiency (η), and surface coverage (θ) were calculated from the values of corrosion current density in the presence and absence of inhibitor respectively. From Table 1 it is evident that I_{corr} value considerably reduced in the presence of CRRE signifying that CRRE components strongly adsorb on the metal surface in 1 M HCl solution. From Fig. 1 it is also observed that the potentiodynamic polarization shape are similar in the presence and absence of inhibitor suggesting that CRRE retarded the mild steel corrosion by adsorption on metal surface. This process occur without changing the mechanism of metal corrosion [21, 24]. It is also observed that in the addition of CRRE E_{corr} values did not cause any significant change suggesting that it is a mix type inhibitor [23]. The inhibitor can be considered as a characteristic anodic or cathodic type, if the displacement in E_{corr} is more than ±85 mV with respect to the corrosion potential of blank solution. In the present study, the average displacement of E_{corr} was not more than 85 mV, suggesting that the CRRE performed like a mix-type inhibitor [20]. Usually the anodic Tafel branch represents the iron dissolution reaction, however the cathodic Tafel branch represent the hydrogen evolution reaction [12]. Maximum inhibition efficiency 91.28 was obtained at optimum concentration of CRRE at 298 K (Table 1).

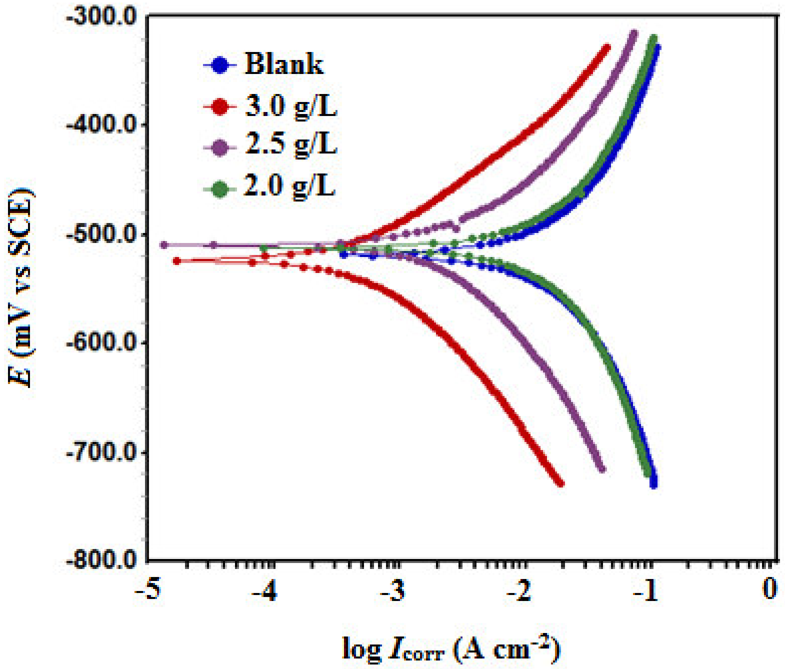

Fig. 1 Tafel polarization behaviour of metal in 1 M HCl solution with different concentration of CRRE at 298 K.

Table 1 Potentiodynamic polarization parameters for the corrosion of mild steel in 1 M HCl solution with different concentration of CRRE at 298 K for 30 min of immersion period.

Conc. (g/L)	I_{corr} mA/cm^2	E_{corr} mV/SCE	β_a mV/dec	β_c mV/dec	θ	$\%\eta$
Blank	28.32	-522	266.8	307.3	-	-
2.0	7.067	-527	53.22	58.62	0.750	75.04
2.5	4.280	-508	108.9	191.0	0.848	84.88
3.0	2.469	-513	68.6	128.6	0.912	91.28

3.2 Electrochemical impedance spectroscopy (EIS)

Impedance method provides information about the surface properties and kinetics of electrode process of the studied system [32]. Inhibition efficiency ($\%\eta$) of CRRE at different concentrations (0, 2.0, 2.5 and 3.0 g/L) was calculated against the acid corrosion of mild steel at 298 K by EIS measurements. Nyquist plot for mild steel in 1 M HCl solution in the absence and presence of inhibitor shown in Fig. 2. Inhibition efficiency and corrosion kinetic parameters (R_s, R_{ct} and C_{dl}) were calculated from Nyquist plot and corresponding results are given in Table 2. All the impedance diagrams were studied in the terms of the equivalent circuit shown in Fig. 3. The double layer capacitance (C_{dl}) is calculated using the following equation [32]:

$$C_{dl} = Y_0 (\omega_{max})^{n-1} \qquad (5)$$

Where n is *CPE* exponent (phase shift), Y_0 is *CPE* coefficient, ω is the angular frequency and ω_{max} shows the frequency at which the imaginary component reaches the maximum. It is clear from the Nyquist plot (Fig. 2) that the diameter of semicircle increase with increasing the concentration of CRRE. It is also clear from Table 2 that in the absence of inhibitor the value of capacitance (C_{dl}) decreases from 120.77 µ F cm^{-2} to 68.19 µ F cm^{-2} on addition of optimum concentration of CRRE. On addition of CRRE the decrease in C_{dl} may be due to increase in dielectric constant or/and may be due to increase in double layer thickness. The increase in the thickness of the double layer, showing that CRRE strongly inhibited the corrosion of mild steel by adsorbing at acid/metal interfaces [33].

Fig. 3 represent the corresponding Bode impedance and phase angle plots for mild steel electrode in the absence and presence of CRRE in 1 M HCl at its open circuit potential. It is apparent from Fig. 3 that phase angle and log |Z| fall to almost zero at the high frequency region. It is also apparent from Fig. 3 that addition of CRRE causes an increase in the interfacial impedance, which further increases upon increasing concentration of CRRE. The phase angle plots indicate a single narrow peaks, direct a single time constant for corrosion process at the acid solution/metal interface in the absence and presence of inhibitor [34]. The metal surface roughness increase in the absence of inhibitor therefore reduced the phase angle in the corrosion process. However increase in the phase angle in the presence of CRRE suggests the surface homogeneity [2].

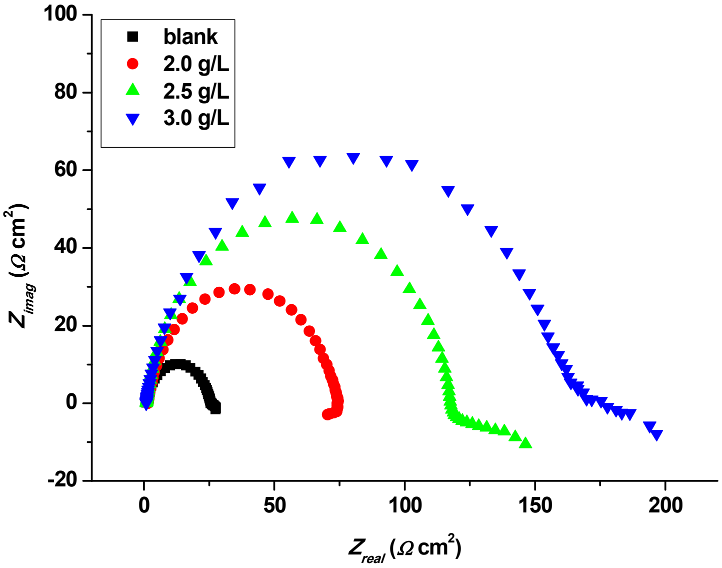

Fig. 2 Nyquist plot of mild steel in 1 M HCl solution with different concentration of CRRE at 298 K.

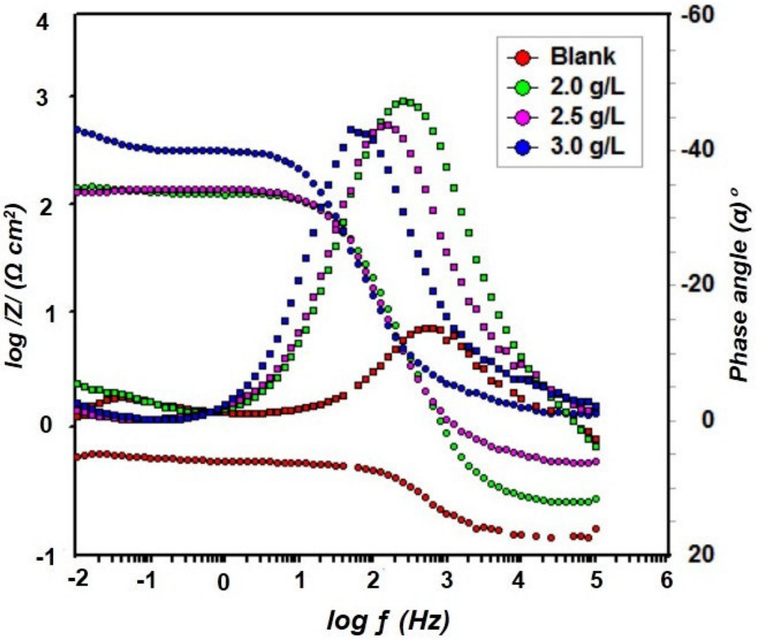

Fig. 3 Bode-phase plots of mild steel corrosion in 1 M HCl solution with different concentration of CRRE at 298 K.

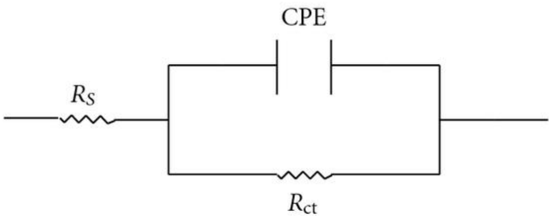

Fig. 4 Electrochemical equivalent circuit model used to fit the impedance spectra

Table 2 Impedance parameters for mild steel in 1 M HCl in the absence and presence of different concentration of CRRE at 298 K for 30 min of immersion period.

Conc. (g/L)	R_s (Ω)	R_{ct} (Ω cm^2)	C_{dl} (μ F cm^{-2})	θ	%η
Blank	0.977	23.97	120.77	-	
2.0	1.510	70.85	82.57	0.661	66.16
2.5	0.892	120.40	81.43	0.800	80.08
3.0	0.820	171.58	68.19	0.860	86.07

3.3 SEM analysis

The SEM microphotographs of polished mild steel in the presence and absence of inhibitor in 0.5 M H_2SO_4 solution shown in Fig. 5a and b respectively. Fig. 5a show the uncorroded, and homogeneous polished mild steel surface. However Fig. 5b represents that the whole surface is severely corroded exposed for 6h in 1 M HCl solution. Fig. 5c shows a formation of protective film by the CRRE components on the mild steel surface which may be responsible for the inhibition of corrosion.

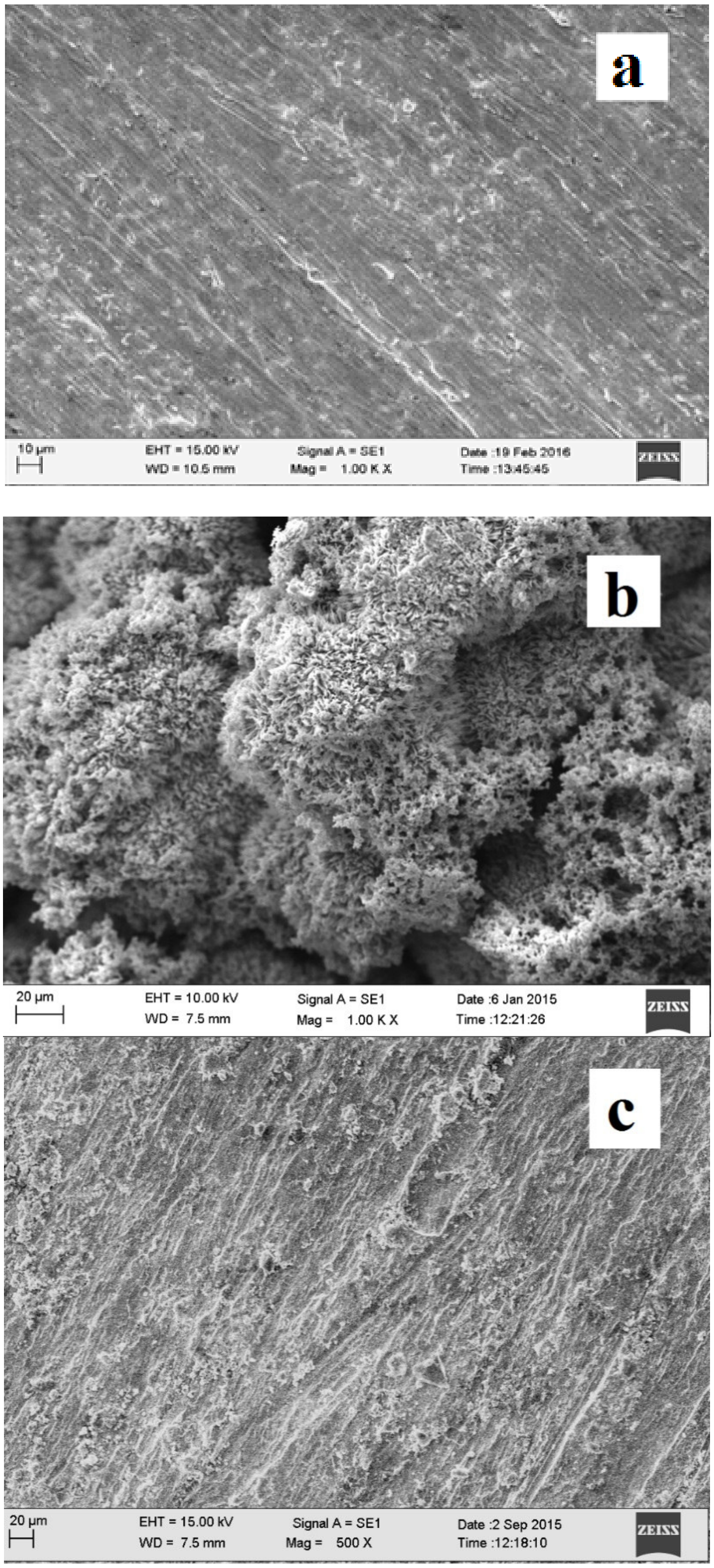

Fig. 5 SEM micrographs of (a) mild steel, (b) mild steel in 1 M HCl, and (c) mild steel in presence of CRRE.

4. Mechanism of inhibition

It can be concluded from the weight loss, potentiodynamic polarization and surface measurements that CRRE inhibits mild steel corrosion in 1 M HCl by adsorption process. Adsorption of CRRE components on the metal surface from the acidic solution will change it in to a passive state from active dissolution state through the formation of a protective layer. In acidic solution surface of mild steel is protected due to rapid adsorption of inhibitor components [38]. Electronic characteristics and molecular structure of inhibitor molecules are the main factors in founding the adsorption ability of inhibitor components on metal surfaces. Most of the inhibitors are organic compounds containing O, N, and S atoms aromatic rings in their structure [39]. The presence of chloride ions in the acidic medium also stabilized the adsorption of inhibitor components by the formation of a stabilized co-ordination inter medium on the mild steel surface. The chloride ion(s) acts as a bridge ligand between inhibitor molecules and mild steel surface [40]. Adsorption of inhibitor molecules on the metal surface may be credited by one or more of the following mechanism: 1 Interaction between lone pair electron(s) of inhibitor molecules with metal surface(s); 2 electrostatic interaction between charged inhibitor molecules and the charged metal surface; 3 interaction between filled p-orbital electrons of inhibitors with vacant d-orbital of the metal; and/or 4 a combination of all [1]. The inhibitive action of CRRE could be attributed due to the presence of quercetin, cuscutine, and kaempferol (Fig.6) thus inhibit mild steel surface from corrosion. The free energy adsorption value (ΔG_{ads}) is around <-20 kJ mol^{-1}, indicating the physical adsorption (physisorption) of the CRRE components on mild steel surface [41].

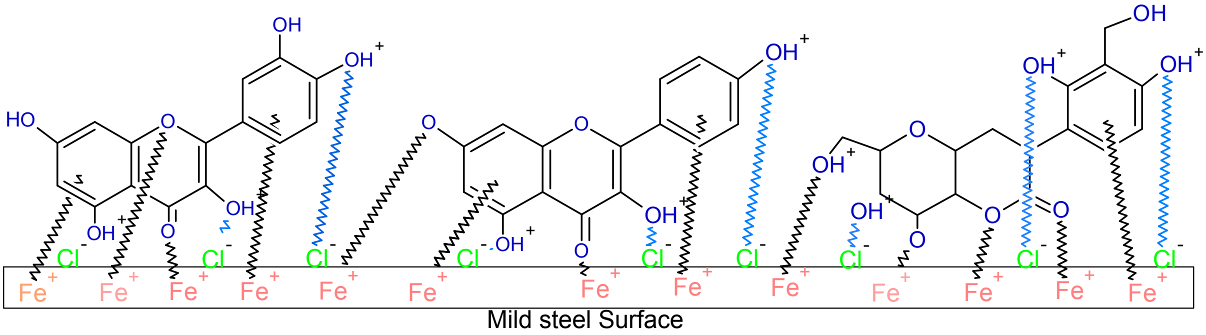

Fig. 6 The schematic illustration of possible mechanism of adsorption of molecules present in CRRE on acid/metal interface.

5. Conclusions

The electrochemical measurements show that the CRRE is good corrosion inhibitor for mild steel in 1 M HCl. Potentiodynamic polarization parameters indicate that the CRRE affects both cathodic and anodic reactions and acts as a mixed inhibitor. 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 1 M HCl solution.

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