

Application of a Natural Inhibitor for Corrosion Inhibition of J55 Steel in CO₂ Saturated 3.5% NaCl Solution

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Received: 26 September 2013 / Accepted: 18 October 2013 / Published: 20 October 2013

The inhibition behavior of *Momordica charantia* seeds extract (MCSE) as an environmental benign corrosion inhibitor for J55 steel was investigated in 3.5 wt.% NaCl saturated with CO₂ solution by means of polarization curve, AC impedance and X-ray diffraction (XRD). The results showed that MCSE can inhibit the corrosion of J55 steel. The maximum inhibition efficiency is achieved when MCSE concentration is 1000 ppm by weight in this study. The adsorption of the studied inhibitor obeyed the Langmuir's adsorption isotherm.

Keywords: J55 steel; Inhibitor, Corrosion; EIS; XRD

1. INTRODUCTION

Aqueous carbon dioxide (carbonic acid) is corrosive and corrodes the carbon steel pipelines. Carbon dioxide corrosion has been of interest to researchers in oil industries for many years and there exists many theories about the mechanism of CO₂ corrosion [1]. The mechanisms of CO₂ corrosion and the formation and removal of protective iron carbonate films are not fully understood due to the complex reaction mechanisms and the presence of many critical environmental factors such as pH, temperature, dissolved species concentration and hydrodynamics that can appreciably change the corrosion rate [2].

Due to its low cost and availability, steel is used as the primary construction material for pipelines in oil and gas industries, but it is very susceptible to corrosion in CO₂ environments. It is easy to form a thin film saturated with CO₂ on the surface of J55 steel in this environment where J55 steel is active and easily corroded. Chloride is well known to play a crucial role in steel corrosion, but its effect depends on whether the aqueous system is deaerated (oxygen-free), oxygen-aerated, or deaerated but CO₂-bearing. In deaerated acidic solutions, chloride accelerates the anodic kinetics of iron dissolution via a catalytic mechanism [3-5]. Use of corrosion inhibitors is the most common method used to retard corrosion of metals as no special equipments required, low cost and easy operation. It is highly desired that new inhibitors for J55 steel are non-toxic and environment-friendly. [6-10].

Momordica charantia often called bitter melon, bitter gourd or bitter squash in English, has many other local names. The cultivar common to China is 20–30 cm long, oblong with bluntly tapering ends and pale green in color, with a gently undulating, warty surface. The plant contains several biologically active compounds, chiefly charantine, glycosides, momordicine, karavilagenin, karaviloside, kuguacin, terpenoids and fatty acids [11, 12].

In present study we have investigated MCSE as corrosion inhibitor of J55 steel in 3.5% NaCl solution using electrochemical and XRD methods.

2. EXPERIMENTAL

2.1. Preparation of inhibitor

Fifty grams of dried *Momordica charantia* plant seeds were soaked in 900 ml of reagent grade ethanol for 24 h and refluxed for 5 h. The ethanolic solution was filtered and concentrated to 500 ml. This extract was used to study the corrosion inhibition properties.

2.2. Materials and Solutions

J55 steel having the following chemical composition (wt %): C 0.24; Si 0.22; Mn 1.1; P 0.103; S 0.004; Cr 0.5; Ni 0.28; Mo 0.021; Cu 0.019; Fe balance were used for all studies. J55 steel coupons having dimensions of 10 mm × 10 mm × 3 mm were used for the electrochemical study. The specimens were welded with copper wire and covered with epoxy resin. The specimens were metallographically polished according to ASTM A262, degreased and dried before experiment. The test solution of 3.5% NaCl was prepared by analytical grade NaCl with double distilled water. All experiments were performed at room temperature.

2.3. Electrochemical measurements

The electrochemical experiments were performed by using three electrode cell, connected to Potentiostat/Galvanostat AUTOLAB model GSTAT302N. Software package incorporated with

AUTOLAB was used for data fitting. J55 steel was used as working electrode, platinum electrode as an auxiliary electrode, and saturated calomel electrode (SCE) as reference electrode. All potentials reported were measured versus SCE. Tafel curves were obtained at a scan rate of 1.0 mVs^{-1} . EIS measurements were performed under potentiostatic conditions in a frequency range from 100 kHz to 0.01 Hz, with amplitude of 10 mV AC signal. The experiments were carried out when the electrochemical system was in steady state in 3.5% NaCl saturated with CO_2 in absence and presence of different concentrations of MCSE.

2.4. X-Ray Diffraction (XRD)

The J55 steel specimens were immersed in CO_2 saturated 3.5% NaCl solution in absence and presence of inhibitor for a period of 3 hr. After then, the specimens were taken out and dried. The surface film formed on the surface of the mild steel specimen was analyzed by using X-ray diffractometer, X Pert PRO incorporated with Higscore software.

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

3.1.1. Electrochemical Impedance Spectroscopy (EIS)

EIS measurements (Figure 1a and 1b) were performed to study the corrosion resistance (proportional to the diameter of the semicircle) and solution resistance in the absence and presence of inhibitor concentration. Nyquist plots of J55 steel in 3.5% NaCl solution in the absence and presence of different concentrations of MCSE are shown in figure 2.

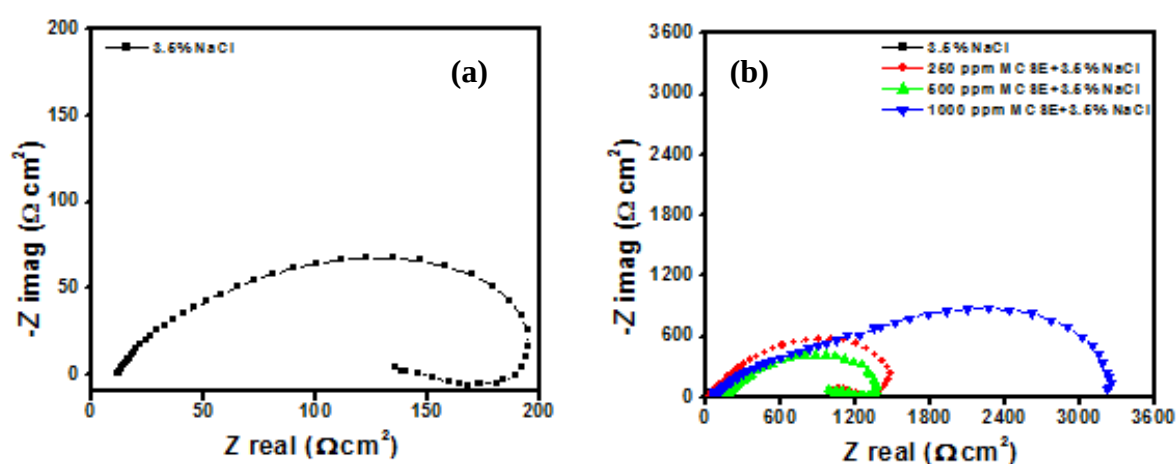


Figure 1. Nyquist plots for J55 steel (a) 3.5% NaCl and (b) in absence and presence of MCSE.

Although the appearance of Nyquist plots remained the same, their diameter increased after the addition of MCSE to the corrosive solution. This increase was more and more pronounced with

increasing inhibitor concentration indicating the adsorption of inhibitor molecules on the metal surface [13]. However, after the addition of MCSE, the impedance modulus of the system gradually increased and was a maximum in the case of MCSE at 1000 ppm. The impedance diagram (Nyquist) contains depressed semicircles with the center under the real axis with one capacitive loop in the high frequency (HF) zone, and one RL – L inductive loop in the lower frequency (LF) zone. As usually indicated in an EIS study, the HF capacitive loop is related to the charge-transfer resistance process of the metal corrosion and the double-layer behavior, and these loops are not perfect semicircles. The charge transfer resistance increased with increase in concentration of inhibitor. The LF inductive loop may be a consequence of the layer stabilization byproducts of the corrosion reaction on the electrode involving inhibitor molecules and their reactive products [14-18]. The curve in the Nyquist plot is depressed, which we attribute to surface roughness and the resulting distortion of the double layer.

The model used for fitting consist of R_s (the resistance of solution between working electrode and counter electrode), R_{ct} , inductive elements L , RL and the constant phase angle element (CPE) as shown in figure 3.

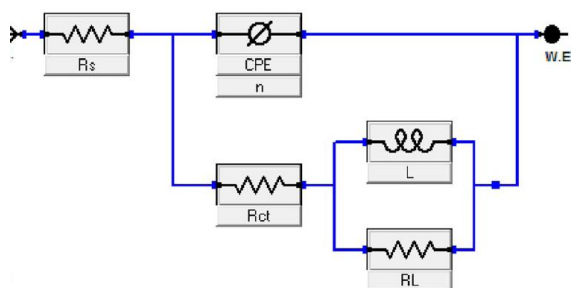


Figure 2. Equivalent circuit used to fit the Nyquist curves.

The inhibition efficiency is calculated using charge transfer resistance (R_{ct}) as follows,

$$\eta\% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (1)$$

Where $R_{ct(inh)}$ and R_{ct} are the values of charge transfer resistance in presence and absence of inhibitor in 3.5% NaCl respectively. At different concentrations MCSE showed increase in value of R_{ct} with respect to blank 3.5% NaCl solution. The increase in R_{ct} values as shown in table 2 is attributed due to increase in resistance and adsorption of inhibitor molecules on J55 steel surface [19-22].

Table 1. Nyquist data for J55 steel in 3.5% NaCl at different concentration of MCSE.

Solutions	Conc.(ppm)	$R_s (\Omega \text{ cm}^2)$	$R_{ct} (\Omega \text{ cm}^2)$	$\eta\%$	θ	n
3.5% NaCl	-	5.0	159	-	-	0.861
MCSE	250 ppm	5.1	1285	87	0.87	0.854
MCSE	500 ppm	4.8	1466	89	0.89	0.829
MCSE	1000 ppm	4.9	3260	95	0.95	0.858

3.1.2. Potentiodynamic polarization measurements

Electrochemical kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic (β_a) and cathodic (β_c) slopes are obtained by the anodic and cathodic regions of the tafel plots shown in table 2.

Table 2. Tafel polarization data for J55 steel in 3.5% NaCl at different concentration of MCSE.

Solutions		Tafel data					
	Conc.(ppm)	E_{corr} (V vs. SCE)	I_{corr} (A cm ⁻²)	b_a (V d ⁻¹)	b_c (V d ⁻¹)	$\eta\%$ (%)	θ
3.5% NaCl	-	-0.434	8.96	0.08	0.92	-	-
MCSE	250 ppm	-0.538	1.25	0.09	0.24	86	0.86
MCSE	500 ppm	-0.448	1.12	0.09	0.12	87	0.87
MCSE	1000 ppm	-0.539	0.53	0.09	0.11	94	0.94

The corrosion current density (I_{corr}) can be obtained by extrapolating the tafel lines to the corrosion potential and the inhibition efficiency ($\eta\%$) values were calculated from the relation:

$$\eta\% = \frac{I_{\text{corr}} - I_{\text{corr}(i)}}{I_{\text{corr}}} \times 100 \quad (2)$$

Where I_{corr} and $I_{\text{corr}(i)}$ are the corrosion current density in absence and presence of inhibitor. The polarization curves for J55 steel in the absence and presence of the inhibitor are given in figure 3.

The liberation of H^+ ions is reduced due to addition of the inhibitor. The inhibitor molecules are first adsorbed on the surface and blocked the active sites of the steel surface.

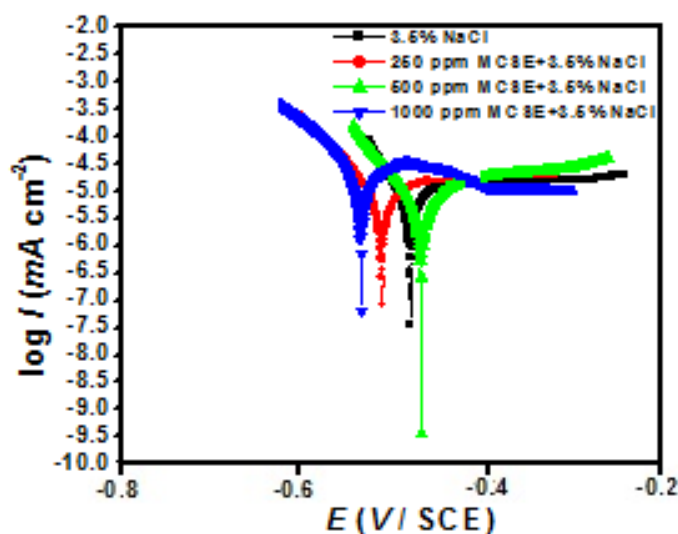


Figure 3. Tafel polarization plots for J55 steel in absence and presence of MCSE.

The values of b_a were shifted to higher values and b_c values shifted to lower values with reference to blank in the presence of MCSE. This showed that MCSE inhibits the corrosion process by controlling anodic and cathodic reactions predominantly of the metal surface [23]. I_{corr} values decreased with increase in concentration inhibitor. This result confirmed the inhibitive action of MCSE toward corrosion of the J55 steel.

But, analysis of both anodic (b_a) and cathodic (b_c) tafel slope values indicated that both anodic and cathodic reactions were suppressed during the addition of the inhibitor, which suggested that the MCSE reduced anodic dissolution and also retarded the hydrogen evolution reaction [24-26]. Since both the anodic and cathodic sites were suppressed therefore MCSE acted as a mixed type inhibitor.

3.2. Adsorption isotherm

Adsorption isotherms always play a vital role in determining mechanism of corrosion reactions. The adsorption of an organic adsorbate on to metal-solution interface can be represented by a substitutional adsorption process between the organic molecules in the aqueous solution phase ($\text{Org}_{(\text{sol})}$) and the water molecules on the metallic surface ($\text{H}_2\text{O}_{(\text{ads})}$) [27].



where, x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate. Basic information on the interaction between the inhibitor and the J55 steel surface can be provided by the adsorption isotherm. It is essential to know the mode of adsorption and the adsorption isotherm that can give important information on the interaction of inhibitor and metal surface.

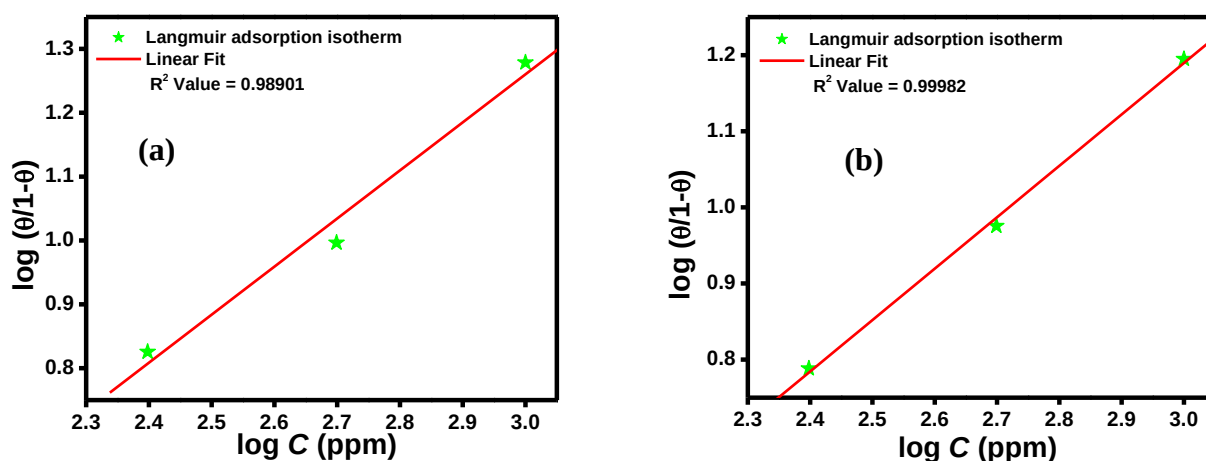


Figure 4. The Langmuir adsorption isotherm plots for mild steel at different concentrations of MCSE by (a) EIS and (b) Tafel method.

The linear regression coefficient values (R^2) determined from the plotted curve of Langmuir was found to be in the range of 0.98901 for EIS and linear regression coefficient values (R^2) for tafel was 0.99982 (figure 4). The straight line in both the case is close to 1 elucidating that EIS and tafel plot values followed Langmuir's adsorption isotherm.

$$\theta = \frac{bC_{inh}}{1 + bC_{inh}} \quad (\text{Langmuir Isotherm}) \quad (4)$$

3.3. Surface Analysis

3.3.1. X-Ray Diffraction (XRD)

X-ray diffraction was used to determine film formation of the J55 steel under various test solutions. The corrosion product over the surface of the J55 steel in 3.5 wt% NaCl solution is shown in figure 5(a). Peaks at $2\theta = 17-18^\circ$, 30° , 38° , 45° , 57° and 69° can be assigned to the oxides of iron. The peaks due to iron appear at $2\theta = 17-18^\circ$, 45° and 69° in presence of MCSE (figure 5b).

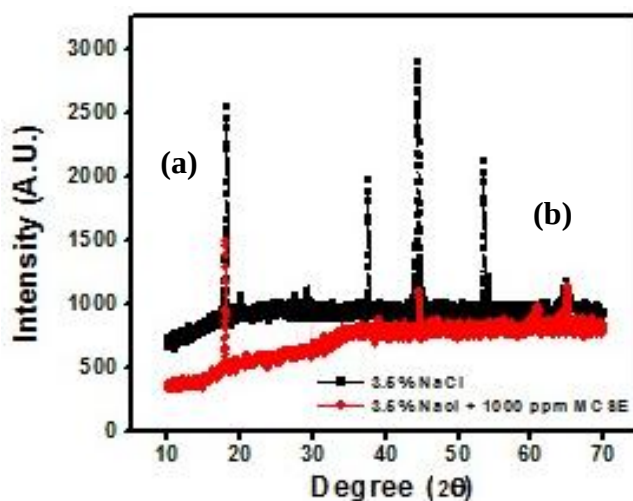


Figure 5. XRD spectrum of J55 steel corrosion in the (a) absence and (b) presence of MCSE.

Thus, it is observed that in absence of inhibitor, the surface of the metal contains iron oxides of iron. The XRD patterns of inhibited surface (figure 5(b)) showed the presence of iron peaks only, the peaks due to oxides of iron are found to be absent [28, 29]. The formation of adsorbed protective film on the surface of metal in the presence of MCSE is clearly reflected from these observations.

4. MECHANISM OF ADSORPTION AND INHIBITION

MCSE constitutes of glycosides, oils, fatty acids, saponins which are very rich in heteroatoms (N, O), which meet the general consideration of typical corrosion inhibitors. These molecules may be

adsorbed on the mild steel surface via (a) physical adsorption or (b) chemical adsorption or (c) a combination of both types of adsorption. It is a well-established fact that chloride ions being adsorbed on a metal surface, promote adsorption of positively charged ions on metals by making a bridge between cations and positively charged metals [30]. Probably inhibitor molecules (protonated form of organic moieties) interacted with the J55 steel through the above stated mechanism and formed a layer at the metal-NaCl interface, due to which, corrosion of the steel was inhibited in 3.5% NaCl solution. Since there are many chemical constituents in MCSE so they may inhibit the J55 steel surface due to the synergism between them. Another possibility is that the large size of the molecules covers the entire surface thereby reducing corrosion. It is also possible that the layer at the NaCl-steel interface was formed due to chemical bonding between π electrons or lone pair electrons (from N, O atoms or aromatic rings of organic moieties) and vacant d-orbital electrons of iron [31-33].

5. CONCLUSIONS

In this study, corrosion inhibition efficiency of MCSE on J55 steel in 3.5% NaCl was determined by electrochemical and surface analysis. The potentiodynamic polarization data indicated that the MCSE is mixed type inhibitor. Electrochemical impedance spectroscopy data reveals increase in R_{ct} values which accounted for good inhibition efficiency. The adsorption of the inhibitor molecules on the J55 steel surface was found to obey the Langmuir adsorption isotherm. The XRD study confirmed the blockage of metal surface through adsorption process.

ACKNOWLEDGEMENTS

Authors are thankful to the financial assistance provided by the National Natural Science Foundation of China (No. 51274170) and the research grants from the Colonel Technology Fund of Southwest Petroleum University (Project No.2012XJZ013).

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