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Cheery Sticks Plant Extract as a Green Corrosion Inhibitor Complemented with LC-EIS/ MS Spectroscopy

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The acid corrosive consumption hindrance process by Cherry Sticks extraction as a green corrosion inhibitor had been explored by utilizing the weight loss method. Impact of temperatures on the consumption conduct in the existence of the inhibitor at a concentration of $50*10^{-2}$ g/L was examined at the temperatures of 30, 40, 50 and 60 °C. The results demonstrate that the green, inhibitor, CSCI (Cherry Sticks Corrosion Inhibitor), guarantees the inhibitive impacts on the corrosion of metal (mild steel) in one molar hydrochloric acid for all inspected conditions. The efficiency increment with concentration augmentation of the green inhibitor achieves its maximum of 89.5% at $50*10^{-2}$ g/L, and its adsorption on a metal surface obeys Langmuir isotherm. To examine the surface morphology of an inhibitor, SEM (scanning electron microscopy) was utilized before and after submersion in HCl. Green inhibitor was extracted and its structures were clarified and affirmed utilizing the following spectroscopical methods: infra_red (IR), and liquid-Chromatography Electrospray-Ionization Mass-Spectrometry (LC-EIS/ MS).

Keywords: Cheery Sticks, LC-EIS/ MS spectroscopy, SEM, weight loss method.

1. INTRODUCTION

The utilization of chemicals as inhibitors had a great attention because of the capacity of these compounds to counteract corrosion in different corrosive environments [1-3]. An assortment of organic chemicals had been utilized effectively as corrosion inhibitors through acidizing in industrial cleaning methods [4,5]; these organic compounds also hinder the adsorption of chlorides and the figuration of a safer oxide film on the metal [6]. The inhibition proficiency of synthesized or natural organic compounds principally depends on the structure and trait of the adsorbed-layer on the mild steel [7–18]. Availableness of the unshared or π-electrons in inhibitor structure encourages the exchange from the inhibitor to the mild steel because of the vacant *d-orbital* for the transition elements and the formation of the coordination bond. Coordination bonds, including the exchange of electrons between inhibitor-molecules and the surface of the metal, might occur. The solidity of the chemical-bond relies on the electron intensity of the benefactor atoms in the functional groups and the polarization of the groups [19, 20]. Electrons intensity in the mild steel for the purpose of connection ex-changes brings about hindrance of the cathodic or anodic reactions [21-23]. Inhibition effectiveness is ascribed to a combination of a balance of the film pH, the lessening of chlorides effectiveness, and the attending arrival of the inhibitor anion [24-28]. Green corrosion inhibitors are very important due to biodegradable ability and not toxic in addition to have not heavy metals. In the past years, Umoren and Obots has published different articles close to the valuations of plant extracts as corrosion inhibitors [29-35]. Due to the high cost of synthesized corrosion inhibitor, we focus on simple, practical and economical corrosion inhibitors, so in this study we were used cherry sticks aqueous extract as inhibitor on metal corrosion in hydrochloric acid medium utilizing the weight-loss method.

2. METHODOLOGY

2.1. General

All chemicals in this work were utilized as received. FT-IR (Fourier transform infrared) were recorded utilizing a ThermoScientific Nicolate 6700 FT-IR Spectrometer. Fragments were computed by utilizing a GC:FID & GC:MS 7890A systems that supply from Agilent Technology (Sources types ESI, Ion Polarities-Positive, Set Capillary 4500 V, Set End Plate Offset -500 V, Set Dry Gas 5.0 l/min, Scanning rang 100-1000 m/z), liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) test strategy has been utilized to characterize the chemical compounds of cherry sticks extract.

2.2. Extraction of CSCI (Cheery sticks corrosion inhibitor).

In order to isolate corrosion inhibitor from the sticks of Cheery, the sticks were subjected to extraction with 500 mL of distilled water. The gained, extract was dense by utilizing of rotary evaporator at room temperature.

2.3. Gravimetric Experiments

2.3.1. Mild steel specimens.

Specimens were purchased from Metal-Samples and utilized in our work and it composed in weight percent accordingly: Carbon 0.210, Silicone 0.380, Phosphorous 0.090, Sulfur 0.050, Manganese 0.050, Iron 99.210 & Aluminum 0.010. Cleaning for the specimens were done in proportion to ASTM method G1-03 [36]. Methods were done without stirred hydrochloric acid solution that include variety conc. of CSCI as green inhibitor.

2.3.2. Weight loss method

Specimens that utilized with dimensions 2.5×2.0×0.025 cm and were hang (repeat 2 times) in 200.0mL., of the examined solution in presence and absence of variety conc., (0, 5×10^{-2}, 10×10^{-2}, 15×10^{-2}, 20×10^{-2}, 25×10^{-2} and 50×10^{-2}) g/L of the CSCI. In accordance with the periods of inundation times 1.0; 2.0; 3.0; 4.0; 5.0; 10.0; 24.0; 48.0 & 72.0 hrs, the specimen was took out, then washed and weighed accurately after drying. IE % was estimated utilizing Equation (1):

$$Inhibition\ Efficiency\ (IE\ \%) = (1 - w_2/w_1)\ x\ 100 \qquad (1)$$

w_1 & w_2, weight loss of the specimens in absence and presence of the green inhibitor.

CR (corrosion rate) was estimated by utilizing equation (2) [37,38].

$$C_R(mm/y) = \frac{87.6W}{at\rho} \qquad (2)$$

w, weight loss; ρ, mild steel density; a, specimen area; t, immersion time.

3. RESULTS AND DISCUSSION

3.1. Chemistry of Cherry Sticks Extract

3.1.1. LC-EIS/ MS

A basic, fast and delicate LC-ESI-MS/MS (liquid chromatography electro-spray ionization mass spectro-metry strategy has been utilized to characterize chemical compounds of cherry sticks extract. Electrospray ionization was firstly published by M. Yamashita and J. Fenn in 1984 [39]. The advancement of ESI for the investigation of organic macromolecules [40] was rewarded Nobel Prize [41]. Among the various working parameters in ESI-MS, the electrospray voltage has been distinguished as an essential parameter to consider in ESI LC/MS inclination elution [42]. From Figure 1, it can be demonstrated that the cherry sticks extract have eighteen compounds with diverse retention time as in table 1. Six of them are the primary compounds and they have the activity as corrosion inhibitor.

Table 1. The retention time and area of cherry sticks extract

No.	RT [min]	Area	S/N	Intens.
1.	12.9	489317	84.0	71625
2.	13.15	302931	62.6	61372
3.	13.69	6136557	952 .0	757523
4.	14.09	4288421	573.3	463432
5.	15.98	521182	100.4	88161
6.	16.65	581124	121.1	104223
7.	17.45	2971575	518.8	416981
8.	17.82	7555870	1164.8	928400
9.	18.52	778698	112.3	92350
10.	19.66	2185395	150.1	159686
11.	20.76	947641	123 .0	110459
12.	21.25	629358	107.8	109885
13.	22.05	2081983	204.3	172485
14.	23.29	424053	91.9	100613
15.	23.47	433675	85.5	109353
16.	23.71	2819888	369.2	319512
17.	27.32	1018205	95 .0	78563
18.	28.48	3568514	291.1	234528

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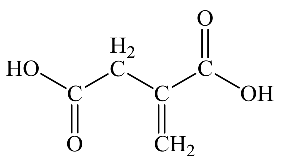
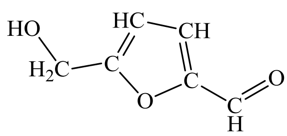
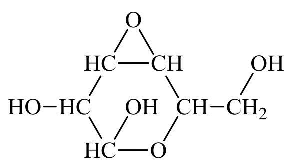


2-methylenesuccinic acid



5-(hydroxymethyl)furan-2-carbaldehyde carbaldehyde



2-(carbinol)-3,7-dioxabicyclo [4.1.0]-4,5-heptanediol

Scheme 1. The active compounds of plant aqueous extract of cheery sticks.

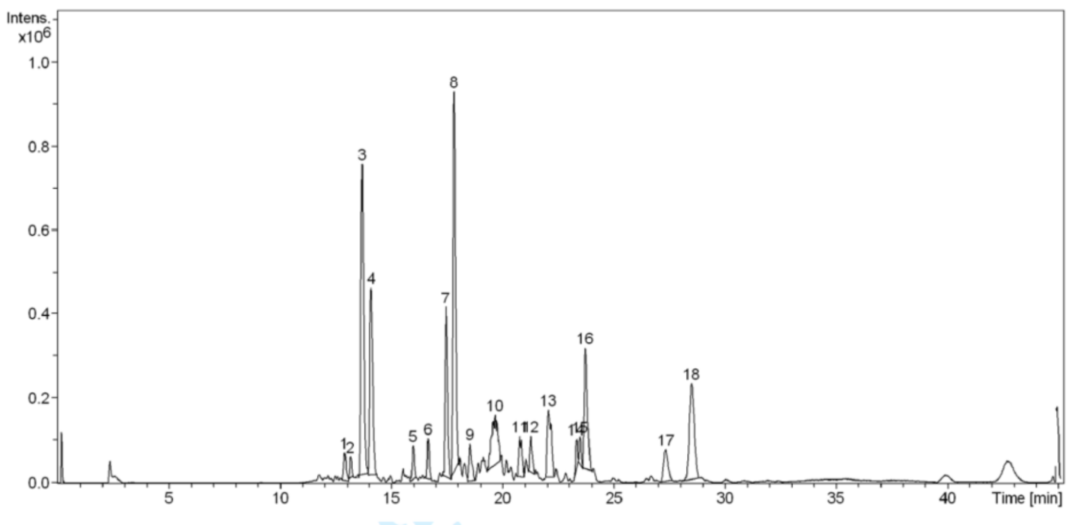


Figure 1. LC-ESI-MS/MS for Cherry sticks extract

Based on their mass spectra and fragmentation patterns related to corrosion inhibition, three compounds namely 2-methylenesuccinic acid, 5-(hydroxymethyl)furan-2-carbaldehydecarbaldehyde and 2-(hydroxymethyl)-3,7-dioxabicyclo[4.1.0]heptane-4,5-diol have the activities of action as inhibitors, Scheme 1

3.1.2. FT-IR spectroscopy

Infra-red spectrum of cherry sticks extract demonstrated a broad band at 3100cm^{-1}, due to hydroxyl group and another band at 1718.5cm^{-1} for C=O. From FT-IR we can conclude that the main compounds of cherry sticks extract were alcohols, carbonyls with long alkyl chains. From the LC-EIS/ MS and FT-IR spectroscopy we can determined the main structures of the extract "2-methylenesuccinic acid, 5-(hydroxymethyl)furan-2-carbaldehydecarbaldehyde and 2-(carbinol)-3,7-dioxabicyclo[4.1.0]-4,5-heptanediol ".

3.2. Weight loss method

3.2.1. Effect of concentration

The simple and confirmed, test for assessing compounds synthetic or natural as corrosion inhibitors is weight loss analysis. The results of the corrosion of mild steel exposed to different concentration in presence and absence of CSCI with different immersion times at 30 °C are summarized in Figures 2 & 3. It is indicated from Figures 2 & 3, that the *CSCI* diminished the corrosion of metal in hydrochloric acid media markedly. The Inhibition efficincy increment with addition of the inhibitor and came to greatest IE (%) at 50*10^{-2} g/L *CSCI*.

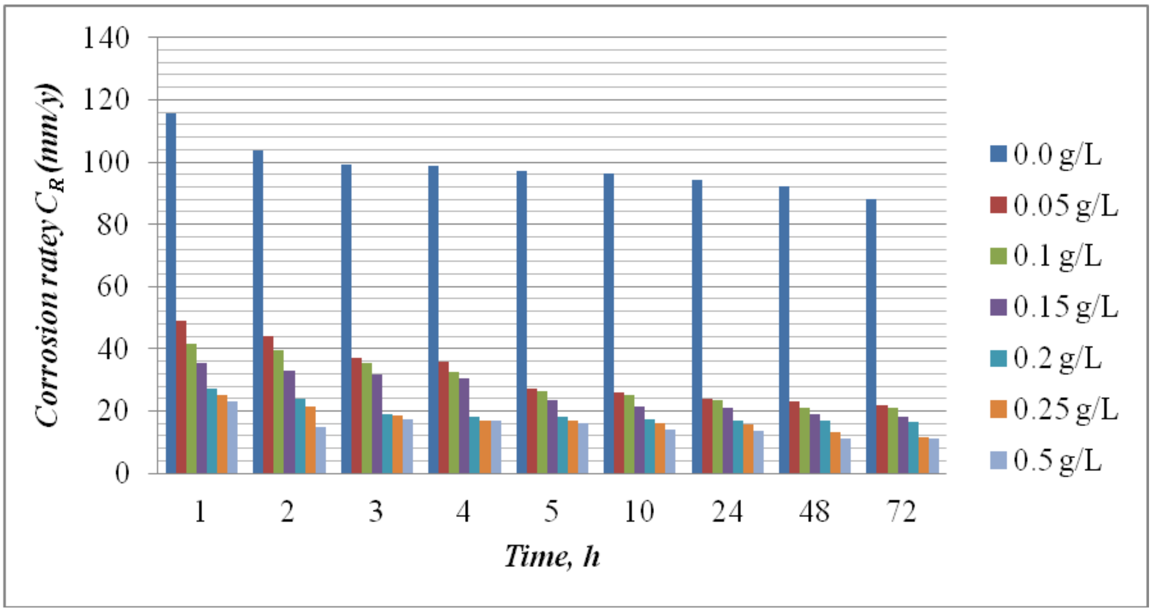


Figure 2. Effect of concentration of *CSCI* and time on corrosion rate at 303 K.

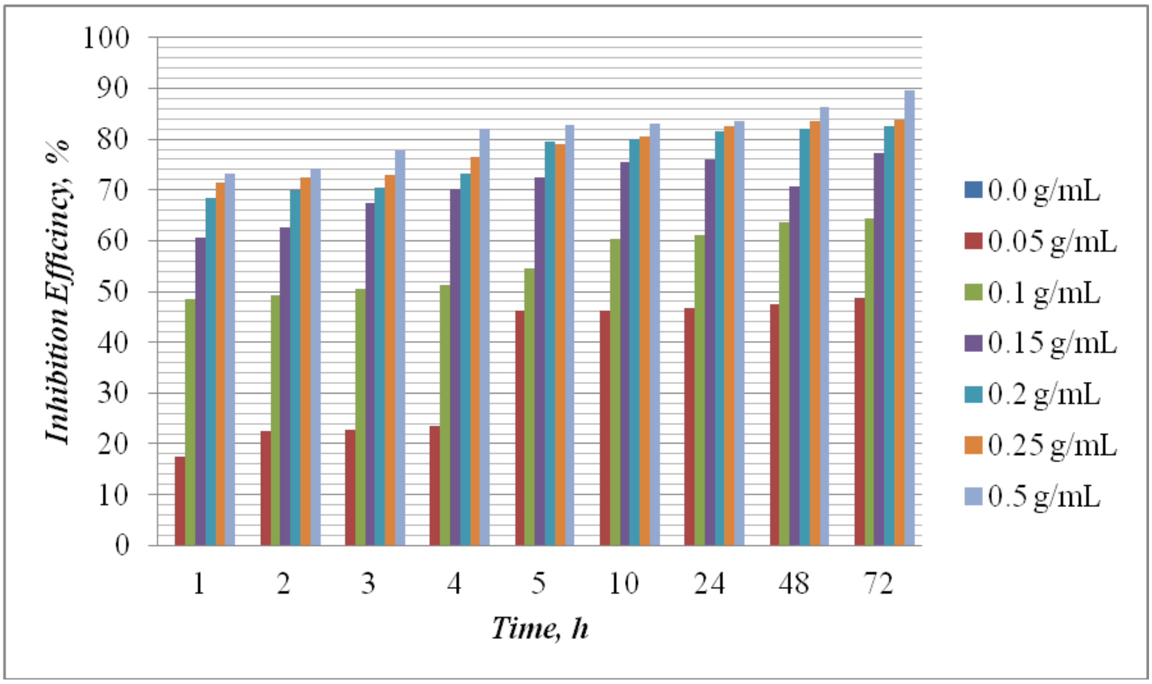


Figure 3. Effect of concentration of *CSCI* and time on inhibition efficiency at 303 K.

3.2.2. Impact of Temperature

A correlation of the IE of CSCI on metal in hydrochloric acid solutions with and without of different concentrations of CSCI at different temperatures (303.0; 313.0; 323.0 & 333.0) K demonstrated that IE upgraded with an increment in temperature as shown in Figure 4. With this procedure, the heat-adsorption is negative, and this demonstrated an exothermic reaction [43]. Rising temperature is mainly reason behind the decreases of the IE.

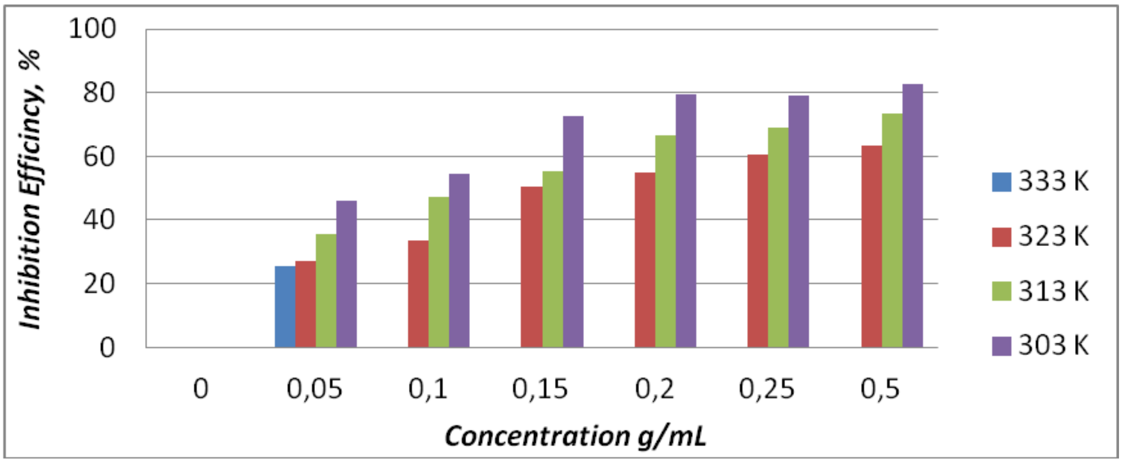


Figure 4. Impact of temperature on IE of *CSCI* with different concentrations.

3.2.3. Adsorption Isotherm

Adsorption of molecules on the metal surfaces plays an important role in inhibition of corrosion. The inhibitors diminish the corrosion rate chiefly by increase or decrease the cathodic or anodic reaction, diminishing the reactants diffusion rate compare to MS (metal surface) and the electrical resistance [44]. It depends primarily on the electronic characteristics of surface of the metal. Adsorption isotherm (AI) depicts the adsorptive conduct of synthetic or natural inhibitors which is important to show the mechanism of inhibition to MS. Langmuir, Temkin, Frumkin, and Freundluich are generally utilized as AIs (adsorption isotherms). AIs can give fundamental data related to the interactions of inhibitor and MS surface [45]. The adsorption process impacted by the structure of the organic compounds, distribution charge, nature of the surface and the types of media utilized [46]. Interaction between MS and inhibitor molecules can be better seen regarding the AI. It is realized that the AIs are critical for the grasp of the mechanism of inhibition. [47]. Values of θ (surface coverage) for the various concentrations of *CSCI* utilized to understand the AI and explain process of adsorption. θ, can be estimated from equation (3) [48],

$$\theta = \frac{IE\ \%}{100} \quad (3)$$

θ was estimated from equation (3) utilizing the inhibition efficiency estimated depending on weight loos method.

Straight line was produced from the plots $\frac{C_{inh}}{\theta}$ vs C_{inh} with a slope, showing that the *CSCI* obeys the Langmuir AI [49], as in the equation (4),

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

The Conc. Of *CSCI* was represented by C_{inh}; The adsorption constant K_{ads} was represent the intercept of the straight line.

Free energy, ΔG°_{ads} where given in equation (5):

$$\Delta G^{o}_{ads} = -RT\ln\,[55.5\ K_{ads}] \quad (5)$$

55.5 is the molar concentration of water in solution; R is the gas constant; T is the absolute temperature [37,38].

The values of k_{ads} and ΔG^{o}_{ads} were estimated depending on Figure 5. It was shown that ΔG^{o}_{ads} was −27.60 kJmol^{-1}. As a rule, if ΔG^{o}_{ads} approximately −20 kJmol^{-1} is proper with physical-adsorption, while a if ΔG^{o}_{ads} ds approximately −40 kJmol^{-1}or higher is proper with chemical-adsorption .The Estimated value of ΔG^{o}_{ads} is around −40 kJmol^{-1}and demonstrated mechanism via chemical-adsorption [49].

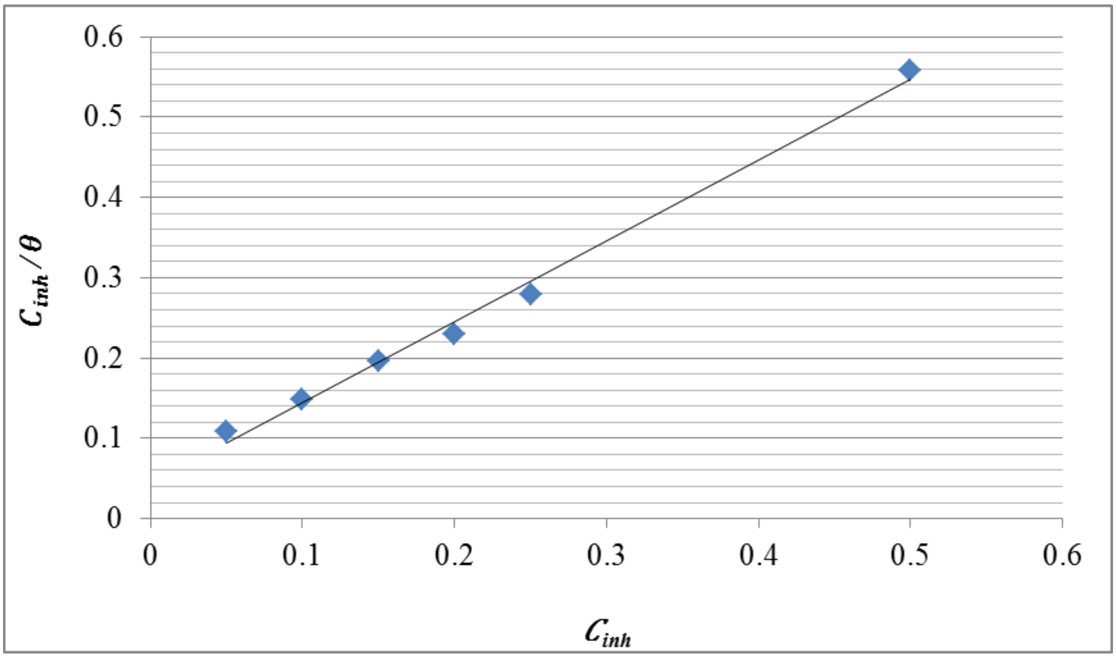


Figure 5. Adsorption isotherm for mild steel in 1.0 M HCl with different concentrations of the corrosion inhibitor

3.3. SEM.

A scanning electron microscope test was directed at the University Kebangsaan Malaysia Electron Microscopy Unit. In view of Figure 6a, obviously, risky corrosion happened where the metal surface, which was initially smooth, got to be harsh. According to Figure 6b, the surface of the metal doesn't suffer risky corrosion. *CSCI* become as a film with the provision prevention to surface from the hydrochloric acid attack.

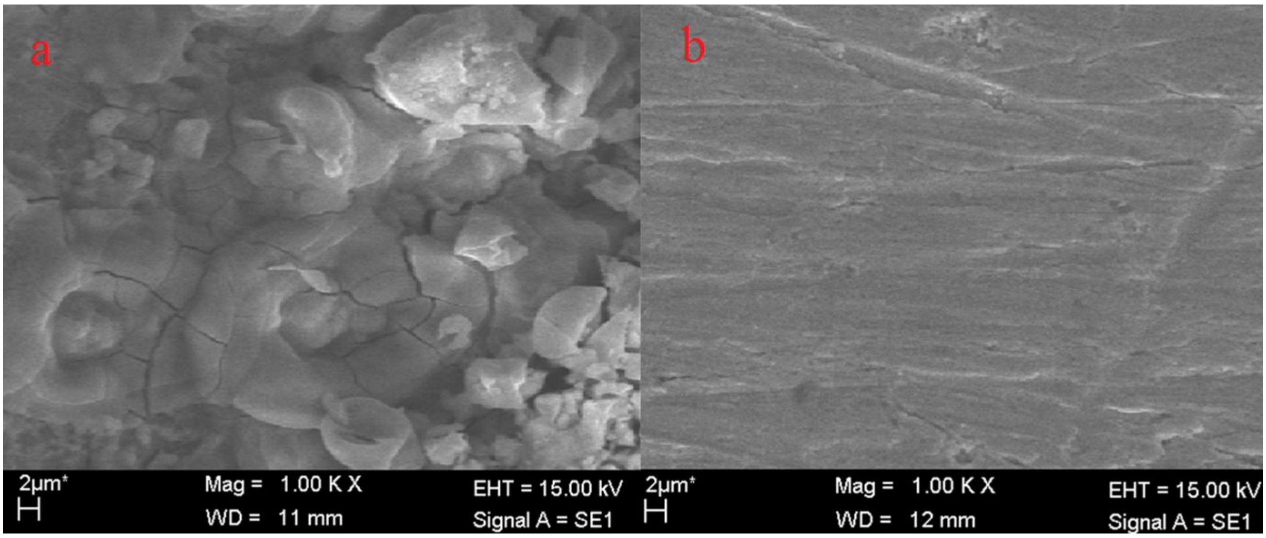


Figure 6. The scanning electron microscope micrographs 5000X, (a, without inhibition; b, with inhibition).

4. CONCLUSION

Sweet Cherry Sticks extract is used as corrosion inhibitor for metal in acid media. Inhibitor demonstrated highest IE up to 89.5% at the highest concentration. Isothermal study demonstrated that CSCI inhibited metal through adsorption mechanism. CSCI is demonstrated as a proficient natural inhibitor having great inhibition properties because of vicinity of natural compounds namely 2-methylenesuccinic acid, 5-(hydroxymethyl)furan-2-carbaldehydecarbaldehyde and 2-(carbinol)-3,7-dioxabicyclo[4.1.0]-4,5-heptanediol that they have hydroxyl and carbonyl groups.

Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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