

Environment Friendly Inhibitor for Mild Steel by *Artemisia Halodendron*

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Corrosion inhibition effect of *Artemisia Halodendron* leaves extract (AHLE) on mild steel in 1 M HCl medium has been investigated by electrochemical potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS) techniques. The polarization studies showed that AHLE acts as mixed-type inhibitor. The Nyquist plots showed that on increasing AHLE concentration, increases charge transfer resistance and decrease double layer capacitance. AHLE obeys the Langmuir adsorption isotherm. The corrosion inhibition efficiency of mild steel in hydrochloric acid solution by AHLE was discussed in terms of adsorption of protonated species and formed the protective film.

Keywords: Mild steel, Corrosion, Polarization, EIS, Acidic solutions, Plant extract

1. INTRODUCTION

Mild steel is most widely used as a significant material in many industries due to its excellence of mechanical properties and low costs. The most commonly used include chemical processing, petroleum production and metal processing equipment, etc. Acid solutions are always used in such applications, for example, chemical cleaning, descaling and pickling. However, these processes will leads to corrosive attack and the corrosion of mild steel caused heavy loss of the use. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption [1-3].

A number of organic compounds have been reported as effective corrosion inhibitors [4-6]. But, most of them are highly toxic to both human being and environment. Currently, research in corrosion is oriented to the development of “green corrosion inhibitors”, compounds with good inhibition efficiency but low risk of environmental pollution [7,8]. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple

procedures with low cost and are biodegradable in the environment. Thus, since the 1990s, many investigations have been related to the evaluation of natural compounds as corrosion inhibitors. For instance, the plants extracts of Hibiscus subdariffa [9], Azadirachta [10], Vernonia amygdalina [11], henna [12], Nypa fruticans Wurmb [13], Azadirachta indica [14], Acalypha indica [15], Zenthoxylum alatum [16], Damsissa [17], Phyllanthus amarus [18], Murraya koenigii [19], Justicia gendarussa [20], Oxandra asbeckii [21], ginkgo [22] and Stevia rebaudiana [23] etc. have been test as corrosion inhibitors for metals. These plant extracts are low cost, nontoxic, readily available, and ecofriendly substances. Therefore, finding naturally occurring substance as corrosion inhibitors is a subject of great practical significance.

The literature study reveals that the inhibition performance of plant extract is normally ascribed to the presence in their composition of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with N, S, O atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers. However, confronting with the vast varieties of plant, the data regarding the use of plant leaves extract as the corrosion inhibitor are still poor. In the present work, Artemisia Halodendron leaves extract is chosen to be the corrosion inhibitor.

Artemisia Halodendron belongs to the family Asteraceae, possesses diverse medicinal properties, and is used for the treatment of cough, asthma, expectorant, and bronchial asthma. These medicinal properties are due to the presence of natural organic compounds containing heteroatoms. It is well known that the acid corrosion of metals can be inhibited by compounds containing heteroatoms.

The present work was established to study the corrosion inhibition of mild steel in 1M HCl solution by employing novel plant Artemisia Halodendron leaves extract (AHLE) as a potential corrosion inhibitor using potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS). The thermodynamic parameters were also obtained and discussed.

2. EXPERIMENTAL

2.1 Preparation of plant extract

Dried *Artemisia Halodendron* (5g) plant leaves were soaked in deionized water (500ml) and refluxed for 5 h. The aqueous solution was filtered and concentrated to 100 ml. This concentrated solution was used to prepare solutions of different concentrations by dilution method. The *Artemisia Halodendron* plant extract was characterized by Fourier transform infrared (FT-IR) spectroscopy. FT-IR spectra was recorded in an AVATAR-FTIR-360 spectrophotometer (Thermo Nicolet Company), which extended from 4000 to 400 cm^{-1} , using the KBr disk technique.

2.2 Electrochemical measurements

Electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a fine Luggin

capillary as the reference electrode. To minimize the ohmic contribution, the tip of Luggin capillary was kept close to working electrode (WE). The WE was embedded in Teflon holder using epoxy resin with an exposed area of 0.785 cm². Before measurement the electrode was prepared by grinding with emery paper (grade 600, 800, 1000 and 1200), cleaned with double distilled water, degreased with acetone and dried, and then immersed in test solution at open circuit potential (OCP) for 2 h to be sufficient to attain the stable state. The temperature of the solutions used in electrochemical tests was held at 25 ± 2°C by a thermostat water bath. All electrochemical experiments were carried out using CHI660E electrochemical workstation. Each experiment was repeated at least three times to check the reproducibility and the good reproducible results were reported.

The potential of potentiodynamic polarization curves was started from cathodic potential of -250 mV to anodic potential of +250 mV vs. OCP at a sweep rate of 1 mV s⁻¹. Inhibition efficiency η_p (%) is defined as:

$$\eta_p (\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100$$

Where i_{corr}^0 and i_{corr} are the corrosion current density values without and with inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were carried out at open-circuit potential over a frequency range of 0.05 Hz - 100 kHz. The sinusoidal potential perturbation was 5 mV in amplitude. Electrochemical data were obtained after 1 h of immersion with the working electrode at the rest potential, and all tests have been performed in non-de-aerated solutions under unstirred conditions. Electrochemical data were analyzed by a Zsimpwin 3.30 Demo Version software. The values of η are calculated by the charge transfer resistance as follows:

$$\eta_E (\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

Where R_{ct} and R_{ct}^0 are the charge transfer resistance in presence and absence of inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of plant extract

The transmission vibrational spectrum of AHLE and the FT-IR peaks are given in Figure 1. Original absorption at 3419 cm⁻¹ (associated hydroxyl) was overlapped by the strong stretching mode of N-H or O-H, and that at 2927 cm⁻¹ is related to C-H stretching vibration. The strong band at 1630 cm⁻¹ is assigned to C=C and C=O stretching vibration. Owing to the conjugation effect of flavonoids of AHLE, the C=O peak shifts from about 1700 cm⁻¹ to lower wavenumber (approximately 1630 cm⁻¹), C=C and C=O stretching vibration bands are superposition [24]. The C-H bending bands in -CH₂ and -CH₃ are found to be at 1409 cm⁻¹. The absorption bands at 1272 cm⁻¹ could be assigned to the framework vibration of aromatic ring. Besides these, there are absorption bands at 1152 cm⁻¹, 1083 cm⁻¹ and 1027 cm⁻¹, which can be ascribed to the C-N or C-O stretching vibration. The absorption bands below 1000 cm⁻¹ correspond to aliphatic and aromatic C-H group. These results indicate that AHLE

contains O and N atoms in functional group (O-H, N-H, C=C, C=O, C=N, C-N, C-O) and aromatic ring. This shows that this plant extract contains mixtures of compounds, that is, alkaloids, flavonoids, and oils [25].

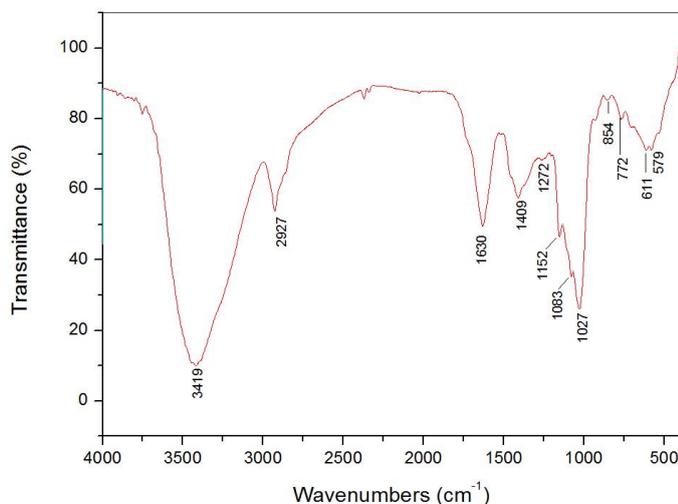


Figure 1. FT-IR transmittance spectra of AHLE.

3.2 Potentiodynamic polarization

Figure 2 shows potentiodynamic polarization curves for mild steel in 1 M HCl solutions without and with various concentrations of AHLE at 298 K (immersion time is 2 h). The corrosion kinetic parameters derived from these curves are presented in Table 1.

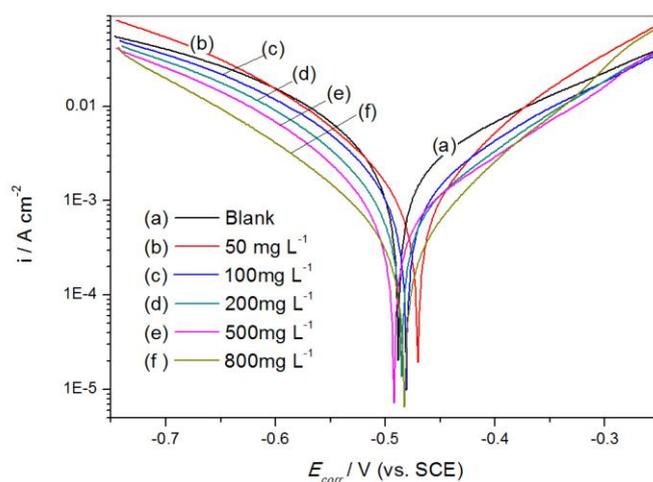


Figure 2. Potentiodynamic polarization curves for mild steel in 1 M HCl without and with different concentrations of AHLE at 298 K (immersion time is 2 h).

It was observed that both the cathodic and anodic curves showed lower current density in the presence of the plant extract than that recorded in the acid solution without the extract. This indicates that the addition of AHLE to acid solution reduces the anodic dissolution of metal and also impedes the cathodic hydrogen evolution reaction [26]. In Table 1 the potentiodynamic polarization parameters including corrosion current densities (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a), and inhibition efficiency (η_p). It can be seen from the Table 1 that i_{corr} decreased noticeably with increase in AHLE concentration which implies that AHLE behaves as a very good corrosion inhibition for mild steel in 1 M HCl solution. An inhibitor, in general, can be classified as an anodic-type or cathodic-type when the change in E_{corr} value is larger than 85 mV [27]. But in this study, the largest displacement exhibited by the extract was 18 mV, from which it can be concluded that AHLE acts as a mixed type inhibitor. On the other hand, the anodic and cathodic slope values of inhibited solution have changed with respect to uninhibited solution which also reiterates that the extract is mixed type effect.

Table 1. Potentiodynamic polarization parameters derived from potentiodynamic polarization measurements.

Concentration (mg L ⁻¹)	E_{corr} (vs SCE/ V)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	β_c (mV dec ⁻¹)	η_p (%)
Blank	-0.488	2.789	165.9	-146.0	-
50	-0.470	1.419	103.9	-114.1	49.1
100	-0.481	1.143	133.8	-131.6	59.0
200	-0.485	0.870	120.1	-120.9	68.8
500	-0.492	0.582	130.9	-119.7	79.1
800	-0.483	0.393	96.7	-114.9	85.9

3.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) has been widely used in investigating corrosion inhibition processes since it provides more information on both the resistive and capacitive behavior at metal/solution interface [28]. The corrosion behavior of mild steel in 1 M HCl solution in the absence and presence of the extract was investigated using this technique. The impedance data are presented as Nyquist and Bode plots in Figures 3 and 4, respectively. The electrochemical equivalent circuit employed to analyze impedance spectra is shown in the inset of Figure 3. In the equivalent circuit, R_s represents the solution resistance, R_{ct} represents the charge transfer resistance, and CPE represents the constant phase element describing the interface double layer. The impedance (Z_{CPE}) of CPE can be represented as follows [8]:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n}$$

Where Y_0 is a proportional factor, n has the meaning of a phase shift. For $n=0$, CPE represents a resistance, for $n=1$ a capacitance, for $n=0.5$ a Warburg element and for $n=-1$ an inductance. According

to Hsu and Mansfeld [29], the value of the double-layer capacitance (C_{dl}) can be obtained from the equation:

$$C_{dl} = Y_0(\omega'')^{n-1}$$

Where ω'' is the frequency at which the imaginary part of the impedance has a maximum. The impedance parameters such as R_s , R_{ct} , C_{dl} and inhibition efficiency (ηE , %) are listed in Table 2.

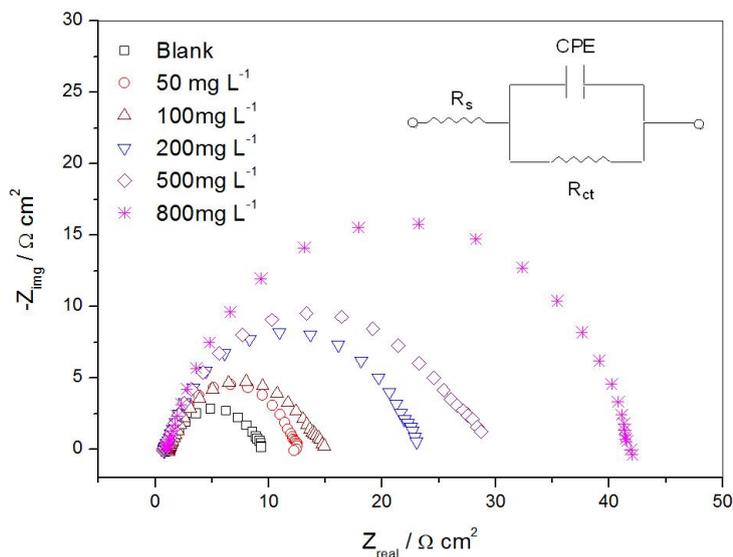


Figure 3. Nyquist plots (solid line shows fitted results) for mild steel in 1 M HCl in the absence and presence of different concentrations of AHLE.

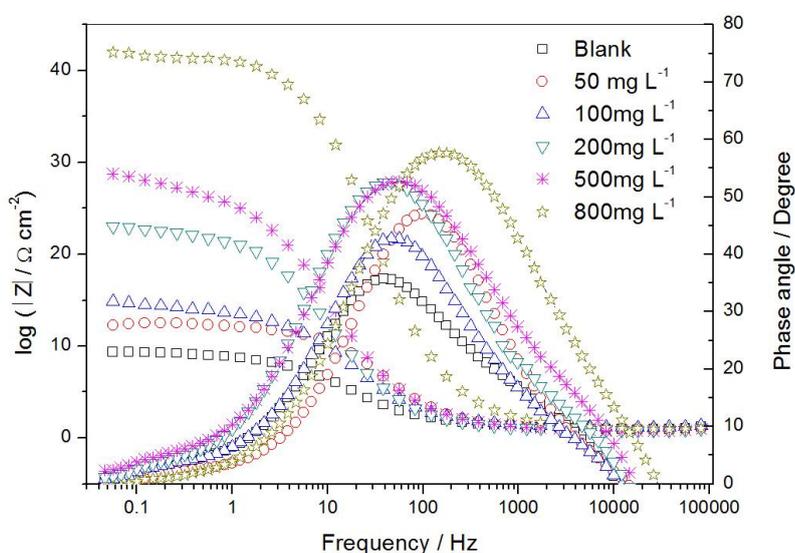


Figure 4. Bode plots for mild steel in 1 M HCl in the absence and presence of different concentrations of AHLE.

Table 2. The impedance parameters for mild steel in 1 M HCl solutions without and with various concentrations of AHLE.

Concentration (mg L ⁻¹)	R_s (Ω cm ²)	R_{ct} (Ω cm ²)	C_{dl} (μ F cm ⁻²)	η_E (%)
Blank	0.68	18.05	392	—
50	0.94	31.55	224	42.8
100	0.71	52.47	133	65.6
200	0.68	52.62	136	65.7
500	0.79	73.97	95	75.6
800	0.46	162.61	43	88.9

It can be concluded from the Figure 3 that a single semicircle has been observed at high frequency. This can be attributed to charge transfer of the corrosion process, and also, the diameter of the semicircle increases in increasing AHLE concentration. It is apparent from the Table 2 that the presence of AHLE in acid media leads to decrease in C_{dl} values. The decrease in C_{dl} values can be attributed to the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [7]. Meanwhile the increase in R_{ct} values indicates that the extent of adsorption with increase in extract concentration and also the adsorbed extract forms a protective film on the mild steel surface which becomes a barrier to hinder the mass and charge transfer processes. On the other hand, one time constant was observed in the Bode diagram (Figure 4). The maximum phase angle for corroding system represented by a simple RC parallel combination should be 90° when $R_s=0$. However, depressed semicircles are usually obtained for an electrode/solution interface, which has been known to be associated with a rough electrode surface [30]. The corrosion of mild steel in acid media increases the roughness of the electrode surface and therefore reduces the phase angle. But in Figure 4, the phase angle increase with increase in extract concentration which indicates the decrease in surface inhomogeneity. Due to all these factors as the concentration of AHLE increases, the protection efficiency also increases. These results confirm that AHLE exhibits good inhibitive performance for mild steel in 1 M HCl solutions, and the data obtained from EIS are in good agreement with those obtained from potentiodynamic polarization method.

3.4 Adsorption isotherm

It is generally assumed that the adsorption of inhibitor on the metal surfaces is the essential step in the mechanism of inhibition. The establishment of isotherms that describe the adsorption behavior of corrosion inhibitors is essential because they provide important clues about the nature of metal inhibitor interaction. For this purpose, the values of surface coverage (θ) corresponding to different concentrations of AHLE have been used to determine the adsorption isotherm. The values of θ were calculated using the data obtained from the potentiodynamic polarization and EIS measurements by the equation given below [6,31]:

$$\theta = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \quad \text{and} \quad \theta = \frac{C_{dl(\theta=0)} - C_{dl,\theta}}{C_{dl(\theta=0)} - C_{dl(\theta=1)}}$$

Where $C_{dl(\theta=0)}$ and $C_{dl(\theta=1)}$ are the double layer capacitances of the inhibitor-free and entirely inhibitor-covered surfaces, respectively. $C_{dl,\theta}$ is the composite total double layer capacitance for any intermediate coverage θ . Unfortunately, the $C_{dl(\theta=1)}$ value is impossible to be obtained through experimental measurements. However, the adsorption of organic adsorbate at a metal/solution interface can be represented as a substitutional adsorption process between the organic molecules and the water molecules on the metal surface [32]. Due to the decrease in local dielectric constant and/or the increase in the thickness of the electrical double layer, the doublelayer capacitance values of the metal surface fully covered by the inhibitive molecules can be far less than that of the metal surface fully covered by water molecules, i.e., $C_{dl(\theta=1)} \ll C_{dl(\theta=0)}$. Thus the Equation of θ calculation using the data of double-layer capacitance (C_{dl}) can be simplified as follows [33]:

$$\theta = \frac{C_{dl(\theta=0)} - C_{dl,\theta}}{C_{dl(\theta=0)}}$$

Attempts were made to fit experimental data to various isotherms including Frumkin, Langmuir, Temkin, Freundlich and Flory-Huggins isotherms. However the results were well fitted by Langmuir [34] adsorption isotherms:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

Where C is the inhibitor concentration, K_{ads} is the equilibrium constant of adsorption process. For both methods, the plots of C/θ versus C were straight lines with almost unit slopes and are given in Figure 5. From the intercept of the straight lines, K_{ads} are obtained and listed in Table 3. In addition, the free energy of adsorption process ΔG_{ads}^0 can be calculated from the equation [35]:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right)$$

Where 55.5 is the concentration of water in the solution in mol dm^{-3} , K = equilibrium adsorption constant, R = the universal gas constant, and T = the thermodynamic temperature. The value of ΔG_{ads}^0 from the Langmuir adsorption isotherm in 1 M HCl for both methods were calculated and listed in Table 3. Generally, values of ΔG_{ads}^0 around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption); those around -40 kJ mol^{-1} or higher involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [36]. The calculated ΔG_{ads}^0 value shows, therefore, that the adsorption mechanism of the AHLE on mild steel in 1 M HCl solution was typical of physisorption.

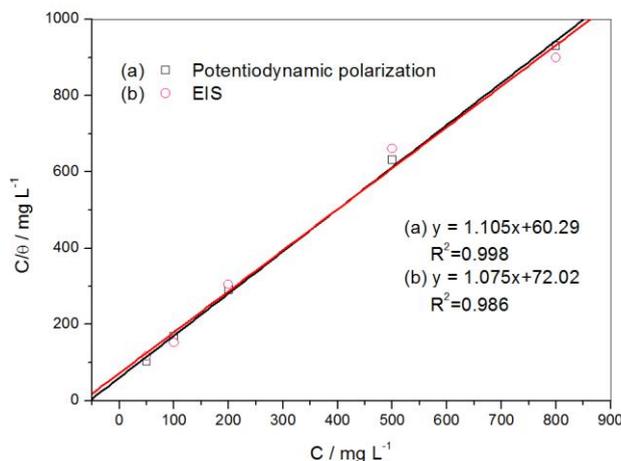


Figure 5. Langmuir adsorption plots of mild steel in 1 M HCl solution containing different concentrations of AHLE determined from potentiodynamic polarization and EIS measurements.

Table 3. Thermodynamic parameters acquired from Langmuir adsorption isotherm in case of both potentiodynamic polarization and EIS techniques.

Parameter	potentiodynamic polarization	EIS
K_{ads} (L mg ⁻¹)	0.01659	0.01389
$-\Delta G_{ads}^0$ (kJ mol ⁻¹)	16.91	16.47

3.5 Inhibition mechanism

The observed corrosion inhibition of mild steel in 1 M HCl solution with increase in AHLE concentration can be explained by the adsorption of the components of the *Artemisia Halodendron* extract on the metal surface. The phenomenon of adsorption is influenced by the nature and surface charge of the metal and by the chemical structure of inhibitors. The surface charge of the metal is due to the electrical field which emerges at the interface on immersion in the electrolyte. It is also well known that steel surface in 1 M HCl charges with a negative charge because of $E_{corr} - E_{q=0}$ (zero charge potential) < 0, thus, it is easy for the positively charged inhibitor (i.e., chemical components which contained N atoms) to approach the negatively charged steel surface due to the electrostatic attraction. When an inhibited solution contains adsorbable anions, such as halide ions, these adsorb on the metal surface by creating oriented dipoles and consequently increase the adsorption of the organic actions on the dipoles (physical adsorption). Also, the AHLE contains many oxygen atoms with the two sets of lone-pair electrons. In neutral aqueous solution, it exists in the form of neutral molecule, in acidic solution, however, the so-called atoms can be protonated, leading to the positive charge in the molecule (cationic form). This is the possible adsorption mechanism of the *Artemisia Halodendron* extract on mild steel in 1 M HCl solution as physical adsorption. Accordingly, the values of K_{ads}

obtained in the present study indicated that the adsorption mechanism of AHLE on mild steel was typical physical adsorption. This mechanism is in good agreement with the experimental data obtained from potentiodynamic polarization and EIS techniques. It could therefore be concluded that the corrosion inhibition of mild steel in hydrochloric acid solution by *Artemisia Halodendron* extract was afforded by adsorption of protonated species rather than neutral molecules onto the metal surface.

4. CONCLUSIONS

The extract of *Artemisia Halodendron* leaves acts as a mixed-type inhibitor for mild steel in 1 M HCl solution. The protection efficiency of AHLE increases with the increasing of the concentration. The adsorption of the extract follows Langmuir adsorption isotherm. The inhibition efficiency values obtained from potentiodynamic polarization measurements are comparable with those obtained from the EIS techniques. The corrosion inhibition of mild steel in hydrochloric acid solution by *Artemisia Halodendron* extract was afforded by adsorption of protonated species rather than neutral molecules onto the metal surface.

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