# *Launaea nudicaulis* as a Source of New and Efficient Green Corrosion Inhibitor for Mild Steel in Acidic Medium: A Comparative Study of Two Solvent Extracts

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The inhibitive effect of *Launaea nudicaulis* methanolic (MLN) and aqueous acidic (ALN) extracts on the corrosion of mild steel in 1.0 M HCl solution was investigated by using weight loss, Tafel plots, linear polarization, electrochemical impedance spectroscopy (EIS) as well as SEM and EDS techniques. It was found that both extracts (MLN and ALN) inhibit remarkably the corrosion of mild steel in acidic solution and inhibition efficiencies increased with the increase of extracts concentration. The results revealed that MLN and ALN behaved as mixed type corrosion inhibitors with predominant anodic effectiveness. Inhibition efficiencies obtained from weight loss and electrochemical experiments were in good agreement and they were up to 92.5 % for MLN and 87.2 % for ALN. The effect of temperature on the corrosion behavior of mild steel was studied in the range of 298K–328$\pm$1K. Adsorption behavior of both green inhibitors on the MS surface followed the Langmuir adsorption isotherm and they inhibited the corrosion of mild steel by adsorption mechanism where the adsorption process involved was spontaneous, exothermic and physically adsorbed (physisorption). Surface morphology study through scanning electron microscope (SEM) and energy dispersive X-ray spectrometry (EDS) analysis showed a significant improvement on the surface morphology of the mild steel plate in the presence of MLN as well as ALN in 1.0 M HCl media. However, MLN was found to be more potent than ALN. The results showed that *L. nudicaulis* extracts could serve as efficient corrosion inhibitor for mild steel in hydrochloric acid environment.

## 1. INTRODUCTION

Corrosion is a very common phenomenon in industries where it creates major problems due to its hazardous nature on metals [1]. The damage done by corrosion generates not only high cost for

inspection, repairing and replacement, but in addition it also leads to a public and environmental risk. Mild steel is extensively used as a constructional material in many industries because of its excellent mechanical properties, ductability, weldability and low cost. However, when exposed to the corrosive industrial environment, it is easily corroded [2]. Metals corrosion starts mainly when they come in contact with water in the presence of air and corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions which change the composition and properties of both metal surface and the local environment (for example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes, and change of electrochemical potential). Other major reason for corrosion of metals is due to the use of acids in various industrial processes. Acidic solutions are frequently used in various industries during acid pickling, chemical cleaning and processing, ore production, industrial cleaning, acid rescaling, oil-well acidification, and petrochemical processes. Comparing to other mineral acids such as sulphuric acid, nitric acid and phosphoric acid, use of hydrochloric acid in industrial processes is more common as it is considered to be more economical, efficient and trouble-free [3,4]. Therefore, in order to minimize the corrosion of the industrial equipments and facilities, it is of immense importance to develop environmental friendly, practical and economical way to protect metals from corrosion caused by acidic solutions, especially with hydrochloric acid. This goal can be achieved by using various corrosion inhibitors [5-10]. Corrosion inhibitors are chemicals (either synthetic or natural) that, when added in small quantities in the corrosive media, either they stop or slow down the corrosion of metals. A large number of synthetic compounds [11-16] including heterocyclic compounds [17-22] are known to be applicable as good corrosion inhibitors for mild steel [23,24]. However, most of them are found to be toxic, and expensive, hence, their popularity and use as corrosion inhibitors is being diminished as they have adverse effects on living beings and environment [25]. Therefore, there exists a need to develop a new class of corrosion inhibitors with low toxicity, eco-friendly and with good inhibition efficiency.

In recent years, plants have been emerged as an excellent source for the development of novel and effective green corrosion inhibitors for metals. Consequently, research into the use of plant extracts and several pure organic molecules (phytomolecules) from the plant origin as effective green corrosion inhibitors for metals have been intensified [25-35] as they are well thought-out to be environmentally acceptable, non-toxic, renewable, easily accessible, and biodegradable [36-39]. Moreover, plants have been described as chemical factories that are capable of synthesizing unlimited numbers of highly complex and unusual chemical substances whose structures could escape the imagination of synthetic chemists forever. Plants can supply us with various classes of phytochemicals such as alkaloids, flavonoids, proteins, tannins and carbohydrates. Molecular structures of these hetero phytomolecules consist of polar function like nitrogen, sulfur, oxygen atoms as well as conjugated double bonds and aromatic rings, which have the capability to adsorb strongly on the metal surfaces and thus, effectively retard the corrosion of metals [40].

As part of our ongoing research on Saudi Arabian plants for the development of products of potential economic values [41,42], in the present study, we report here for the first time a detailed investigation of the corrosion inhibitive action of two extracts of *Launaea nudicaulis* on mild steel. *Launaea* is a relatively small genus consists of about 40 plant species growing in dry, saline and sandy habitats. They belong to the tribe Lactucaea of the daisy family Asteraceae [43,44]. Various *Launaea*

species possesses antitumor, insecticidal, cytotoxic and antioxidant activities and are well known in traditional medicine due to their various medicinal properties such as diuretic, aperients, soporific, galactagouge, febrifuge, and stomachic [45-47]. *L. nudicaulis* is an important plant species of this genus and in Saudi Arabia it is one of the most fairly widespread plants, famous with its local Arabic name 'Al-Hewa' [48-50]. It is a perennial naked-stemmed herbs containing yellow flowers of about 2 cm wide with sweet scent and is frequently and popularly used in folk medicine by local people for the treatment of fever, itches, ulcers, cuts, swellings, toothache, eczema eruptions and rheumatism [45,50,51]. Due to the wide applications of *L. nudicaulis* in folk medicine and its various potent biological activities including insecticidal, cytotoxic, antimicrobial, hypoglycaemic and anti-inflammatory [47,52,53], this plant has been extensively investigated and reported to be a rich source of various classes of compounds such as flavonoids, terpenoids, acetylenes, shingolipids, steroids and their glycosides [52,54-57]. Among them many classes of compounds specially flavonoids and acetylenes could play a possible role and find potential applications as anticorrosive agents. However, to the best of our knowledge, *L. nudicaulis* has never been investigated for its corrosion inhibitive properties which prompted us to carry out detail study on corrosion inhibitive actions of *L. nudicaulis* on mild steel in acidic media.

Here in, we reports corrosion inhibitive properties of methanolic and aqueous acidic extracts of *L. nudicaulis* on mild steel in 1.0 M HCl using weight loss, Tafel plots, linear polarization, and electrochemical impedance spectroscopy (EIS) as well as SEM and EDS methods.

## 2. EXPERIMENTAL

### 2.1 Collection of plant material and identification

The whole plant of wild growing *L. nudicaulis* was collected from Rowdah Khuraim, central part of Saudi Arabia in the month of March 2011. Identification of the plant species was confirmed by a plant taxonomist, Herbarium Division, College of Science, King Saud University, Riyadh, KSA. A voucher specimen of the plant material has been maintained in our laboratory as well as in the herbarium division of King Saud University with voucher specimen no. KSU-21700.

### 2.2 Extraction of plant materials

Shade air-dried and powdered whole plant materials (150.0 g) of *L. nudicaulis* were first defatted with *n*-hexane three times at room temperature for 72 h each. The defatted plant materials were then extracted three times with methanol at room temperature for 72 h each. The combined methanol extracts were concentrated under vacuum at 40 °C until methanol was completely removed. This dried methanolic extract (7.5 g) was used to prepare test solutions of different required concentration in 1.0 M aqueous hydrochloric acid solution. In case of aqueous acidic extraction method, 100 g of dried and powdered plant material of *L. nudicaulis* was soaked in 1.0 M aqueous hydrochloric acid solution and kept for 24 h at room temperature, filtered out and the resultant stock

solution was used to prepare the test solutions of required concentration. The concentration of the stock solution was determined by evaporating 10 ml of stock solution on a rotary evaporator and weighing the resultant residue.

## 2.3 Materials, preparation of test specimen and solutions

The material used for constructing the working electrode was mild steel purchased from Goodfellow, England with chemical composition (wt %) as follows; C-0.2 %, Mn-0.94 %, Si-0.3 % and rest being iron with an exposed area of 0.9498 cm$^2$. The exposed area was mechanically abraded with a series of emery papers of variable grades, starting with a coarse one (600) and proceeding in steps to the finest (1000) grade. The sample was then washed thoroughly with double distilled water and degreased with acetone just before insertion in the cell. All chemicals, reagents used were of analytical grade and double distilled water was used for preparing solutions. The aggressive solutions of 1.0 M HCl was prepared by dilution of AR grade 37 % HCl with distilled water.

## 2.4 Weight loss measurements

Firstly, mild steel specimens were abraded with a series of emery paper (grade 600-800-1000), washed with distilled water, degreased with acetone, and dried with a cold air stream then used for weight loss measurement. After weighing accurately on an analytical balance with sensitivity of $\pm 0.1$ mg, three parallel MS specimens were completely immersed in an open beaker containing 100 mL of 1.0 M HCl with and without different concentrations of inhibitors at different temperatures (298, 313 and 328$\pm$1 K) for 3 h. Then, the mild steel specimens were removed, washed with distilled water, dried and weighed accurately. In order to get good reproducibility, experiments were carried out in triplicate and the weight losses were averaged. Inhibitor concentrations starting from 100 to 400 ppm were used. The percentage inhibition efficiency (*IE* %) and degree of surface coverage ($\theta$) were calculated by the following equations:

$$IE\ \% = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

$$\theta = \frac{IE\ \%}{100} \qquad (2)$$

where $W_0$ and $W_i$ are the weight loss of the mild steel specimens in absence and in presence of inhibitors, respectively.

The corrosion rate ($C_R$) of mild steel was calculated using equation (3):

$$C_R\ (mm\ year^{-1}) = \frac{87.6\ W}{AtD} \qquad (3)$$

where $W$ is the corrosion weight loss of mild steel (mg), A the area of the specimen, t the exposure time (h) and D is the density of mild steel ($\text{gcm}^{-3}$).

## 2.5 Electrochemical studies

The electrochemical studies were carried out in a conventional three-electrode cell assembly at room temperature using an ACM potentiostat serial number-784 with EIS software, ACM instruments Inc., U.K. A platinum foil of 1 cm$^2$ was used as a counter electrode (CE), and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary was used as the reference electrode. The tip of Luggin capillary was kept close to working electrode (WE) to minimize the ohmic contribution. The WE was in the form of a circular rod of mild steel with aforementioned composition tightly embedded in a Teflon rod using epoxy resin leaving only one exposed surface area of 0.9498 cm$^2$. Prior to the electrochemical measurements the working electrode was immersed in test solution for approximately 30 min until a steady open-circuit potential (OCP) was reached. The Tafel polarization curves were studied from cathodic potential of $-250$ mV to an anodic potential of $+250$ mV at a constant sweep rate of 1 mV/s to study the effect of inhibitor on mild steel corrosion. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities ($I_{corr}$). The inhibition efficiency was calculated from the measured ($I_{corr}$) values using equation (4):

$$IE\ \% = \frac{I^0_{corr} - I^i_{corr}}{I^0_{corr}} \times 100 \qquad (4)$$

where $I^i_{corr}$ and $I^0_{corr}$ are the corrosion current densities in presence and absence of inhibitors, respectively

The linear polarization resistance (LPR) measurements were carried out by polarizing the specimen from $-25$ to $+25$ mV with respect to corrosion potential ($E_{corr}$) at a scanning rate of 0.125 mV/s to measure the polarization resistance ($R_p$). From the measured polarization resistance value, the inhibition efficiency was calculated by using the equation:

$$IE\ \% = \frac{R^i_p - R^0_p}{R^i_p} \times 100 \qquad (5)$$

where $R^i_p$ and $R^0_p$ are the polarization resistance in presence and absence of inhibitors, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential (OCP) by using ac signals of 10 mV amplitude in a frequency range of 30 kHz to 10 mHz . The charge transfer resistance values were obtained from the diameter of the semicircles of the Nyquist plots. The electrical equivalent circuit for the system is shown in Fig. 1. In the given electrical equivalent circuit, $R_{ct}$ is the charge transfer resistance, $R_s$ is the solution resistance and $C_{dl}$ is the

double layer capacitance. The inhibition efficiencies of the inhibitors have been calculated from the charge transfer resistance values by using equation (6):

$$IE \% = \frac{R_{ct}^i - R_{ct}^0}{R_{ct}^i} \times 100 \qquad (6)$$

where $R_{ct}^0$ and $R_{ct}^i$ are the charge transfer resistance in absence and in the presence of inhibitors, respectively.
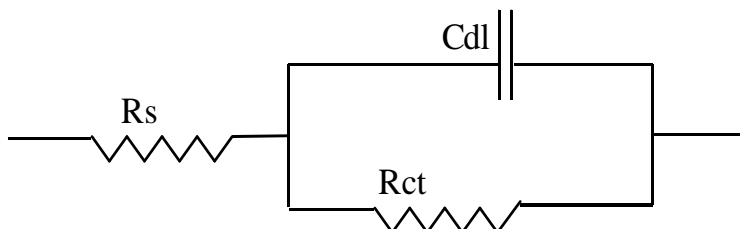


**Figure 1.** The electrical equivalent circuit for ac impedance measurement.

To assure the reliability and reproducibility of the measurements, all the experiments were done in triplicate in each case under the same conditions and the mean of each experiment were reported.

*2.6 SEM and EDS analysis*

The mild steel coupons were immersed in 100 mL of 1.0 M HCl without and with the inhibitors (MLN and ALN) concentration of 400 ppm for the period of 3 h. Then they were removed, rinsed quickly with acetone and dried. The surface morphology of the specimens was examined using a JEOL–JSM-6380LA Scanning Electron Microscope (SEM–EDS).

## 3. RESULTS AND DISCUSSION

*3.1 Weight loss measurements*

The effect of both green inhibitors, methanolic (MLN) and aqueous acidic extracts (ALN) of *L. nudicaulis* concentration on mild steel in 1.0 M HCl were studied using weight loss measurement at $298 \pm 1$ K for 3 h immersion period. The values of percentage inhibition efficiency ($IE \%$), corrosion rate and surface coverage ($\theta$) obtained are given in Table 1, whereas Fig. 2 shows the effect of inhibition efficiency with different concentrations of MLN and ALN.

**Table 1.** Inhibition efficiency, weight loss, surface coverage and corrosion rate for various concentrations of inhibitors for the corrosion of mild steel in 1.0 M HCl from weight loss measurements at 298±1 K.

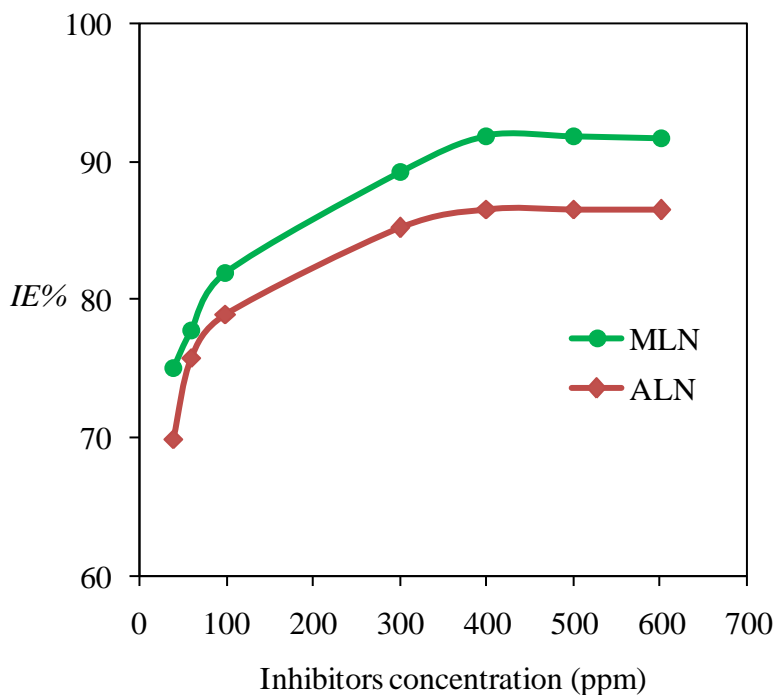| Inhibitors | Concentration of inhibitor (ppm) | Weight loss (g) | Surface coverage ($\theta$) | Corrosion rate $C_R$ (mm year$^{-1}$) | (*IE* %) |
|---|---|---|---|---|---|
| | 0 (Blank) | 0.2587 | - | 16. 18 | - |
| | 40 | 0.0643 | 0.7508 | 4.03 | 75.1 |
| | 60 | 0.0574 | 0.7775 | 3.60 | 77.8 |
| **MLN** | 100 | 0.0467 | 0.819 | 2.93 | 81.9 |
| | 300 | 0.0278 | 0.8922 | 1.74 | 89.2 |
| | 400 | 0.0209 | 0.919 | 1.31 | 91.9 |
| | 500 | 0.0211 | 0.918 | 1.33 | 91.8 |
| | 600 | 0.0215 | 0.917 | 1.35 | 91.7 |
| | 40 | 0.0776 | 0.699 | 4.86 | 69.9 |
| | 60 | 0.0625 | 0.758 | 3.92 | 75.8 |
| **ALN** | 100 | 0.0544 | 0.789 | 3.41 | 78.9 |
| | 300 | 0.0383 | 0.852 | 2.40 | 85.2 |
| | 400 | 0.0347 | 0.866 | 2.17 | 86.6 |
| | 500 | 0.0347 | 0.866 | 2. 17 | 86.6 |
| | 600 | 0.0350 | 0.865 | 2. 19 | 86.5 |



**Figure 2.** Variation of inhibition efficiency with different concentrations of MLN and ALN.

It can be seen from Table 1 and Fig. 2 that both green inhibitors showed efficient anticorrosive property for mild steel in 1.0 M HCl aggressive media. It is noted that inhibition efficiencies increases

with the increase of inhibitors concentration. This may be due to the increase in adsorption of more phytomolecules at the metal/solution interface on increasing the concentration of inhibitors. The increase in inhibition efficiencies was noticed until the inhibitors concentration reached up to 400 ppm and beyond that further increase in inhibitors concentration did not show any marked improvement in the performance of both extracts (Fig. 2). This may be due to the removal of extracts molecules back into the inhibitive solution when the concentration of inhibitor reaches beyond the critical concentration [33]. This effect leads to the weakening of metal–inhibitor interactions, resulting in the replacement of inhibitor by water or chloride ions with decrease in inhibition efficiency [58]. Thus, 400 ppm was considered to be optimum concentration at which maximum inhibition efficiency was achieved for both extracts (MLN and ALN). Having determined the optimum concentration for both inhibitors, effect of different temperature (298±1-328±1 K) at optimum inhibitor concentration for both extracts was carried out during 3 h of immersion time and the results are shown in Table 2 and Fig. 3.

**Table 2.** Inhibition efficiency, weight loss, surface coverage and corrosion rate at various temperatures for the corrosion of mild steel in 1.0 M HCl in the presence of 400 ppm of inhibitors from weight loss measurements.

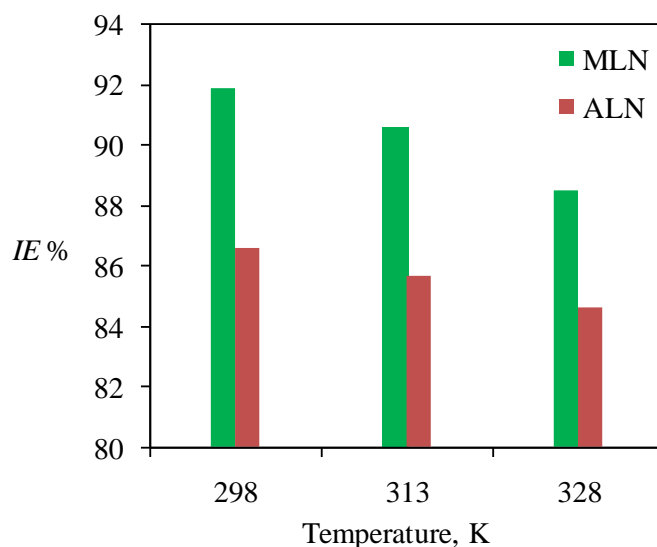| Inhibitors | Temperatures (K) | Weight loss (g) | Surface coverage ($\theta$) | Corrosion rate $C_R$ (mm year$^{-1}$) | (*IE* %) |
|---|---|---|---|---|---|
| **MLN** | 298±1 | 0.0209 | 0.919 | 1.31 | 91.9 |
| | 313±1 | 0.0243 | 0.906 | 1.52 | 90.6 |
| | 328±1 | 0.0297 | 0.885 | 1.86 | 88.5 |
| **ALN** | 298±1 | 0.0347 | 0.866 | 2.17 | 86.6 |
| | 313±1 | 0.0551 | 0.857 | 2.31 | 85.7 |
| | 328±1 | 0.0659 | 0.846 | 2.49 | 84.6 |



**Figure 3.** Variation of inhibition efficiency in the presence of optimum concentration of MLN and ALN at various temperatures of solutions.

It is evident from Table 2 and Fig. 3 that the inhibition efficiencies for both extracts at their optimum concentration decreases as temperature of inhibitive solution increases. This may be due to the equilibrium that exists between adsorption and desorption of inhibitor molecules that continuously occurs at the metal surface at a specific temperature. As temperature increases, the equilibrium between adsorption and desorption is shifted towards desorption until equilibrium is reestablished. As a result, the lower inhibition efficiencies were obtained at higher temperatures (313±1 and 328±1 K), which indicates that the mechanism of adsorption of the inhibitor is physisorption [59] as physisorption is an electrostatic interaction, which generally loses its effect at elevated temperatures [27].

### 3.2 Potentiodynamic polarization measurements

The inhibitive effect of *L. nudcaulis* methanolic (MLN) and aqueous acidic (ALN) extracts were studied by using potentiodynamic polarization measurements. Cathodic and anodic polarization curves of mild steel in 1.0 M HCl solution, in the absence and presence of various concentrations of MLN and ALN are shown in Fig. 4. Whereas, their corresponding electrochemical parameters such as corrosion current density ($I_{corr}$), anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel constants, corrosion potential ($E_{corr}$), polarization resistance ($R_p$) and inhibition efficiency ($IE$ %) are listed in Table 3.
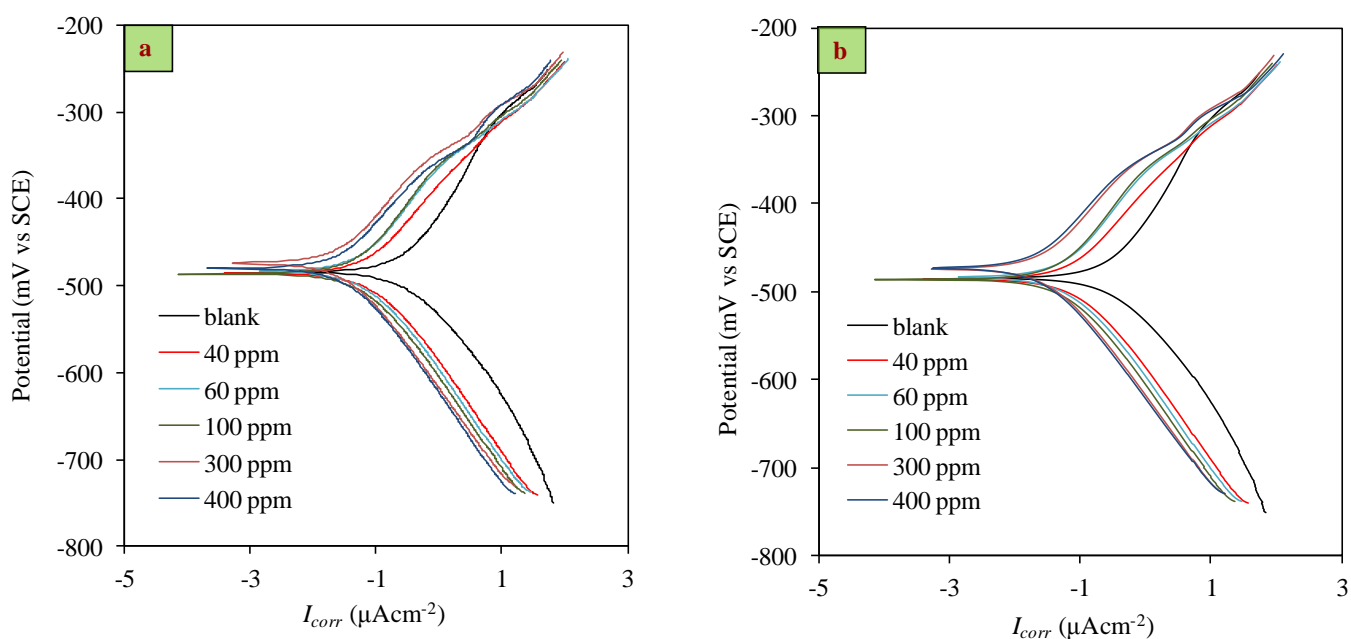


**Figure 4.** Polarization curves in the absence and presence of different concentrations of (a) MLN and (b) ALN in 1.0 M HCl.

The inhibition efficiencies for potentiodynamic polarization and linear polarization measurements were calculated from the measured ($I_{corr}$) and ($R_p$) values using equations (4) and (5)

respectively. In Table 3, it can be clearly seen that the values of corrosion current density ($I_{corr}$) decreased while the values of polarization resistance ($R_p$) increased with increasing concentrations of both extracts as expected. Due to the inverse relationship between corrosion current density ($I_{corr}$) and polarization resistance ($R_p$), with increasing concentration of the inhibitor, it can be assumed that the adsorption of the inhibitors phytomolecules on metal surface increases which makes a physical barrier for the mass and charge transfer, providing a high degree of protection to the metal surface by blocking the active sites [60].

**Table 3.** Potentiodynamic polarization parameters obtained from Tafel plots for the corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentrations of MLN and ALN.

| Inhibitors | Concentration (ppm) | $E_{corr}$ (mV) | $I_{corr}$ ($\mu Acm^{-2}$) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | $R_p$ ($\Omega cm^2$) | (IE %) Tafel | (IE %) LPR |
|---|---|---|---|---|---|---|---|---|
| MLN | 0 (Blank) | −485.2 | 213 | 98.8 | 74.5 | 54.5 | - | - |
| | 40 | −484.9 | 47.6 | 75.0 | 80.4 | 228.0 | 77.7 | 76.1 |
| | 60 | −480.2 | 40.7 | 80.5 | 85.3 | 252.5 | 80.9 | 78.4 |
| | 100 | −480.8 | 34.0 | 83.6 | 87.1 | 298.0 | 84.0 | 81.7 |
| | 300 | −467.3 | 17.7 | 71.6 | 76.9 | 520.8 | 91.1 | 89.5 |
| | 400 | −462.0 | 11.3 | 64.2 | 76.1 | 730.3 | 94.7 | 92.5 |
| ALN | 40 | −484.6 | 59.6 | 84.8 | 75.6 | 185.7 | 72.0 | 70.7 |
| | 60 | −483.4 | 48.9 | 93.3 | 80.2 | 215.5 | 77.0 | 74.8 |
| | 100 | −485.0 | 41.0 | 90.7 | 76.8 | 265.8 | 80.8 | 79.5 |
| | 300 | −474.0 | 25.4 | 88.9 | 84.7 | 364.4 | 88.1 | 85.1 |
| | 400 | −473.8 | 20.5 | 89.3 | 78.0 | 425.2 | 90.4 | 87.2 |

From Fig. 4, it is evident that both the cathodic and anodic curves showed lower current density values in the presence of both extracts than those recorded in the absence of green inhibitors (MLN and ALN). This confirmed the adsorption of extracts phytomolecules on the mild steel/acid solution interface and consequently inhibits the corrosion process [61,62]. Moreover, results in Fig. 4 also suggested that the studied extracts influence both anodic as well cathodic corrosion processes; hence it reveals the properties of mixed type inhibitors with predominant anodic inhibitors as they showed pronounce influence on anodic corrosion process. This statement can be further supported from the values of corrosion potential ($E_{corr}$), anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel constants. From Table 3, it is evident that the addition of both extracts changes the values of $E_{corr}$ towards anodic direction, hence extracts can be considered as slightly anodic inhibitors. However, on the addition of extracts the maximum displacement in $E_{corr}$ values was 23 mV for both extracts which suggests that both inhibitors act as mixed type inhibitors with predominant anodic effectiveness as it has been well known that if the displacement in $E_{corr}$ is >85 mV the inhibitor can be recognized as a cathodic or anodic type inhibitor and if the displacement of $E_{corr}$ is <85 mV, the inhibitor can be seen as mixed type [33, 62]. Furthermore, from Table 3 it can be noticed that the inhibitors concentrations have more pronounce influence on anodic Tafel constant ($\beta_a$) values whereas they have little influence on

cathodic Tafel constants ($\beta_c$) values. This indicates that both extracts have slightly more influence on the mechanism of anodic reaction and have very little effect on the process of cathodic dissolution [63]. In Table 3, the values of inhibition efficiency (*IE %*) obtained from the Tafel plot experiments were slightly higher than those obtained through the linear polarization resistance. This behavior suggests that the inhibitor action is dependent on the potential applied and time of polarization, since in the linear polarization experiments only $\pm 25$ mV around $E_{corr}$ was applied to the working electrode and the duration of the experiment was shorter [64]. Nevertheless, the data clearly showed that the mild steel electrochemical corrosion rate decreased in the presence of both extracts.

### 3.3 Electrochemical impedance spectroscopic (EIS) measurements

The anticorrosive behavior of *L. nudcaulis* methanolic (MLN) and aqueous acidic (ALN) extracts on mild steel in 1.0 M HCl aggressive media were investigated using EIS measurements at room temperature after an exposure period of 30 min. Fig. 5 shows results of EIS experiment in the form of Nyquist plots for mild steel obtained at the interface in the absence and presence of both extracts at different concentrations. In Fig. 5, the general trend of the curve shape is found to be very similar for all samples and curve shape is maintained throughout the whole concentration range, indicating that similar mechanism of inhibition is involved [65, 66].
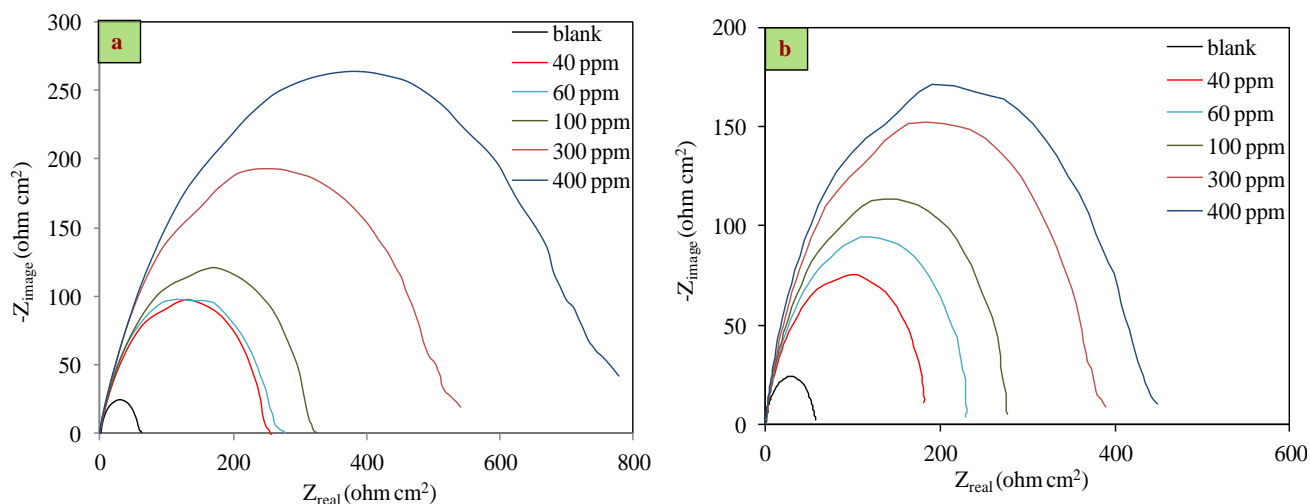


**Figure 5.** Nyquist plots in the absence and presence of different concentrations of (a) MLN and (b) ALN in 1.0 M HCl.

It is also clear from Fig. 5 that the diameter of Nyquist plots increases on increasing the concentration of both extracts. This might suggest that a protective film was formed on mild steel through the deposition of phytomolecules of plant extracts and the formed inhibitive film was strengthened by addition of inhibitors. Moreover, the Nyquist plots consist of a depressed semi-circle with the centre below the real X-axis, this type of behavior represent the characteristic of solid electrodes and often refers to frequency dispersion which arises due to the roughness and

inhomogeneities of solid surface [67,68]. The impedance parameters, that is, solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), double layer capacitance ($C_{dl}$) and inhibition efficiency (*IE %*) derived from the Nyquist plots are shown in Table 4.

**Table 4.** Electrochemical impedance parameters obtained from Nyquist plots for the corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentrations of MLN and ALN.

| Inhibitors | Inhibitors Concentration (ppm) | $R_{ct}$ ($\Omega cm^2$) | $C_{dl}$ ($\mu F\ cm^{-2}$) | *IE %* |
|---|---|---|---|---|
| **MLN** | 0 (Blank) | 57.1 | 7.7 | - |
| | 40 | 231.6 | 1.8 | 75.3 |
| | 60 | 263.7 | 1.5 | 78.4 |
| | 100 | 324.1 | 1.7 | 82.4 |
| | 300 | 519.6 | 1.4 | 89.0 |
| | 400 | 749.0 | 1.3 | 92.4 |
| **ALN** | 40 | 190.8 | 2.3 | 70.1 |
| | 60 | 238.9 | 2.4 | 76.1 |
| | 100 | 283.3 | 2.1 | 79.8 |
| | 300 | 381.1 | 1.5 | 85.0 |
| | 400 | 433.7 | 1.3 | 86.8 |

Inhibition efficiency values are calculated using equation (6) while the double layer capacitance ($C_{dl}$) is calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad (7)$$

where $f_{max}$ is the frequency at the *apex* of the Nyquist plot and $R_{ct}$ is the charge transfer resistance.

From Table 4, it is clear that charge transfer resistance ($R_{ct}$) and inhibition efficiency (*IE %*) values of inhibited substrates are increased as the concentration of inhibitors increases whereas as expected, double layer capacitance ($C_{dl}$) values tend to decrease with increase in inhibitors concentration. The decrease in $C_{dl}$ values may be due to the increase in thickness of the electrical double layer and /or decrease in local dielectric constant, suggesting that both extracts (MLN and ALN) act through adsorption at the mild steel/solution interface [67,69,70]. It may be assumed that the decrease of $C_{dl}$ values is due to the gradual replacement of water molecules by adsorption of phytomolecules on the MS surface, providing more surface coverage to the active site of mild steel by inhibitors, thus decreasing the extent of the mild steel dissolution [71]. Moreover, the EIS measurement reveals that both extracts showed promising anticorrosive property for mild steel in 1.0 M HCl. However, methanolic extract (MLN) was found to be more effective with maximum corrosion inhibition of 92.4 % at optimum concentration of 400 ppm than that obtained for aqueous acidic extract (ALN) which showed maximum corrosion inhibition of 86.8 % at optimum concentration of

400 ppm. The data obtained from EIS measurement is in good agreement with those obtained from weight loss, Tafel plots and LPR methods (Fig. 6).
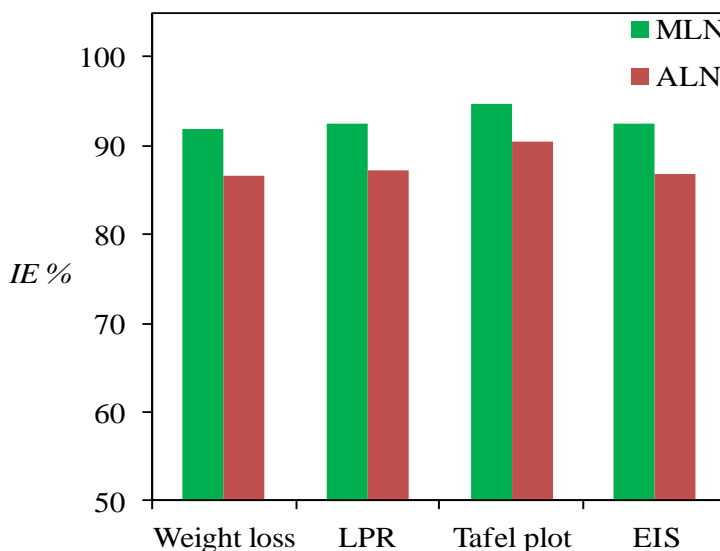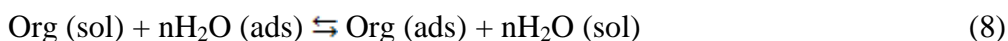


**Figure 6.** Inhibition efficiency obtained from various methods in the presence of optimum concentrations of MLN and ALN

*3.4 Adsorption isotherm and inhibition mechanism*

The adsorption process of inhibitor is a substitutional adsorption process between the organic molecules in the aqueous solution Org(sol) and the water molecules $H_2O$(ads) from the surface of metals and can be represented as [72]:

Org (sol) + $nH_2O$ (ads) ⇆ Org (ads) + $nH_2O$ (sol)        (8)

Where Org (sol) and Org (ads) are the organic molecules in the aqueous solutions and those adsorbed on the metallic surface, respectively. While $H_2O$ (ads) is the water molecules on the metallic surface and (n) is the coefficient representing the number of water molecules replaced by one molecule of organic adsorbate.

An inhibitor can be considered as an effective corrosion inhibitor in aqueous solution only when the interaction force between metals and inhibitor is greater than the interaction force of metal and water molecules [73].

Most commonly applied adsorption isotherms are Temkin, Langmuir and Frumkin isotherms. According to these isotherms, ($\theta$) is related to the concentration of inhibitor:

$$\log \left(\frac{\theta}{C}\right) = \log K - g\theta \qquad \text{(Tempkin isotherm)} \qquad (9)$$

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad \text{(Langmuir isotherm)} \qquad (10)$$

$$\log\left\{\frac{\theta}{(1-\theta)C}\right\} = \log K - g\theta \quad \text{(Frumkin isotherm)} \quad (11)$$

Where $(\theta)$ is the surface coverage, $K$ is the adsorption–desorption equilibrium constant, $C$ is the concentration of inhibitor and $(g)$ is the adsorbate parameter.

By using degree of surface coverage $(\theta)$ values for different concentrations of inhibitors (MLN and ALN) at 298$\pm$1 K, attempts were made to fit aforementioned isotherms.
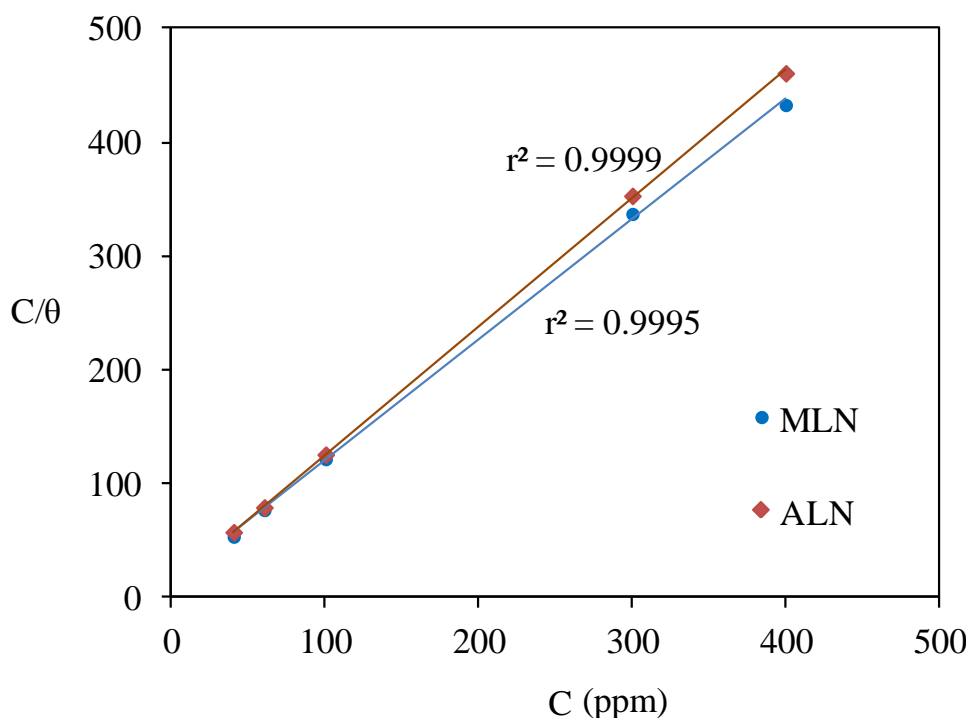


**Figure 7.** Langmuir isotherms in the presence of different concentrations of MLN and ALN in 1.0 M HCl.

As can be seen in Fig. 7, the best fit was obtained with Langmuir isotherm which gave straight line with the slope of the unit, where the regression coefficient $r^2$ values for Langmuir isotherm were 0.9995 and 0.9999 for MLN and ALN, respectively. This suggested that Langmuir isotherm shows the best correlation with the experimental data and also explains the monolayer formation of the inhibitor on the surface of mild steel [74, 75]. Moreover, Thermodynamic parameters for the adsorption of both extracts (MLN and ALN) on the mild steel calculated from Langmuir isotherms using surface coverage $(\theta)$, calculated from the results of weight loss method, is shown in Table 5.

**Table 5.** Thermodynamic parameters for mild steel in 1.0 M HCl in the absence and presence of optimum concentration (400 ppm) of inhibitors

| Extract | $\Delta G_{ads}$ (kJmol$^{-1}$) | $\Delta H_{ads}$ (kJmol$^{-1}$) | $\Delta S_{ads}$ (JK$^{-1}$) |
|---------|---------------------------------|---------------------------------|------------------------------|
| MLN     | -16.42                          | -10.33                          | 20.43                        |
| ALN     | -16.24                          | - 4.33                          | 39.97                        |

The value of free energy of adsorption provides important information about the nature of adsorption of inhibitor onto the surface of mild steel and can be calculated by using the following equation:

$$\Delta G_{ads} = -RT \ln(K \times 55.5) \qquad (12)$$

In Table 5, the negative values of free energy of adsorption ($\Delta G_{ads}$) revealed that both inhibitors (MLN and ALN) spontaneously adsorbed on the mild steel surface [76]. It is generally accepted that with the values of $\Delta G_{ads}$ around $-20$ kJ mol$^{-1}$ or lower, types of adsorption were regarded as physisorption and the inhibition acts through the electrostatic interaction between the charged molecules and the charged metal. In contrast, for the values around $-40$ kJ mol$^{-1}$ or higher, interactions are seen as chemisorptions where the charge sharing or a charge transfer from the inhibitor molecules to the metal surface occurs to form covalent bond [77, 78]. In present study the values of free energy of adsorption ($\Delta G_{ads}$) for both inhibitors (MLN and ALN) were around $-20$ kJ mol$^{-1}$. Hence, it is clear that both inhibitors are physically adsorbed on the surface of mild steel. This statement can also be supported with weight loss study where we observed decrease in inhibition efficiency ($IE \%$) with increase in temperature of inhibition solutions. As the temperature increases the number of adsorbed molecules on the metal surface decreases, leading to a decrease in inhibition efficiency ($IE \%$) [79]. The other thermodynamic parameters such as enthalpy and entropy of adsorption can also be calculated from the following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (13)$$

where $\Delta H_{ads}$ and $\Delta S_{ads}$ are the enthalpy and entropy of adsorption respectively.

The results obtained are shown in Table 5. The negative sign of $\Delta H_{ads}$ in Table 5 revealed that the adsorption of inhibitors (MLN and ALN) on the MS surface is exothermic [60].

*3.5 SEM and EDS analysis*

Scanning electron microscope (SEM) has become an important tool to study surface morphology of corroded and uncorroded metals [60]. To establish the interactions of inhibitors (MLN

and ALN) with mild steel samples, the SEM images were recorded for mild steel in the absence and presence of optimum inhibitors concentration and results are shown in Fig. 8.

Fig. 8a shows the characteristic surface of finely polished mild steel surface where some minor scratches can be seen which might have arisen during the polishing process. Fig. 8b shows the image of mild steel sample treated in 1.0 M HCl for the period of 3 hr. It reveals that the MS specimens were highly corroded and appeared full of pits and cavities which may result from the aggressive attack of 1.0 M HCl solution. On the other hand, Fig. 8c shows the SEM image of mild steel treated with optimum concentration (400 ppm) of both inhibitors (MLN and ALN) in 1.0 M HCl for a period of 3 hr. In Fig. 8c a very smooth surface of mild steel was observed which appeared closely similar to that of polished mild steel surface (Fig. 8a).
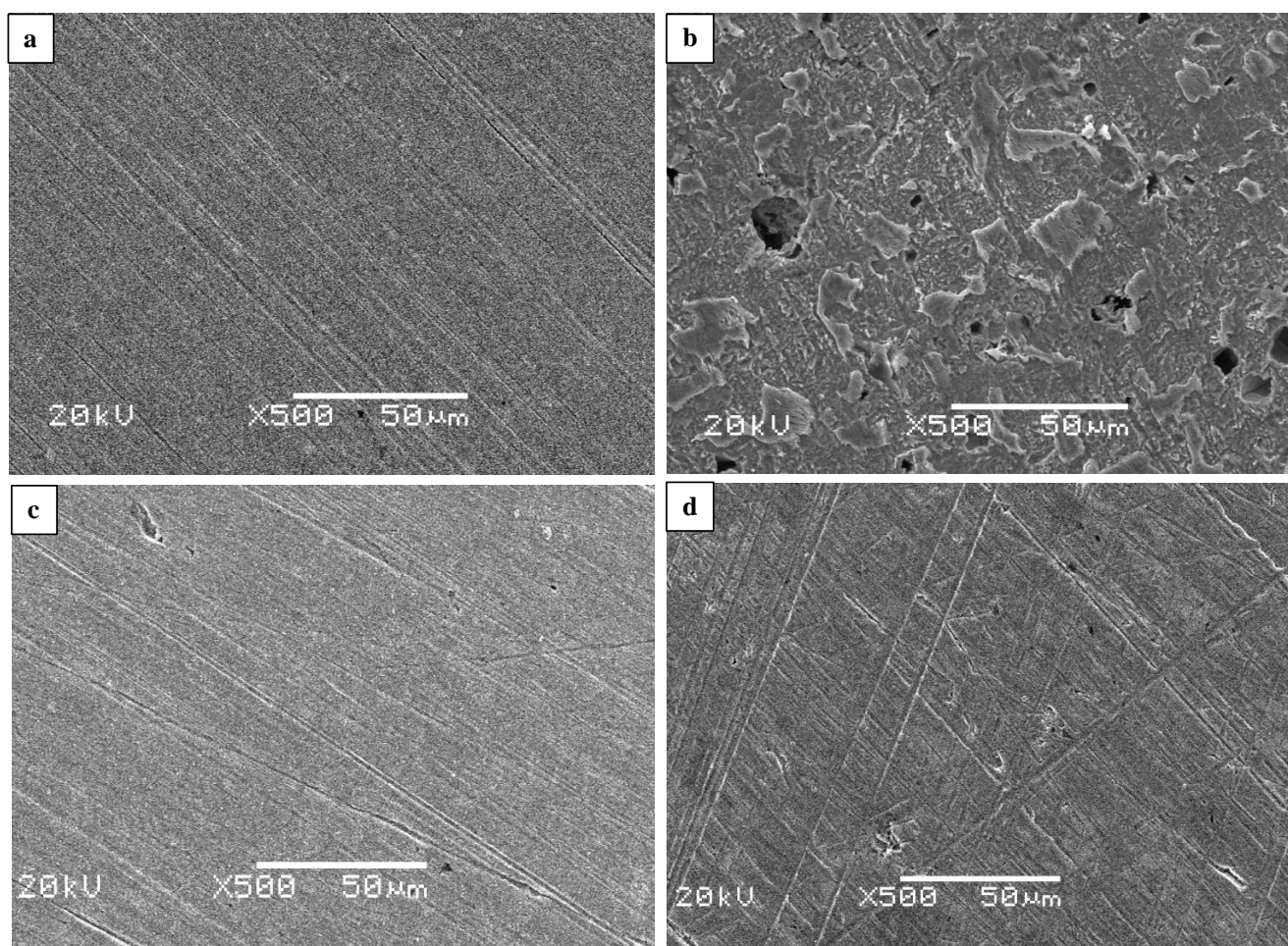


**Figure 8.** SEM images of (a) polished mild steel coupon (b) mild steel coupon in 1.0 M HCl (c) mild steel coupon in 1.0 M HCl with optimum concentration of MLN (d) mild steel coupon in 1.0 M HCl with optimum concentration of ALN

This indicates that a protective film was formed by the inhibitor molecules on the mild steel surface which inhibits the corrosion of mild steel significantly in 1.0 M HCl solution [80].

Energy dispersive spectrometry (EDS) analysis of mild steel samples in the absence and presence of optimum concentration of both inhibitors (MLN and ALN) were done mainly to determine the percentage of chloride content present on the surface of mild steel in the absence and presence of optimum inhibitors concentration and the results obtained are shown in the form of EDS spectrum in Fig. 9. The data in Fig. 9a revealed that the surface of untreated polished MS was chlorine free. Whereas, in the case of MS treated with 1.0 M HCl solution showed the presence of chloride ions in significant amount (Fig. 9b) which may be due to the aggressive attack of the acidic solution. Figures 9c and 9d referred to the spectrum of mild steel treated with optimum concentration (400 ppm) of MLN and ALN, respectively in 1.0 M HCl for a period of 3 hr. This spectrum showed almost negligible amount of chloride ions on the surface of mild steel compared to the mild steel treated with 1.0 M HCl. This indicates that both green inhibitors efficiently protect the mild steel in acidic medium [60,65].
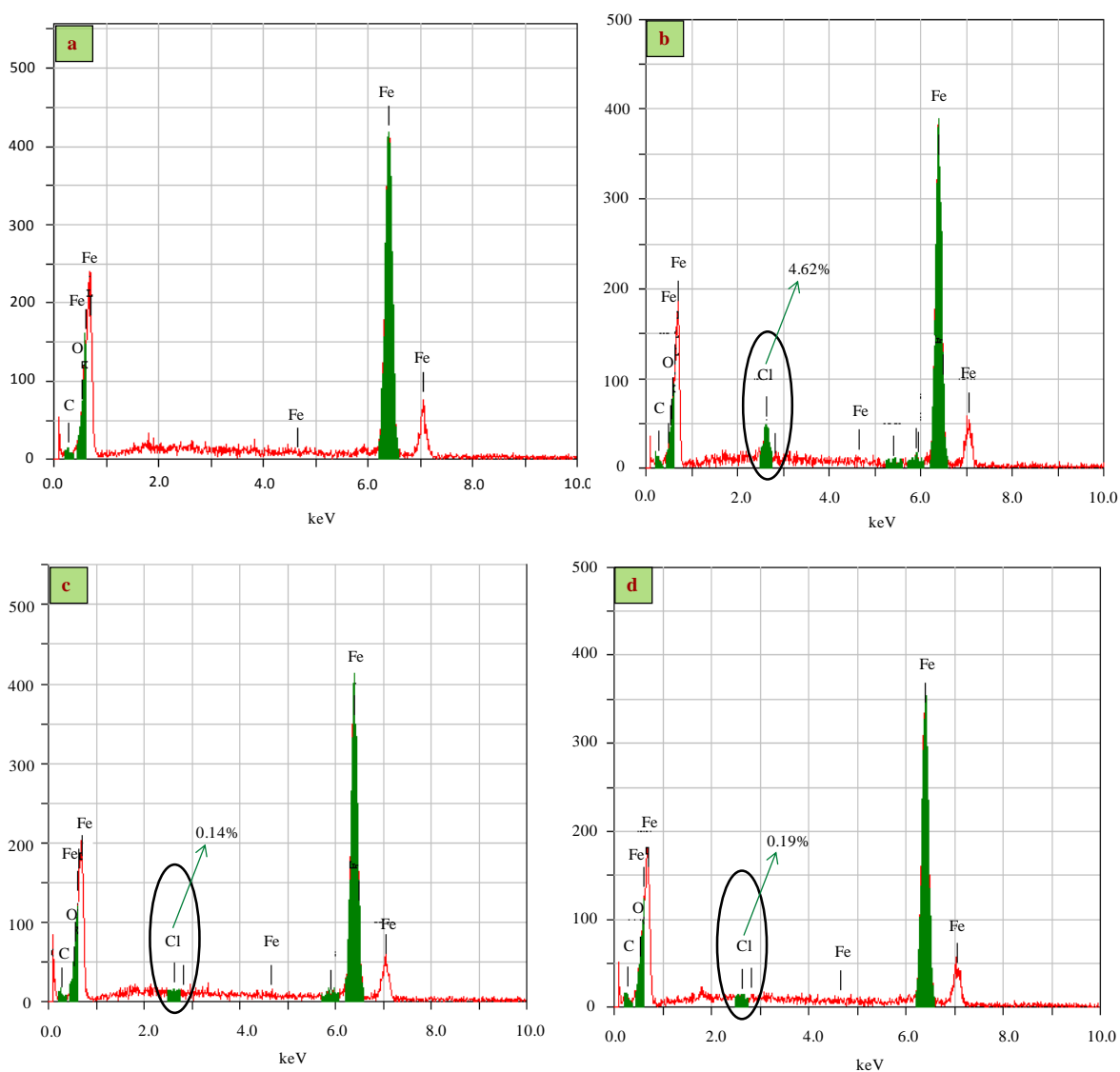


**Figure 9.** EDS spectrum of (a) polished mild steel coupon (b) mild steel coupon in 1.0 M HCl (c) mild steel coupon in 1.0 M HCl with optimum concentration of MLN (d) mild steel coupon in 1.0 M HCl with optimum concentration of ALN.

## 4. CONCLUSION

Plant extracts have been proven to be an excellent source for the development of environmental benign and effective corrosion inhibitors for metals in various aggressive media and research on the topic is ever increasing in order to find cost effective and efficient corrosion inhibitors from this cheaply available, renewable, environmental friendly and excellent source of phytochemicals. The results obtained from weight loss, Tafel plots, linear polarization, electrochemical impedance spectroscopy and SEM-EDS methods indicate that both *L. nudicaulis* extracts (MLN and ALN) exhibit significant corrosion inhibition properties for mild steel in 1.0 M HCl and act as mixed type of inhibitors with predominant anodic effectiveness. Both extracts follows Langmuir adsorption isotherm and inhibit the corrosion of mild steel in acidic media by adsorption mechanism and the adsorption process of inhibitors was spontaneous, exothermic and physisorption (physically adsorbed). The inhibition efficiency for all electrochemical tests and weight loss measurements were in good agreement. Our present study is the first report on *L. nudicaulis* extracts as an efficient corrosion inhibitor for mild steel in acidic media. Hence, it is a contribution to a better valorization of this medicinal plant growing abundantly and widely in Saudi Arabia. Moreover, further study such as anticorrosive assay guided isolation of active phyotconstituents from the methanolic extract of this plant would be worthwhile carrying out. Therefore, our next approach will be focused on isolation of pure active compounds from methanolic extract of *L. nudicaulis* which may result in the identification and characterization of pure anticorrosive phytoconstituents with better inhibition efficiency at lower concentration.

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