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# Alchemilla Vulgaris Extract as Green Inhibitor of Copper Corrosion in Hydrochloric Acid

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This paper aims to assess the anti-corrosion capability of Alchemilla Vulgaris (ALV) extract in 1 M HCl on pure copper with the perspective of exploring and developing an eco-friendly or natural corrosion inhibitor. Therefore, in the current study, the extraction of ALV was made from its leaves and its anticorrosion potential was studied by utilizing weight loss experiment, potentiodynamic polarization test, scanning electron microscopy (SEM) analysis and electrochemical impedance spectroscopy (EIS). It has been found that in 1 M HCl solution, the ALV was effectively inhibited the corrosion on pure copper metal. The results obtained from the electrochemical tests and weight loss way proved that the anti-corrosion capability of ALV was increased with increasing its concentration. Inhibition is achieved through the adsorption of Alchemilla molecules onto the pure copper surface by adopting the Langmuir adsorption isotherm model. SEM study also indicates that the inhibitor gave positive results when adsorption on the surface of copper. This study directs attention to highly inhibitive properties of some natural compounds as the ALV extract. Hence, it is considered the first time to investigate the efficiency of ALV extract as a potential pure copper corrosion inhibitor in a 1M HCl solution. The anti-corrosion effect of ALV extract has been proven by standard methods. The findings of this research are important because ALV, as a natural inhibitor material, could find use in industries where pure Cu is used.

**Keywords**: Copper, Corrosion inhibitors, ALV extract, Eco-friendly, Hydrochloric acid.

## 1. INTRODUCTION

Copper is a significant metal that attracted researchers because of its wide scope of properties and applications in industry [1, 2]. For example, it can be utilized in electronics, wires, sheets, tubes, heating and cooling system, condensers, and so on [3-6]. Although this metal is resistant toward the atmosphere environments and the influence of using chemicals, however, it is oversensitive to corrosion in media which is aggressive. Therefore, it is necessary for such conditions to utilize copper corrosion inhibitors in case when no protective passive layer can be expected. So, numerous corrosion inhibitors were widely investigated and used by researchers to reduce the rate of copper corrosion to the minimum. However, most of these inhibitors are of toxic nature, high cost, and harmful to living things [7]. It is importance to explore plant as a natural product to be used as a corrosion inhibitor thus helps to overcome these deficiencies. The problem that faces most researchers recently is to search and choose the non-toxic, cheap and eco-friendly compounds to be used as corrosion inhibitors. During recent years, several natural green inhibitors have been used by most of the investigators for the prevention of corrosion.

## 2. MATERIAL & METHODS

### *2.1 Preparation of specimens*

The copper metal used in this study with a chemical composition 99.99% purity, the Cu specimens of the size 2 × 2 × 0.2 $cm^3$ utilized for weight reduction method and 2 cm × 2 cm × 2 cm embedded in epoxy resin leaving its square cross-section is used for electrochemical measurements. The Cu samples were abraded mechanically with 600 to 2000 grade of emery papers. Then it was successively washed with double filtered water and acetone. These samples were first desiccated at the room temperature then stocked in a desiccator.

### *2.2 Preparation of solution*

The corrosive solution was infectious by the analytical grade 37% HCl with a molecular weight of 36.5 g/mL was used for preparing the acid electrolyte. The dilution of acid was made exactly with double filtered water to prepare 1 M HCl solution. To avoid the undesirable effect of any pollution, it is therefore necessary that each combination of experiment newly prepared 1M HCl solutions and used properly.

### *2.3 Preparation of plant extract*

50 g of each ALV leaves powder was extracted with 100 mL of sterilized distilled water using magnetic stirrer for 24 h. at room temperature. Using whatman filter paper No.1, the extract was first filtered and then it was concentrated in vacuum at 40℃ using rotary evaporator. The dried extracts were stored properly.

### *2.4 Plant description*

Alchemilla (ALV) can be classified as a kind of perennial herb in the family Rosacea, widely known as lady’s mantle, or lion’s foot ". The majority of Alchemilla’s species consist of clump-forming perennial plants with basal leaves growing from woody rhizomes. Generally Alchemilla consists of long-stalked, gray-green to green leaves that often covered with soft hairs, and show a high level of water-resistance. This plant has a widely known history as it was used as traditional medicinal in different countries. The most important and extensive chemical composition in this plant is the tannins, salicylic acid, essential oil, and bitter substances. It also includes vitamin C as well as numerous minerals.

### *2.5 Weight loss method*

Weight loss technique has been used to research anti-corrosion property. Experiment was accomplished using six specimens of the copper block (Good fellow, 99.99%) with the dimensions of 2 cm length, width of 2 cm and thickness of 0.2 cm with an exposed total area of 9.6 $cm^2$. The coupons were polished and dried as copper rods were, weighed ($W_1$), and then completely immersed in 150 mL of 1 M HCl solution with and without the different concentration of ALV extracts for different exposure periods (24 h). At the end of a run, the top surface of the sample was gently wiped with a soft brush, rinsed with tap water, and then it was washed with a 1.0% HCl solution, then with filtered water, absolute ethanol, acetone, and weighed again ($W_2$) precisely by utilizing LP 120 digital balance with ± 0.1 mg sensitivity.

The loss in weight, the corrosion rate, and the effectiveness percentage of the inhibition were calculated according to the following equation.

$$CR(mmpy) = \frac{87.6 \times \Delta w}{DAT} \qquad (1)$$

Where mmpy = millimeter per year, ΔW = weight loss (mg), D = Density (g/cm3),
A = Area of specimen ($cm^2$), T = time (h).
The inhibition efficiency (IE%) calculated using the following equation [8-11].

$$IE\% = \frac{W_1 - W_2}{W_1} \times 100 \qquad (2)$$

where $W_1$ and $W_2$ are the Weight loss which measured in the presence and absence of the inhibitor respectively.

### *2.6 Electrochemical Measurements*

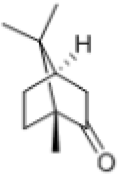
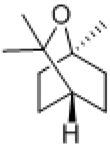
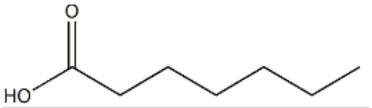
Before the experiments of potentiodynamic polarization curve, the Cu electrode was freely allowed to oxidize and its open circuit potential ($E_{OCP}$) was recorded when the function of time was up to (580 s). After this period of time a steady-state $E_{OCP}$, the polarization measurement was made using Chi660e electrochemical workstation. The Cu electrode that was in the square shape (1 × 1 $cm^2$) commonly made of the copper sample and the remaining part of the surface was wrapped with epoxy resin. Platinum was used as the auxiliary electrode and the reference electrode as a standard calomel electrode. Before running each group of test, the working electrode was abraded with a string of emery papers and cleaned out with filtered water followed by acetone. The polarization curves were gained from –300 to +300 mV with the scan rate of 1 mV/s. In fact, the selection of the scan rates was based mainly on the linearity of the polarization curves. The linear Tafel segments of the cathodic curves and the calculated anodic Tafel lines were extrapolated to obtain the corrosion potential (*Ecorr*), corrosion current density ($I_{corr}$), and the inhibition efficiency. IE% was calculated by equation (5). All experiment sets were achieved solutions at room temperature.

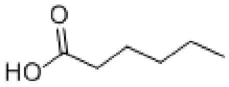
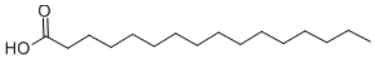
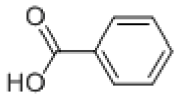
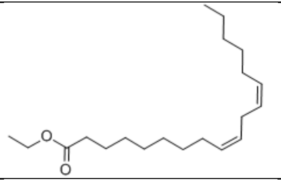
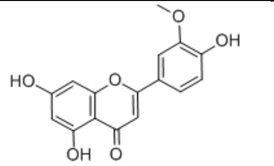
## 3. RESULTS AND DISCUSSION

### *3.1 GC-SM analysis*

Alchemilla Vulgaris (ALV) extracts, like other plant extracts that have corrosion inhibitor effect, can be considered as one of the complex chemical compositions which make it rather difficult to determine the inhibitive effect to a particular compound present in that extracts. The corrosion inhibition effectiveness of this plant extract has been confirmed by previous studies [12-22] (see table 1 below). In the present study, the technique used for identifying the composition of Alchemilla Vulgaris (ALV) extracts was GC-mass spectrum. Table 1 below showed the main components identified using GC-mass method with their chemical structures and the qualifications of the molecules regarding their adsobtion activation supported with refferences that confirmed the effectiveness of these components as inhabitor corrosion. This important method is used to analysis the (ultra)trace levels of plant extracts components that may occur in such complex Alchemilla Vulgaris (ALV).

**Table 1.** Classification of the main components of Alchemilla Vulgaris (ALV) extract and their chemical structure

| No. | Components | Chemical Formula | Chemical structure | Qual | References [12-22] |
|---|---|---|---|---|---|
| 1 | Camphor | $C_{10}H_{16}O$ |  | 93 | [12-13] |
| 2 | 1,3,3-trimethyl-2-oxabicyclo[2.2.2] octane | $C_{10}H_{18}O$ |  | 96 | [14] |
| 3 | Heptanoic acid | $C_7H_{14}O_2$ |  | 78 | [15] |
| 4 | Octanoic acid (CAS) | $C_8H_{16}O_2$ |  | 27 | [16] |

| | | | | | |
|---|---|---|---|---|---|
| 5 | Hexanoic acid | $C_6H_{12}O_2$ |  | 38 | [17] |
| 6 | Hexadecanoic acid | $C_{17}H_{32}O_2$ |  | 95 | [17] |
| 7 | Stearic acid | $C_{18}H_{36}O_2$ |  | 74 | [17-18] |
| 8 | Benzoic acid | $C_7H_6O_2$ |  | 27 | [19] |
| 9 | Linoleic acid ethyl ester | $C_{20}H_{36}O_2$ |  | 99 | [18, 20] |
| 10 | Luteolin 3'-methyl ether | $C_{16}H_{12}O_9$ |  | 55 | [21-22] |

### *3.2 Weight loss tests*

The ALV extract at diverse concentrations effect on the corrosion of copper in 1 mol/L HCl was researched by using weight loss measurements at room temperature. After 24 h. of the immersion period. Weight loss, Fractional Surface coverage (θ), corrosion rate (Rc) and inhibition efficiency of the extract obtained by weight loss way for diverse inhibitor concentrations at diverse periods of immersion in 1 mol/L HCl are presented in (Table 2). It is clear find that the ALV extract inhibits the corrosion of Cu in 1 mol/L HCl at all concentrations made use of in this research. These findings showed that the corrosion rate (Rc) decreases constantly by increasing the additive concentration of ALV. Indeed. This behavior can be attributed to the increase of the surface covered, due to the adsorption of phytochemical components of the essential ALV extract when it was adsorbed on the Cu surface resulting in the blocking of the reaction spots, which consequently led to the protection of the metal surface from the attack of the corrosion active ions in the acid medium. Accordingly, we can conclude and discover that the ALV extract can exhibit excellent corrosion inhibition performance for copper in hydrochloric acid.

**Table 2.** The Corrosion parameters of pure copper in the 1 mol/L HCl at room temperature for 24 h of immersion period.

| Inhibitor concentration (g/L) | Weight loss (mg/cm$^2$ h) | Corrosion Rate (Rc) (mmpy) | IE% | θ |
|---|---|---|---|---|
| 0 | 80 | 3.41 | – | – |
| 1 | 9.99 | 0.43 | 87.39 | 0.8739 |
| 2 | 7.73 | 0.33 | 90.32 | 0.9032 |
| 4 | 5.98 | 0.25 | 92.67 | 0.9267 |
| 6 | 4.46 | 0.19 | 94.43 | 0.9443 |
| 7 | 3.5 | 0.15 | 95.60 | 0.9560 |

### *3.3. Adsorption isotherm research*

The adsorption isotherm research described the interaction between inhibitors and the metal surface. They believe that this interaction depends on the effective components in plant extracts. The inhibitors of this corrosion are always explained depending on the molecular adsorption. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) at different concentrations of ALV inhibitor in 1 M HCl has been calculated by using equation θ=IE/100. In previous studies, Frumkin, Temkin and Langmuir isotherms are the most frequently used adsorption isotherms. In this work, an attempt was followed to fit data obtained from weight loss data with different adsorption isotherms, and the Langmuir adsorption isotherm gave the best results [23-27].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (3)$$

where θ is the degree of surface coverage, $C_{inh}$ is the inhibitor concentration, and $K_{ads}$ stands for the equilibrium constant of the adsorption isotherm. Plot of C/ θ against C as shown in Figure 1 gave straight lines, which clearly show that Cu in 1 mol/L HCl by ALV extract at room temperature accord with Langmuir monolayer adsorption isotherm. The correlation parameters including coefficient ($R^2$), slopes, and adsorption coefficients are shown in Table 3. The free energy of adsorption, ($\Delta G_{ads}$), is related with adsorption constant ($K_{ads}$) and water adsorption equilibrium and ($\Delta G_{ads}$), can be obtain using the following Equation (4) [28-31].

$$\Delta G^{o}_{ads} = -RT\ln(55.5K_{ads}) \qquad (4)$$

where the 55.5 is the molar concentration of $H_2O$, R stands for the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and T stands for temperature (K). The negative value of ($\Delta G_{ads}$), suggests that the adsorption of inhibitors on pure Cu surface is a spontaneous process. The correlation coefficient ($R^2$) and slope obtained was nearly equal to unity best-fit experimental data. The value of $\Delta G_{ads}$ indicates that the adsorption on Cu surface is physical. If the value of $\Delta G_{ads}$ is $-20$ kJ/mol or less this would indicate physical adsorption, while the value of $\Delta G_{ads}$ is $-40$ kJ/mol or higher imply chemical adsorption, which involves charge sharing, or a transfer from the inhibitor molecules to the metal surface and then to form a physical bond [32-38].

**Table 3.** Langmuir adsorption isotherm of ALV extract on pure copper in 1M HCl.

| Adsorption isotherms | Slope | $K_{ads}$ | $R^2$ | $-\Delta G_{ads}$ kJ/mol |
|---|---|---|---|---|
| Langmuir | 1.05 | 17.13 | 0.9997 | 17.633 |

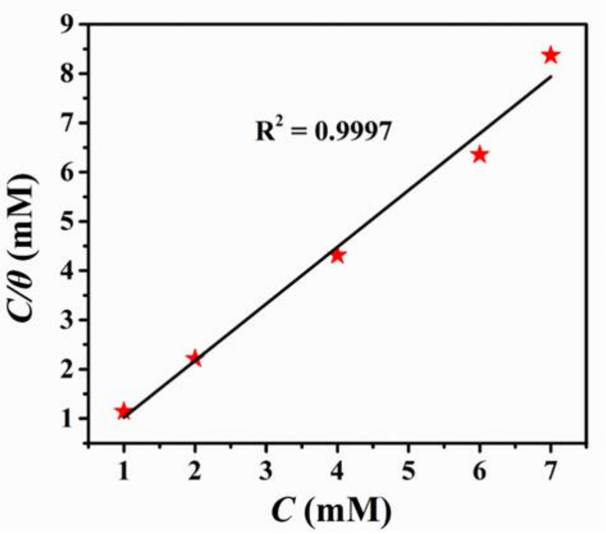


**Figure 1.** Langmuir adsorption isotherm of ALV on pure copper in 1M HCl.

### *3.4 Open circuit potential (OCP)*

Figure 2 shows the $E_{OCP}$ with time obtained for Cu in 1 mol/L HCl in the presence and absence of different concentrations of ALV extracts at 298 K. The figure showed that $E_{OCP}$ in the blank started at $-105$ mV and the stable state was reached after 580 s. This indicated that the initial dissolution of the air formed an oxide film on the Cu specimen and then begins of the attack of the bare metal on the bare metal. In the presence of ALV extracts at 1 g/L concentration $E_{OCP}$ started at$-84$ mV a and then shifted anodically, and the steady state was reached after 570 s relatively positive potential with respect to in its absence, and when adding 2,4,6,7 g/L respectively ALV extracts inhibitor, $E_{OCP}$ increases in the positive direction. Consequently, we can conclude that the ALV can exhibit excellent corrosion inhibition performance for copper in hydrochloric acid [10].

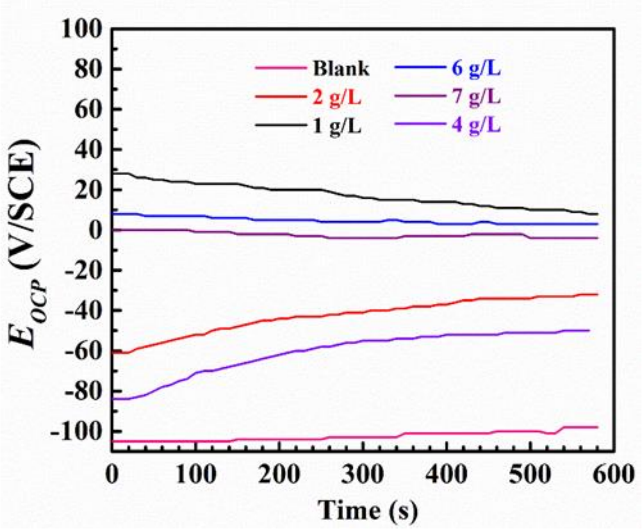


**Figure 2.** Open circuit potential (OCP), for Cu specimen immersed in 1 mol/L HCl at 298 K.

### *3.5 Potentiodynamic polarization curve measurements*

Figure 3 shows the Tafel curves for Cu in the absence and presence of various concentrations of ALV extract in 1 M HCl solution at 298 K. The corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), cathodic and anodic Tafel slopes ($\beta c$, $\beta a$) and inhibition efficiency (IE %) are given in Table 4. Where the inhibition efficiency was calculated by following the equation [39-45].

$$IE\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \qquad (5)$$

Where $I^{\circ}_{corr}$ and $I_{corr}$ are corrosion current with and without inhibitor, respectively.

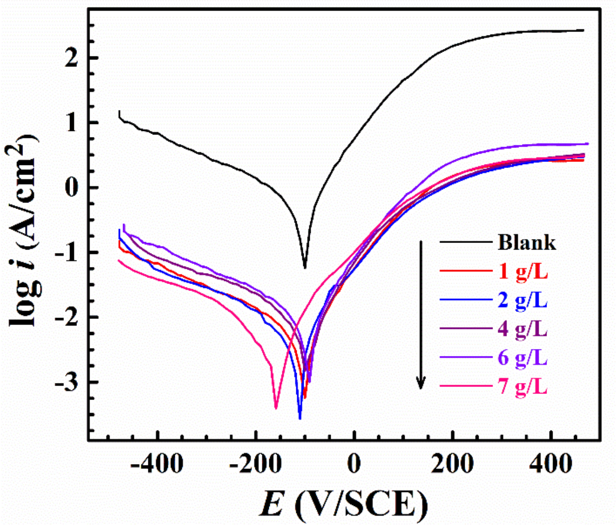


**Figure 3**. Potentiodynamic polarization curves of Cu 1 mol/L HCl with and without ALV inhibitors.

Table 4 showed that the ($I_{corr}$) decreased with increasing the concentration of the extracts, which decreased from 44.43 to 1.84 μA cm$^2$ with the addition of the highest concentration of ALV extract (7 g/L). Indicating that the inhibitive property of these extracts on the corrosion of pure copper in 1 M HCl solutions was attributed to the coverage surface through adsorption process.

It was noticed in the table 4 that the IE% augment with the addition of different ALV extract until reaching a maximum value of 96% at 7 g/L, which represented the excellent inhibitive property. A change in the $E_{corr}$ value is noticed in the presence of ALV extract. If the displacement $E_{corr} > 85$ mV, it acts as a cathodic or anodic type inhibitor, but if the displacement $E_{corr} < 85$ mV, it is considered as mixed-type inhibitor [46].

In the present study, as shown in, it can be seen that the displacement was at most 59 mV with respect to $E_{corr}$ for ALV extract, indicating that the inhibitors studied are a mixed inhibitor.

**Table 4.** Electrochemical parameters obtained at pure copper in 1 M HCl solution with and without of different concentrations of ALV extract at room temperature.

| Inhibitors concentration (g/L) | $E_{corr}$ (mVvs.SCE) | $I_{corr}$ (µA) | *IE* (%) |
|---|---|---|---|
| blank | −49 | 44.43 | — |
| 1 | −105 | 3.75 | 91.5 |
| 2 | −100 | 3.17 | 92.8 |
| 4 | −110 | 2.62 | 94.0 |
| 6 | −93 | 2.55 | 94.3 |
| 7 | −160 | 1.84 | 96.0 |

### *3.6 Electrochemical impedance spectroscopy (EIS)*

The electrochemical impedance technique of Cu in 1 mol/L HCl were studied with a frequency range of 0.01 Hz to 100 KHz with a signal amplitude perturbation of 5 mV.

The Nyquist plots of copper in 1 mol/L HCl acidic solution at room temperature with and without disparate concentrations of ALM extract are appeared in Figure 4. It is clear that the plots appear non-perfect semi-circle. Which indicated that the frequency dispersion and increasing diameter as the concentration of the ALM extract increases.

The $R_{ct}$, $R_s$ and $C_{dl}$ values, all the electrochemical parameters obtained from Nyquist plots were calculated and iisted in Table 5. We find the $R_{ct}$ values increase with increasing the concentration of inhibitor ALM extract. Maximum inhibition efficiency (95.5%) at 7 g/L. Thus, result indicates a charge-transfer process was mainly controlling to the copper corrosion.

The values of double layer capacitance ($C_{dl}$) decrease with an increase in inhibitor concentration. The decrease in $C_{dl}$ values indicates that the active constituents of ALM extract were adsorption on the copper surface leading to the formation of a layer of film or compound of the acid solution. Thus, result indicates good inhibitive efficacy of ALM extract.

The values of inhibition efficiency were calculated from $R_{ct}$ according to the following equation. The IE is defined as [47-52]:

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

Where $R_{ct}$ and $R_{ct(inh)}$ are the values of the charge transfer resistance with and without of the inhibitor, respectively. In order to analysis of the Nyquist plots, the corresponding equivalent circuit given in Figure 5, where $R_s$ stands for the solution resistance, $R_{ct}$ stands for the charge transfer resistance and $C_{dl}$ is the electrochemical double layer capacitance.

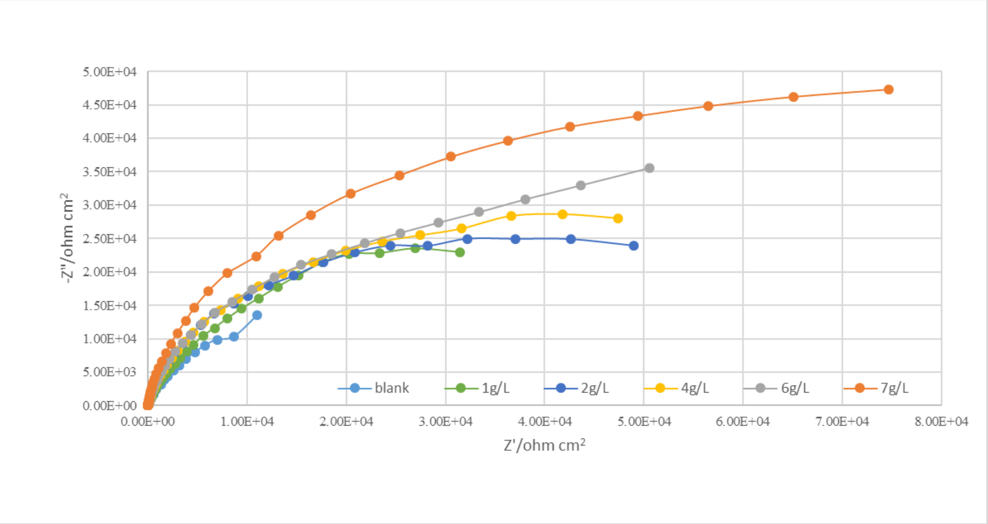


**Figure 4.** Nyquist plots for Cu in 1mol/L HCl acidic solution with and without different concentrations of ALM extract inhibitor.

**Table 5.** Electrochemical Impedance parameters for copper in 1M HCl solution with and Without different concentrations of ALV extract inhibitor.

| ALV g/L | $R_f$ (Ω cm$^2$) | $C_f$ (µF/cm$^2$) | $R_s$ (Ω cm$^2$) | $Y_0$ (µF/cm$^2$) | $n$ | $R_{ct}$ (kΩ cm$^2$) | W (µF/cm$^2$) | IE% |
|---|---|---|---|---|---|---|---|---|
| 0 | 2.72 | 0.198 | 3.9 | 87 | 0.9 | 22.8 | 83 | - |
| 1 | 1.99 | 0.39 | 6.39 | 57.5 | 0.94 | 249.9 | 154 | 90.8 |
| 2 | 3.01 | 12.1 | 11.01 | 44. 8 | 0.91 | 258.6 | 218 | 91.2 |
| 4 | 12 | 26.98 | 8.49 | 33.2 | 0.78 | 329.4 | 268 | 93.1 |
| 6 | 5.28 | 19.01 | 10.1 | 36.3 | 0.86 | 433.7 | 225 | 94.7 |
| 7 | 3.1 | 35.01 | 8.99 | 27.4 | 0.56 | 513.2 | 209 | 95.5 |

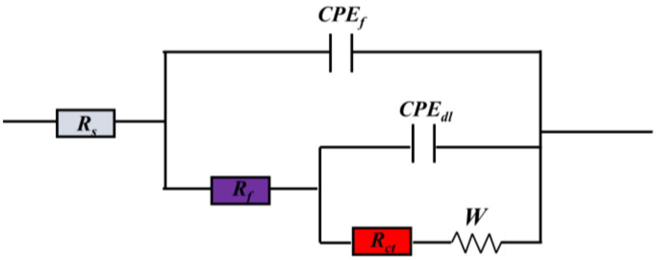


**Figure 5.** The equivalent circuit for EIS measurements data.

### *3.7 SEM analysis*

As shown in Figure 6, was observed the effects on the copper metal surface after immersion for 24 h in solution 1 mol HCl in the absence of the ALV extract. In the case of using the inhibitor (ALV), Figure 6a, showed that the surface of the copper metal is high corrosion and cracks in the surface. In the presence of inhibitor the surface of the metal was more smooth and uniform in Figure 6b, this indicates that the inhibitor gave positive results when adsorption on the Cu surface and this compatible to the results obtained from electrochemical and weight loss method.

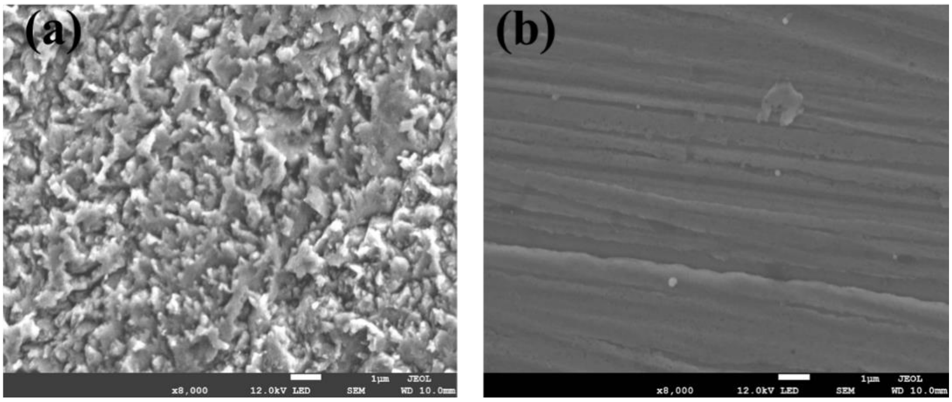


**Figure 6.** Surface morphology of the Cu substrate (a) in the absence and (b) presence of ALV extract after 24 hours of immersion in 1 mol/L HCl.

## 4. CONCLUSIONS

This study has investigated the inhibiting effect of the ALV extract in 1 M HCl on the pure copper by using weight loss, electrochemical potentiodynamic polarization curve methods, electrochemical impedance spectroscopy (EIS) and SEM-EDX analysis. The results obtained from all of Tafel, EIS, weight loss and SEM-EDX measurements were in good agreement and almost identical. ALV extract was found to be an effective inhibitor for copper in 1 M HCl solutions and its inhibition efficiency increases with increases in concentration. Reaching a maximum value of 96% at 7 g/L of the ALV extract, which obviously represented an excellent inhibitive property. Thus, ALV extract can be considered as a mixed-type inhibitor that adsorbed on the pure copper surface based on Langmuir isotherm model. The inhibition efficiency of ALV in EIS method we obtained the maximum inhibition efficiency (95.5%) at (7 g/L). Thus result indicates good inhibitive efficacy of ALM extract. The inhibition efficiency of ALV in weight loss method increases when immersion time reaching a maximum value (95.60%) at 24 h.

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