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Electrochemical Noise Analysis of Different Herbal Compounds for Copper Exposed to Chloride Media.

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Four different herbal compounds,), Caraway (*Carum Carvi*), Cumin (*Cuminum Cyminum*), Anise (*Pimpinella Anisum)* and Hibiscus (*Hibiscus Sabdarriffa*) have been tested as green corrosion inhibitor for copper exposed to 0.5 M NaCl. The corrosion Inhibition has been studied using electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS). The comparative analysis of the results obtained showed that EN is an effective tool for screening of new corrosion inhibitors. Polynomial trend removal method has been used to remove the trend in the potential and current fluctuations during the measurement periods. The results gathered showed very good inhibition efficiency. Generally, EN showed a good correlation with EIS in this study

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Keywords: Copper, EN, EIS, Herbal compounds

1. INTRODUCTION

Due to the environmental restriction of application of corrosion inhibitors, researchers reoriented to use natural compounds (green corrosion inhibitors). Green inhibitors will help keep the environment more salubrious, safely and under pollution control. Recently, the use of different herbal compounds as corrosion inhibitors have been widely used, of these some data has been reported for the use of Anise, Caraway, Cumin and Hibiscus as corrosion inhibitors [1-7].

A great interest concerning the utilization of electrochemical noise in corrosion studies has magnetized the attentions of many corrosion scientists due to its simplicity and low cost; however, the technique is still under investigation [8-11]. It was not possible to collect corrosion rate from noise analysis with a traditional electrochemical cell that has only one working electrode. The use of two identical working electrode configuration in noise studies was first introduced by Eden et al, this configuration allowed the collection of both current and potential simultaneously, so that corrosion rate can be calculated [12]. Analysis of noise data can be performed both in the time and frequency domains, Mansfeld et al studied the validity of both statistical parameters such as localization index (LI),skewness and kurtosis and frequency parameters such as power spectral noise (PSD) slopes [13,14]. LI is defined as the ratio of the standard deviation and the root mean square of current fluctuation in EN measurements; accordingly LI will have values between 0 and 1. It was assumed that LI could be used to differentiate between different kinds of corrosion mechanisms [15]. An experimental and theoretical analysis showing the importance of trend that may appear in both potential and current fluctuation has been carried out by Mansfeld et al [10]. Recently, EN has been used to study green inhibitors such as Aloe plant extract, Salvia officinalis and coconut oil modified [16-18]. This study aims to investigate the inhibition efficiency of different herbal compounds as green inhibitors for copper exposed to sodium chloride solution by using electrochemical noise technique.

2. EXPERIMENTAL PROCEDURE

Four different herbal compounds, Hibiscus (*Hibiscus Sabdarriffa*), Caraway (*Carum Carvi*), Cumin (*Cuminum Cyminum*) and Anise (*Pimpinella Anisum*) were used in this study. The herbal samples were prepared by refluxing 10 gm of each dried herbal in 100 ml of deionized water for a period of 1 hour, then the refluxed solution was cleaned by filtration process. Concentrations of the herbal were determined after evaporating 10 ml of the cleaned filtrate and weight the residue [19]. The symbols K, C, J and W in this study will refer to Hibiscus, Cumin, Anise and Caraway, respectively. For each experiment, electrochemical measurements were carried out in a two identical electrodes configuration cell (2E) with a saturated calomel reference electrode (SCE). The tested electrode was pure copper sheet (99.9%) with exposed area of 1 cm^2. All corrosion measurements were conducted in 0.5 M NaCl solution. Prior to corrosion testing copper samples were subjected to mechanical polishing up to the grit size of 1200 silicon carbide paper, then cleaned in acetone and dried with nitrogen. All corrosion experiments were carried out for a duration varying between 6 hours to 96 hours at 25 ^{0}C. Electrochemical impedance spectroscopy (EIS) and electrochemical noise analysis (EN) were used in this study [9]. EN was performed in a set-up with an electrochemical cell consisting of two identical copper electrodes with an exposed area of 1.0 cm^2 for each electrode and an SCE as a reference electrode within a Faraday cage. An AutoCAD DSP device (ACM Instruments) was used to collect potential and current fluctuations simultaneously. Potential and current fluctuations were obtained with a sampling rate of 2-point s^{-1} during a time period of 1024 seconds, which fixed the frequency range (Δf) in region between 1 Hz and about 1 mHz. The instrument noise was tested and shown to be with no influence on the noise measurements. A polynomial trend removal method was performed to remove the direct current (DC) trend contained in the noise data. The analysis of EN data in time domain was developed using Mathcad PLUS 6 software. EIS was performed with the AutoCAD DSP device (ACM Instruments). A sinusoidal perturbation of 10 mV rms was applied at the cell over the frequency range of 30 kHz-0.005 Hz. EIS was conducted immediately after EN using the same cell [9].

3. RESULTS AND DISCUSSION

Figure 1 shows the time dependent of corrosion potential (E_{corr}) for copper exposed to chloride media with and without different herbal compounds. Generally E_{corr} values showed a slight decrease with time which may indicate acceleration of corrosion. The highest E_{corr} values were observed for solution containing K. For C, W and J, E_{corr} values were less than that obtained for solution without herbal compounds. These results may suggest that C, W and J will electrochemically behave different than K.

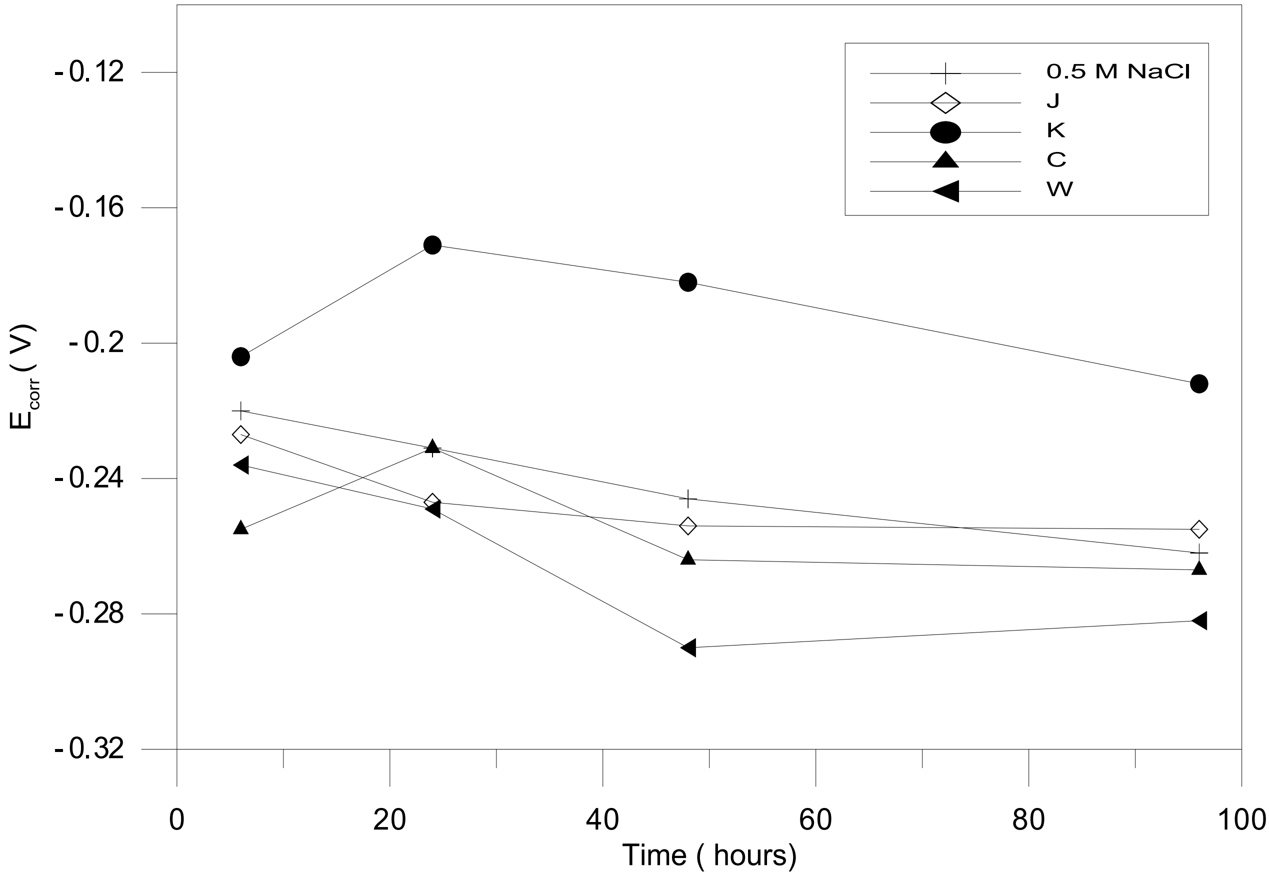

Figure 1. Time dependence of E_{corr} for copper exposed to 0.5M NaCl with and without different herbal compounds.

Figure 2 shows Bode plots for copper exposed to 0.5 M NaCl with and without different herbal compounds after 6 hours. There are clear differences between the spectra obtained in solution containing herbal compounds and in its absence. The appearance of second phase angle not exceeding 45^0 at the lowest frequency region is considered to be an indicative of diffusion process [10, 14]. For copper exposed to 0.5M NaCl a diffusion process was observed with a maximum phase angle of about -50^0 and Rp value of about $3x10^2$ ohm (Figure 2). It is clear that the impedance was much higher for copper exposed to NaCl in the presence of W, C and J than in its absence. No significant change in the impedance was observed in case solution containing k. A similar effect was observed for copper exposed to NaCl with and without herbal compounds after 4 days (Figure 3). The increased impedance followed the following sequence; C > J > W> K.

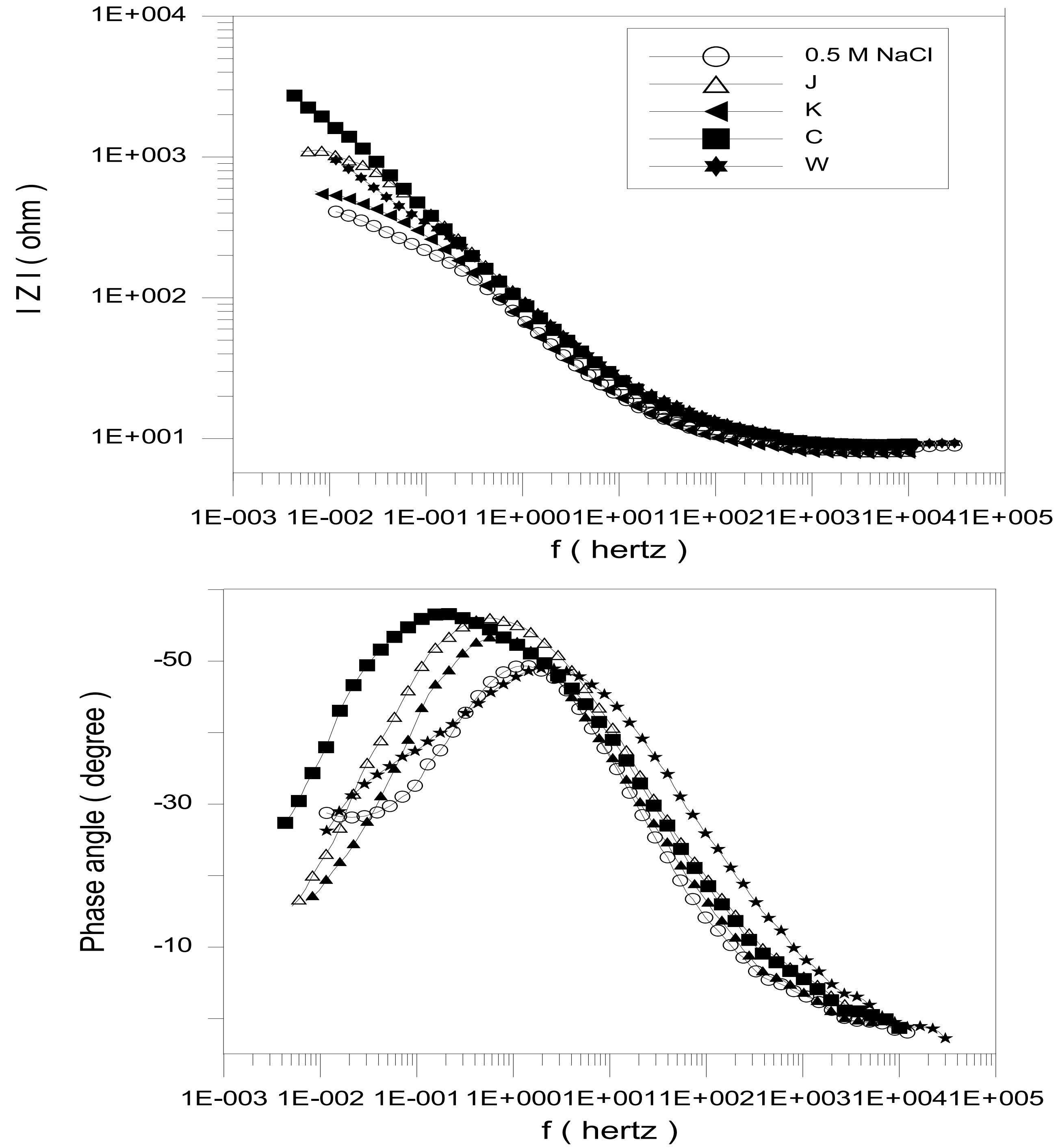

Figure 2. Bode plots for copper exposed to NaCl with and without different herbal compounds after 6 hours.

Organic corrosion inhibitors usually have nitrogen, Sulfur and oxygen atoms in their structure. It was believed that the presence of such atoms will ease the adsorption of these inhibitors on metal surface by donation of their free electron lone pairs to the metal vacant d orbitals [20-22]. It has been reported that the chemical composition of the studied herbals were rich in oxygen functional groups such as aldehyde, hydroxyl and hydroxyl acid [23-26]. The presence of such groups might be the main cause of the expected corrosion inhibition. The presence of free lone pairs of electrons on the oxygen atom will establish the adsorption of these compounds with metals surface. Copper like most transition elements has vacant d orbitals that might be occupied by the free lone pairs found in these herbal compounds. The major chemical compounds that have been found in Hibiscus extracts are hibiscus acid, hydroxycitric acid, citric acid, malic and tartaric acids. Oxalic and ascorbic was found with minor quantity [26]. Accordingly, the presence of such organic acid will accelerate the corrosion rate of copper exposed to chloride media containing K.

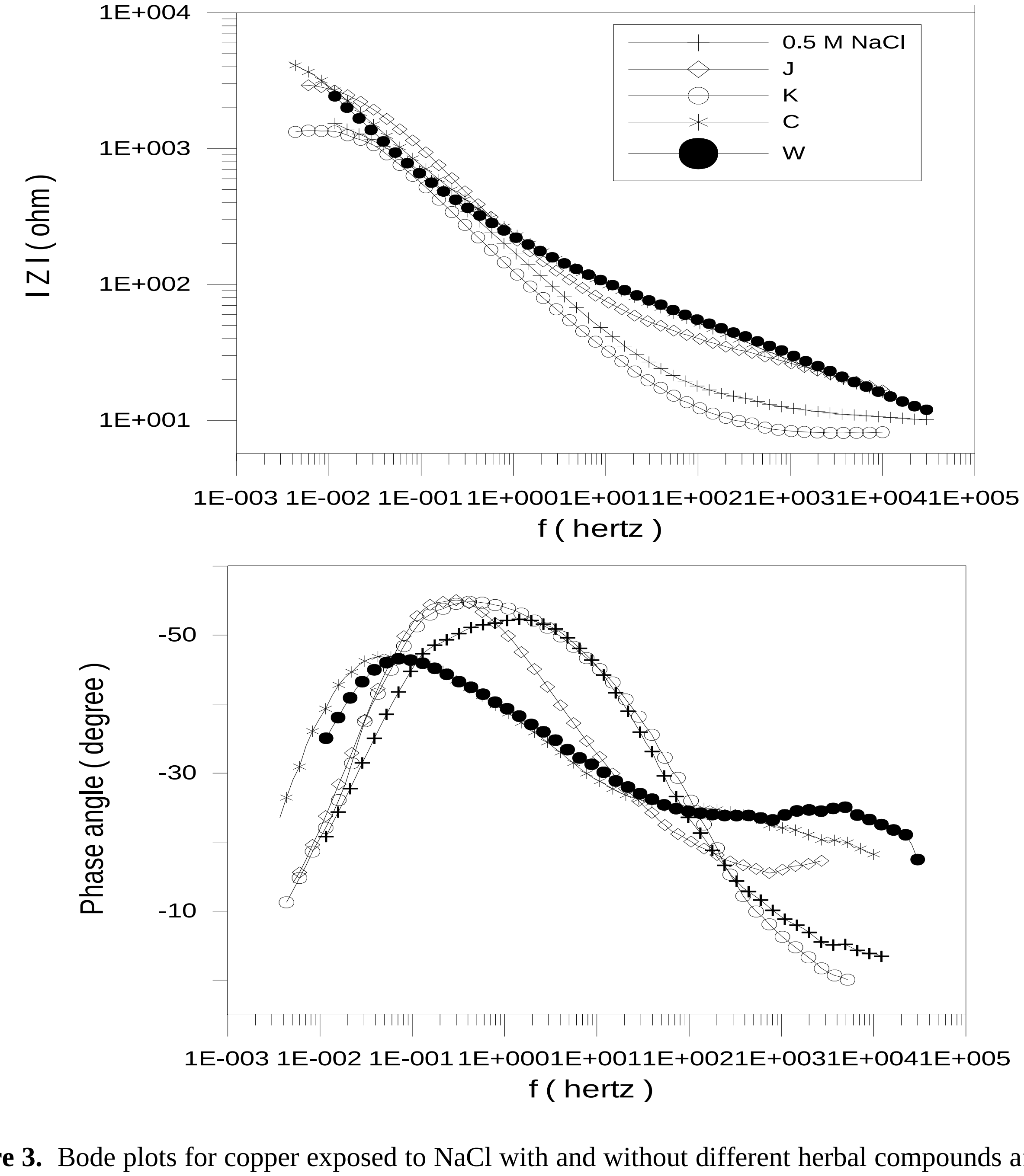

Figure 3. Bode plots for copper exposed to NaCl with and without different herbal compounds after 4 days.

The impedance response of copper samples is approximated by an appropriate equivalent circuit. In this study the impedance spectra were analyzed using the open boundary finite length diffusion model [10,14]. Figure 4 shows the time dependence of R_p in absence and presence of different herbal compounds. R_p values obtained for all the tested herbal compounds except K were much higher than those obtained for copper exposed to NaCl only. The increased values of R_p will reflect the inhibitive effect of the corrosion of copper due to the presence of such compounds. It is also clear that the corrosion inhibition reached its maximum values for solution containing C. R_p values were slightly increased for all of the tested solutions, which indicate improvement of corrosion inhibition with time. The increased R_p values followed the following sequence; C>J>W>K.

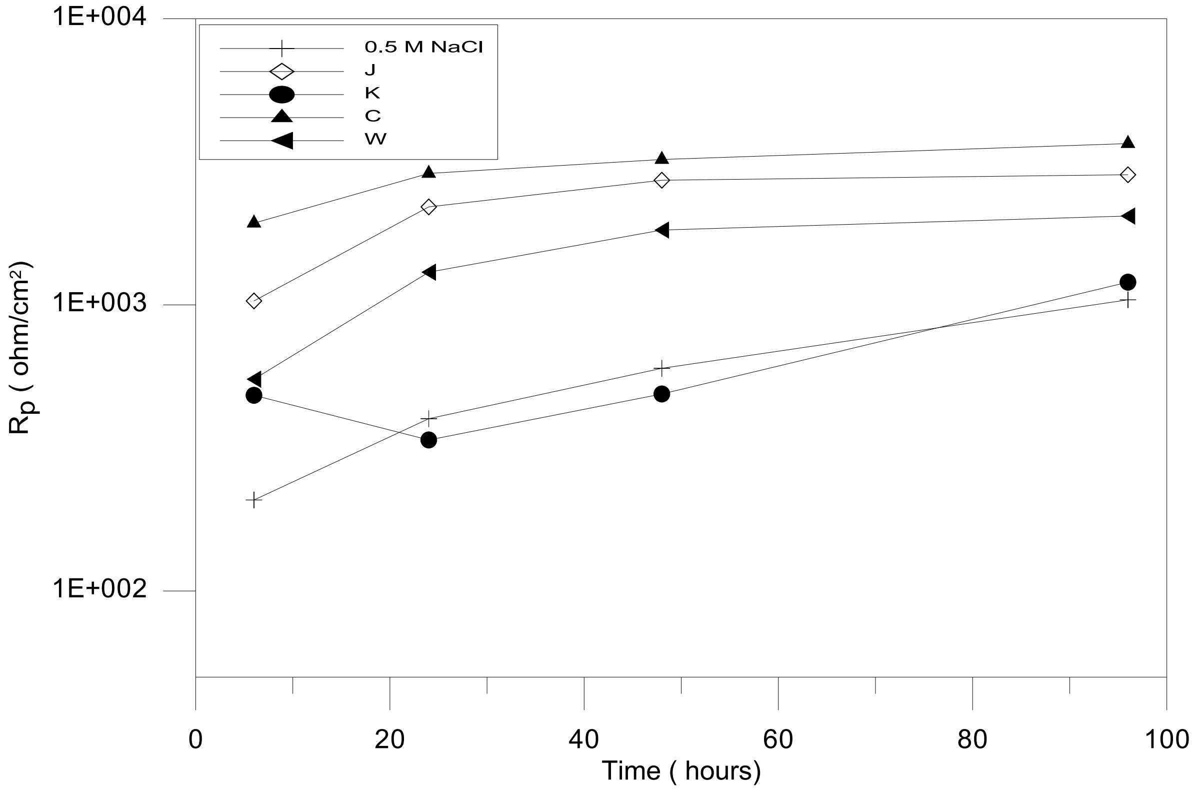

Figure 4. Time dependence of R_p for copper exposed to 0.5M NaCl with and without different herbal compounds.

As was described in the experimental section, the potential and current noise fluctuations were recorded simultaneously. The noise data has been analysis both in the time and frequency domains. Figure 5 shows the experimental EN data for copper exposed to 0.5M NaCl containing w after 6 hours in the time domain (Figure 5 (a), (b)) and the frequency domain (Figure 5 (c)-(e)), while Figure 6 represents the corresponding EN data after trend removal. As was discussed before the presence of trend can mask the shape and current fluctuations and may affect the slopes of PSD plots [9, 13, 14].

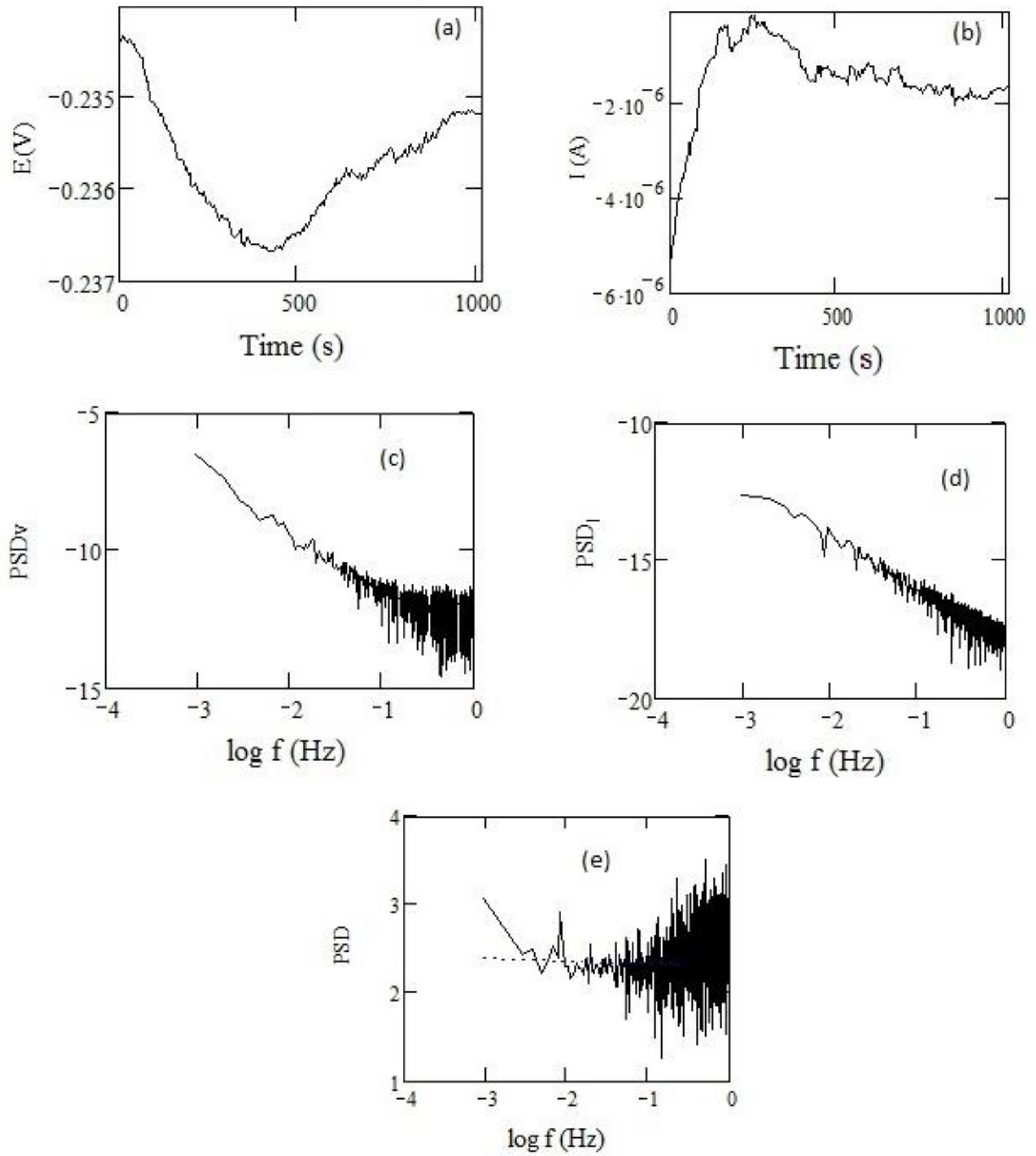

Figure 5. EN data in the time (a and b) and frequency domains(c-e) for copper exposed to NaCl containing W. for 6 hours

Analysis of the noise data in the time domain will allow us to calculate the noise resistance (R_n) which is define as the ratio of the standard deviation of potential noise (σV) to that of current noise (σI), ($R_n = \sigma V/\sigma I$). This parameter can be used to calculate the corrosion rate, assuming that R_n is equivalent to polarization resistance R_p [27].

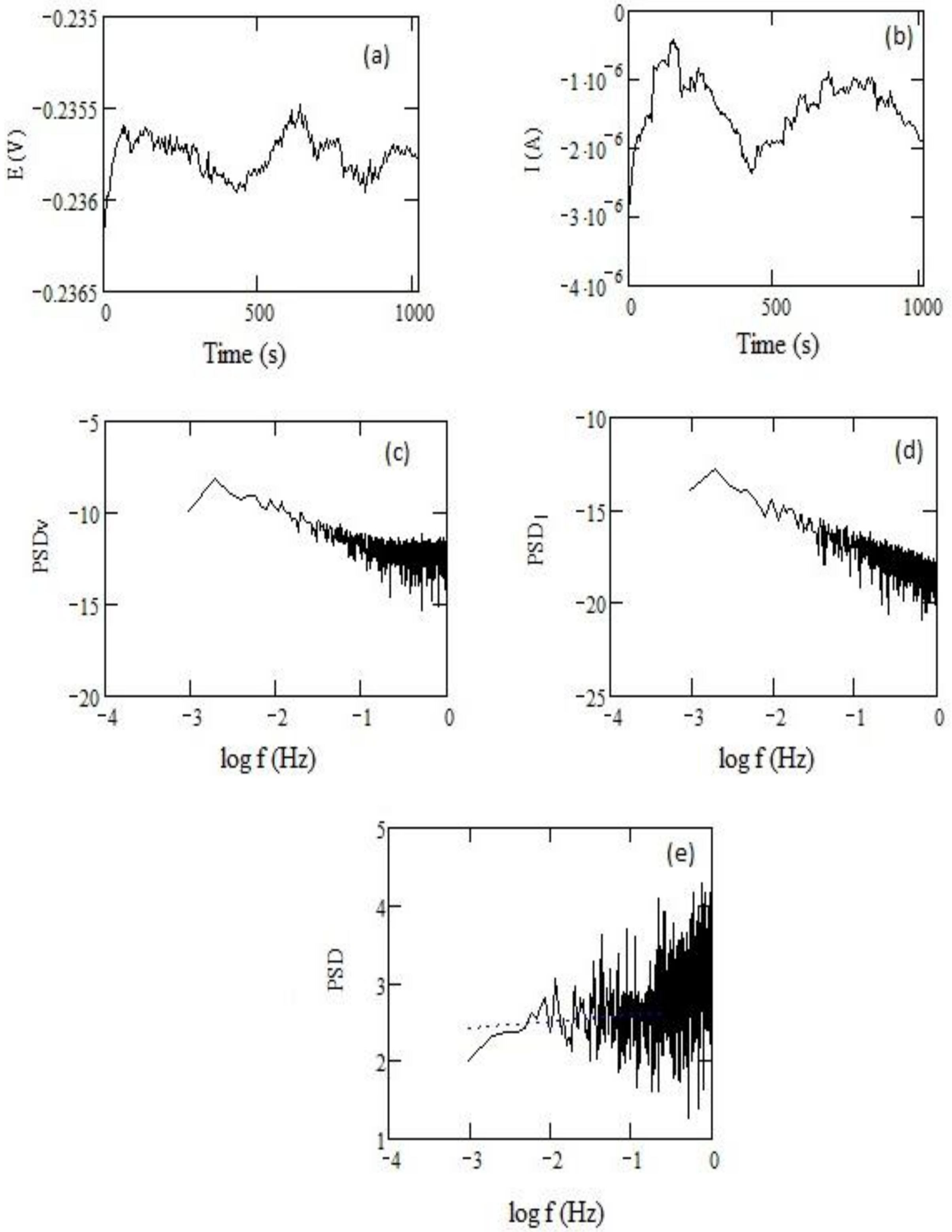

Figure 6. EN data in the time (a and b) and frequency(c-e) domains for copper exposed to NaCl containing W. for 6 hours after trend removal.

Figure 7 shows the time dependence of R_n for copper exposed to NaCl with and without different herbal compounds. The high R_n values obtained for W, C and J coincided with the corresponding R_p values obtained from impedance study. R_n values for W, K and C slightly increased with time, which indicate improvement of corrosion inhibition. These results also coincided with R_p values obtained before. After 4 days of exposure R_n values reached its maximum value (Figure 7). Accordingly, the obtained results suggested that these inhibitors could be very effective for the studied period.

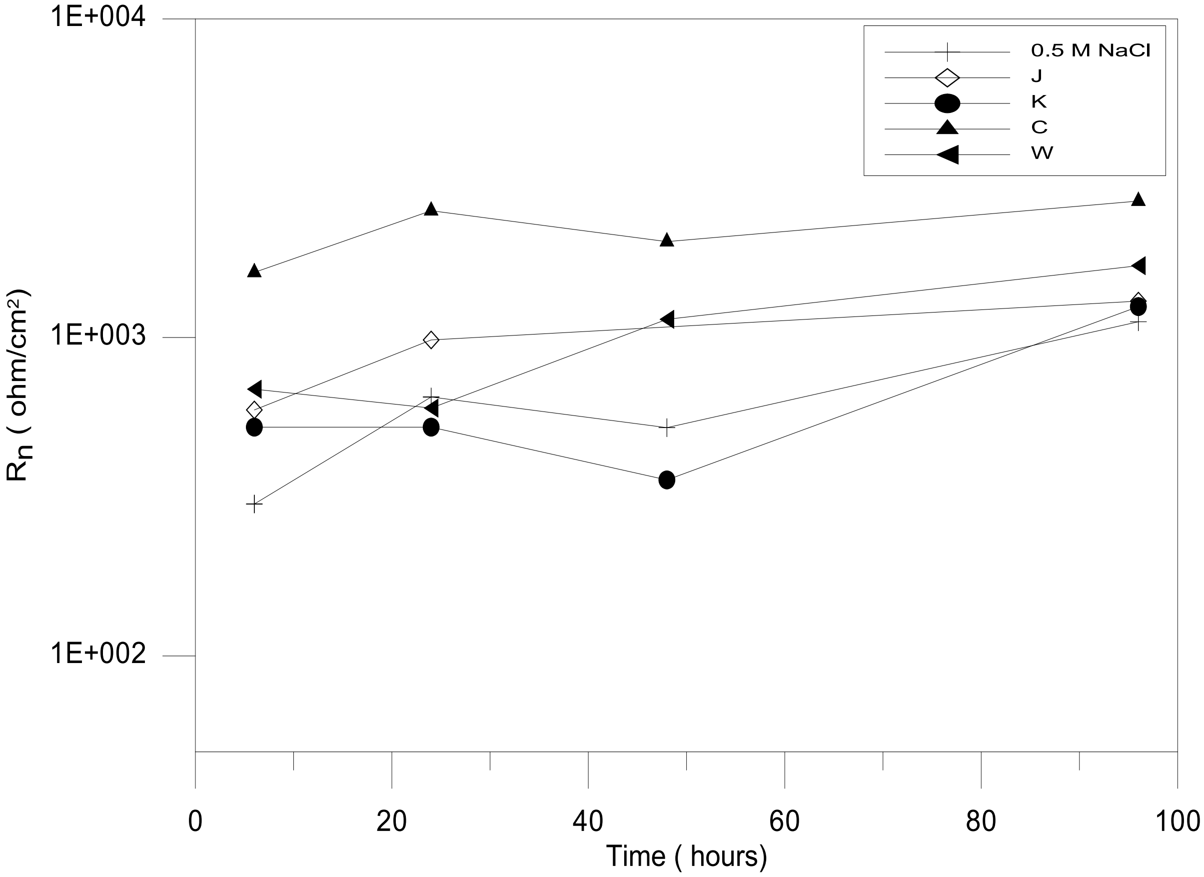

Figure 7. Time dependence of R_n for copper exposed to 0.5 M NaCl with and without different herbal compounds.

The localization index (LI) is defined as the ratio of the standard deviation of σ_i and the root mean square of the current I_{rms}. LI has values between 0 and 1. It has often been assumed that LI values can be used to differentiate between different types of corrosion, for example LI close to 1 corresponds to localized corrosion, while LI close to zero suggests general corrosion [14,15]. LI data obtained for copper exposed to 0.5M NaCl with and without different herbal compounds are shown in Figure 8. It is clear that LI values were close to zero, regardless the tested solutions, which is in agreement with previous findings that LI could not be used to determine the corrosion mechanisms [9, 13, 14].

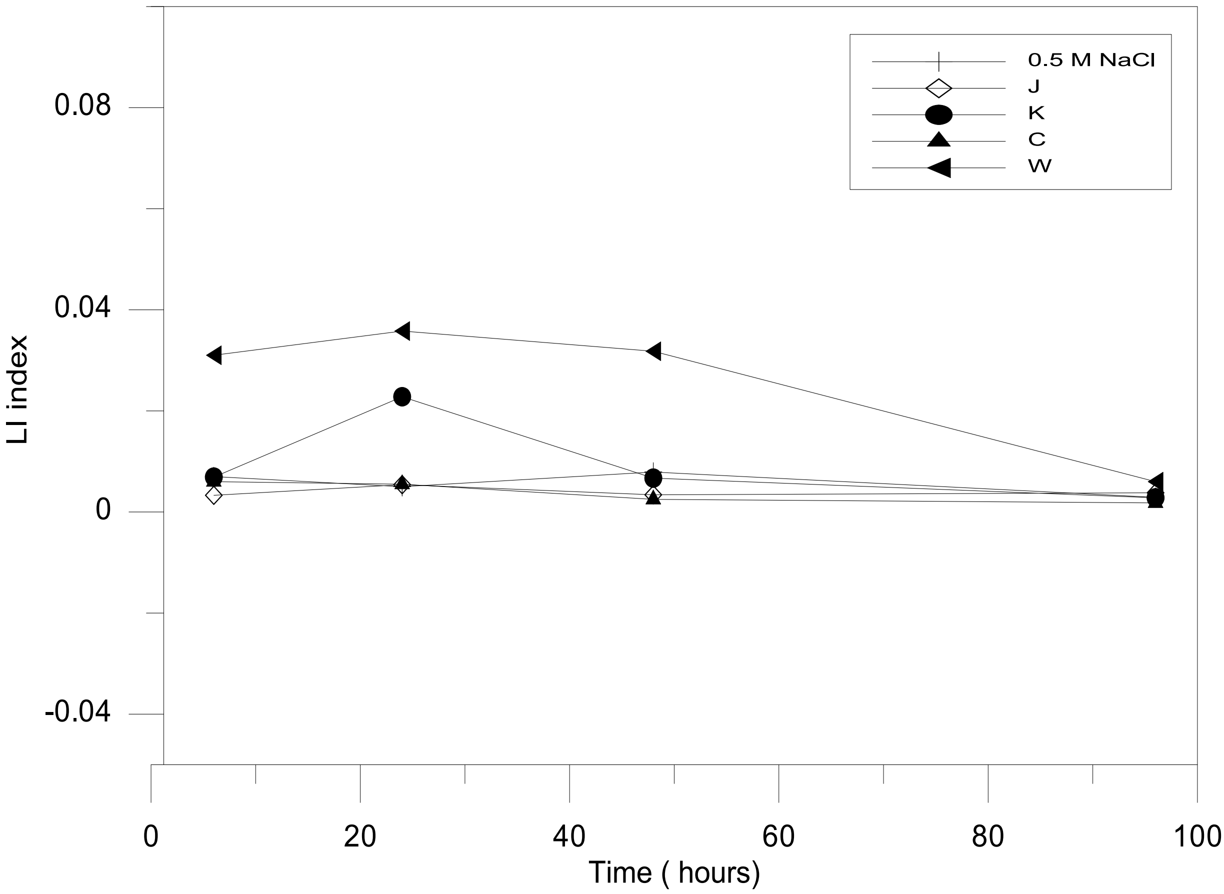

Figure 8. Time dependence of LI for copper exposed to 0.5 M NaCl with and without different herbal compounds.

Kurtosis can be used as a measure of the shape of the distribution of the random fluctuation of both potential and current data. For kurtosis value equal to 3 the data will have the shape of a normal distribution, while for values more or less than 3 the shape of the disruption peak will be more sharped or flatted [9, 28]. The asymmetry of the probability distribution of the EN data can be measured by Skewness. If the skewness equals to zero the shape of the noise data will have a symmetric shape. Negative values imply that the distribution is skewed to the left and the distribution is focused in its rightmost section with an extended thin tail to the left. On the other hand, the symmetric distribution will be skewed to the right for positive skewness values [10, 28]. I_{skew} and E_{skew} are the skewness of the current and potential fluctuations, respectively. I_{kurt} and E_{kurt} are the kurtosis of the current and potential fluctuations, respectively.

Time dependence of skewness and kurtosis for both current and potential fluctuations for copper exposed to 0.5M NaCl with and without different herbal compounds are shown in figure 10. It is obvious that both skewness and kurtosis were independent of both time and different inhibitors used. This results agreed with what has been reported before and confirmed that skewness and kurtosis will only give an indication about the shape of the noise data and cannot provide any mechanistic information [9,10,14].

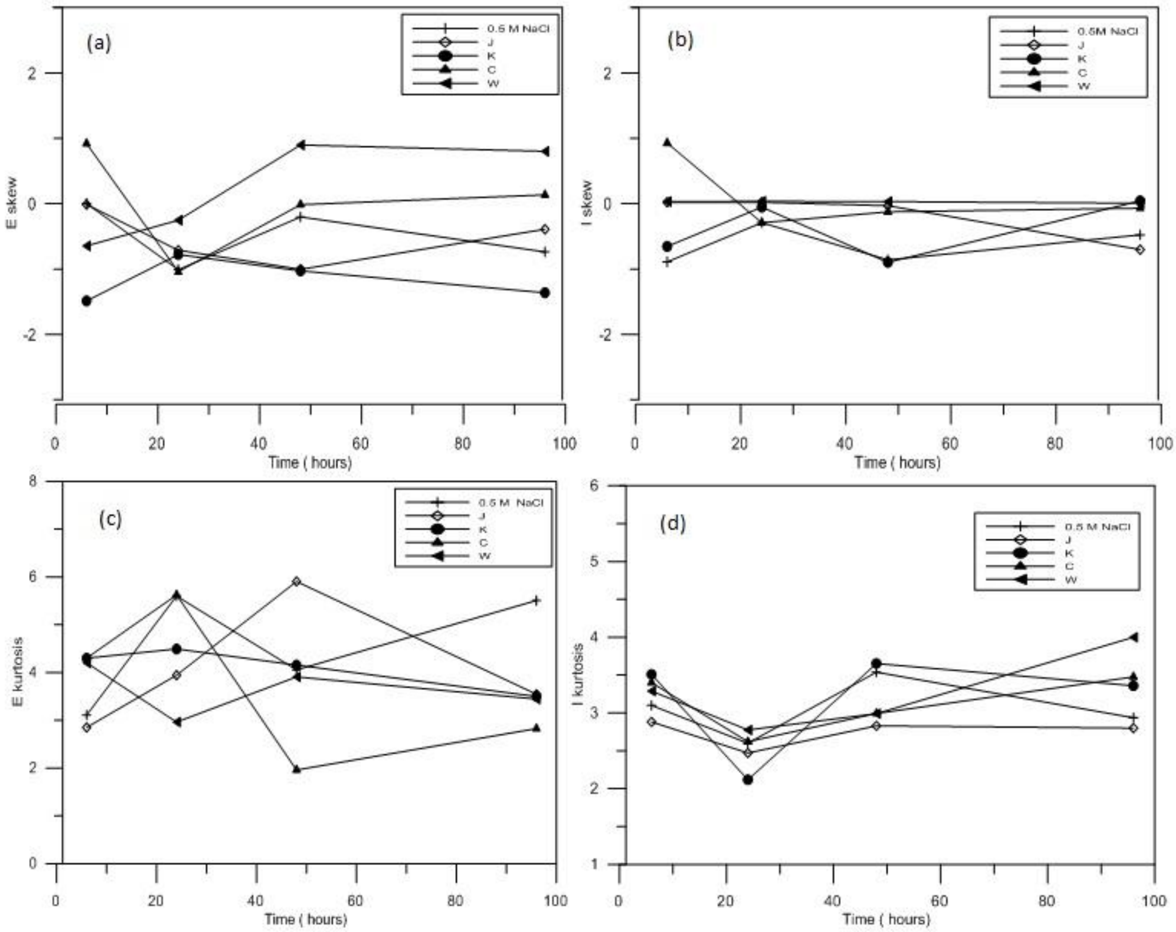

Figure 9. Time dependence of E_{skew} (a), I_{skew} (b), E_{kurt} (c), and I_{kurt} (d) for copper exposed to 0.5 M NaCl with and without different herbal compounds.

The noise data in time domain has been converted to frequency domain by using Fast Fourier transform (FFT). The spectral noise plot (R_{sn}) is defined as [29, 30]:

$$R_{sn}\,\mathbf{(f)} = \left| \frac{V_{FFT}(f)}{I_{FFT}(f)} \right| = \left(\frac{V_{PSD}(f)}{I_{PSD}(f)} \right)^{1/2}$$

Where, V_{FFT} and I_{FFT} will refer to the Fast Fourier Transformer functions of the potential and current noise, respectively, and V_{PSD} and I_{PSD} are the corresponding PSD plots.

Figure 10 shows a comparison between the spectral noise plots and impedance plot for copper exposed to NaCl solution containing K before (a) and after trend removal (b). It is obvious that no agreement between the noise and impedance plots was observed before trend removal (Figure. 10 (a)) however, after trend removal a very good agreement was observed (Figure 10 (b)). Examination of noise data confirmed the necessity for the removal of the drifts both in potential and current fluctuations during the measurement periods

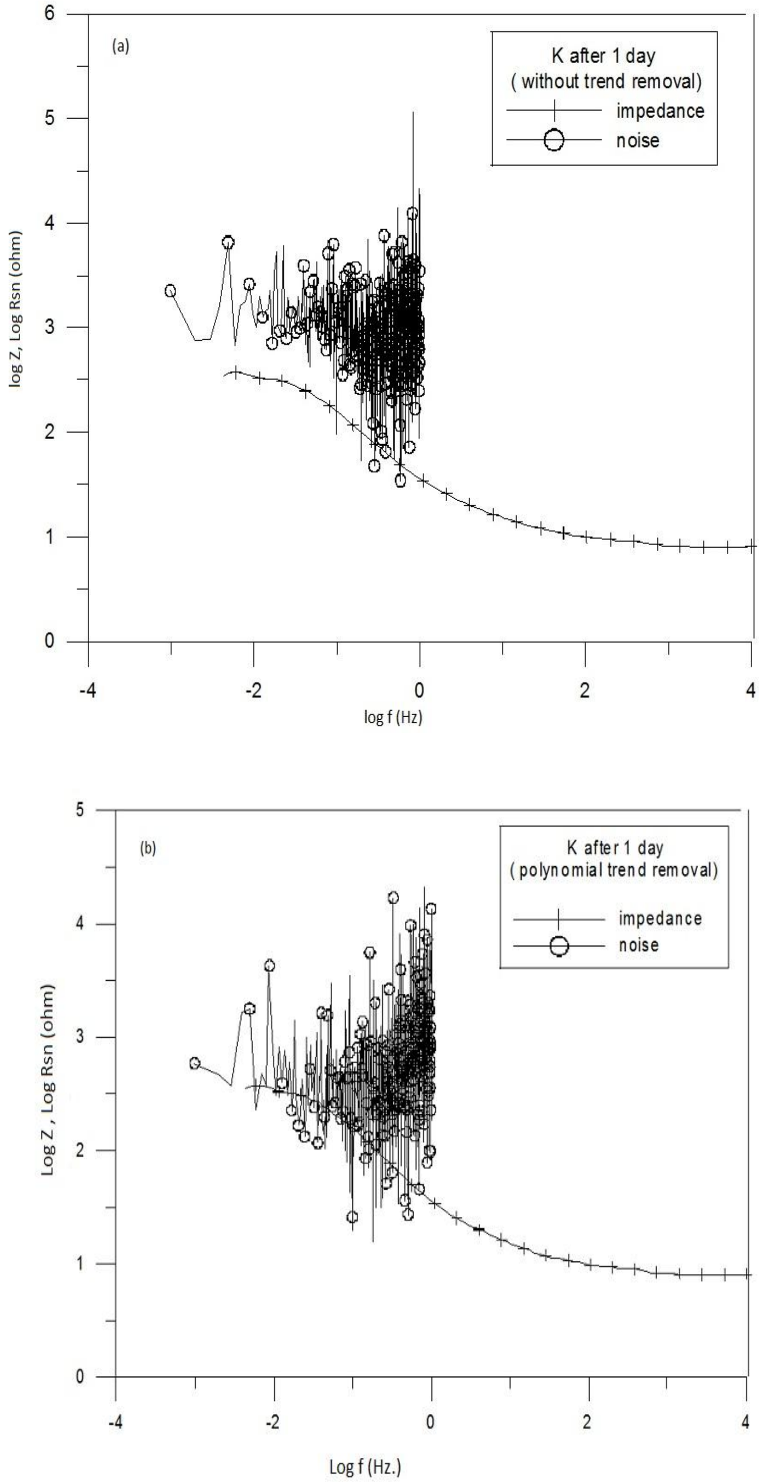

Figure 10. Impedance and spectral noise plots comparison for copper exposed to 0.5 M NaCl with k for 1day (a) before and (b) after trend removal.

5. CONCLUSIONS

The experimental results show that the tested herbal compounds are good corrosion inhibitors of pure copper exposed to solution of 0.5 M NaCl. Negative shift in E_{corr} values for NaCl containing herbal compounds (W, C and J) may indicate that they worked as cathodic inhibitors. EIS showed that the corrosion mechanism is controlled by diffusion process. R_p values were increased to a large extent in the presence of herbal compounds. The increased impedance followed the following sequence; C>J>W>K. The obtained R_n values were nearly similar to R_p values. It can be concluded that R_n successfully followed the corrosion behavior of copper exposed to NaCl in the presence and absence of herbal compounds, like EIS. Analysis of noise data demonstrated the need of removal of the trends in the potential and current fluctuations during the measurement periods Analysis of skewness and kurtosis data were independent on the corrosion environment. Accordingly, No mechanistic information could be obtained from skewness and kurtosis data. Noise data showed a good agreement with Impedance data in the frequency domain, so that Noise analysis can be used to detect the corrosion rate but was not found to give mechanistic information. The comparative analysis of the results obtained showed that EN is an effective tool for screening of new corrosion inhibitors. Further studies are required to clarify why one herb works better than the other by going into the structural part of the inhibitor molecule and its inhibition mechanism.

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