Int. J. Electrochem. Sci., 12 **(2017)** 5867 – 5887, doi: 10.20964/2017.07.13

International Journal of
ELECTROCHEMICAL
SCIENCE
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Electrochemical study on the Efficiency of Curcuma extract as a green Inhibitor for Corrosion of α- brass in 1MHCl

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Received: 12 February 2017 / *Accepted:* 25 April 2017 / *Published:* 12 June 2017

The effect of Curcuma as a corrosion inhibitor compound for the corrosion of α-brass in 1.0 M HCl was studied using chemical and electrochemical techniques. The inhibition effect was attributed to the adsorption of the compound on the α-brass surface. The data obtained fit well to Freundlich and Henry adsorption isotherms. Potentiodynamic measurements indicated that; Curcuma considers a mixed-type inhibitor for α-brass in 1.0 M HCl. Curcuma was found to have high corrosion inhibition efficiency as indicated from the results of weight loss, potentiodynamic polarization, EFM and electrochemical impedance spectroscopy (EIS) measurements. AFM technique was performed and the results showed superior inhibition efficiency of Curcuma. The efficiencies obtained from all different techniques were in a good agreement, which prove the validity of these tools in the measurements of the tested inhibitor.

Keywords: α-brass; corrosion inhibition;Curcuma; HCl;EIS; AFM;FTIR

1. INTRODUCTION

The alloys of copper have different uses in heat exchanger tubes in absorption refrigeration systems and water distribution systems due to their excellent electrical and thermal conductivity, good machineability, corrosion resistance, and low cost [1-3]. Brass is used as tubing material for condensers in cooling water systems. The alloys of copper are resistant toward the influence of atmosphere and many chemicals, they are susceptible to corrosion problems such as dezincification and pitting corrosion in aggressive media. The most of the marine propellers are made from copper and its alloys. Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass [4,5]. Many techniques have been used to minimize the dezincification and corrosion of brasses. The brass which has more than 15% of zinc is exposed to a corrosive medium, they are affected by dezincification (preferential dissolution of zinc) process, leaving a spongy mass of copper on the alloy surface and general corrosion damage[6]. From the important techniques for minimizing corrosion is the use of inhibitors. The effectiveness of the inhibitors varies with their concentrations, the corrosive medium and the surface properties of the alloy. Many inhibitors have been used to minimize the corrosion of brass in different media [7-12]. The natural products of plant origin are readily available, inexpensive and eco-friendly corrosion inhibitors[13-15]. The extracts from their leaves, barks, seeds and roots compose of mixture of organic compounds and some have been reported as effective inhibitors for various metals. Usually organic compounds contain polar functions as oxygen, sulfur and nitrogen atoms. Also these compounds have conjucated or triple double bonds with aromatic rings in their molecular structures, which are the major adsorption centers[16,17]. Curcuma (turmeric) is used in spice in Southeast Asia, household medicine and food colorant. Figure 1demonstrates curcumin chemical structure.

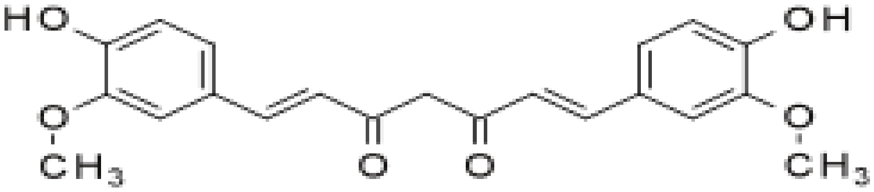

Figure 1. Chemical structure of curcumin**.**

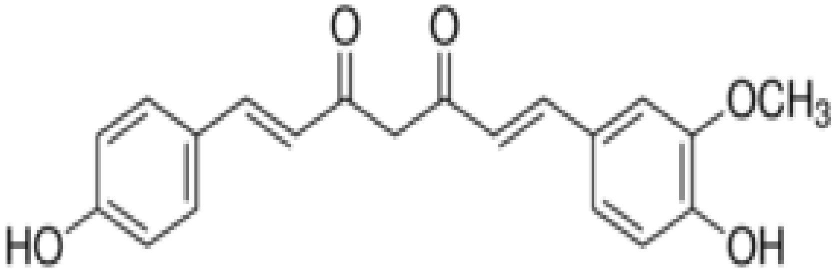

Figure 2. Chemical structure of demethoxy curcumin

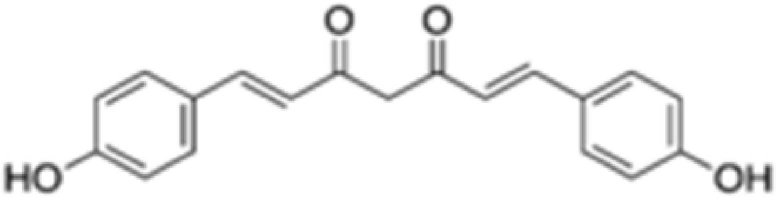

Figure 3. Chemical structure of bis-demethoxy curcumin.

The chemical structure of other two compounds demethoxy curcumin and bis-demethoxy curcumin show in Figures 2, 3 respectively. These three compounds are natural phenols, also they are responsible for the yellow colour of turmeric. These compounds possess heterocyclic compounds with polar functional group, hydroxyl, oxygen, conjugated double bonds and the non-toxicity factors that show the ability to act as organic corrosion inhibitors [18,19].

The aim of this work is to investigate the corrosion inhibition effect of Curcuma on α-brass in 1.0 M HCl solution, using some electrochemical measurements and weight loss method.

2. EXPERIMENTAL

2.1.Materials and solutions

The experiments were performed with local commercial α-brass (Helwan Company of Non-Ferrous Industries, Egypt) with the following composition (mass %) Cu 67.28, Pb 0.029, Fe 0.002, Zn 32.689. Brass coupons were cooled and annealed in an electric oven maintained at 600 °C. After that the specimens were quenched in air to reach the ambient temperature. For weight loss measurements, α-brass specimens of size (10 x 10 x 2) mm were used. Electrodes for electrochemical studies were embedded in araldite with an exposed surface area of 1cm^2. The specimens and electrodes were abraded with emery paper (up to 1200 grit size), degreased with acetone and rinsed with bidistilled water. 1.0 M HCl solution was used as a test (corrosive) electrolyte and was prepared from an analytical reagent grade of HCl by diluting concentrated HCl (37%) to a required concentration using bidistilled water. Curcuma extract was obtained directly from the powder curcumin. Curcuma was soaked in methanol and left standing for 5 days. The solution was filtered and further distilled at 40°C to remove the methanol from the Curcuma solution extract and then concentrated to dryness.

2.2.Weight loss method

For weight loss measurements, the coupons of α-brass were immersed in glass beakers containing 100 ml of uninhibited and inhibited solutions and allow standing for several intervals in water thermostat. After definite times, the coupons were taken out, washed by bidistilled water, dried and weighed accurately. The weight loss measurements were performed at different temperatures (25-55°C) for 3 hours.

The corrosion rate (C.R) and the percentage inhibition efficiency (%IE) over the exposure time are calculated according to the following equations:

$$CR = \Delta W/at \qquad (1)$$

$$IE\% = \theta \text{ x } 100 = (W_0\text{-}W/W_0) \text{ x } 100 \qquad (2)$$

where ΔW is the weight loss in mg cm^{-2}, a is the area of specimens in cm^2 and t is the time in min., θ is the degree of surface coverage, W_o and W are the values of the average weight loss without and with addition of the inhibitor respectively.

2.3. Electrochemical measurements

The electrochemical measurements were carried out by using cell with three-electrodes, α-brass as a working electrode, platinum electrode of approximately 1 cm^2 as the auxiliary electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The electrochemical measurements were carried out using Gamry Potentiostat/Galvanostat /ZRA (model PCI4-G750) with a Gamry framework system based on ESA400. Gamry applications include DC105 for DC corrosion measurements, EIS300 for electrochemical impedance spectroscopy (EIS) and EFM140 for electrochemical frequency modulation (EFM) measurements – along with a computer for collecting data. Echem Analyst 5.58 software was applied for graphing and fitting data. All electrochemical measurements were conducted at 25°C ±1 at the OCP after immersion the electrode for 30 minutes (or until a steady-state open circuit potential was obtained) in the test solution.

2.3.1 Potentiodynamic polarization measurements

By using scan rate of 1 mV s^{-1} in the potential range from -500 to + 500 mV with respect to the open circuit potential (E_{ocp}) we obtained Tafel polarization plots. Both cathodic and anodic polarization curves were recorded. The corrosion current density (i_{corr}) was used for calculating the inhibition efficiency and surface coverage (θ) as shown below:

$$\%IE = \theta \times 100 = [1 - (i_{corr} / i^{o}_{corr})] \times 100 \qquad (3)$$

Where i^{o}_{corr} and i_{corr} are the corrosion current densities without and with the inhibitor respectively.

2.3.2 Electrochemical impedance spectroscopymeasurements (EIS)

For electrochemical impedance measurements, the AC signal was 10 mV peak to peak and the frequency range measured was between 100 kHz and 0.2 Hz. The efficiency of the inhibition and the surface coverage(θ) obtained from the impedance measurements are defined by the following relation:

$$\%IE = \theta \times 100 = [1 - (R^{o}_{ct} / R_{ct})] \times 100 \qquad (4)$$

where R^{o}_{ct} and R_{ct} represent the charge-transfer resistance without and with the inhibitor respectively.

2.3.3 Electrochemical frequency modulation technique (EFM)

Electrochemical frequency modulation (EFM) was studied with two sine waves of 2 and 5 Hz. The results of EFM technique are a spectrum of current response as a function of frequency. The spectrum is named the intermodulation spectrum. The spectra contains current responses assigned for harmonical and intermodulation current peaks. The larger peaks were examined to study the corrosion current density (i_{corr}), the causality factors (CF-2 and CF-3) and the Tafel slopes (β_c and β_a) [20]. The great strength of the EFM is the causality factors which demonstrate an internal check on the validity of the EMF measurement [21].

The inhibition efficiency (% IE) can be calculated from EFM measurements by the following relation:

$$\%IE = \theta \times 100 = 1 - [(i_{corr})_{EFM} / (i^{o}_{corr})_{EFM})] \times 100 \qquad (5)$$

2.4 Surface analysis

For surface analysis, the coupons were immersed in 100 ml of 1.0 M HCl solution prepared without and with addition of 200 ppm of Curcuma inhibitor at 25^{o}C. The coupons were taken out and dried in open air after immersion for one day. The surface morphology of the electrode surface was evaluated by atomic force microscopy (AFM). Also, the UV-Visible absorption spectra of 1.0 M HCl solution containing 200 ppm of Curcuma inhibitor before and after immerssion of the carbon steel for 24 h were studied . FTIR spectra were recorded for the plant extract without and with adsorbtion on α-brass immersed in 1.0 M HCl.

3. RESULTS AND DISCUSSION

3.1 Weight – loss measurements:

The effect of different concentrations (50, 100, 150 and 200 ppm) from Curcuma extract on the corrosion of α-brass in 1.0 M HCl solution was investigated by weight loss technique. The weight loss method was used in order to estimate average corrosion rates and inhibition efficiency. Figure 4 shows the effect of increasing concentrations of Curcuma on the corrosion rate of α-brass at 25-55 °C. It is obvious that the weight loss of α-brass in the presence of Curcuma inhibitor is much lower than that obtained in the blank solution, also the weight loss decreases with increasing inhibitor concentration.

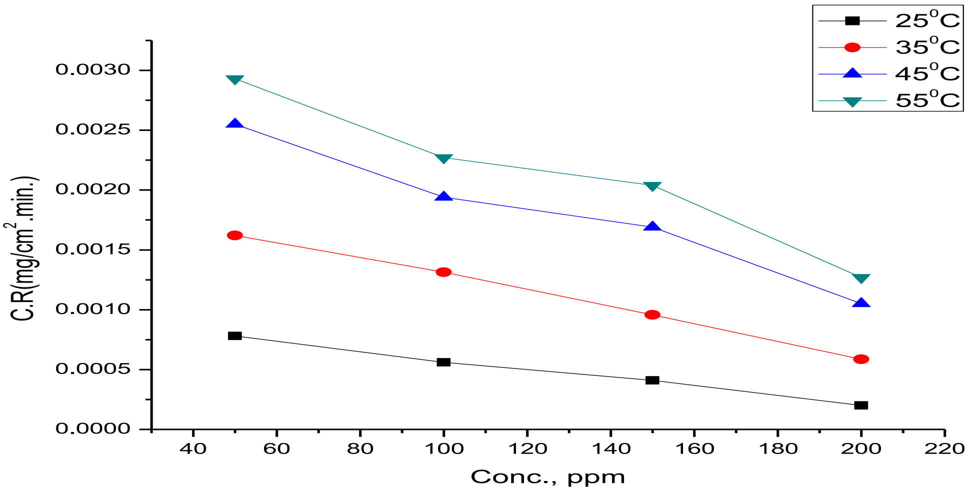

Figure 4. Corrosion rates of various concentrations of curcuma extract on α- brass in 1.0 M HCl at 25 - 55^{0}C.

3.2. Effect of temperature

The effect of different temperatures (25, 35, 45 and 55^{o}C) on corrosion of α-brass in 1.0 M HCl without and with different concentrations of Curcuma inhibitor was determined by weight loss method.

Figure 5 shows the effect of different temperatures on corrosion of α-brass in 1.0 M HCl in the presence of different concentrations of Curcuma.

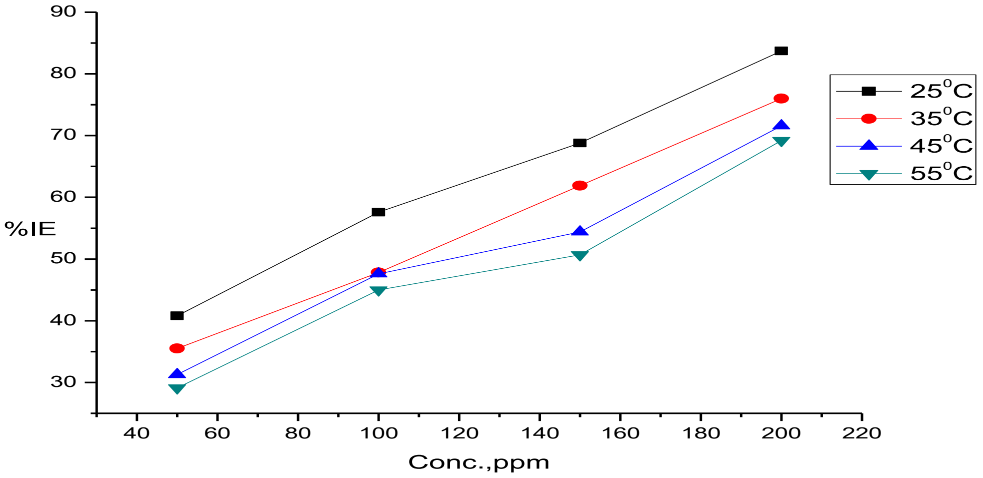

Figure 5. The variation of inhibition efficiency with curcuma extract concentration on α-brass in 1.0 M HCl solutions

Table 1. Data from weight loss of α-brass in1.0 M HCl for various concentration of Curcuma after 90 min. immersion at different temperature.

Temp, °C	Conc., ppm	ΔW, mg/cm^2	θ	%IE	C.R., mg/cm^{2}min
25	Blank	0.119	——	——	0.001320
	50	0.070	0.408	40.8	0.000780
	100	0.050	0.576	57.6	0.000560
	150	0.037	0.688	68.8	0.000410
	200	0.019	0.837	83.7	0.000200
35	Blank	0.226	——	——	0.002510
	50	0.146	0.355	35.5	0.001621
	100	0.118	0.478	47.8	0.001314
	150	0.086	0.619	61.9	0.000958
	200	0.053	0.760	76.0	0.000586
45	Blank	0.333	——	——	0.343590
	50	0.229	0.313	31.3	0.002550
	100	0.175	0.476	47.6	0.001940
	150	0.152	0.544	54.4	0.001690
	200	0.095	0.716	71.6	0.001050
55	Blank	0.295	——	——	0.004420
	50	0.264	0.291	29.1	0.002930
	100	0.204	0.450	45.0	0.002270
	150	0.183	0.507	50.7	0.002040
	200	0.115	0.692	69.2	0.001270

The values of C.R and %IE obtained from the weight loss technique for various concentrations of Curcuma in 1.0 M HCl solution at different temperatures are shown in Table 1.

The results demonstrated that, C.R decreases by increasing in Curcuma concentration, so the values of %IE improves with the inhibitor concentration. This is due to the fact that the extent of adsorption and the resultant coverage by inhibitor on α-brass surface increases with the inhibitor concentration[22]. Inspection of Table 1 reveals that, the inhibition efficiency increases with increasing the inhibitor concentration and decreases with raising the temperature. This behavior as a result of increasing of the number of adsorbed molecules at the metal surface.

The decrease in inhibition efficiency with increases in the temperature can be explained in terms of physical adsorption of Curcuma inhibitor molecule on α-brass surface. In case of physical adsorption, the desorption increases by raising the temperature and the adsorption decreases. Some information on the mechanism of the inhibitor action can be obtained by comparing apparent activation energy (E^*_a) obtained in the presence of inhibitor with that in its absence. The values of E^*_a were calculated using Arrhenius equation:

$$\log C.R = -E^*_a/2.303RT + \log A \qquad (6)$$

where, A is the Arrhenius pre-exponential factor. The plots of log C.R versus 1/T without and with different concentrations of Curcuma gave straight lines Figure 6. The values of E^*_a are calculated from the slopes of the straight lines.

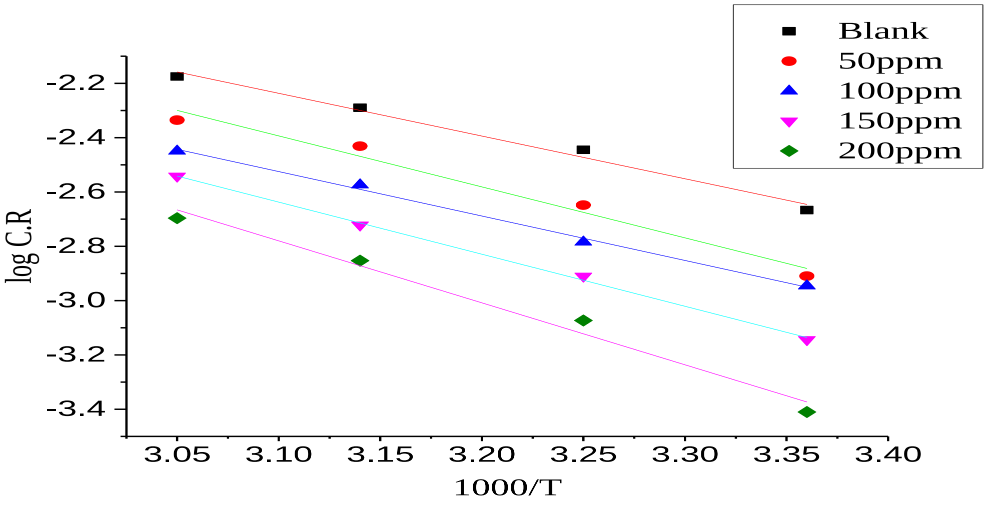

Figure 6. log C.R vs. 1/T for α-brass in 1.0 M HCl without and with different concentrations of Curcuma.

The values of standard enthalpy of activation (ΔH^*) and standard entropy of activation (ΔS^*) for the dissolution of α-brass were calculated using the following equation:

$$CR=RT/Nh\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (7)$$

The plots of log (C.R/T) versus (1/T) gave straight lines Figure7 with slope values equal to ($-\Delta H^*/2.303R$) and intercept of [{log (R/Nh) + ($\Delta S^*/2.303R$)}].

Table 2 demonstrates the calculated values of E^*_a, ΔH^* and ΔS^*without and with different concentrations of Curcuma. Higher values of activation energy in the presence of Curcuma extract demonstrate that, the extract of Curcuma acts as an efficient inhibitor by forming a physical barrier to the charge and mass transfer reactions, leading to reduction in corrosion rate. It is further noted that, the observed value of E^*_a in the presence of Curcuma extract at each concentration is greater than that in its absence. The increase in E^*_a with increases in concentration of inhibitor is in line with the concentration dependent nature of the inhibitive property.

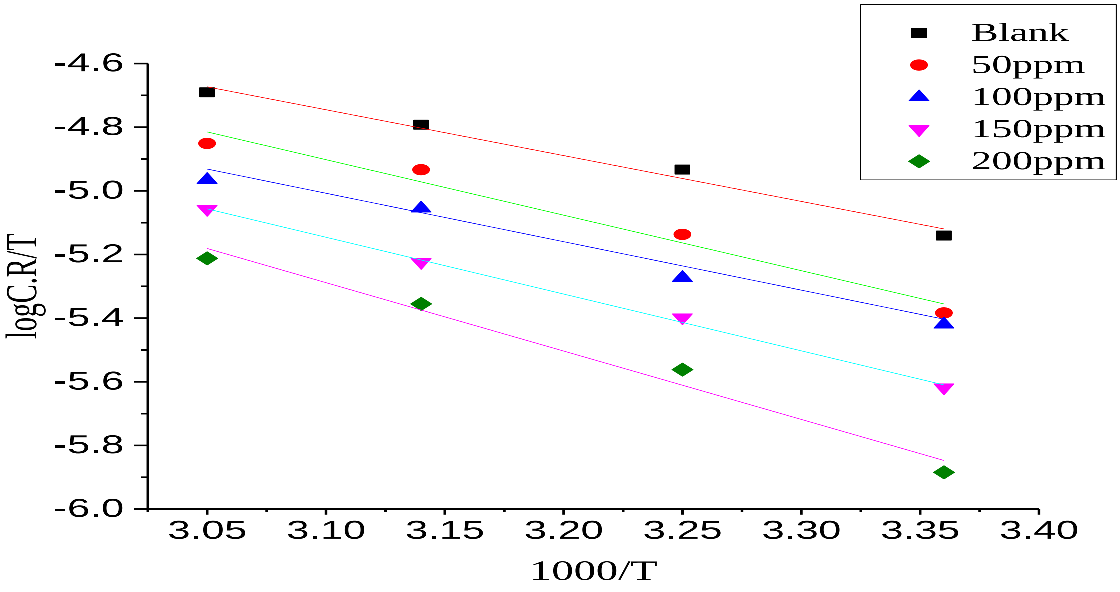

Figure 7. log C.R/T vs. 1000/T for α-brass in 1.0 M HCl before and after addition different concentrations of Curcuma

In the ideal case values of E^*_a and ΔH^* should be equal for a chemical reaction in electrolytic solutions, but from the recorded values of these parameters there is almost a constant and small difference between the two values in all the cases.

The values of ΔS^* are negative. With increasing of Curcuma concentration, ΔS^* becomes less and less negative. This indicates that the activated complex is less ordered in the presence of Curcuma.

Free energies of activation (ΔG^*) were calculated by applying the Eyring equation:

$$\Delta G^* = RT\left[\ln\frac{K''T}{h} - \ln CR\right] \qquad (8)$$

where C.R is the corrosion rate, h is Planck's constant, K" is Boltzman's constant, R is the universal gas constant and T is the absolute temperature. The values of ΔG^* was registerd in Table 2. The values of ΔG^* increase with increasing temperature where the constantly values of ΔH^* indicated that, the behavior of the corrosion reaction was not changed by raising the temperatures from 25°C to 55°C.

Table 2. Kinetics parameters of Arrhenius equation and transition state equation.

Conc., ppm	E^*_a, KJmol^{-1}	A, mgcm^{-2}	ΔH^*, KJmol^{-1}	ΔS^*, Jmol^{1}K^{-1}	ΔG^* KJmol^{-1}			
					298K	308K	318K	328K
Blank	30.10	4.37x10^{2}	27.57	-202.6	87.94	89.97	91.81	93.83
50	35.94	2.66x10^{3}	33.40	-187.6	89.30	91.20	92.87	94.93
100	31.40	4.88x10^{2}	29.13	-192.7	86.55	88.27	90.19	92.33
150	36.72	3.55x10^{3}	34.20	-189.8	90.52	92.67	94.40	96.45
200	43.70	19.62x10^{3}	41.13	-171.0	92.10	93.80	95.50	97.22

3.3. Adsorption isotherm

More information regarding the mechanism of corrosion inhibition can be obtained from the study of adsorption isotherm. From the adsorption isotherms, Freundlich and Henry adsorption isotherms (equation 9 and 10, respectively) are the most fundamental. According to these isotherms, the fraction of the metal surface covered with the inhibitor θ is related to inhibitor concentration C by the relations:

$$\log\theta = \log K + n \log C \qquad (9)$$

$$\theta = K C \qquad (10)$$

where K is the equilibrium constant of the adsorption process. Straight lines were obtained by plotting the two equations at (25-55°C) as shown in Figures (8,9).

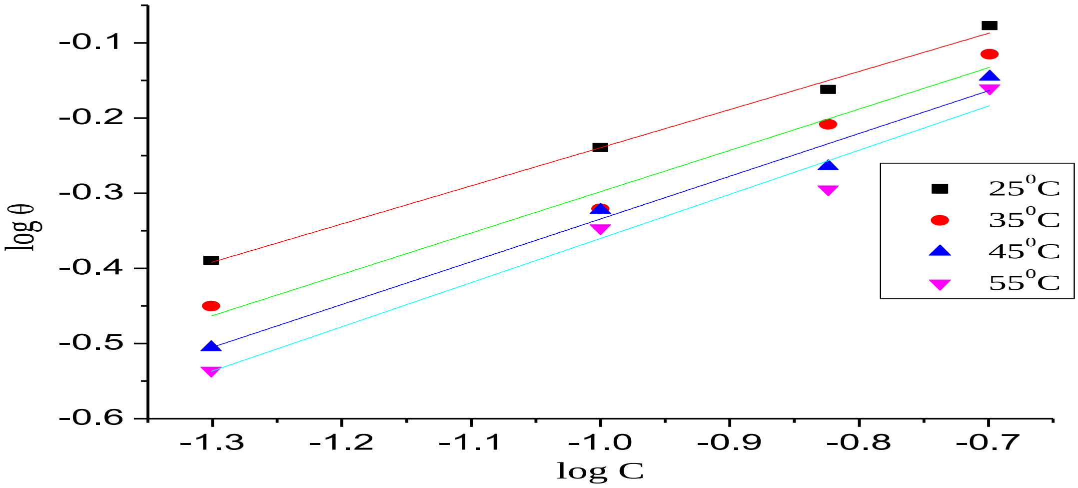

Figure 8. Freundlich adsorption isotherm for Curcuma on α-brass surface in 1.0 M HCl at different temperatures (25-55) ^{0}C

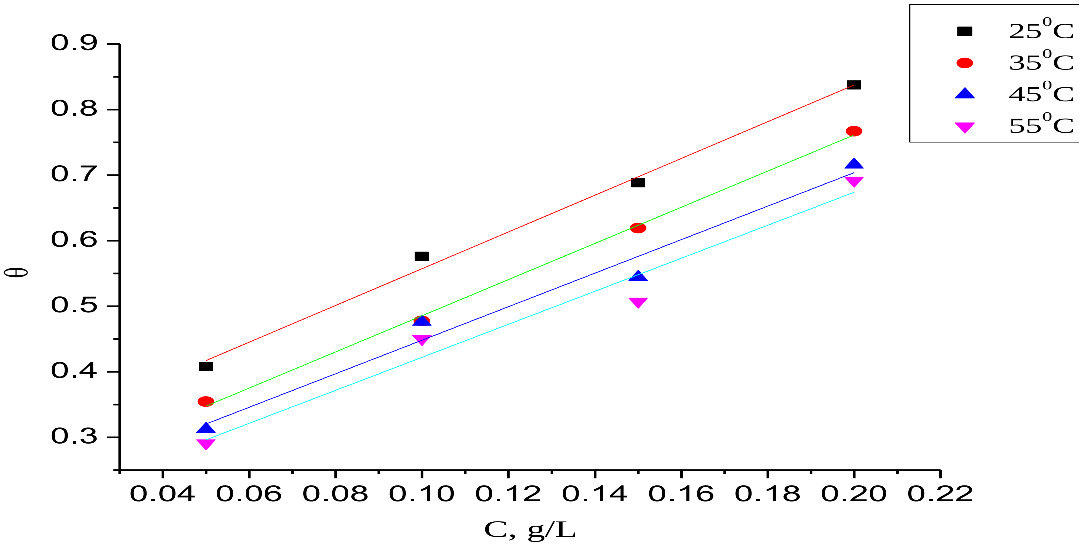

Figure 9. Henry adsorption isotherm for Curcuma on α-brass surface in 1.0 M HCl at different temperatures (25-55) ^{0}C

where the R^2 values for Freundlich isotherm were more than Henry isotherm. Consequently, Freundlich adsorption isotherm was found to be the best description for the adsorption behaviour of Curcuma extract on α- brass surface.

The values of equilibrium constant (K) calculated from Freundlich and Henry adsorption isotherms are related to the standard free energy of adsorption (ΔG^o_{ads}) by the following equation:

$$K = 1/55.5 \exp(-\Delta G^o_{ads}/RT) \qquad (11)$$

where 55.5 is the concentration of water molecule in (mol L^{-1}) at metal/solution interface.The calculated values of ΔG^o_{ads} are listed in Table 3. The negative values of ΔG^o_{ads} revealed that the adsorption of Curcuma onto α-brass surface is a spontaneous process. The values of ΔG^o_{ads} up to -20 kJ mol^{-1} are consistent with electrostatic interaction between the charged molecules and the charged metal and the adsorption is physical adsorption, but when the negative values more than -40 kJ mol^{-1} involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond and the adsorption is chemical adsorption[23-25].

The heat of adsorption was calculated using the Van't Hoff equation[26]:

$$\ln K = -\Delta H^o_{ads}/RT + \text{const.} \qquad (12)$$

Figure10 shows a plot of log K_{ads} vs. 1/T for α-brass dissolution in 1.0 M HCl in the presence of Curcuma. The ΔH^o_{ads} values Table 3 are negative, which show that, the adsorption is an exothermic process[27]. The standard adsorption entropy ΔS^o_{ads} can be calculated by the following equation:

$$\Delta S^o_{ads} = (\Delta H^o_{ads} - \Delta G^o_{ads})/T \qquad (13)$$

From Table 3, the values of ΔS^o_{ads} are positive. So the adsorption is an exothermic process and this exothermic process is accompanied by an increases in the entropy.

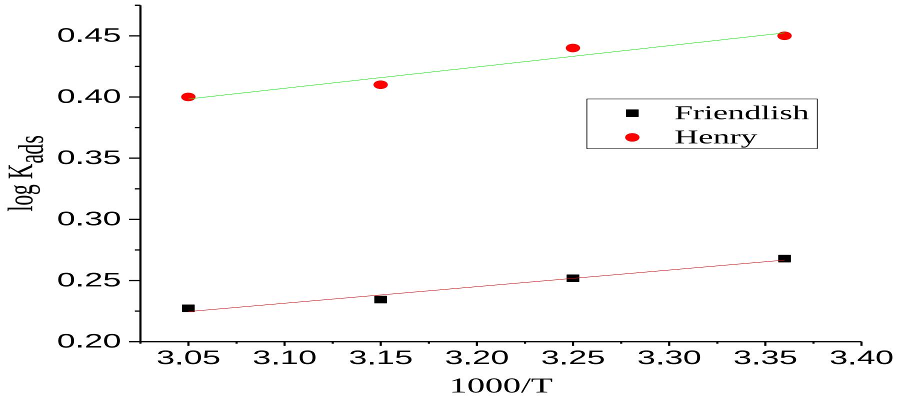

Figure 10. Plots of log C.R/T vs. 1000/T for α-brass in 1.0 M HCl for Freundlich and Henry adsorption isotherms at different temperatures.

Table 3. Freundlich and Henry adsorption parameters of adsorption of Curcuma on α-brass surface in 1.0 M HCl after 90 min.immersion at different temperatures.

Temp.,	Freundlich						Henry				
^{0}C	logK	N	R^2	$-\Delta G^o_{ads}$	$-\Delta H^o_{ads}$	ΔS^o_{ads}	logK	R^2	$-\Delta G^o_{ads}$	$-\Delta H^o_{ads}$	ΔS^o_{ads}
25	0.2679	0.5073	0.993	11.48	2.58	29.9	0.45	0.992	12.50	3.32	30.8
35	0.2518	0.5497	0.975	11.77		29.8	0.44	0.997	12.89		31.1
45	0.2344	0.5687	0.970	12.04		30.9	0.41	0.964	13.10		30.7
55	0.2272	0.5873	0.960	12.38		32.2	0.40	0.949	13.50		32.0

3.4. Potentiodynamic polarization

Figure11 represents the anodic and cathodic polarization curves for α-brass in 1.0 M HCl solution without and with different concentrations of Curcuma at 25°C. The potentiodynamic curves indicate that, the shift the anodic and cathodic curves to the lower values of corrosion current densities in the presence of Curcuma extract. This causes decreasing in the corrosion rate. In other words, both cathodic and anodic reactions of α-brass electrode are retarded by Curcuma in 1.0 M HCl.

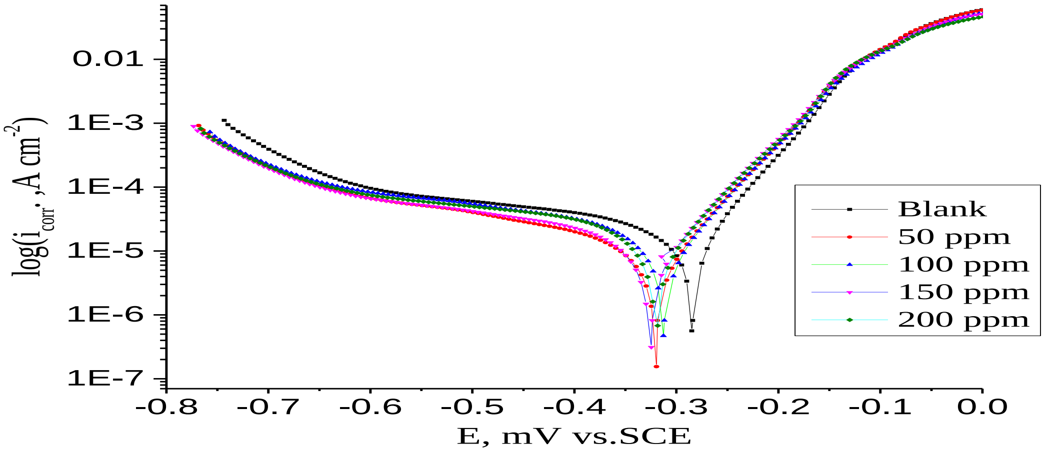

Figure 11. Potentiodynamic polarization curves of α-brass in 1.0 M HCl without and with different concentrations of Curcuma at 25°C.

The derived parameters of corrosion from the polarization curves without and with different concentrations of Curcuma for α-brass in 1.0 M HCl such as corrosion current density (i_{corr}), the potential of corrosion (E_{corr}), Tafel slopes (β_a and β_c), the surface coverage degree (θ) and the inhibition efficiency (%IE) are reported in Table 4. From this Table, Tafel slopes (β_a and β_c) were slightly changed when the concentration of Curcuma increases and also the presence of Curcuma does not change the mechanism of hydrogen evolution and the metal dissolution process.

Table 4. Corrosion parameters derived from the polarization curves for α-brass in 1.0 M HCl in absence and presence of (50-200 ppm) of Curcuma at 25°C.

Conc, ppm	$-E_{corr,}$ mV	$i_{orr.}$ μAcm^{-2}	β_a mV dec^{-1}	β_c mV dec^{-1}	θ	%IE
Blank	284	29.7	90.5	535.0	——	——
50	312	17.7	78.5	335.6	0.404	40.4
100	319	12.6	71.7	320.9	0.575	57.5
150	320	9.3	79.6	328.9	0.687	68.7
200	325	5.11	71.8	296.5	0.830	83.0

When the shift of corrosion potential in the presence of the inhibitor is more than 85 mV, an extract can be classified as anodic or cathodic type, with respect to that in the absence of the inhibitor[28,29]. In the presence of Curcuma, E_{corr} shifts to more negative but with very small rate which indicates that Curcuma can be considered as a mixed-type inhibitor. The lower values of i_{corr} in the presence of Curcuma extract indicates that, the increases in the inhibition efficiency may be as a result of the adsorption of Curcuma on α-brass surface.

3.5. Electrochemical impedance spectroscopy (EIS)measurements

The corrosion parameters of α-brass in 1.0 M HCl solution without and with different concentrations of Curcuma were also examined by EIS at 25°C. The obtained Nyquist and Bode plots are shown in Figures (12,13) respectively.

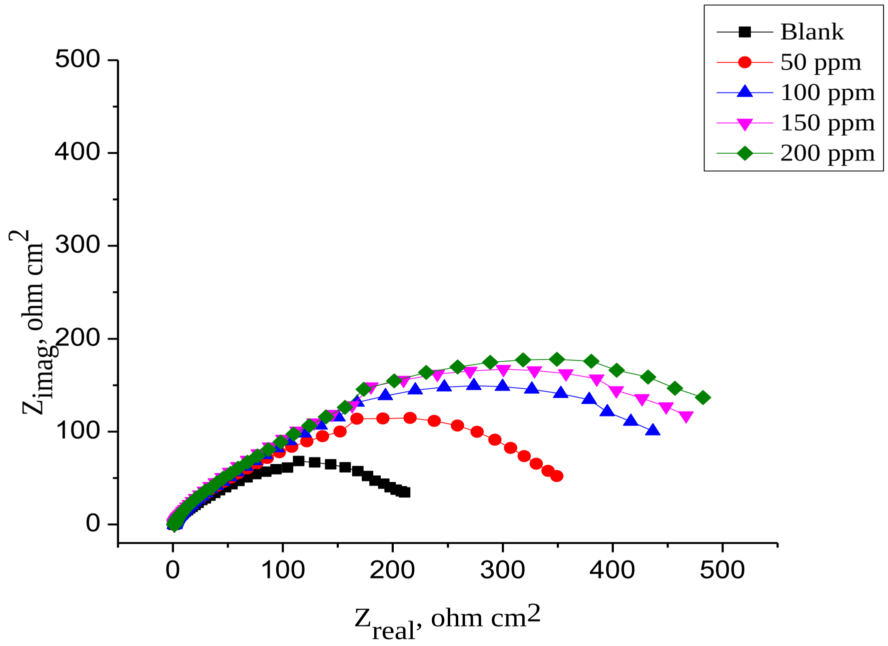

Figure 12. Nyquist plots for the corrosion of α-brass in 1.0 M HCl without and with different concentrations of Curcuma at 25^0C.

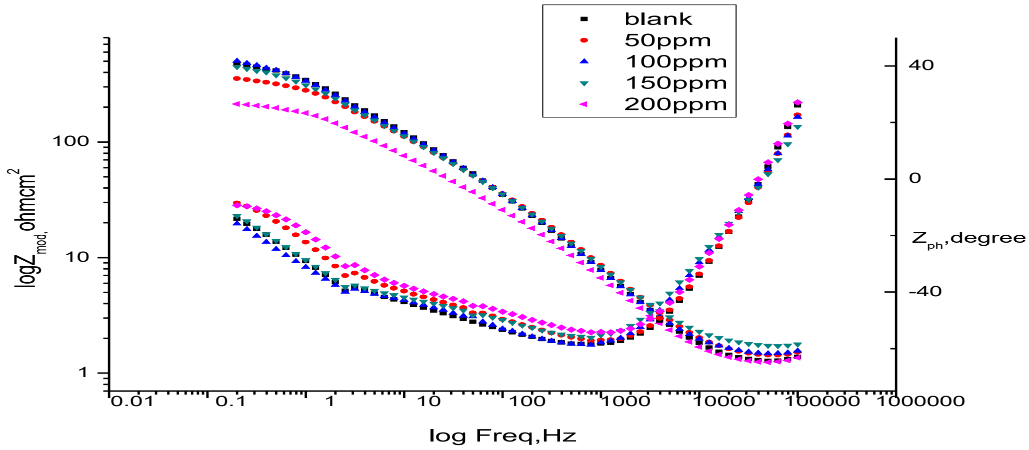

Figure 13. Bode plots for the corrosion of α-brass in 1.0 M HCl without and with ifferent concentrations of Curcuma at 25^oC.

The Nyquist plots of curcuma extract is not perfect semicircles, which is attributed to nonhomogeneity of the surface and roughness of the metal [30,31]. From the plots, the impedance response of copper is increased by the addition of curcuma extract [32]. Although the appearance of Nyquist plots remained the same and their diameter increased after the addition of Curcuma to the corrosive solution[33]. Nyquist plots show that the curves are approximated by single capacitive semicircles, so the corrosion process was mainly charge transfer-controlled[34,35]. The shape of the curves is very similar in without and with the extract showing that, no change in the corrosion mechanism[36].

By using the equivalent circuit Figure14, EIS spectra of Curcuma were analyzed, where R_s represents the solution resistance, R_{ct} represents the charge transfer resistance and CPE represents the constant phase element. CPE is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit[33].

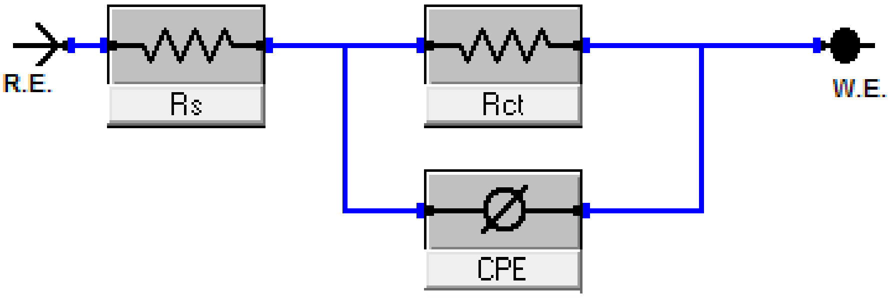

Figure 14. Electrical equivalent circuit used to fit the impedance data.

The values of the double layer capacitance (C_{dl}) were calculated from the following eqution[37]:

$$C_{dl} = Y_o (\omega_{max})\, n^{-1} \qquad (14)$$

Where Y_o is the magnitude of the CPE, $\omega_{max} = 2\pi f_{max}$, f_{max} is the frequency at which the imaginary component of the impedance is maximum and n is an adjustable parameter that usually lies between 0.50 and 1.0.

In the Bode plots Figure 13, the high frequency limits corresponds to the solution resistance $R_{S(\Omega)}$, while the lower frequency limits corresponds to ($R_{ct} + R_s$). The low frequency shows the kinetic response of the charge transfer reaction[38].

The corrosion parameters from impedance measurements are shown in Table 5. The obtained results show that the value of R_{ct} increases with increasing the concentration of Curcuma, which leads to an increase in %IE. Value of double layer capacitance (C_{dl}) decreases in the presence of the inhibitor. The decrease in CPE/C_{dl} results from a decrease in local dielectric constant and/or an increases in the thickness of the double layer, suggesting that organic derivatives inhibit the α-brass corrosion by adsorption at metal/acid[39,40].

Table 5. Electrochemical kinetic parameters obtained by EIS technique for the corrosion of α-brass in 1.0 M HCl without and with different concentrations of Curcuma at 25^{o}C.

Conc., ppm	R_{ct}, Ω cm^{-2}	Rct, Ω cm^{-2}	Y° x 10^{6}, μΩ-1sn	C_{dl}, μF cm^{-2}	θ	%IE
Blank	0.983	213.4	566.5	195.4	——	——
50	1.129	361.1	385.9	149.6	0.409	40.9
100	1.383	498.8	460.0	209.0	0.572	57.2
150	1.015	685.5	377.3	177.4	0.689	68.9
200	1.178	1300.5	416.9	202.05	0.836	83.6

3.6 Electrochemical frequency modulation measurements (EFM):

Electrochemical frequency modulation EFM Likes EIS has a small signal AC technique, but this technique has two sine waves (at different frequencies) are applied to the cell simultaneously. EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Figure 15 shows the EFM spectra (current vs. frequency) without and with different concentrations of Curcuma for corrosion of α-brass in 1.0 M HCl solution at 25^{o}C.

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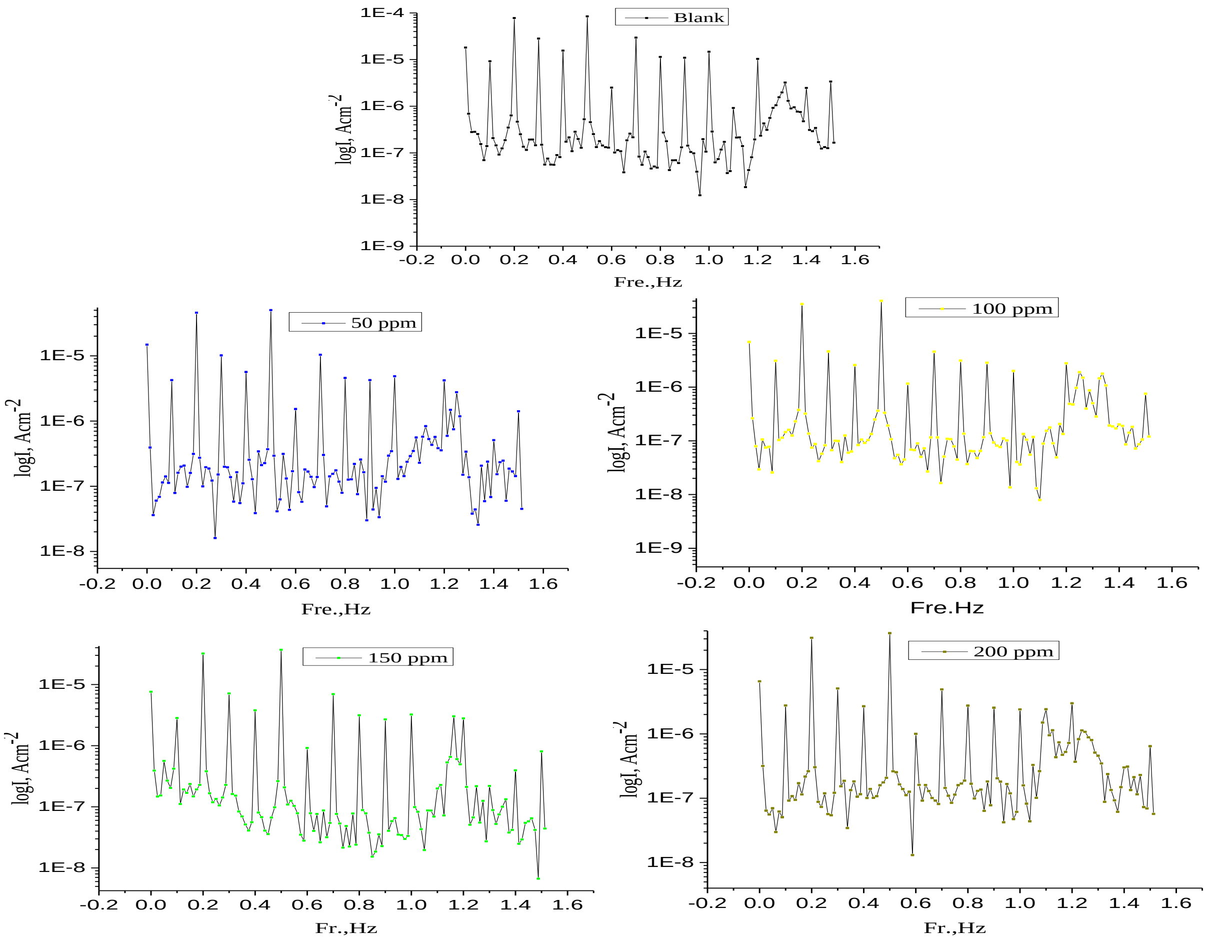


Figure 15. EFM Intermodulation spectra (current vs frequency) without and with different concentrations of Curcuma for corrosion of α- brass in 1.0 M HCl solution at 25^{o}C.

The calculated corrosion kinetic parameters (i_{corr}, βa, βc, CF-2, CF-3 and %IE) without and with variable concentrations of Curcuma for corrosion of α-brass in 1.0 M HCl solution at 25^{o}C are given in Table 6. It is clear from the obtained data that, i_{corr} values decrease by increasing the concentration of Curcuma and the inhibition efficiencies increase. The causality factors in Table 6 are very close to the theoretical values according to the EFM theory[41].

Table 6. Electrochemical kinetic parameters obtained by EFM technique for α-brass in 1.0 M HCl without and with different concentrations of Curcuma at 25 °C.

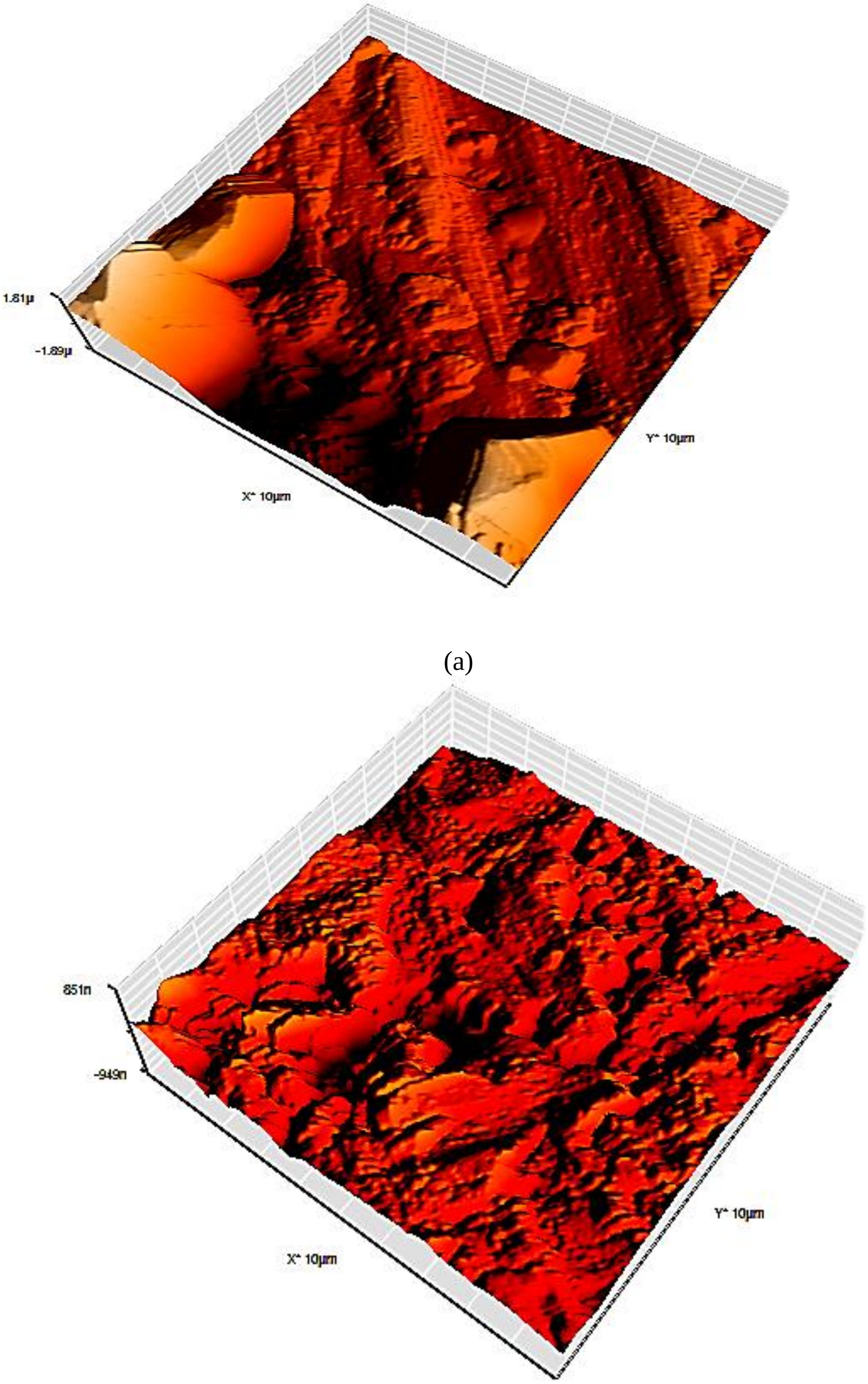
Conc., ppm	i_{corr} μA cm^{-2}	β_a mV dec^{-1}	β_c mV dec^{-1}	C.R Mpy	CF-2	CF-3	θ	%IE
Blank	50.08	27.96	72.04	58.73	1.907	3.55	—	—
50	29.9	34.74	61.52	36.91	2.008	3.32	0.403	40.3
100	21.54	33.35	59.32	29.13	1.953	2.937	0.570	57.0
150	16.1	35.69	52.67	27.62	1.964	3.362	0.679	67.9
200	8.8	36.83	50.69	27.62	2.011	3.091	0.824	82.4

The deviation of causality factors from their ideal values might due to that, the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough, also another possible explanation, the inhibitor is not performing very well. If the causality factors are approximately equal to the predicted values of 2.0 and 3.0, i.e. there is a causal relationship between the perturbation signal and the response signal, then the data are assumed to be reliable[42]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [43].

3.7 Atomic force microscopy (AFM)

Further investigation of the corrosion inhibition ability of Curcuma for α-brass in 1.0 M HCl was studied by atomic force microscopy (AFM) technique in order to characterize the α-brass surface microstructure. Figure 16 illustrates three-dimensional AFM images of α-brass surface after 24 h exposure to 1.0 M HCl at 25^{o}C without (Figure 16a) and with 200 ppm Curcuma (Figure 16b).

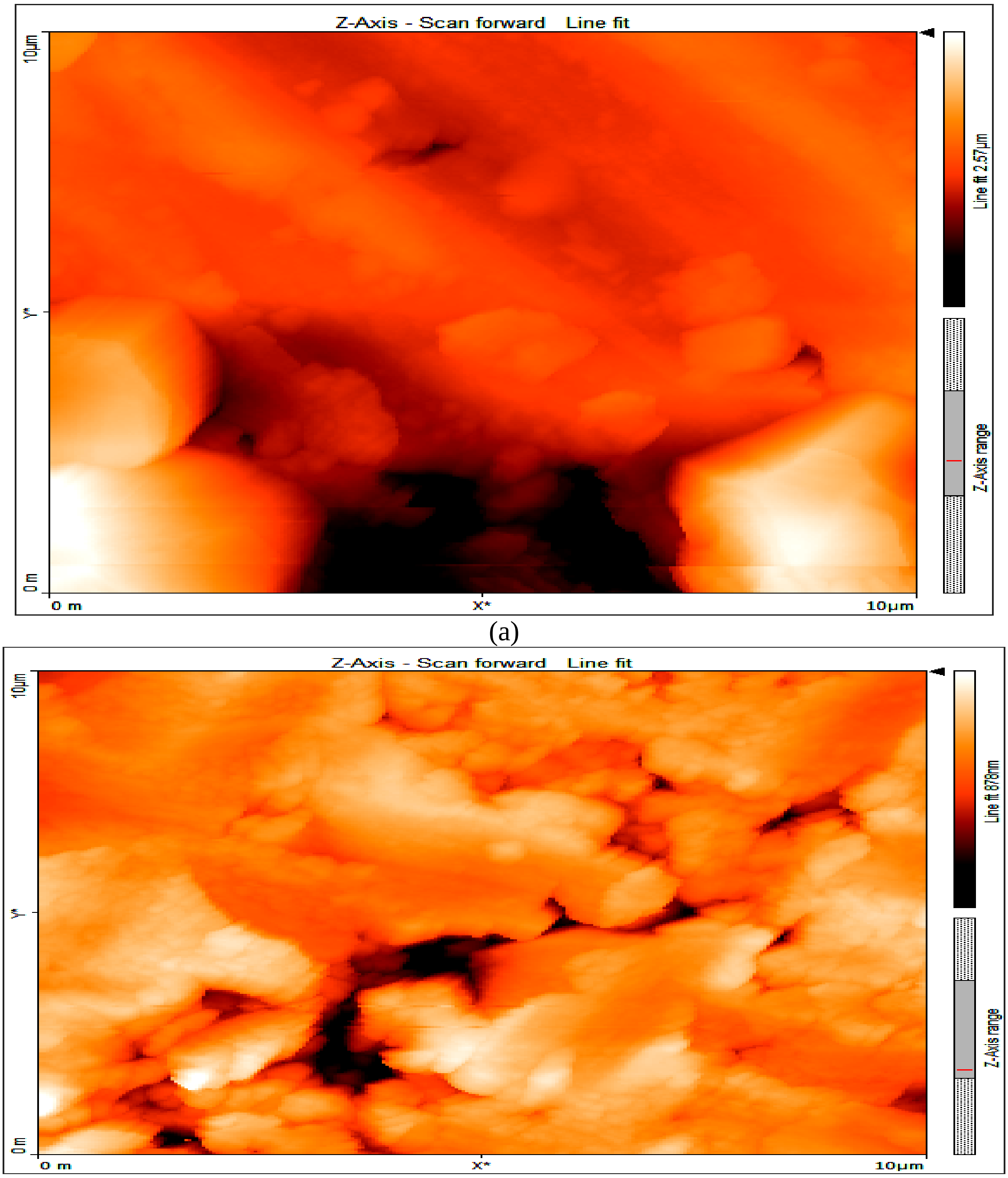
Two-dimensional AFM images of the α-brass surface are shown in Figure 17. In uninhibited system, the α-brass surface was fairly damaged due to dissolution in corrosive medium with roughness of 306.18 nm. The roughness of inhibited α-brass surface was 82.406 nm due to formation of a protective layeron α-brass surface which causes the decrease of the surface roughness and effectively protects it from corrosion.



(a)

(b)

Figure 16. Three-dimensional AFM images of α-brass surface after one day exposure to 1.0 M HCl at 25°C without (a) and with (b) 200 ppm Curcuma.



(a)

(b)

Figure 17. Two-dimensional AFM images of α-brass surface after one day exposure to 1.0 M HCl at 25°C without (a) and with (b) 200 ppm Curcuma.

3.8 UV–visible spectroscopy

A substantial support for the formation of metal complex is often obtained by UV–visible spectroscopic investigation. UV–visible absorption spectra obtained from 1.0 M HCl solution containing 200 ppm Curcuma before and after 24h of α-brass immersion are shown in Figure 18. The electronic absorption spectra of curcuma extract before immersion have absorption maximum at 245nm, and this as result to n- π^* and π- π^* transitions. After 24hrs immersion of α-brass, the change in the absorbance values or the change in the position of absorption maximum demonstrates the complex formation between two species in solution. Also, not change in the shape of absorption spectra. These experimental findings provide the formation of complex between Cu^{2+} and curcuma extract and confirm the inhibition of α-brass from corrosion [44].

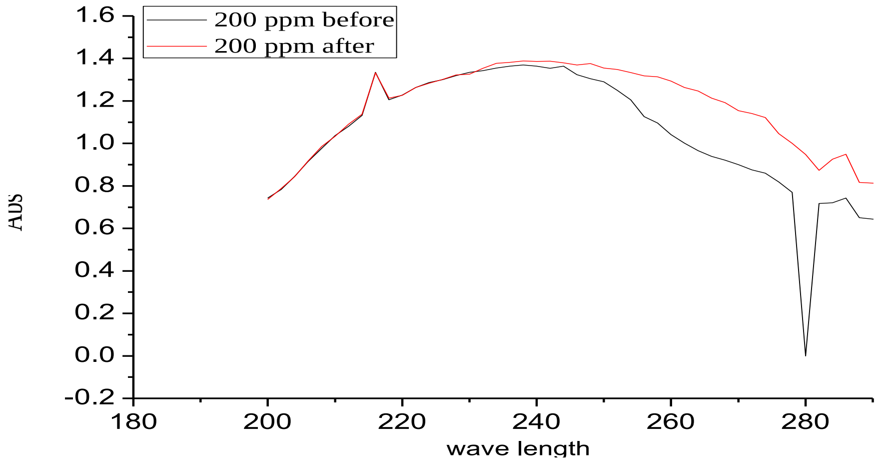
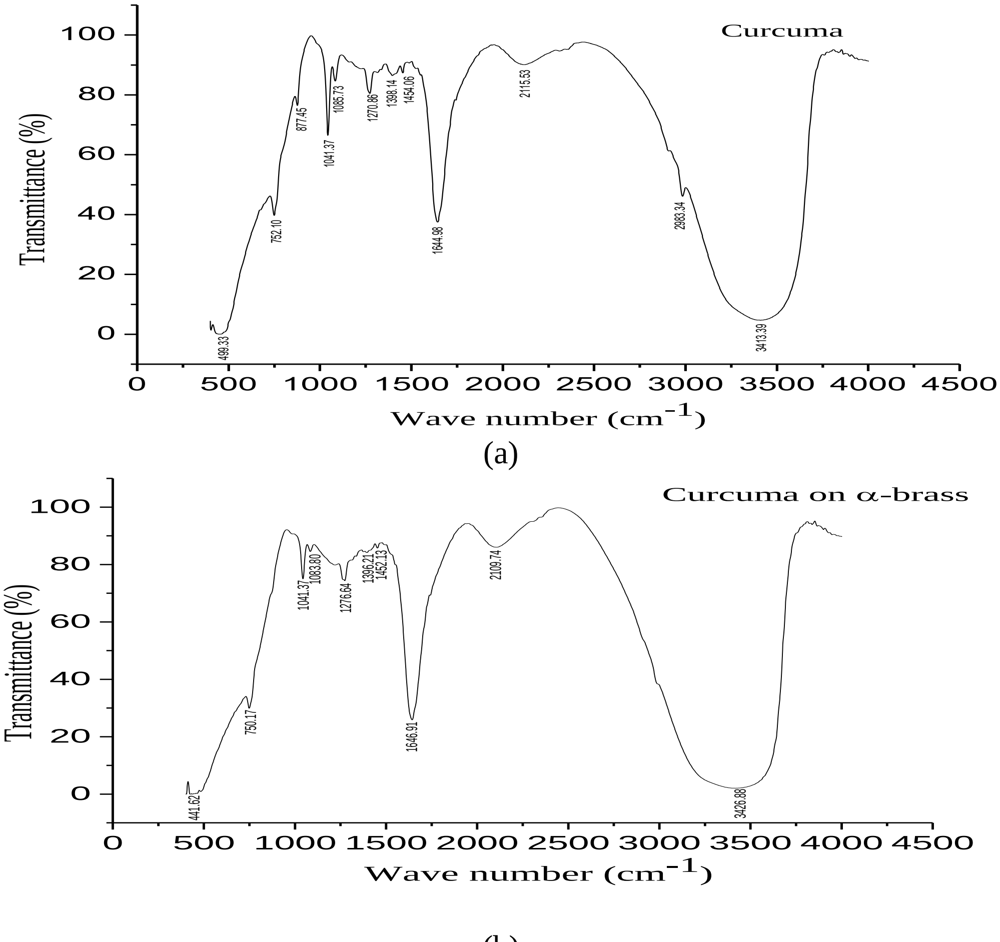


Figure 18. UV-Visible spectra of the solution from 1 M HCl containing 200 ppm Curcuma before and after 24h of α-brass immersion.

3.9 Analysis of FT-IR spectra

FT-IR spectroscopy is used to analyze the protective film formed on the α-brass.The spectrum of the 200 ppm Curcuma in 1.0 M HCl (Fig. 19a) shows that broad peaks appeared at 3413.39, 1644.98, 1454.06 and 2983.34 cm^{-1}, which corresponds to the O–H, C=O, C=C and aliphatic C-H stretching vibration frequencies respectively. Thus, Curcuma was characterized by IR spectroscopy[45].

The FT-IR spectrum of 200 ppm Curcuma adsorbed on the α-brass specimen (Fig. 19b) shows that, the -OH has shifted to 3426.88 cm^{-1}, the C=O stretching frequency has shifted to 1646.91 cm^{-1}, the C=C stretching frequencyhas shifted to 1452.13 cm^{-1} and the aliphatic C-H stretching frequency (2983.34 cm^{-1}) disappeared.This shows that there is an interaction between the curcuma extract and the α-brass substrate which resulted in inhibition. The shifts in the spectra consider as a result of the interaction between the extracts and α-brass occurred through the functional groups presents in them. So, it can be affirmed that the functional group has coordinated with Cu^{2+} formed on the metal surface resulting in the formation of Cu^{2+} extract complex on the metal surface, which promotes the inhibition of the metal sample. FT-IR analysis was carried out using FT/IR-4100typeASerial Number B117761016.



(a)

(b)

Figure 19. FT-IR spectrum of Curcuma (a) and Curcuma adsorbed α-brass surface (b).

4. CONCLUSIONS

The effects of Curcuma on the corrosion inhibition on α-brass in 1.0 M HCl solution was investigated in the present work using weight loss measurements, potentiondynmic polarization measurements, EIS, EFM and AFM surface analysis, resulting in the following experimental evidences:

1- Weight loss measurements show that the addition of Curcuma to α-brass in 1.0 M HCl solution significantly reduced the corrosion rate, while the inhibition efficiency increases by increasing the Curcuma concentration and decreases with temperature.

2- Adsorption isotherm of Curcuma on α-brass surface can be described by Freundlich and Henry adsorption isotherms. According to the obtained values of ΔG^o_{ads} from the Freundlich and Henry adsorption isotherms, the physicsorption mechanism was considered as adsorption processes.

3- The obtained values of ΔG^o_{ads} at different temperatures indicate that adsorption of Curcuma on α-brass surface is spontaneous. The ΔH^o_{ads} values are negative, which show that the adsorption is an exothermic process and the values of ΔS^o_{ads} are positive; this means that the adsorption is an exothermic process and this exothermic process is accompanied by an increase in entropy.

4- Affecting both anodic and cathodic branches of polarization curves, the Curcuma was suggested to be a mixed type adsorptive inhibitor.

5- The concentration dependence of inhibition efficiency was indicated from the EIS data. It was found from EIS measurements that the inhibition efficiency increases by increasing the Curcuma concentration.

6- The inhibition effect of Curcuma was further confirmed by AFM measurements, where it was shown that Curcuma decreases the α-brass surface roughness and effectively protects α-brass from corrosion due to the formation of the inhibitor film.

7- Based on the results of weight loss, potiondynmic polarization measurements, EIS and EFM, curcuma was shown to be an effective inhibitor in 1.0 M HCl on α-brass.

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