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RESEARCH ARTICLE

Adsorption and Corrosion Inhibition of Alkanna Tinctoria Extract (ATE) on Copper in 1 M HNO₃ Solution

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Abstract

Alkanna Tinctoria Extract (ATE), was investigated as a green corrosion inhibitor for copper in 1 M HNO₃ solution using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The effect of the temperature on corrosion behavior with addition of different concentrations was studied in the temperature range of 25-40 °C by weight loss method. Polarization curves reveal that the investigated extract is a mixed type inhibitor. The inhibition efficiency was found to increase with increase in the investigated extract concentration and decrease with increase in solution temperature. The adsorption of the inhibitor on copper surface was found to obey the Langmuir's adsorption isotherm. The results obtained from chemical and electrochemical techniques are in good agreement.

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INTRODUCTION

Copper is a metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. The use of copper corrosion inhibitors in acid solutions is usually to minimize the corrosion of copper during the acid cleaning and descaling. The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated^[1-3]. Most well-known acid inhibitor are organic compounds containing nitrogen, sulfur, and oxygen atoms. Among them, organic inhibitors have many advantages such as high inhibition efficiency and easy production^[4-7]. Organic heterocyclic compounds have been used for the corrosion inhibition copper^[8] in different corroding media. Although many of these compounds have high inhibition efficiencies, several have undesirable side effects, even in very small concentrations, due to their toxicity to humans, deleterious environmental effects, and high-cost^[9]. Plant extract is low-cost and environmental safe, so the main advantages of using plant extracts as corrosion inhibitor are economic and safe environment. Up till now, many plant extracts have been used as effective corrosion inhibitors for copper in acidic media, such as: Zenthoxylum alatum^[10], Azadirachta Indica^[11], caffeine^[12] Cannabis^[13]. The inhibition performance of plant extract is normally ascribed to the presence of complex organic species, including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products in their composition. These organic compounds usually contain polar functions with nitrogen, sulfur, or oxygen atoms and have triple or conjugated double bonds with aromatic rings in their molecular structures, which are the major adsorption centers. Zygophyllum coccineum L, is a type genus of flowering plants in Zygophyllaceae family. The eleven species it contains are known generally as White Alratrit, is widely distributed in Mediterranean, The whole

plant has great medicinal importance, as Uses repellent worms, hypotensive , decrease the percentage of sugar in the blood and used as Antipyretic and anti-fever^[14].

The objective of this study was to investigate the inhibitor effect of *Alkanna Tinctoria* Extract (ATE) as a green corrosion inhibitor for copper in 1 M HNO₃ using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM) techniques.

2. EXPERIMENTAL METHODS

2.1. Materials and Solutions

The working electrode was made from Copper specimens (99.98%) rod. The rod was mounted into a glass tube and fixed by araldite leaving a circle surface geometry of 1 cm diameter to contact the test solution. Prior to each experiment, the working electrode was polished with a different grades of emery paper up to 1200 grade, rinsed with acetone and finally with doubly distilled water. The auxiliary electrode was platinum wire, while a saturated calomel electrode (SCE) connected to conventional electrolytic cell of capacity 100 ml. The aggressive solution used was prepared by dilution of analytical reagent grade 70% HNO₃ with bidistilled water. The stock solution (1000 ppm) of ATE was used to prepare the desired concentrations by dilution with bidistilled water. The concentration range of ATE used was 25-150 ppm.

2.2. Preparation of Plant Extracts

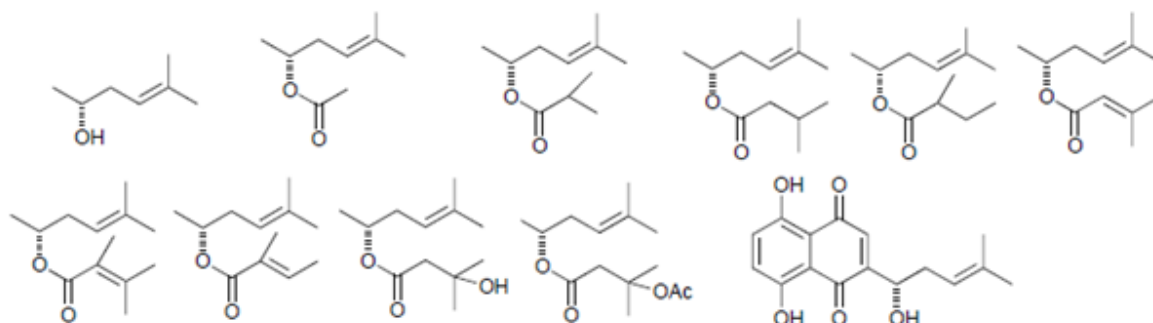
Fresh aerial parts of *Alkanna Tinctoria* Extract (ATE) sample were crushed to make fine powder. The powdered materials (250 g) were soaked in 500 ml of dichloromethane for 5 days and then subjected to repeated extraction with 5× 50 ml until exhaustion of plant materials. The extracts obtained were then concentrated under reduced pressure using rotary evaporator at temperature below 50°C. The dichloromethane evaporated to give solid extract that was prepared for application as corrosion inhibitor.

Chemical studies have demonstrated that the ATE contain: Zygophyllin (28% in leaves, 0.18% in stems and 0.26% in fruits), Quinovic acid (0.36% in leaves, 0.31% in fruits and 0.47% in stems) and Flavonoids e.g, kaempferol-1-3- rutinoside^[15,16].

Alkanna tinctoria:

Kingdom: Plantae
(unranked): Angiosperms
(unranked): Eudicots
(unranked): Asterids
Order: (unplaced)
Family: Boraginaceae
Genus: *Alkanna*
Species: *A. tinctoria*





Scheme (1): Structure of alkannin compounds isolated form *Alkanna tinctoria* root

2.3. Weight Loss Method

For weight loss measurements, square specimens of size 2 cm x 2 cm x 0.2 cm were used. The specimens were first polished to a mirror finish using 400 and 800 grit emery paper, immersed in methanol and finally washed with bidistilled water and dried before being weighed and immersed into the test solution. The weight loss measurements were carried out in a 100 ml capacity glass beaker placed in water thermostat. The specimens were then immediately immersed in the test solution without or with desired concentration of the investigated compound. Triplicate specimens were exposed for each condition and the mean weight losses were reported in order to verify reproducibility of the experiments.

2.4. Electrochemical Measurements

2.4.1. Potentiodynamic Polarization Measurements

Polarization experiments were carried out in a conventional three-electrode cell with platinum gauze as the auxiliary electrode (1 cm²) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The working electrode was in the form of a square cut from copper sheet of equal composition embedded in epoxy resin of polytetrafluoroethylene so that the flat surface area was 1 cm². Prior to each measurement, the electrode surface was pretreated in the same manner as the weight loss experiments. Before measurements, the electrode was immersed in solution at natural potential for 30 min. until a steady state was reached. The potential was started from - 600 to + 400 mV vs. open circuit potential (E_{ocp}). All experiments were carried out in freshly prepared solutions at 25°C and results were always repeated at least three times to check the reproducibility.

2.4.2 Electrochemical Impedance Spectroscopy Measurements

Impedance measurements were carried out using AC signals of 5 mV peak to peak amplitude at the open circuit potential in the frequency range of 100 kHz to 0.1 Hz. All impedance data were fitted to appropriate equivalent circuit using the Gamry Echem Analyst software.

2.4.3 Electrochemical Frequency Modulation Technique

EFM experiments were performed with applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5 Hz was based on three arguments^[17]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF-2 and CF-3^[18]. All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 corrosion software, EIS300 electrochemical impedance spectroscopy software, EFM140 electrochemical frequency modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

3- Results and discussion

3.1. Weight Loss Measurements

Figure (1) represents the weight loss-time curves for copper in 1 M HNO₃ in the absence and presence of different concentrations of Alkanna Tinctoria Extract (ATE). The weight loss values are used to calculate the corrosion rate (R) in mmy⁻¹ by Eq. (1):

$$R = (\text{weight loss in gram} \times 8.75 \times 10^4) / DAT \quad (1)$$

Where D is copper density in g cm⁻³, A is exposed area in cm²; T is exposure time in hr. The inhibition efficiency (%IE) and the degree of surface coverage (θ) were calculated from Eq. (2):

$$\%IE = \theta \times 100 = [(R^* - R) / R^*] \times 100 \quad (2)$$

Where R* and R are the corrosion rates of copper in the absence and in the presence of inhibitor, respectively.

Table (1) collects the values of inhibition efficiency obtained from weight loss measurements in 1 M HNO₃ at 25°C.

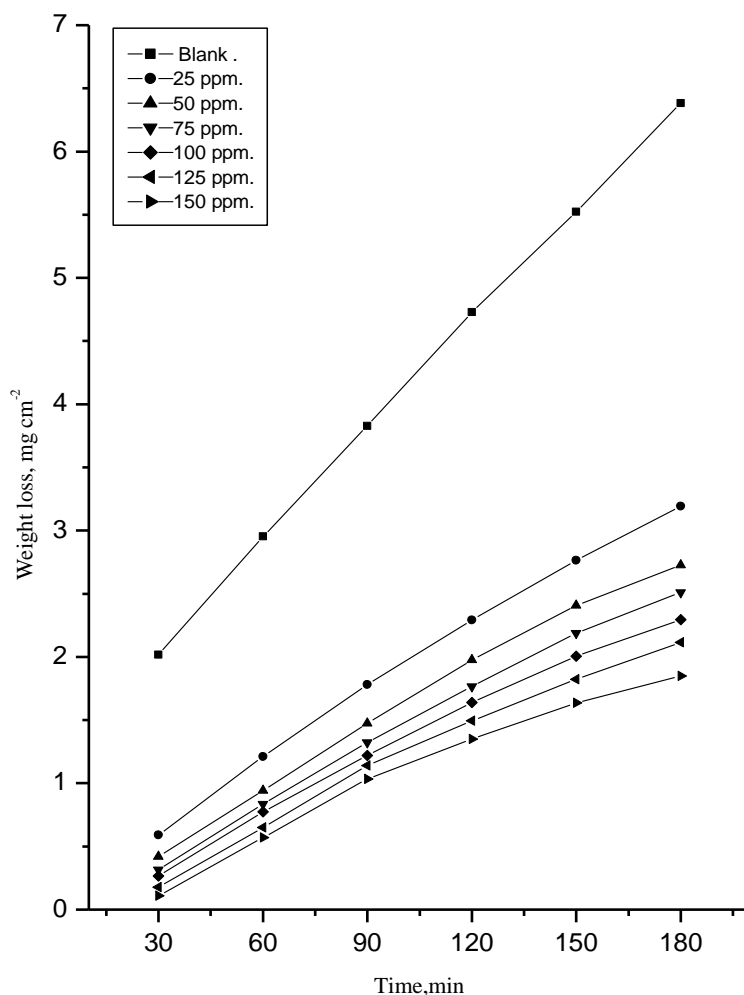


Figure (1). Weight loss-time curves for the dissolution of copper in the absence and presence of different concentrations of Alkanna Tinctoria Extract (ATE) in 1 M HNO₃ at 25°C.

Table 1: Variation of inhibition efficiency (%IE) of *Alkanna Tinctoria* Extract (ATE) with its different concentrations at 25°C from weight loss measurements at 60 min immersion in 1 M HNO₃.

Compound	Conc., ppm	CR mg cm ⁻² min ⁻¹	%IE
Blank	---	0.049	----
(ATE)	25	0.020	58.98
	50	0.016	68.10
	75	0.014	71.66
	100	0.013	73.80
	125	0.011	78.00
	150	0.010	80.65

3.2. Adsorption Isotherm

It is generally assumed that the adsorption of the inhibitors on the metal surface is essential step in the inhibition mechanism^[19].

To calculate the surface coverage (θ) it was assumed that the inhibitor efficiency (%IE) is due mainly to the blocking effect of the adsorbed species so (%IE = $\theta \times 100$)^[20]. In order to gain insight into the mode of adsorption of ATE on copper surface, the surface coverage values from weight loss technique were theoretically fitted into different adsorption isotherms and the values of correlation coefficient (R^2) were used to determine the best-fit isotherm. Figure (2) shows the plot (C/θ) vs. (C), which is typical of Langmuir adsorption isotherm at different temperatures. The deviation of the slope from unity, as observed from this study, could be interpreted to mean that there are interaction between adsorbate species on the copper surface as well as changes in adsorption heat with increasing surface coverage^[21, 22], factors that were ignored in the derivation of Langmuir isotherm.

The Langmuir isotherm is given by Eq. (3)^[23]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

Where (C) is the inhibitor concentration and (K) is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption ($\Delta G^\circ_{\text{ads}}$) by Eq. (4):

$$k = \frac{1}{55.5} \exp\left(\frac{-\Delta G^\circ_{\text{ads}}}{RT}\right) \quad (4)$$

The value of (55.5) is the concentration of water in solution expressed in mole per liter, (R) the universal gas constant and (T) the absolute temperature. The calculated ($\Delta G^\circ_{\text{ads}}$) values were also given in Table.(2). The negative values of ($\Delta G^\circ_{\text{ads}}$) ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the copper surface^[24]. It is well known that values of ($\Delta G^\circ_{\text{ads}}$) of the order of -40 kJ mol⁻¹ or higher involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond (chemisorption); those of order of -20 kJ mol⁻¹ or lower indicate a physisorption^[25, 211 26]. The calculated ($\Delta G^\circ_{\text{ads}}$) values Table (2) were less negative than -20 kJ mol⁻¹ indicate, therefore, that the adsorption mechanism of ATE on copper in 1 M HNO₃ solution is typical of physisorption. The lower negative values of ($\Delta G^\circ_{\text{ads}}$) indicate that this inhibitor is not strongly adsorbed on the copper surface. Moreover, the adsorption heat can be calculated according to the van't Hoff equation^[27]:

$$\text{Ln}K_{\text{ads}} = \Delta H^\circ_{\text{ads}}/RT + \text{const} \quad (5)$$

That is:

$$\ln(K_{2ads}/K_{1ads}) = -\Delta H^0_{ads}/R(1/T_2 - 1/T_1) \quad (6)$$

Where ΔH^0 is the adsorption heat, R is the gas constant, T is the absolute temperature, K_1 and K_2 are the adsorptive equilibrium constants at T_1 and T_2 , respectively. In consideration that the experiments precede at the standard pressure and the solution concentrations are not very high, which are close to the standard condition, the calculated adsorption heat thus can be approximately regarded as the standard adsorption heat ΔH^0_{ads} . The negative values of ΔH^0 Table (2) reflect the exothermic behavior of the adsorption of ATE on the copper surface. Finally, the standard adsorption entropy ΔS^0_{ads} can be calculated by the following Eq. (7):

$$\Delta S^0_{ads} = (\Delta H^0_{ads} - \Delta G^0_{ads}) / T \quad (7)$$

The (ΔS^0_{ads}) values from Table (2) are positive, which are opposite to the usual expectation that the adsorption is an exothermic process and always accompanied by a decrease of entropy. The reason can be explained as follows: the adsorption of ATE inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the ATE in the aqueous phase and water molecules at the electrode surface $[H_2O_{(ads)}]^{[28-31]}$. In this situation, the adsorption of ATE is accompanied by the desorption of water molecules from the copper surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent $^{[32]}$. The thermodynamic values obtained are the algebraic sum of the adsorption of ATE inhibitor molecules and the desorption of water molecules. Therefore, the gain in entropy is attributed to the increase in solvent entropy. The positive values of (ΔS^0_{ads}) suggest that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of ATE on the copper surface. Table (2) lists all the above calculated thermodynamic parameters.

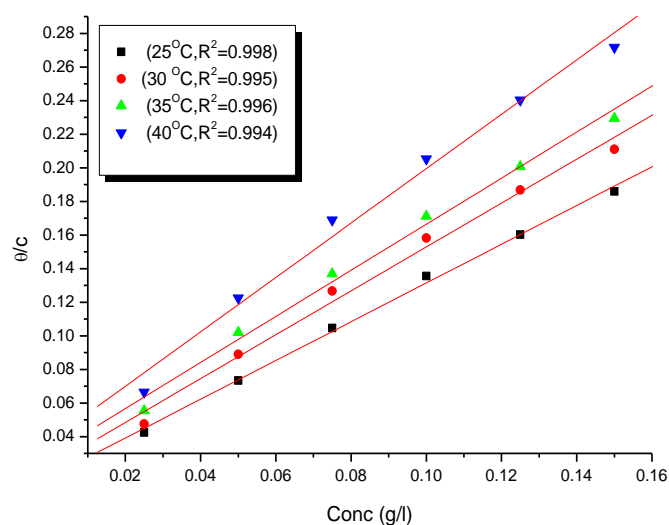


Figure (2): Langmuir adsorption plots for copper dissolution in 1M HNO₃ are containing various concentrations of Alkanna Tinctoria Extract (ATE) at different temperatures.

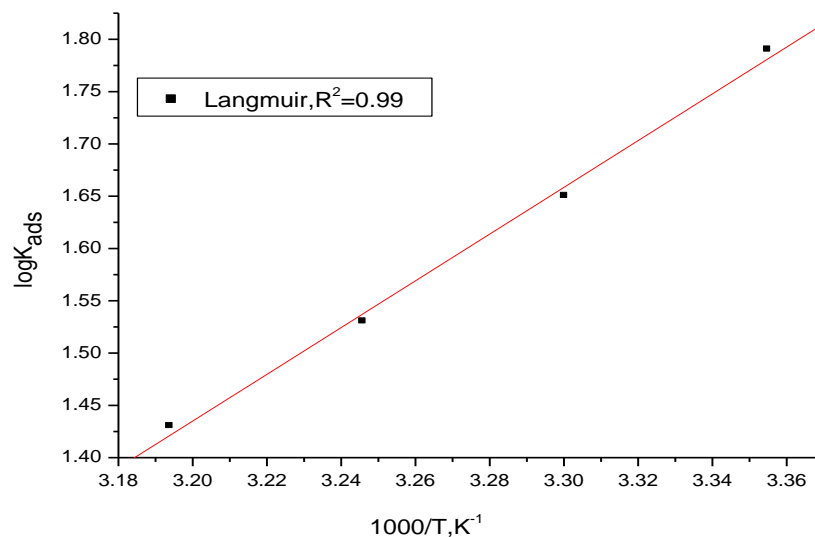


Figure (3): ($\log k_{ads}$) vs. ($1/T$) for the corrosion of Copper in 1M HNO_3 in the presence of Alkanna Tinctoria Extract (ATE).

Table (2): Thermodynamic parameters for the adsorption of Alkanna Tinctoria Extract (ATE) on copper surface in 1M HNO_3 at different temperatures

Langumir Isotherm				
Temp. K	K_{ads} M ⁻¹	$-\Delta G_{ads}^{\circ}$ kJ mol ⁻¹	$-\Delta H^{\circ}$ kJ mol ⁻¹	$-\Delta S^{\circ}$ J mol ⁻¹ K ⁻¹
298	62.073	20.1	42.8	67.6
303	45.454	19.7	42.8	64.0
308	34.482	19.3	42.8	62.7
313	27.027	19.0	42.8	60.7

3.3. Effect of Temperature

The effect of temperature on the inhibited acid-metal reaction is highly complex, because many changes occur on the metal surface, such as rapid etching and desorption of the inhibitor and the inhibitor itself, in some cases, may undergo decomposition and/or rearrangement. Generally the corrosion rate increases with the rise of temperature. It was found that the inhibition efficiency decreases with increasing temperature and increases with increasing the concentration of the inhibitor. The activation energy (E_a^*) of the corrosion process was calculated using Arrhenius Eq. (8) [33]:

$$K = A \exp(-E_a^* / RT) \quad (8)$$

Where K. corrosion rate, A is Arrhenius constant, R is the gas constant and T is the absolute temperature.

The values of activation energies E_a^* can be obtained from the slope of the straight lines of plotting $\log K$ vs. $1/T$ in the presence and absence of Alkanna Tinctoria Extract (ATE) at various temperatures Figure. (4) and are

given in Table (3), it is noted that the values of activation energy increase in the presence of inhibitor and with increase of the concentration of the inhibitor. This is due to the presence of a film of inhibitor on copper surface. The activation energy for the corrosion of copper in 1 M HNO₃ was found to be 42.4 kJ mol⁻¹ which is in good agreement with the work carried out by Fouda et al [34] and others [35,36]. An alternative formulation of the Arrhenius equation is the transition state Eq. (9) [37]:

$$K = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (9)$$

where h is Planck's constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Figure (5) shows a plot of $\log(K/T)$ vs. $(1/T)$. Straight lines are obtained with a slope of $(\Delta H^*/2.303 R)$ and an intercept of $(\log R/Nh + \Delta S^*/2.303 R)$ from which the values of ΔH^* and ΔS^* are calculated and also listed in Table (3). From inspection of Table (3) it is clear that the positive values of ΔH^* reflect that the process of adsorption of the inhibitors on the copper surface is an endothermic process; it is attributable unequivocally to chemisorption. Typically, the enthalpy of a chemisorption process approaches 100 kJ mol⁻¹ [38]. More interesting behavior was observed in Table (3) that positive ΔS^* values is accompanied with endothermic adsorption process. This agrees with what expected, when the adsorption is an endothermic process, it must be accompanied by an increase in the entropy energy change and vice versa [39].

It is seen that investigated ATE has inhibiting properties at all the studied temperatures and the values of %IE decrease with temperature increase. This shows that the inhibitor has experienced a significant decrease in its protective properties with increase in temperature. This decrease in the protective properties of the inhibitor with increase in temperature may be connected with two effects; a certain drawing of the adsorption-desorption equilibrium towards desorption (meaning that the strength of adsorption process decreases at higher temperatures) and roughening of the metal surface which results from enhanced corrosion. These results suggest that physical adsorption may be the type of adsorption of the inhibitor on the copper surface.

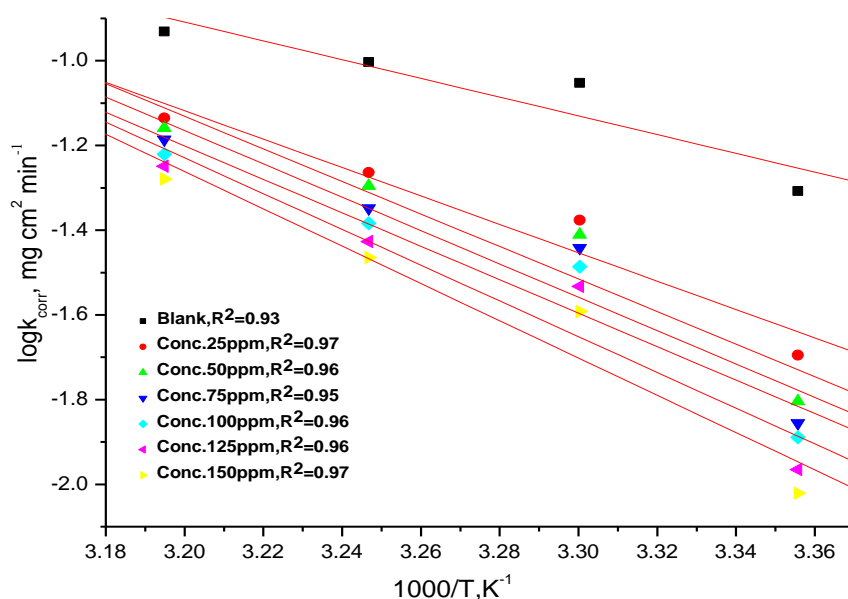


Figure (4): Arrhenius ($\log k$ vs $1/T$) for corrosion of copper in 1M HNO₃ in the absence and presence of different concentrations of Alkanna Tinctoria Extract (ATE).

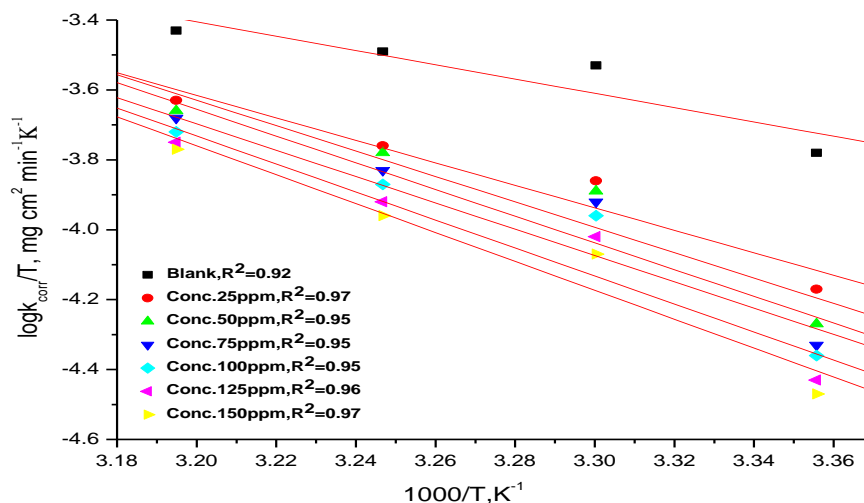


Figure (5): Plots of $(\log k/T)$ vs. $1/T$ for corrosion of copper in 1 M HNO_3 in the absence and presence of different concentrations of Alkanna Tinctoria Extract (ATE).

Table (3): Activation parameters for copper corrosion in the absence and presence of various concentration of Alkanna Tinctoria Extract (ATE) in 1 M HNO_3 .

Conc. ppm	Activation parameters		
	E_a^* (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	$-\Delta S^*$ (J mol K ⁻¹)
Blank	42.4	17.0	137.5
25	64.2	26.8	69.5
50	73.6	30.2	44.4
75	75.4	31.3	37.4
100	75.6	31.8	33.7
125	80.8	33.3	23.5
150	84.3	34.4	16.2

3.4. Potentiodynamic Polarization Measurements

Theoretically, copper can hardly be corroded in the deoxygenated acid solutions, as copper cannot displace hydrogen from acid solutions according to the theories of chemical thermodynamics^[40-42]. However, this situation will change in nitric acid. Dissolved oxygen may be reduced on copper surface and this will allow corrosion to occur. It is a good approximation to ignore the hydrogen evolution reaction and only consider oxygen reduction in the nitric acid solutions at potentials near the corrosion potentials^[43].

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Figure (6) shows the polarization behavior of copper electrode in 1M HNO_3 in the absence and presence of various concentrations of Alkanna Tinctoria Extract (ATE). Figure (6) shows that both the anodic and cathodic reactions are affected by the addition of investigated Alkanna Tinctoria Extract (ATE) and the inhibition efficiency increases as the inhibitor concentration increases, but the cathodic reaction is more inhibited, meaning that the addition of Alkanna Tinctoria Extract (ATE) reduces the anodic dissolution of copper and also retards the cathodic reactions. Therefore, investigated Alkanna Tinctoria Extract (ATE) is considered as mixed type inhibitor. The values of electrochemical parameters such as corrosion current densities (i_{corr}), corrosion potential (E_{corr}), the cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency (% IE) were calculated from the curves of Figure (6) and are listed in Table (4). The results in Table (4) revealed that the corrosion current density decreases obviously after the addition of inhibitor in 1 M HNO_3 and %IE increases with increasing the inhibitor concentration. In the presence of inhibitor E_{corr} was enhanced with no definite trend, indicating that

Alkanna Tinctoria Extract (ATE) act as mixed-type inhibitor in 2 M HNO₃. The inhibition efficiency was calculated using Eq. (10):

$$\%IE_p = [(i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0] \times 100 \quad (10)$$

Where i_{corr}^0 and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

Also it is obvious from Table. (4) that the slopes of the anodic (β_a) and cathodic (β_c) Tafel lines remain almost unchanged upon addition of Alkanna Tinctoria Extract (ATE), giving rise to a nearly parallel set of anodic lines, and almost parallel cathodic plots results too. Thus the adsorbed inhibitor act by simple blocking of the active sites for both anodic and cathodic processes. In other words, the adsorbed inhibitor decrease the surface area for corrosion without affecting the corrosion mechanism of copper in 1M HNO₃ solution, and only causes inactivation of a part of the surface with respect to the corrosive medium^[44,45].

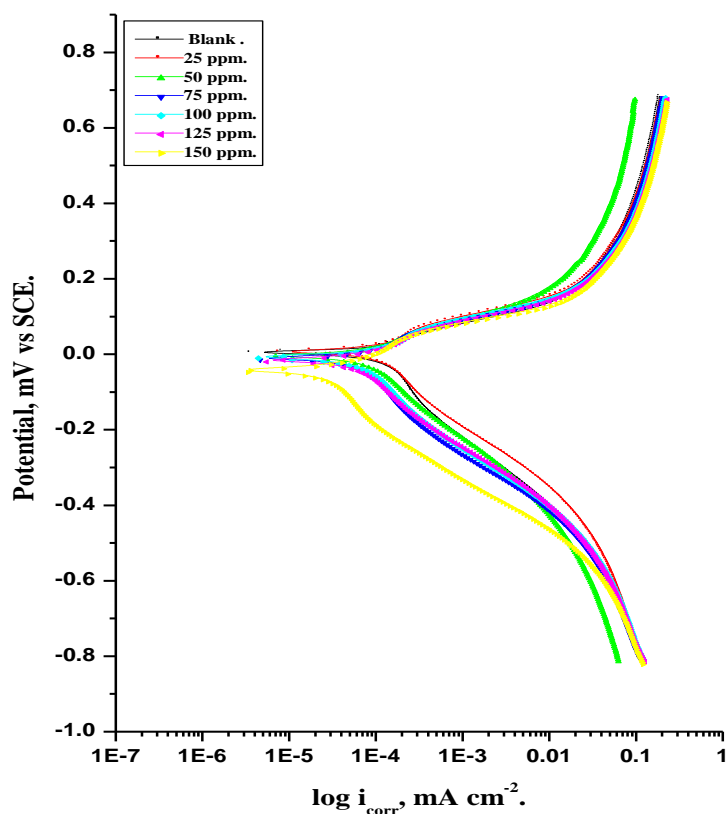


Figure (6): Potentiodynamic polarization curves for the corrosion of Copper in 1 M HNO₃ in the absence and presence of various concentrations Alkanna Tinctoria Extract (ATE) at 25°C.

Table (4): The effect of concentration of the investigated concentrations of Alkanna Tinctoria Extract (ATE) on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (% IE), and degree of surface coverage for the corrosion of Copper in 1 M HNO_3 at 25 °C.

Compound	Conc., ppm.	$-E_{\text{corr.}}$, mV(vs SCE)	$i_{\text{corr.}} \times 10^{-5}$, $\mu\text{A cm}^{-2}$	$\beta_a \times 10^{-3}$, mV dec ⁻¹	$\beta_c \times 10^{-3}$, mV dec ⁻¹	θ	% IE
(ATE)	Blank	405	9.90	83.7	232.5	----	----
	25	364	9.70	112.5	249.2	0.202	2.02
	50	949	9.61	120.5	372.0	0.1040	10.40
	75	768	8.82	113.3	302.9	0.1090	10.90
	100	145	6.62	93.9	212.4	0.3313	33.13
	125	419	3.72	98.9	339.2	0.6242	62.42
	150	779	2.04	153.6	409.3	0.7939	79.39

3.5 Electrochemical Impedance Spectroscopy (EIS)

EIS is well-established and powerful technique in the study of corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from impedance diagrams^[46-50]. Figure (7) shows the Nyquist (a) and Bode (b) plots obtained at open-circuit potential both in the absence and presence of increasing concentrations of investigated Alkanna Tinctoria Extract (ATE) at 25°C. The increase in the size of the capacitive loop with the addition of Alkanna Tinctoria Extract (ATE) shows that a barrier gradually forms on the copper surface. The increase in the capacitive loop size (Figure 7a) enhances, at a fixed inhibitor concentration. Bode plots (Figure 7b), shows that the total impedance increases with increasing inhibitor concentration (log Z vs. log f). However (log f vs. phase), also Bode plot shows the continuous increase in the phase angle shift, obviously correlating with the increase of inhibitor adsorbed on copper surface. The Nyquist plots do not yield perfect semicircles as expected from the theory of EIS. The deviation from ideal semicircle was generally attributed to the frequency dispersion^[51] as well as to the inhomogeneity of the surface.

EIS spectra of the Alkanna Tinctoria Extract (ATE) were analyzed using the equivalent circuit, Figure. (8), which represents a single charge transfer reaction and fits well with our experimental results. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit^[52]. The double layer capacitance, C_{dl} , for a circuit including a CPE parameter (Y_0 and n) were calculated from Eq. (11)^[53]:

$$C_{dl} = Y_0 \omega^{n-1} / \sin [n (\pi/2)] \quad (11)$$

where Y_0 is the magnitude of the CPE, $\omega = 2\pi f_{\text{max}}$, f_{max} is the frequency at which the imaginary component of the impedance is maximal and the factor n is an adjustable parameter that usually lies between 0.50 and 1.0. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charged-transfer controlled^[54, 55]. The general shape of the curves is very similar for all samples (in presence or absence of inhibitors at different immersion times) indicating that no change in the corrosion mechanism^[56]. From the impedance data (Table 5), we conclude that the value of R_{ct} increases with increasing the concentration of the inhibitor.

In fact the presence of inhibitors enhances the value of R_{ct} in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of CPE follows the order similar to that obtained for i_{corr} in this study. The decrease in CPE/C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggesting that organic

derivatives inhibit the copper corrosion by adsorption at metal/acid [57, 58]. The inhibition efficiency was calculated from the charge transfer resistance data from Eq. (12)^[59]:

$$\%IE_{EIS} = [1 - (R_{ct}^0/R_{ct})] \times 100 \quad (12)$$

Where R_{ct}^0 and R_{ct} are the charge-transfer resistance values without and with inhibitor respectively.

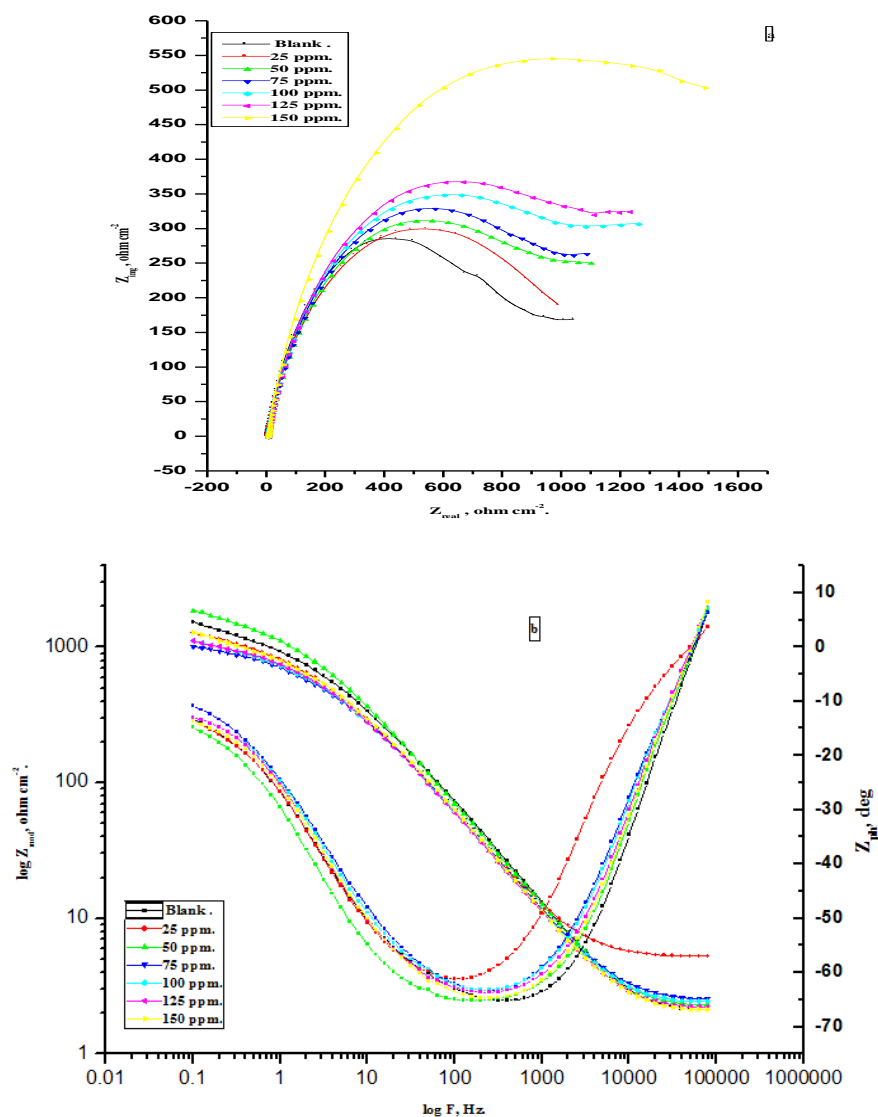


Figure (7): EIS Nyquist plots (a) and Bode plots (b) for copper in 1 M HNO₃ in the absence and presence of different concentrations of Alkanna Tinctoria Extract (ATE) at 25°C.

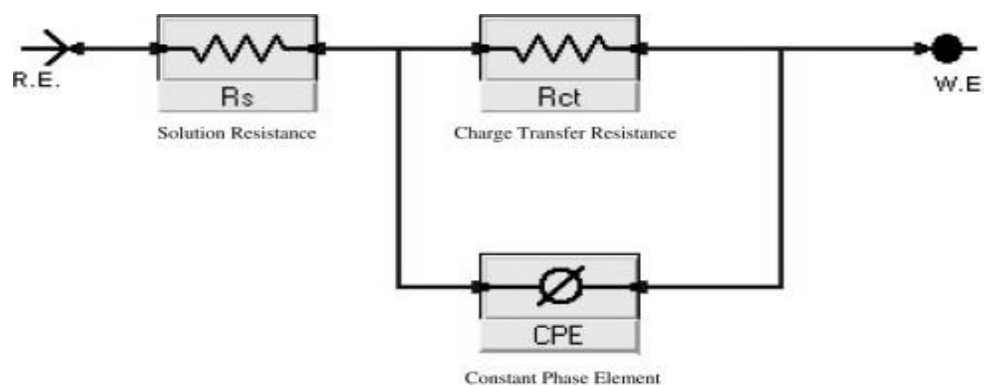


Figure (8): Equivalent circuit model used to fit experimental EIS

Table (5): Electrochemical kinetic parameters obtained by EIS technique for copper in 1 M HNO₃ without and with various concentrations Alkanna Tinctoria Extract (ATE) at 25°C.

Compound	Conc., ppm.	R_s , $\Omega \text{ cm}^2$	$Y_0, \times 10^{-6} \mu\Omega^{-1} \text{ sn}$	$n \times 10^{-3}$	R_{ct} , $\Omega \text{ cm}^2$	$C_{dl} \times 10^{-5} \mu\text{Fcm}^{-2}$	θ	% IE
ATE)(Blank	1.895	90.82	782.8	103.0	6.20	---	---
	25	2.114	90.94	786.6	137.4	5.85	0.2503	25.03
	50	2.353	115.3	769.5	797.9	5.78	0.8709	87.09
	75	2.231	116.0	771.4	825.4	5.64	0.8752	87.52
	100	2.020	114.6	776.0	853.7	5.41	0.8793	87.93
	125	1.949	104.4	783.9	886.4	5.17	0.8837	88.37
	150	4.959	118.9	767.5	982.0	4.70	0.8951	89.51

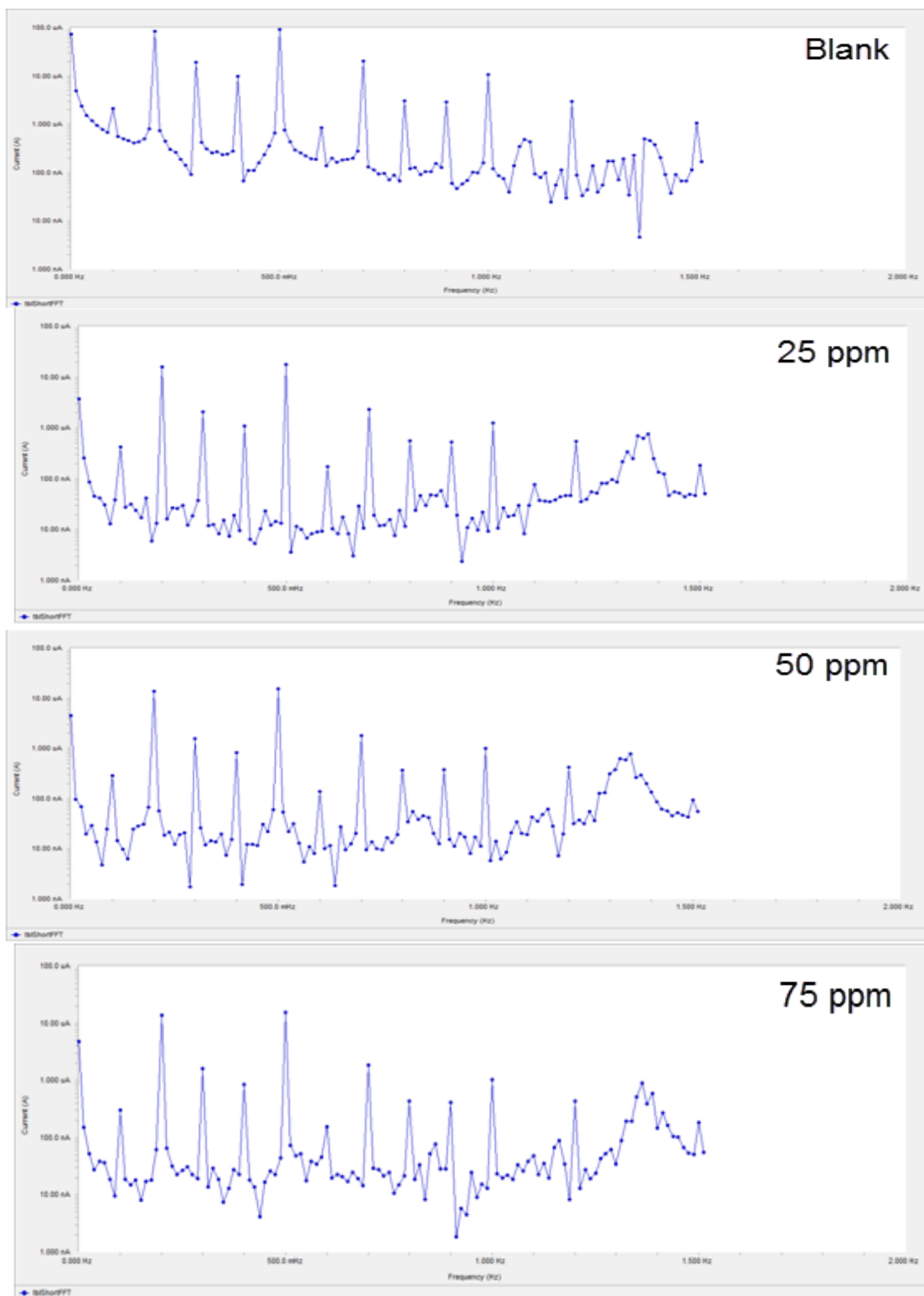
3.6. Electrochemical Frequency Modulation Technique (EFM)

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current values without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring^[60]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses.

Figure (9) shows the EFM Intermodulation spectrums of copper in nitric acid solution containing different concentrations of Alkanna Tinctoria Extract (ATE) at 25°C. The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 200 μA , are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 nA). The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the "activation" model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode^[61]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were listed in Table (6). The data presented in Table (6) obviously show that, the addition of Alkanna Tinctoria Extract (ATE) at a given concentration to the acidic solution decreases the corrosion current density, indicating that Alkanna Tinctoria Extract (ATE) inhibit the corrosion of copper in 1 M HNO₃ through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality. The inhibition efficiencies % IE_{EFM} increase by increasing the inhibitor concentrations and was calculated as from Eq. (13):

$$\% \mathbf{IE}_{\mathbf{EFM}} = [1 - (i_{\mathbf{corr}} / i_{\mathbf{corr}}^0)] \times 100 \tag{13}$$

Where $i_{\mathbf{corr}}^0$ and $i_{\mathbf{corr}}$ are corrosion current densities in the absence and presence of inhibitor, respectively.



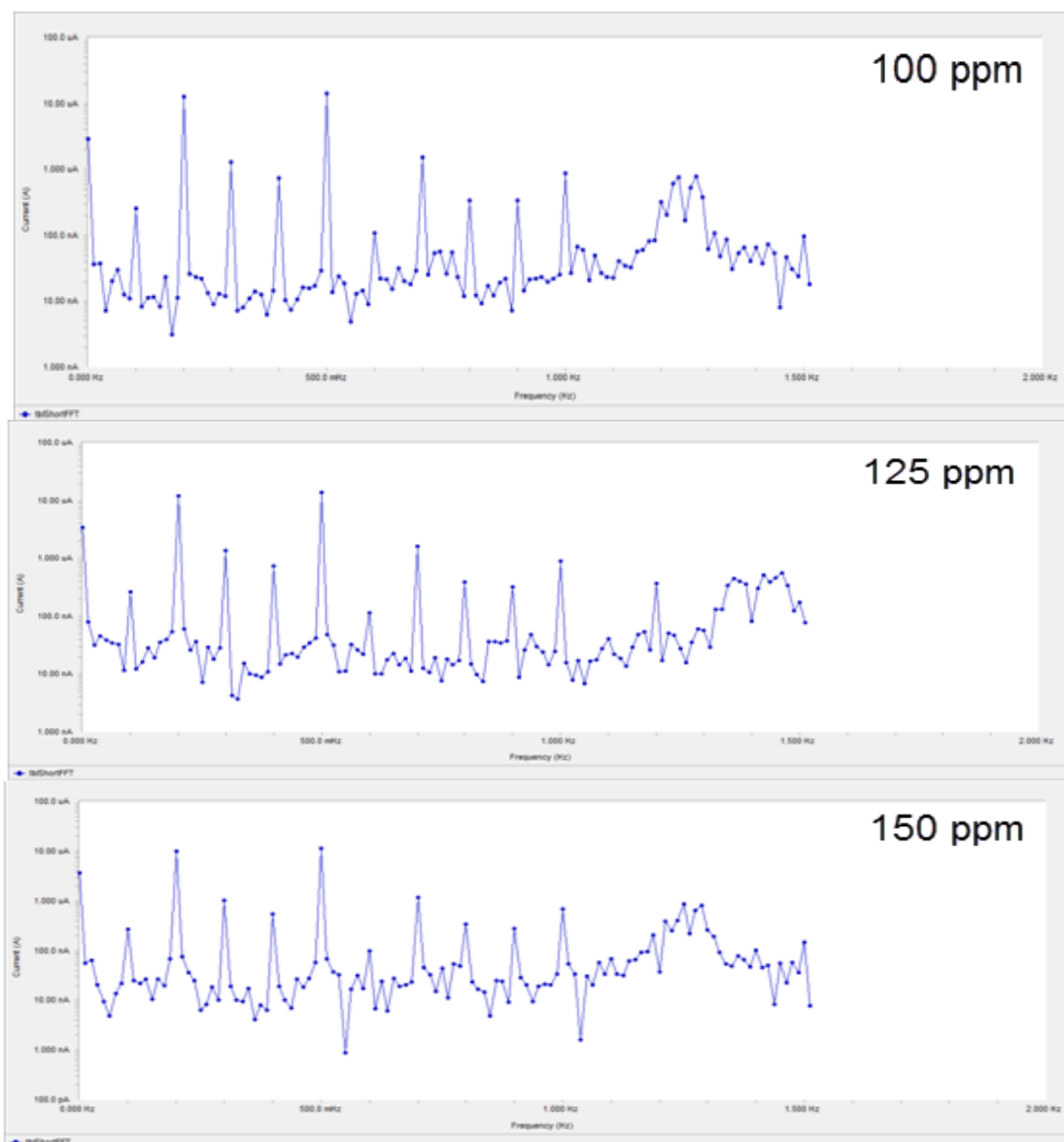


Figure (9): EFM spectra copper in 1M HNO₃ in the absence and presence of different concentrations of Alkanna Tinctoria Extract (ATE) at 25°C.

Table (6): Electrochemical kinetic parameters obtained by EFM technique for Copper in the absence and presence of various concentrations of Alkanna Tinctoria Extract (ATE) in 1M HNO₃ at 25°C.

Compound	Conc., ppm	i_{corr} μA cm^{-2}	$\beta_c \times 10^{-3}$ $mV dec^{-1}$	$\beta_a \times 10^{-3}$ $mV dec^{-1}$	CF-2	CF-3	C.R	θ	% IE
(ATE)	Blank	138.1	59.8	341.3	1.92	2.93	133.10	---	---
	25	18.88	56.8	104.7	1.86	2.88	18.20	0.8332	83.32
	50	18.57	63.6	114.0	1.84	3.13	17.90	0.8655	86.55
	75	17.53	60.8	109.5	1.83	2.93	16.90	0.8730	87.30
	100	17.10	65.2	113.9	1.78	3.08	16.49	0.8761	87.61
	125	15.74	62.0	111.0	1.81	3.02	15.17	0.8860	88.60
	150	14.42	68.3	118.6	1.79	2.88	13.90	0.8955	89.55

3.7. Mechanism of Inhibition

Most organic inhibitors contain at least one polar group with an atom of nitrogen or sulphur or in some cases selenium and phosphorus. The inhibiting properties of many compounds are determined by the electron density at the reaction center^[62].

With increase in electron density in the center, the chemisorption between the inhibitor and the metal are strengthened^[63, 64]. The plant extract ATE is composed of numerous naturally occurring organic compounds. Accordingly, the inhibitive action of ATE could be attributed to the adsorption of its components on the copper surface. The constituents of ATE are phytochemical constituents is Zygophyllin (28% in leaves, 0.18% in stems and 0.26% in fruits), Quinovic acid (0.36% in leaves, 0.31% in fruits and 0.47% in stems) and Flavonoids e.g, kaempferol-3-rutinoside^[15,16]. Most of these phytochemicals are organic compounds that have center for π -electron and presence of hetero atoms such as oxygen and nitrogen; hence, the adsorption of the inhibitor on the surface on copper is enhanced by their presence. The inhibition efficiency of methanol extracts of ATE is due to the formation of multi-molecular layer of adsorption between copper and some of these phytochemicals. Results of the present study have shown that ATE inhibits the acid induced corrosion of copper by virtue of adsorption of its components onto the copper surface. The inhibition process is a function of the metal, inhibitor concentration, and temperature as well as inhibitor adsorption abilities, which is so much dependent on the number of adsorption sites. The mode of adsorption was mixed one, chemisorption and physisorption observed could be attributed to the fact that ATE contains many different chemical compounds, which some can be adsorbed chemically and others adsorbed physically. This observation may derive the fact that adsorbed organic molecules can influence the behaviour of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes^[65].

4. CONCLUSIONS

From the overall experimental results the following conclusions can be deduced:

1. ATE is good inhibitor and act as mixed type for copper corrosion in 1 M HNO₃ solution.
2. The results obtained from all electrochemical measurements showed that the inhibiting action increases with the inhibitor concentration and decreases with the increasing in temperature.
3. Double layer capacitances decrease with respect to blank solution when the plant extract is added. This fact confirms the adsorption of plant extract molecules on the copper surface.
4. The adsorption of inhibitor on copper surface in 1 M HNO₃ solution follows Langmuir isotherm for ATE extract.
5. The negative values of the free energy of adsorption and adsorption heat are indicate that the process was spontaneous and exothermic.
6. The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results

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