CORROSION INHIBITION OF GALVANIZED IRON USING GINGER PLANT EXTRACT AS A GREEN INHIBITOR IN SULFIDE POLLUTED SALT WATER

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ABSTRACT

In this study, extract of ginger has been evaluated as a green inhibitor for the corrosion of galvanized iron in sulfide polluted NaCl solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Potentiodynamic polarization measurements showed that this extract acts as a mixed type inhibitor but mainly inhibits the cathodic polarization part. The inhibition efficiency was found to increase with inhibitor concentration reaching to approximately 83.9 % using 250 ppm of ginger. EIS showed that the film coverage on the metal surface depending not only the type of the inhibitor but also the nature of the metal surface. Moreover, EIS was used to investigate the mechanism of corrosion inhibition. Nyquist plots show a single capacitive loop in uninhibited and inhibited solutions. From EFM the causality factors are very close to theoretical values which indicate that the measured data are of good quality. The adsorption process of the studied extract on galvanized iron surface obeys Temkin adsorption isotherm. The results obtained from the different electrochemical techniques were in good agreement which prove the validity of these tools in the measurement of the tested inhibitor.

INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes, and electrochemical potential. Regarding the chemical structure and chemical behavior, an inorganic compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic compound must have some features that give it the ability to act as a corrosion inhibitor. Among these, the molecule may have a large structure, double bonds, an active center or group, etc. These features give the molecule the ability to cover a large area of a metal surface with a firmly attached film [El-Etre (2007)].

Apart from the structural aspects, there are also economic and environmental considerations. Thus, since the whole subject of corrosion is about its destructive economical effect, the used inhibitor must be cheap. Furthermore, due to the recent increasing awareness of green chemistry, it must be a nontoxic and environmentally friendly chemical. One of the sources of these cheap and clean inhibitors is plants. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Efforts to find naturally organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified. Several reports are available on the various natural products used as green inhibitors. Low-grade gram flour, natural honey, onion, potato, gelatin, plant roots, leaves, seeds, and flowers gums have been reported as good inhibitors. However, most of them have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (millimolar solutions). Plant parts contain several compounds that satisfy the

mentioned criteria. Many recent researches [El-Etre (2006), Benabdellah et al., (2006), Chaieb et al., (2005), Muller (2002), Li et al., (2005), El-Etre (2005), A.Bouyanzer et al., (2006), El-Etre (2003)] have adopted this trend and carried out their work on naturally occurring substances. Promising results were obtained in previous work in this field. It was reported that Khillah extract inhibits steel corrosion in HCl solution with inhibition efficiency as high as 99% [El-Etre (2006)], while opuntia extract inhibits the corrosion of aluminum in the same acid with efficiency of about 96% [El-Etre (2003)].

The aim of this work is to study the effect of ginger extract as green corrosion inhibitor for the galvanized iron in sulfide polluted salt water using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques.

EXPERIMENTAL

The material used is a galvanized iron which was provided from a bridge in a Talkha sanitation plant, Egypt. These samples have the following chemical composition (wt %): 0.005% Si, 0.248% Mn, 1.832% Zn and the remainder is iron. For electrochemical measurements, the sheets were welded with Cu-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active surface of (1 cm^2) geometric area to contact the test solution. Prior to each experiment, these sheets were first briefly ground with no. 800 emery paper, subsequently polished with no. 1200 emery paper, washed with bi-distilled water, degreased with absolute ethanol and then dried. A conventional electrochemical cell of capacity 100 ml was used containing three compartments for working, platinum spiral counter and saturated calomel electrode (SCE) as reference electrode. The measurements were carried out in aerated non-stirred 3.5% NaCl with 16ppm sulfide in the presence of various concentrations of the investigated compound, as environmentally-friendly corrosion inhibitor. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. For each run, a freshly prepared solution as well as a cleaned set of electrodes was used. Each run was carried out in aerated stagnant solutions at the required temperature (25±1°C), using a water thermostat. Potentiodynamic

measurements were performed using a Gamry framework instruments (version 3.20), controlled by a computer which also recorded and stored the data. All experiments were carried out at $25\pm1^{\circ}C$ using circulator thermostat model CW-05GL and solutions were not deaerated. The potentiodynamic polarization curves were carried out at a scan rate of 1 mV s^{-1} starting from -1.7 V up to -0.1 V (SCE). Before polarization, the open circuit potential of the working electrode was measured as a function of time during 20 min, the time necessary to reach a quasi-stationary value for the open-circuit potential. Impedance measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open-circuit potential in the frequency range 100 kHz and 0.2 Hz. All impedance measurements were recorded at open circuit potential (OCP) after immersion the electrode for 20 minutes in the test solution. The measurements were performed with Potentiostat/Galvanostat/Zra analyzer (Gamry PCI300/4). A personal computer with EIS300 software and Echem Analyst 5.21 was used for data fitting and calculating.

PREPARATION OF PLANT EXTRACTS

The present investigation was carried out using the plant namely ginger. The uses parts were the bark and the rhizomes of ginger. The sample were purchased from the local market and ground into a fine powder to give 500g of powdered materials which extracted separately by soaking at room temperature for six times with methanol (5 L), then the methanolic extract of the sample was concentrated to nearly dryness under reduced pressure by using the rotary evaporator at 45 °C to achieve the crude methanolic extract which kept for further investigation.

Botanical aspect of ginger

English name: ginger   **Botanical name:** *Zingiber officinale*

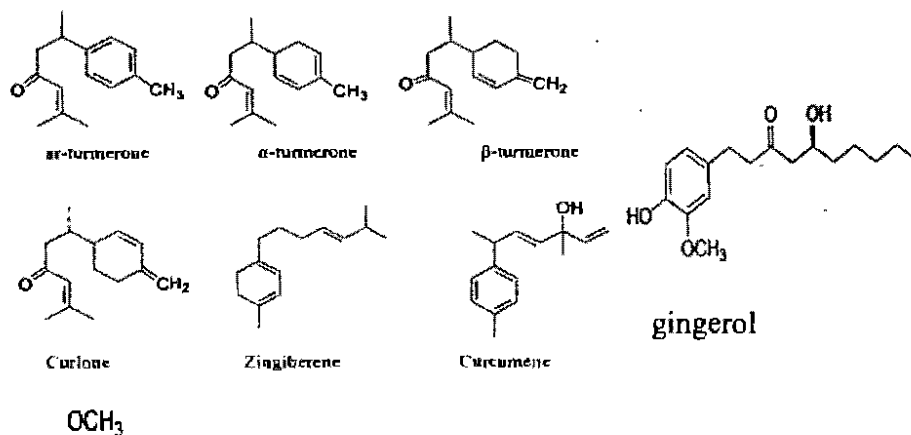   **Family:**   Zingiberaceae

Chemical structures of ginger

ar-turmerone   α-turmerone   β-turmerone

Curlone   Zingiberene   Curcumene

gingerol

OCH$_3$

RESULTS AND DISCUSSION

1. Potentiodynamic polarization measurements

Fig.1 shows the potentiodynamic polarization curves of galvanized iron in sulfide polluted salt water without and with different concentrations of ginger extract at 25°C. The obtained electrochemical parameters; cathodic and anodic Tafel slopes (β_c and β_a) respectively, open circuit potential (E_{OC}), corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion rate (C.R.) and polarization resistance (R_p) were obtained and listed in Table 1. The degree of surface coverage; θ at constant potential is given by the following relation [**Ammar and Darwish (1967), Fisher (1960)**]:

$$\theta = [1 - (R_p / R_{pinh})] \tag{1}$$

where i_{corr} and $i_{corr(inh)}$ are the corrosion current densities of uninhibited and inhibited solutions, respectively, R_p and R_{pinh} are the polarization resistance of uninhibited and inhibited experiments, respectively. The percentage of inhibition efficiency, IE% at each concentration was calculated using the equation:

$$IE\% = (1 - R_p / R_{pinh}) \times 100 \tag{2}$$

The percentage inhibition efficiencies (IE% calculated from i_{corr} and IE% calculated from R_p) of the investigated compound is given in Table 1. An inspection of the results obtained from Table 1 reveals that, the presence of different concentrations of the additive compound reduce the anodic and cathodic current densities by decreasing the hydrogen evolution and the metal dissolution at the cathode which appears from the table that $\beta_c > \beta_a$ this is due to presence of donor atom having alone pair of electrons attached with the surface by charge or electron transfer between the inhibitor and the metal surface also the bulky group of the inhibitor makes strike hindrance at the metal surface for the reach of the corrosive medium to the metal surface and the suppression in current increases as the inhibitor concentration increases, this indicate the inhibiting effects of the investigated compound. The slight shifts of E_{corr} values towards less negative direction are found in the presence of various concentrations of this compound in sulfide polluted salt water. Generally, increase in inhibitor concentration shifts corrosion potential to less negative values. This can be explained by a small domination of the anodic reaction inhibition [Stupnisek-Lisac et al., (2002)]. The %IE was found to increase with increasing the inhibitor concentration.

Table (1): The effect of concentration of ginger on the electrochemical parameters calculated by using potentiodynamic technique for corrosion of galvanized iron in sulfide polluted salt water at 25 °C.

Conc., ppm	$-E_{corr}$, V	j_{corr}, µA cm^{-2}	$-\beta_c$, mV dec^{-1}	β_a, mV dec^{-1}	C.R mmy^{-1}	θ	I %
Blank	1.056	11470	265.0	208.7	133.19	------	-----
50	1.077	6538	253.1	196.3	99.11	0.430	43.0
100	1.063	4269	241.7	165.7	53.24	0.628	62.8
150	1.083	3670	221.2	146.7	35.76	0.680	68.0
200	1.080	2909	219.5	144.2	33.77	0.746	74.6
250	1.058	1858	193.2	123.9	19.11	0.839	83.9
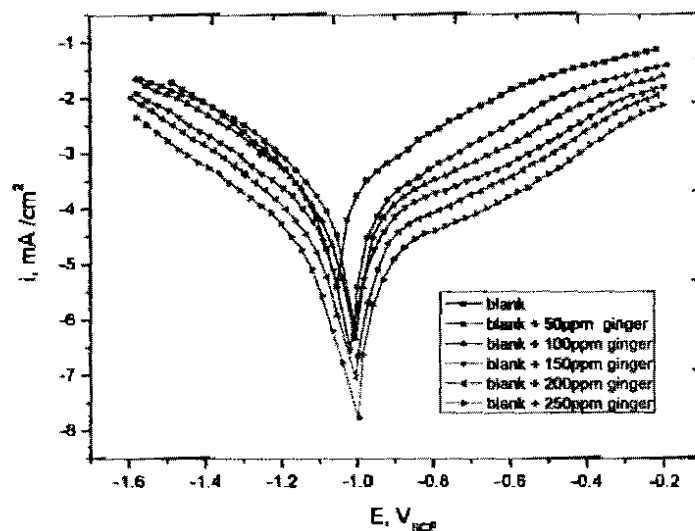
Fig. (1): Potentiodynamic polarization curves for the corrosion of galvanized iron in 3.5% NaCl + 16ppm Na_2S in the absence and presence of different concentrations of ginger at 25 °C.

1.1- Adsorption isotherm

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/environment system [Szklarska-Smiaiowska et al., (1991)]. The values of the degree of surface coverage θ were evaluated at different concentrations of the inhibitor in sulfide polluted salt water. Attempts were made to fit θ values to various adsorption isotherms. The Temkin adsorption isotherm fits the experimental data. A plot of θ against log C for all concentrations of inhibitor shown in Fig. 2 gives a straight line relationship in all cases which suggests that the adsorption of the studied inhibitor on the galvanized iron surface follow Temkin adsorption isotherm. The strong correlation ($R^2 = 0.996$) for the Temkin adsorption isotherm plot confirmed the validity of this approach.

$$KC = \exp(-2a\theta) \qquad (3)$$

where a is molecular interaction parameter, θ is the degree of surface coverage, K is the equilibrium constant of adsorption process and C is the inhibitor concentration. It is well known that the equilibrium constant of adsorption (K) is related to the standard adsorption free energy (ΔG°_{ads}) and can be calculated by the following equation [Khamis (1990)]:

$$K = 1/55.5 \exp [-\Delta G^{\circ}_{ads}/RT] \tag{4}$$

Table 2 shows the calculated values of molecular interaction a, equilibrium constant of adsorption process, K and free energy (ΔG°_{ads}) obtained from Temkin plot. The value of a are positive shows that attraction exists in adsorption layer [Tang et al, (2006)]. The relatively high and negative free energy values may indicate a relatively strong and spontaneous adsorption of the investigated compound on the metal surface, which explains its high corrosion inhibition efficiency. A value of -40 kJ mol^{-1} is usually adopted as a threshold value between chemical and physical adsorption [Oguzie (2007)]. The calculated values of ΔG°_{ads}, for the investigated compound with the metal surface is -35.63 kJ mol^{-1}, which means that the adsorption of this inhibitor is physically through electrostatic interaction between the inhibitor and the metal surface.

Table (2): The equilibrium constant of the adsorption process (K), free energy of binding (ΔG°_{ads}) and the interaction parameter (a) of the investigated compound at 25 °C.

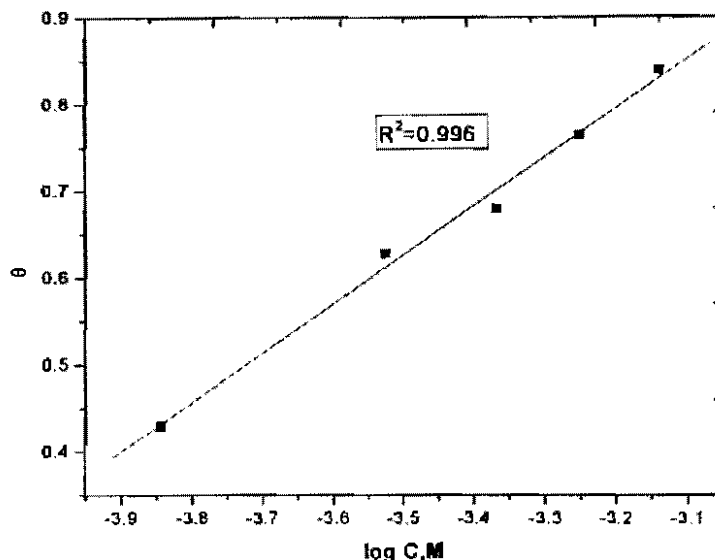| Temkin isotherm		
a	K, M^{-1}	$-\Delta G^{\circ}_{ads}$ kJ mol^{-1}
57.99	1.79×10^{8}	11.18

Fig. (2): Temkin adsorption isotherm plotted as θ vs. log C of ginger for the corrosion of galvanized iron in sulfide polluted salt water.

2. Electrochemical Impedance Spectroscopy (EIS)

Fig. 3 shows the Nyquist plot of galvanized iron in 3.5%NaCl and 16ppm Na_2S in absence and presence of different concentrations of investigated compound was investigated by EIS method at 25°C after 20 min immersion. All the impedance spectra were measured at the corresponding open-circuit potentials. It is apparent that Nyquist plots show a single capacitive loop, both in uninhibited and inhibited solutions. The data described a semi-circular at high frequencies, indicating that the corrosion process was now under diffusion control, through an inhibitor-formed film, whereas at low frequencies a depressed, capacitive-like semicircle was observed, which correspond to a charge transfer-controlled corrosion process. According to Ramachandran [**Ramachandran et al., (1996)**], the film formed in the presence of ginger extract acts as a protective barrier against aggressive ions from the bulk solution. Thus, the corrosion process in the presence of the inhibitor was under addsorption and charge transfer mixed mechanism. The EIS data were simulated using equivalent electric circuits as shown in Fig. 4

where R_S represents the solution or electrolyte resistance, C_{dl} the double layer capacitance, R_{ct} the charge transfer resistance.

Form the Nyquist plot it is obvious that low frequency data are on the right side of the plot and higher frequencies are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true of all circuits). The capacity of double layer C_{dl} can be calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi\,f_{max}\,R_{ct}} \tag{5}$$

where f_{max} is maximum frequency. The parameters obtained from impedance measurements are given in Table 3. It can see from Table 3 that the values of charge transfer resistance increase with inhibitor concentration [**Larabi et al.**, **(2006)**]. In the case of impedance studies, IE% increases with inhibitor concentration in the presence of investigated inhibitors. The impedance study confirms the inhibiting characters of these compounds obtained with potentiodynamic polarization methods. It is also noted that the C_{dl} values tend to decrease when the concentration of these compounds increases. This decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that these compounds molecules function by adsorption at the metal/solution interface [**Lagrenee et al.**, **(2002)**].

EIS data Table 3 shows that the R_{ct} values increase and the C_{dl} values decrease with increasing the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The high R_{ct} values, are generally associated with slower corroding system [**Bessone et al.**, **(1983)**, **Epelboin et al.**, **(1972)**]. The decrease in the C_{dl} can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [**Khaled**, **(2008)**], suggested that the inhibitor molecules function by adsorption at the metal/solution interface.

The inhibiting effect of this compound can be attributed to their parallel adsorption at the metal solution interface. The parallel adsorption is owing to the presence of one or more active center for adsorption. The chemisorptions take place by the formation of a chemical bond between the metal and the adsorbed molecule. Chemisorptions involve charge or

charge transfer from inhibitor molecule to the metal surface forming co-ordinate type bond [Khamis et al, (1991)].

Table (3): Electrochemical kinetic parameters obtained by EIS technique for the corrosion of galvanized iron in 3.5% NaCl +16ppm Na_2S alone and with different concentrations of ginger at $25\,^{\circ}C$.

Conc., M	R_s $\Omega\,cm^2$	C_{dl}, $(\mu F\,cm^{-2})$	n	R_{ct} $\Omega\,cm^2$	Θ	I %
blank	1.294	605.5	0.886	3.863	----	----
50	1.194	433.0	0.878	4.782	0.192	19.2
100	1.181	392.1	0.886	10.24	0.623	62.3
150	1.132	367.1	0.878	11.68	0.669	66.9
200	1.122	356.0	0.861	14.87	0.740	74.0
250	1.110	333.6	0.848	25.49	0.848	84.8
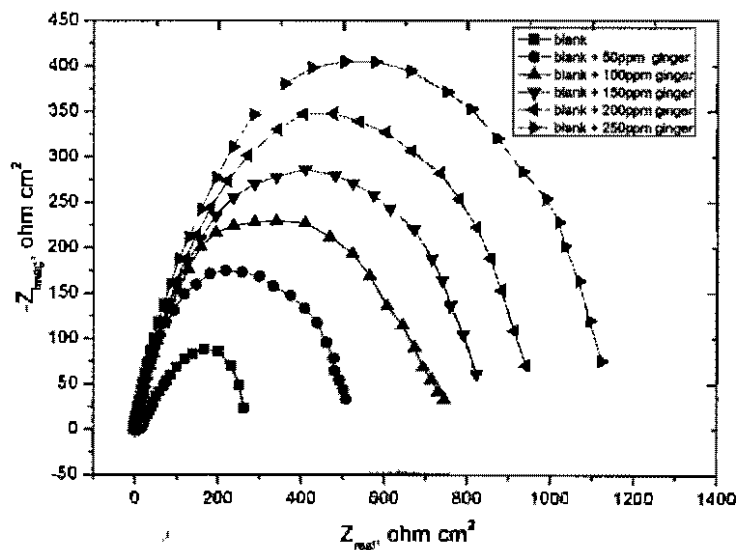
Fig. (3): Nyquist plots recorded for galvanized iron in 3.5% NaCl + 16ppm Na_2S with and without different concentrations of ginger at 25°C.
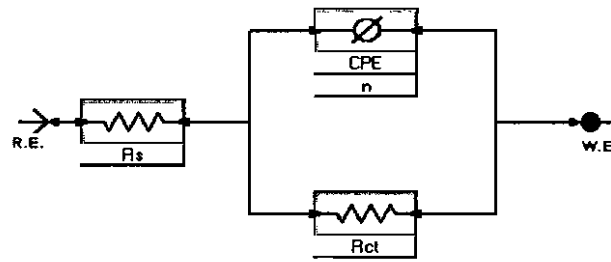
Fig. (4): Electrical equivalent circuit used to fit the impedance spectra.

3. Electrochemical Frequency Modulation (EFM)

Intermodulation spectra obtained from EFM measurements are presented in Fig. (5a-e) as examples of galvanized iron in 3.5% NaCl + 16ppm Na_2S containing different concentrations of ginger at 25 °C. Each spectrum is a current response as a function of frequency. The two large peaks are the response to the 2Hz and 5Hz excitation frequencies. These peaks are used by the EFM 140 software package to calculate the corrosion current and Tafel constants.

The calculated corrosion kinetic parameters in the presence of 3.5% NaCl + 16ppm Na_2S alone and with different concentrations of the investigated inhibitor at 25°C (i_{corr}, β_a, β_c, CF-2 and CF-3) are given in Table 4. From this Table it is obvious that the corrosion current densities decrease by increasing the concentration of inhibitor and hence the inhibition efficiency increases. Also it is clear that the causality factors are very close to theoretical values which according to EFM theory should guarantee the validity of Tafel slope and corrosion current densities. In addition the values of causality factors indicate that the measured data are of good quality [Abdel-Rehim et al., (2006)]. The obtained results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and EFM methods.

Table (4): Electrochemical Kinetic parameters obtained by EFM technique for galvanized iron in 3.5% NaCl +16ppm Na_2S alone and with different concentrations of ginger at 25 °C.

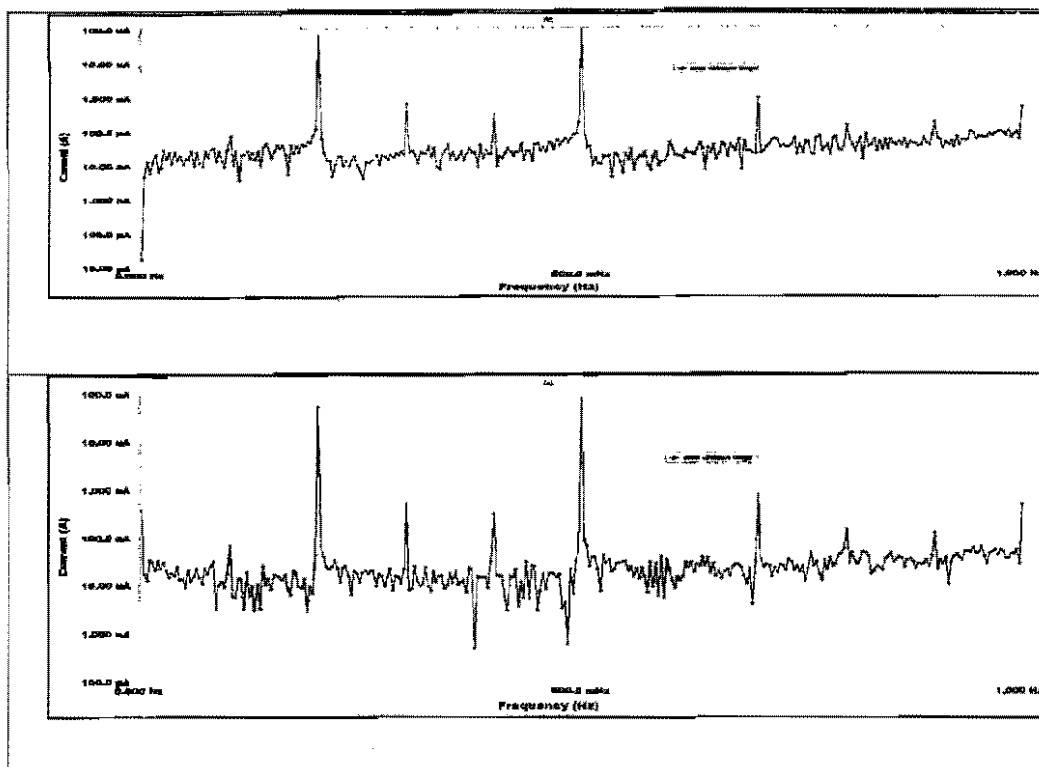| Concentration, ppm	$i_{corr.}$, $\mu A\ cm^{-2}$	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	C.R, mmy^{-1}	Θ	I %
blank	13540	278.0	240.6	1.85	2.85	140.31	------	------
50	7447	272.3	237.16	1.68	2.74	77.17	0.450	45.0
100	4766	267.42	232.41	1.69	2.70	49.38	0.648	64.8
150	4062	264.31	228.31	1.72	2.82	42.10	0.700	70.0
200	3250	257.41	220.62	1.84	2.90	33.68	0.760	76.0
250	1950	250.81	218.41	1.86	2.93	20.21	0.856	85.6
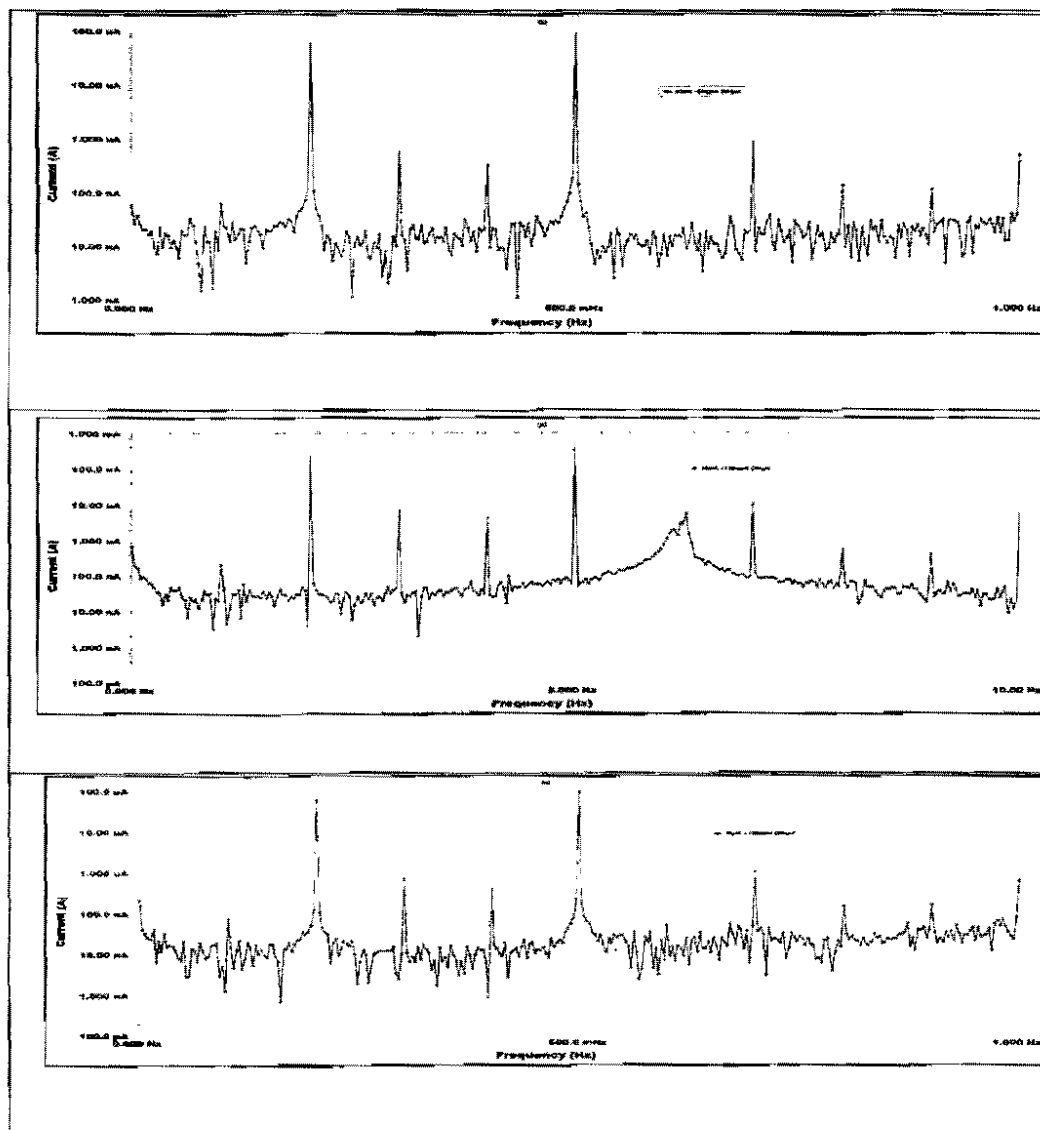
Fig. (5a-e): Intermodulation spectrum for galvanized iron in 3.5% NaCl + 16ppm Na₂S with various concentrations of ginger at 25°C.

CONCLUSION

1- Ginger extract acts as an inhibitor for corrosion of galvanized iron in sulfide polluted salt water.

2- The inhibition efficiency increases with increase in the concentration of the inhibitor.

3- The inhibition is due to the adsorption of the inhibitor molecule on the metal surface by charge transfer or by the diffusion of the inhibitor molecules.

4- The adsorption of these compounds on the metal surface follows Temkin adsorption isotherm.

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تثبيط تأكل الحديد المجلفن بإستخدام مستخلص الجنزبيل كمثبط صديق للبيئة فى ماء البحر
الملوث بأيونات الكبريتيد

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شركة مياه الشرب والصرف الصحى- الدقهلية- مصر

إن الحديد المجلفن من أهم المعادن التى تستخدم فى مياه البحر ومحطات معالجة
مياه الصرف الصحى لكونه يواجه مشكلة التآكل فى وجود أيونات الكبريتيد الضارة وهذا
البحث يناقش كيفية حماية هذا المعدن من التآكل بإستخدام مثبطات صديقه للبيئة رخيصة
الثمن.

تم مناقشة قدرة وكفاءة مستخلص الجنزبيل على تثبيط تأكل الحديد المجلفن فى ماء
البحر الملوث بأيونات الكبريتيد بإستخدام طريقة الإستقطاب الكهربى وطريقة الممانعة
الإسبكتروسكوبية الكهروكيميائية وأيضا طريقة تقنية التردد الكهروكيميائى المعدل. أظهرت
النتائج أن هذا المستخلص النباتى يعمل كمثبط جيد للتآكل. ووجد أيضا أن إمتزاز هذا المركب
على سطح المعدن يتبع أيزوثيرم تمكن.