

Cinnamon Plant Extract as Corrosion Inhibitor for Steel Used in Waste Water Treatment Plants and Its Biological Effect on *Escherichia coli*

Abd El-Aziz S. Fouda*, Ahmed Abdel Nazeer†, Ayman Y. El-Khateeb‡, and Mohamed Fakh§

Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt.

*E-mail: asfouda@mans.edu.eg

†National Research Center, Electrochemistry and Corrosion Lab., Dokki, Cairo, Egypt.

‡Dept. of Agric. Chemistry, Faculty of Agriculture, Mansoura University, Egypt.

§Water and waste water company, Daqahlia, Egypt.

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ABSTRACT. The inhibition effect of cinnamon plant extract as a green corrosion inhibitor for steel in sulfide polluted salt water was studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM). The results showed that cinnamon plant extract in sulfide polluted salt water is a good corrosion inhibitor with inhibition efficiency reached to 80% at 250 ppm of the plant extract. The adsorption of cinnamon obeys Temkin adsorption isotherm, and acts as a mixed-type of inhibitor but dominantly as a cathodic inhibitor in sulfide polluted salt water.

Key words: Steel corrosion, Cinnamon plant extract, Polluted salt water

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. The compound so formed is called corrosion product and metal surface becomes corroded. Prevention would be more practical and achievable than complete elimination. Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal, 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.¹ Inhibitors function by adsorption of ions or molecules onto metal surface. They reduce the corrosion rate by, increasing or decreasing the anodic and/or cathodic reaction, decreasing the diffusion rate for reactants to the surface of the metal and decreasing the electrical resistance of the metal surface.

Inhibitors are often easy to apply and offer the advantage of in situ application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor: cost of the inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge, toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species, availability of the inhibitor will determine the selection of it and if the availability is low, the inhibitor becomes often expensive and environment friendliness.

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 researches²⁻⁹ 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%,² while opuntia extract inhibits the corrosion of aluminum in the same acid with efficiency of about 96%.⁹

The aim of this work is to study the effect of cinnamon plant extract as green corrosion inhibitor for the steel in sulfide polluted salt water using electrochemical techniques, and also to study its biological effect on the activity of *Escherichia coli*.

EXPERIMENTAL

The material used is steel which was provided from a bridge in a Talkha sanitation plant, Egypt. These samples have the following chemical composition (wt%): 0.20 C, 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 cm²) geometric area to contact the test solution. Prior to each experiment, these sheets were first abraded with emery papers up to 1200 grit size, washed with bidistilled water, degreased with absolute ethanol and then dried. A conventional electrochemical cell of capacity 100 ml was used containing three compartments for working, platinum foil counter and saturated calomel electrode (SCE) as reference electrode. The measurements were carried out in aerated non-stirred 3.5% NaCl with 16 ppm sulfide in the presence of various concentrations of the investigated extract, as environmentally-friendly corrosion inhibitor. All solutions were freshly prepared from analytical grade chemical reagents using bi 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. All experiments were carried out at 25±1 °C using circulator thermostat 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 30 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 30 minutes in the test solution.

All electrochemical experiments were carried out using Gamry PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 corrosion software, EIS300 electrochemical impedance spectroscopy software, EFM140 electrochemical frequency modulation software and Echem Analyst 5.21 for results plotting, graphing, data fitting and calculating.

Preparation of Plant Extract

The present investigation was carried out using the plant namely cinnamon. The uses parts were the bark and the rhizomes of cinnamon. The sample were purchased from the local market and ground into a fine powder to give 500 g 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 Cinnamon Plant

English name: *cinnamon*

Botanical name: *cinnamomum zeylanicum*

Family: *Lauraceae*

Chemical Structures of Cinnamon Plant

Preparation of Bacterial Agriculture Media

Suspend 50 grams of the medium in one liter of distilled water and dissolve it by heating. Sterilize in autoclave at 121 °C for 15 min. Cool to 45–50 °C, mix well and dispense into plates. Allow the plates to solidify. The prepared medium should be stored at 8–15 °C. The color is violet-red.

RESULTS AND DISCUSSION

Potentiodynamic Polarization Measurements

Fig. 1 shows the potentiodynamic polarization curves of steel in sulfide polluted salt water without and with different concentrations of cinnamon plant extract at 25 °C. The obtained electrochemical parameters; cathodic (β_c) and anodic (β_a) Tafel slopes, 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 are listed in *Table 1*. The degree of surface coverage; θ and percentage of inhibition efficiency, % IE were calculated using the equation (1)^{10,11}

$$\%IE = \theta \times 100 = [1 - (i_{corr(inh)} / i_{corr(free)})] \times 100 \quad (1)$$

where i_{corr} and $i_{corr(inh)}$ are the corrosion current densities of

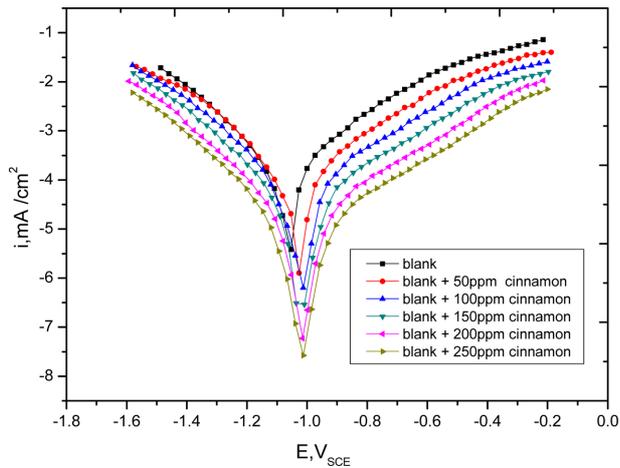


Figure 1. Potentiodynamic polarization curves for the corrosion of steel in 3.5% NaCl + 16 ppm Na₂S in the absence and presence of different concentrations of cinnamon at 25 °C.

uninhibited and inhibited solutions, respectively.

The percentage inhibition efficiencies (% IE) of the extract is given in Table 1. An inspection of the results obtained from Table 1 revealed that, the presence of different concentrations of the extract reduces the anodic and cathodic current densities by decreasing the hydrogen evolution and the metal dissolution reactions. Addition of extract shifts the corrosion potentials slightly in the negative direction without an appreciable change in β_a and β_c values.¹² On the basis of the experimental data, it is not difficult to deduce that in polluted salt water this extract acts as mixed-type inhibitor. The inhibition efficiency was found to increase with increasing concentration of extract. This suggests that the added extract does not change the mechanism of steel dissolution and hydrogen evolution reactions and the extract decreases both reactions by adsorption on steel surface.

Adsorption Isotherm

One of the most convenient ways of expressing adsorption quantitatively and the type of bond formed is by deriving the adsorption isotherm that characterizes the metal/

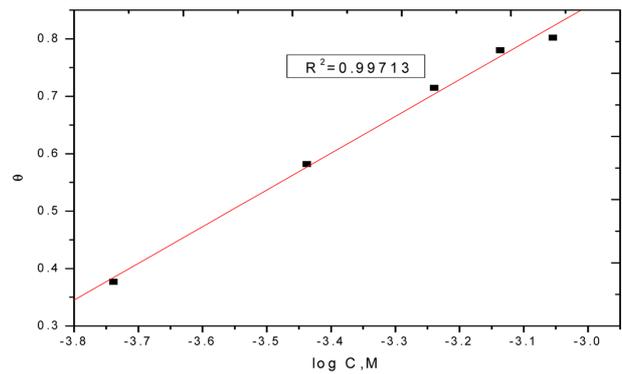


Figure 2. Temkin adsorption isotherm plotted as θ vs. $\log C$ of cinnamon for the corrosion of steel in sulfide polluted salt water.

inhibitor/environment system.¹³ 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 extract on the steel surface follow Temkin adsorption isotherm. The strong correlation ($R^2 = 0.996$) for the Temkin adsorption isotherm plot confirmed the validity of this approach.

$$K_{ads}C = \exp(-2a\theta) \quad (2)$$

where a is molecular interaction parameter, θ is the degree of surface coverage, K_{ads} is the equilibrium constant of adsorption process and C is the inhibitor concentration. It is well known that the equilibrium constant of adsorption (K_{ads}) is related to the standard adsorption free energy (ΔG_{ads}°) and can be calculated by the following equation:¹⁴

$$K_{ads} = 1 / 55.5 \exp[-\Delta G_{ads}^\circ / RT] \quad (3)$$

The value of " a " is positive and equal to 2.77. This shows the presence of attraction between the adsorption layer.¹⁵ The relatively high and negative free energy value indi-

Table 1. The effect of concentration of cinnamon on the electrochemical parameters calculated by using potentiodynamic technique for corrosion of steel in sulfide polluted salt water at 25 °C

Conc., ppm	$-E_{corr}$, Vvs SCE	i_{corr} , $\mu A cm^{-2}$	$-\beta_c$, mV dec ⁻¹	β_a , mV dec ⁻¹	C.R mmy ⁻¹	θ	% IE
blank	1.056	11470	265	209	133.19	–	–
50	1.026	7146	254	200	83.00	0.377	37.7
100	1.001	4794	234	192	56.00	0.582	58.2
150	1.036	3272	228	188	35.00	0.715	71.5
200	1.025	2523	219	170	29.00	0.780	78.0
250	1.012	2271	210	159	26.00	0.802	80.2

icates a relatively strong and spontaneous adsorption of the extract components 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.¹⁶ The calculated values of $\Delta G_{\text{ads}}^{\circ}$ for the extract with the metal surface is $-34.1 \text{ kJ mol}^{-1}$, which means that the adsorption of extract components on steel surface is physically through electrostatic interaction between the inhibitor and the metal surface. The equilibrium constant is high and equal to $63.7 \times 10^2 \text{ M}^{-1}$. This indicates strong adsorption of extract components on the steel surface.

Electrochemical Impedance Spectroscopy (EIS) Measurements

Fig. 3 shows the Nyquist plot of steel in 3.5% NaCl and 16 ppm Na_2S in the absence and presence of different concentrations of extract was investigated by EIS method at 25 °C after 30 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 semicircle at low frequencies, indicating that the corrosion process was now under adsorption control, whereas at high frequencies a depressed, capacitive-like semicircle was observed, which correspond to a charge transfer-controlled corrosion process. According to Ramachandran,¹⁶ the film formed in the presence of cinnamon extract acts as a protective barrier against aggressive ions from the bulk solution. Thus, the corrosion process in the presence of the extract was under diffusion and charge transfer mixed mechanism. The EIS

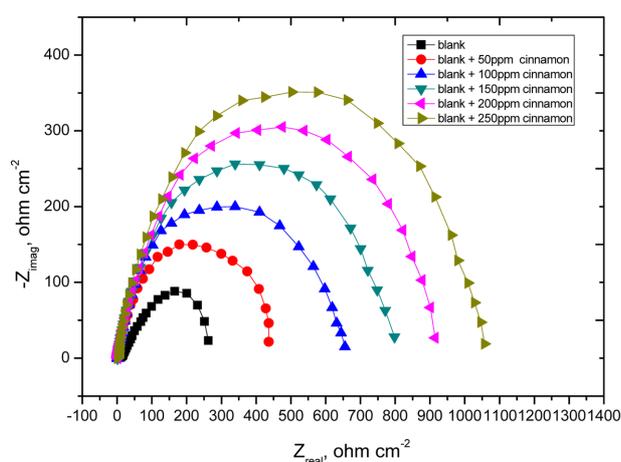


Figure 3. Nyquist plots recorded for steel in 3.5% NaCl + 16 ppm Na_2S with and without different concentrations of cinnamon at 25°C.

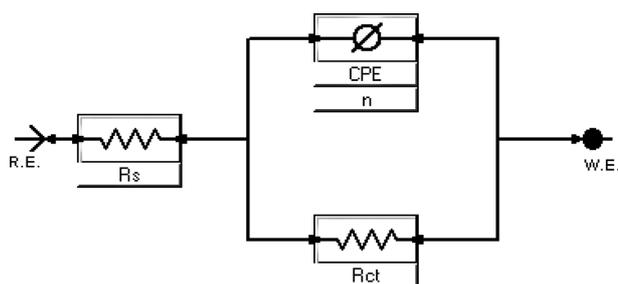


Figure 4. Electrical equivalent circuit used to fit the impedance spectra.

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 equation (4):

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}} \quad (4)$$

where f_{\max} is maximum frequency. The parameters obtained from impedance measurements are given in Table 2. It can see from Table 2 that the values of charge transfer resistance increase with inhibitor concentration.¹⁷ In the case of impedance studies, %IE increases with extract concentration. The impedance study confirms the inhibiting character of this extract obtained with potentiodynamic polarization methods. It is also noted that the C_{dl} values tend to decrease when the concentration of the extract 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.¹⁸

EIS data Table 2 shows that the R_{ct} values increase and the C_{dl} values decrease with increasing the extract concentration. This is due to the gradual replacement of water molecules by the adsorption of the extract molecules on the metal surface, decreasing the extent of dissolution reaction. The high R_{ct} values, are generally associated with slower corroding system.^{19,20} 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,²¹ suggested that the extract components function by adsorption

Table 2. Electrochemical kinetic parameters obtained by EIS technique for the corrosion of steel in 3.5% NaCl +16 ppm Na₂S alone and with different concentrations of cinnamon at 25 °C

Conc., ppm	$R_s \Omega \text{ cm}^2$	$C_{dl} \mu\text{Fcm}^{-2}$	n	$R_{ct} \Omega \text{ cm}^2$	θ	%IE
blank	1.294	605.5	0.886	150	–	–
50	1.127	564.4	0.876	243	0.382	38.2
100	1.113	475.6	0.845	370	0.593	59.3
150	1.142	337.6	0.881	526	0.715	71.5
200	1.135	324.7	0.891	700	0.785	78.5
250	1.112	312.5	0.828	803	0.813	81.3

at the metal/solution interface.

The inhibiting effect of this extract 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.

Electrochemical Frequency Modulation (EFM) Measurements

Intermodulation spectra obtained from EFM measurements are presented in *Figs. (5a–f)* as examples of steel in 3.5% NaCl + 16 ppm Na₂S containing different concentrations

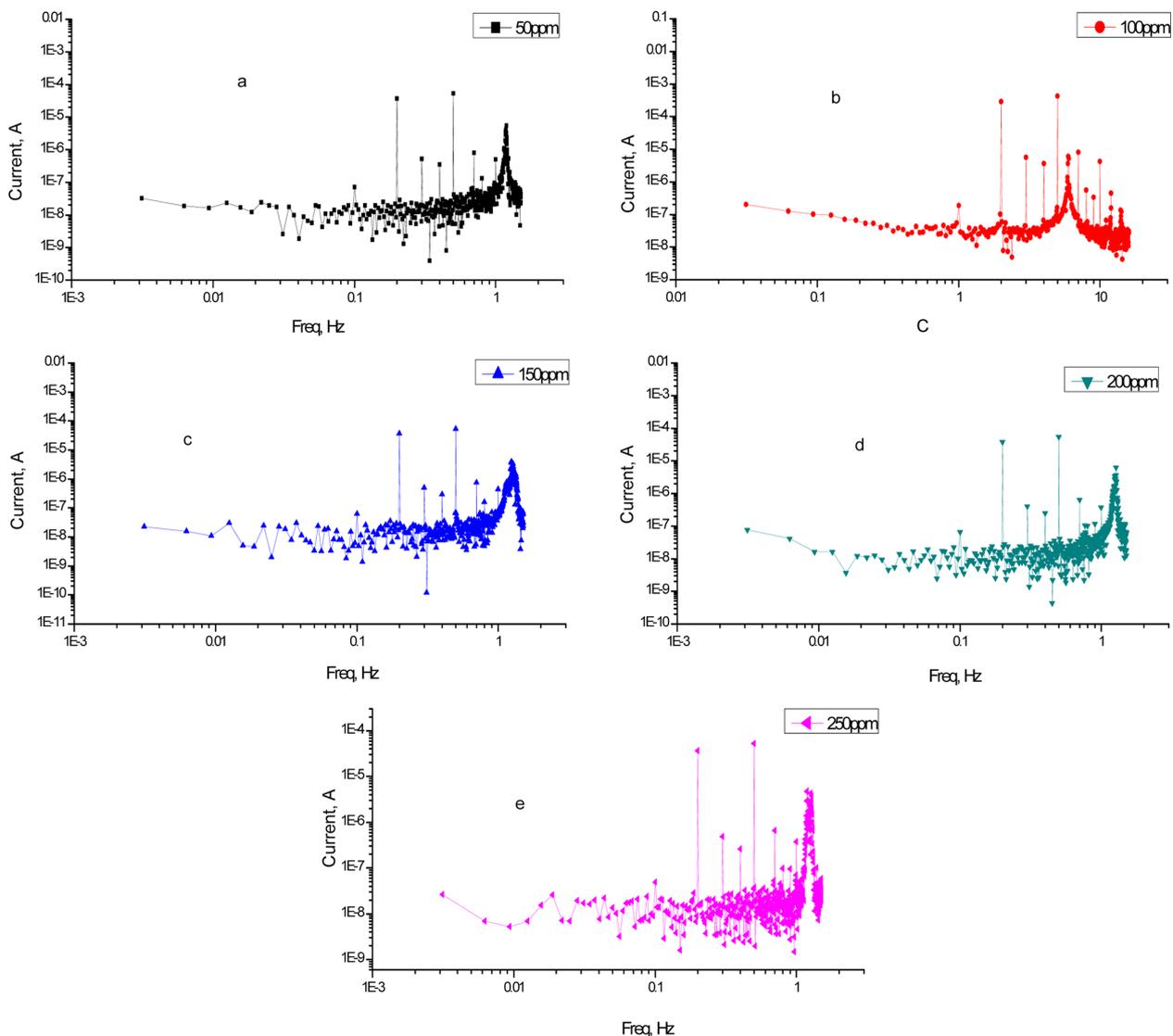
**Figure 5.** (a–f) Intermodulation spectrum for steel in 3.5% NaCl + 16 ppm Na₂S with various concentrations of cinnamon at 25 °C.

Table 3. Electrochemical Kinetic parameters obtained by EFM technique for steel in 3.5% NaCl +16ppm Na₂S alone and with different concentrations of cinnamon at 25 °C

Conc., ppm	i_{corr} , $\mu\text{A cm}^{-2}$	β_a , mV dec^{-1}	β_c , mV dec^{-1}	CF-2	CF-3	C.R, mmy^{-1}	Θ	% IE
blank	13540	278	241	1.85	2.85	140.31	–	–
50	8286	276	239	1.61	2.70	85.86	0.388	38.8
100	5375	270	236	1.68	2.72	55.70	0.603	60.3
150	3453	268	230	1.73	2.86	35.78	0.745	74.5
200	2830	263	229	1.86	2.87	29.33	0.791	79.1
250	2424	254	221	1.90	2.91	25.12	0.821	82.1

of cinnamon 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. The calculated corrosion kinetic parameters in the presence of 3.5% NaCl + 16 ppm Na₂S 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 3. 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.²² The obtained results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and EFM methods.

Biological Effect of Cinnamon on *Escherichia coli*

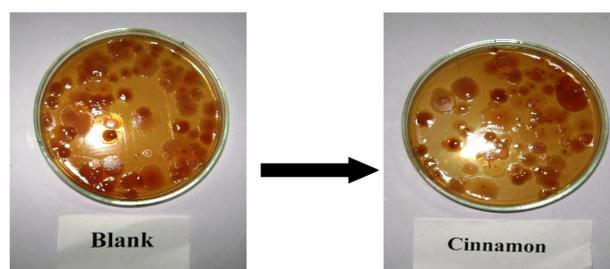
After the bacterial agriculture of *Escherichia coli* in the presence and absence of the inhibitor we found a little effect on the bacterial activity of *Escherichia coli* according to Table 4 and Fig. 6. Cinnamon is suggested that it have oxygen donor atoms attached with the proteins and lipids on the bacterial tissues surface making a little activity for it. So we found that this inhibitor has no toxicity on the bacterial activity, and can be applied on the waste water plants safely without any problems in treating waste water operations.

Mechanism of Corrosion Inhibition

The mechanism of corrosion inhibition of steel in acidic solution by the phytochemical compounds of the extract

Table 4. The results obtained from the plate counter for bacterial agriculture

Samples	CFU (R1)	CFU (R2)	CFU (mean)
Control	89×10^4	95×10^4	92×10^4
Cinnamon	81×10^4	84×10^4	83×10^4

**Figure 6.** Bacterial agriculture in the absence and presence of plant extract inhibitor.

can be explained on the basis of adsorption on the metal surface. This indicates that the inhibition efficiency of the extract is due to the presence of some or all of the above listed phytochemical constituents. The adsorption of the extract molecules on the steel surface is due to the donor - acceptor interaction between - electrons of donor atoms O and aromatic rings of inhibitors and the acceptor, i.e., vacant d orbital of iron surface atoms.²³ The inhibitor molecules can also be adsorbed on the metal surface in the form of negatively charged species which can interact electrostatically with positively charged metal surface, which led to increase the surface coverage and consequently protect efficiency even in the case of low inhibitor concentration. Eddy and Ebenso²⁴ also stated that saponins, tannins and alkaloids are active constituents of most green inhibitors.

CONCLUSIONS

Cinnamon plant extract acts as good inhibitor for corrosion of steel in sulfide polluted salt water.

The inhibition efficiency increases with increasing the concentration of the extract. The potentiodynamic polarization data indicated that this extract is mixed type inhibitor and is adsorbed on steel surface obeying Temkin adsorption isotherm. EIS measurements suggest that this extract inhibits the steel dissolution by adsorption at steel surface thereby causing the decrease in C_{dl} values and increasing

R_{ct} values. This extract has no biological effect on the activity of *Escherichia coli*, so it can be applied safely on waste water treatment plants.

The results obtained from different electrochemical techniques are in good agreement.

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REFERENCES

1. El-Etre, A. Y. *J. Coll. Interf. Sci.* **2007**, *314*, 578.
2. El-Etre, A. Y. *Appl. Surf. Sci.* **2006**, *252*, 8521.
3. Benabdellah, M.; Benkaddour, M.; Hammouti, B.; Bendahhou, M.; Aouniti, A. *Appl. Surf. Sci.* **2006**, *252*, 6212.
4. Chaieb, E.; Bouyanzer, A.; Hammouti, B.; Benkaddour, M. *Appl. Surf. Sci.* **2005**, *246*, 199.
5. Müller, B. *Corros. Sci.* **2002**, *44*, 1583.
6. Li, Y.; Zhao, P.; Liang, Q.; Hou, B. *Appl. Surf. Sci.* **2005**, *252*, 1245.
7. El-Etre, A. Y.; Abdallah, M.; El-Tantawy, Z. E. *Corros. Sci.* **2005**, *47*, 385.
8. Bouyanzer, A.; Hammouti, B.; Majidi, L. *Mater. Lett.* **2006**, *60*, 2840.
9. El-Etre, A. Y. *Corros. Sci.* **2003**, *45*, 2485.
10. Ammar, I. A.; Darwish, S. *Corros. Sci.* **1967**, *7*, 679.
11. Fisher, H. *Ann. Univ. Ferrera. Sez. 3 (Suppl. 3)*, **1960**, 1.
12. Stupnisek-Lisac, E.; Gazivoda, A.; Madzarac, M. *J. Electrochim. Acta* **2002**, *47*, 4189.
13. Szklarska-Smiałowska, Z. *Electrochemical and Optical Techniques for the Study of Metallic Corrosion*; Kluwer Academic: The Netherlands, 1991; p 545.
14. Khamis, E. *Corrosion* **1990**, *46*, 476.
15. Ramachandran, S.; Tsai, M.; Blanco, M.; Chen, H.; Tang, W. A. *Langmuir* **1996**, *12*, 6419.
16. Oguzie, E. E. *Corros. Sci.* **2007**, *49*, 1527.
17. Larabi, L.; Benali, O.; Mekelleche, S. M.; Harek, Y. *J. Appl. Surf. Sci.* **2006**, *253*, 1371.
18. Lagrenee, M.; Mernari, B.; Bouanis, B.; Traisnel, M.; Bentiss, F. *Corros. Sci.* **2002**, *44*, 573.
19. Bessone, J.; Mayer, C.; Tuttnier, K.; Lorenz, W. J. *Electrochim. Acta* **1983**, *28*, 171.
20. Epelboin, I.; Keddou, M.; Takenouti, H. *J. Appl. Electrochem.* **1972**, *2*, 71.
21. Khaled, K. F. *Electrochim. Acta* **2008**, *53*, 3484.
22. Abdel-Rehim, S. S.; Khaled, K. F.; Abd-Elshafi, N. S. *Electrochim. Acta* **2006**, *52*, 3269.
23. Eddy, N. O.; Ebenso, E. E. *Afri. J. Pure Appl. Chem.* **2008**, *2*, 46.