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METHANOLIC EXTRACT OF CURCUM PLANT AS A GREEN CORROSION INHIBITOR FOR STEEL IN NACL POLLUTED SOLUTIONS

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ABSTRACT

The effect of curcum plant extract on the corrosion of steel used in sanitation treatment plants in 3.5% NaCl and 16 ppm Na_2S was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The results obtained showed that the curcum extract is a good inhibitor for steel in NaCl polluted solutions Potentiodynamic polarization curves indicated that the curcum extract behaves as mixed-type inhibitor with predominant cathodic effect. EIS measurements showed that the dissolution process of steel occurs under activation control and the inhibition is due to the adsorption of the extract on the metal surface. Thermodynamic consideration reveals that adsorption of curcum extract on steel surface is spontaneous and occurred according to Temkin adsorption isotherm. Physical adsorption mechanism has also been proposed for the adsorption of the inhibitor. The biological study of the extract on *Escherichia coli* activity shows that this extract is safety for applying in sanitation plants

KEYWORDS : Steel, *Curcum*, Eis, Green Inhibitor, *Escherichia coli*, NaCl Polluted Solution

The use of inhibitors is one of the most practical methods for protection against corrosion1. Among numerous inhibitors that have been tested and applied industrially as corrosion inhibitors, those that are non-toxic or low-toxic are now far more strategic than in the recent past. In the 21st century, the research in the field of green or eco-friendly corrosion inhibitors has been addressed toward the goal of using cheap, effective compounds at low or zero environmental impact. Plant extract is low-cost and environmental safe, and so the main advantage of the using plant extract as corrosion inhibitor is due to both economic and environmental benefits. Up to now, many plant extracts have been used as effective corrosion inhibitors of iron or steel in acidic media (Ekpe et al., 1994). Although many synthetic compounds show good anticorrosive activity, most of them are highly toxic to both human beings and the environment, and they are often expensive and non-biodegradable. Thus, the use of natural products as corrosion inhibitors has become a key area of research because plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that are biodegradable in nature and can be extracted by simple procedures with low cost. 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. Several studies have been carried out on the inhibition of corrosion of metals by plant extracts (Trabanelli, 1991; Maheshwari et al., 2001; Manohari et al., 2001; Prithiba, 2003). Earlier, some worker showed that the actual inhibitors in the plant extracts are usually alkaloids and other organic nitrogen bases, as well as carbohydrates, proteins and their acid hydrolysis products.

In this direction the present study is aimed at investigating the inhibitive and adsorption properties of curcum extract obtained from methanolic destructive distillation of curcum plant for the corrosion of steel in 3.5% NaCl + 16 ppm Na_2S by different electrochemical methods, and also showing its biological effect on *Escherichia coli* activity.

Experimental

Material Composition of The Sample

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.

Preparation of Plant Extract

The present investigation was carried out using the

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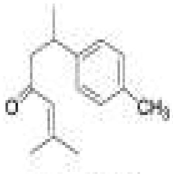
plant namely *Curcum*. The uses parts were the bark and the rhizomes of *Curcum*. The sample were purchased from the local market and ground into a fine powder to give 500 g of powdered materials which extracted separately by soaking at room temperature for six hours with methanol (5L), then the methanolic 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.

Preparation of Bacterial Agriculture Media

Suspend 50g 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.

Solutions

The aggressive solutions of 3.5 % NaCl and 16 ppm Na_2S was prepared by dissolving the required amount of salts in bidistilled water. All chemicals were analytical-grade reagents. The experiments were carried out under non-stirred and naturally aerated conditions. The addition of the extract did not change the pH of the aggressive media.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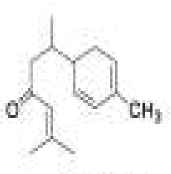
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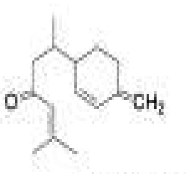
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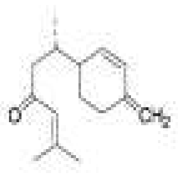
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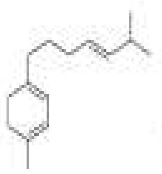
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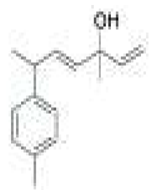
Curcumene


CURCUMIN *Diferuloyl methane*


DEMETHOXY CURCUMIN *p-Hydroxy-cinnamoyl-feruloyl-methane*


BISDEMETHOXY CURCUMIN *pp'-Dihydroxy-dicinnamoyl-methane*

Electrochemical Procedure

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 abraded with different grades of emery papers (800 to 1200 grades), 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 foil counter (1 cm^2) 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 extract, as environmentally-friendly corrosion inhibitor. 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, using a water thermostat. 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. Electrochemical frequency modulation was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1s. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (βc and βa) and the causality factors CF-2& CF-3 Bosch et al., 2001 and Szklarska-

Smiaiowska, 1999.

All electrochemical experiments were carried out using Potentiostat/Galvanostat/Zra analyzer (Gamry PCI300/4). A personal computer with DC 105 software for polarization, EIS 300 software for impedance, EFM140 software for electrochemical frequency modulation and Echem Analyst 5.21 was used for data fitting and calculating.

RESULTS AND DISCUSSION

Potentiodynamic Polarization Measurements

Polarization measurement is an important research tool in the investigation of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and the kinetics of corrosion phenomena on the metal deposition. Figure 1 shows the potentiodynamic polarization curves of steel in sulfide polluted salt water without and with different concentrations of *Curcum* extract at 25°C. The obtained electrochemical parameters; cathodic and anodic Tafel slopes (βc and βa) respectively, corrosion potential (E_{corr}), corrosion current density (i_{corr}), and corrosion rate (C.R.) were obtained and are listed in Table 1. The degree of surface coverage; θ, and inhibition efficiency (% IE) were calculated from Eq. (1):

%IE = θ x 100 = [1(i_{corr}(inh)/i_{corr})] (1) where icorr and i_{corr} (inh) are the corrosion current densities of uninhibited and inhibited solutions, respectively. An inspection of the results obtained from Table 1 reveals that, the presence of different concentrations of the extract reduce the anodic and cathodic current densities by decreasing the hydrogen evolution and the metal dissolution. A similar displacement of cathodic and anodic Tafel lines indicated that the extract inhibited both the hydrogen evolution and the metal dissolution process. Thus this inhibitor acted as a mixed type inhibitor. Tafel slopes of βa and βc for steel in the presence of the inhibitor change uniformly. This behaviour indicated that the molecules are adsorbed on both the anodic and cathodic sites, acting as a mixed type of inhibitor (Figure, 1). No significant change in E_{corr} values also supported the mixed behaviour of the inhibitor.

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. The % IE was found to increase with increasing the inhibitor concentration.

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. 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 extract is shown in Figure, 2 which gives a straight line relationship suggests that the adsorption of the extract on the steel

Table 1 : Effect of concentration of curcum on the electrochemical parameters calculated using potentiodynamic technique for corrosion of steel in sulfide polluted salt water at 25°C

Conc., ppm	$-E_{corr}$, V vs SCE	i_{corr}, mA cm^{-2}	$-\beta_c$, mV dec^{-1}	β_a, mV dec^{-1}	C.R mmy^{-1}		% IE
Blank	1.056	11.470	265	209	133.19	------	-----
50	0.976	7.077	250	200	95.42	0.383	38.3
100	0.962	5.093	230	189	59.00	0.556	55.6
150	0.986	3.739	220	172	43.42	0.674	67.4
200	0.975	2.764	210	160	35.82	0.759	75.9
250	0.962	2.592	211	149	31.43	0.774	77.4

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

Temkin isotherm		
a	K_{ads}, M^{-1}	$-\Delta G^o_{ads}$, kJ mol^{-1}
2.89	5659	30.9

Table 3 : Electrochemical Kinetic Parameters Obtained by EIS Technique For The Corrosion of Steel in 3.5 % NaCl +16 ppm Na_2S alone and with different concentrations of *Curcum* at 25°C

Conc., ppm	R_s Ω cm^2	C_{dl} μFcm^{-2}	n	R_{ct} Ω cm^2	θ	% IE
blank	1.294	605.5	0.886	150	----	----
50	1.154	575.4	0.836	243	0.385	38.5
100	1.123	435.6	0.854	343	0.563	56.3
150	1.157	402.8	0.878	473	0.682	68.2
200	1.162	334.5	0.825	634	0.763	76.3
250	1.123	330.4	0.876	702	0.786	78.6

Table 4 : Electrochemical Kinetic Parameters Obtained By EFM Technique For Steel in 3.5 % NaCl +16 ppm Na_2S Alone $_a$nd With Different Concentrations of *Curcum* at 25°C

Concentration, ppm	$i_{corr.}$, mA cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	C.R, mmy^{-1}	θ	% IE
blank	13.540	278	241	1.85	2.85	140.31	------	------
50	8.151	277	240	1.63	2.68	84.47	0.398	39.8
100	5.795	273	237	1.67	2.71	60.10	0.572	57.2
150	4.279	269	232	1.73	2.82	44.34	0.684	68.4
200	3.141	265	230	1.83	2.91	32.55	0.768	76.8
250	2.789	258	225	1.82	2.93	28.90	0.794	79.4

surface follow Temkin adsorption isotherm. The strong correlation ($R^2 = 0.996$) for the Temkin adsorption isotherm plot confirmed the validity of this approach. Temkin isotherm is given as in Eq. (3):

$$K_{ads}C = \exp(-2a\theta) \quad (3)$$

where a is molecular interaction parameter, θ is the degree of surface coverage, Kads is the equilibrium constant of adsorption process and C is the inhibitor concentration. It is well known that the equilibrium constant of adsorption (Kads) is related to the standard adsorption free energy (ΔG°ads) and can be calculated from equation (4):

$$K_{ads} = 1/55.5 \exp[-\Delta G^{\circ}_{ads}/RT] \quad (4).$$

Table, 2 shows the calculated values of molecular interaction a, equilibrium constant of adsorption process, Kads and free energy (ΔG°ads) obtained from Temkin plot. The value of 'a' are positive shows that attraction exists in adsorption layer. The relatively high and negative free energy values may indicate a relatively strong and spontaneous adsorption of the investigated extract 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. The calculated values of ΔG°ads, for the investigated extract with the metal surface is -30.9 kJ mol^{-1}, which means that the adsorption of extract is physically through electrostatic interaction between the extract and the metal surface.

Electrochemical Impedance Spectroscopy (EIS)

Figure, 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 investigated extract was investigated by EIS method at 25°C after 30 min immersion. 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, 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. The film formed in the presence of curcum extract acts as a protective barrier against

Table 5 : Results Obtained From the Plate Counter for Bacterial Agriculture

Samples	CFU (R1)	CFU (R2)	CFU (mean)
Control	89 X 104	95 X 104	92 X 104
Curcum	85×10^4	87×10^4	86×10^4

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 data were simulated using equivalent electric circuits as shown in Figure, 4 where RS represents the solution or electrolyte resistance, Cdl the double layer capacitance, Rct 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 Cdl can be calculated from equation (5):

$$C_{dl} \quad \frac{1}{2 \quad f_{max} \, R_{ct}} \qquad (5)$$

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. In the case of impedance studies, % IE increases with inhibitor concentration in the presence of investigated extract. The impedance study confirms the inhibiting characters of this extract obtained with potentiodynamic polarization method. It is also noted that the Cdl values tend to decrease when the concentration of this extract increases. This decrease in Cdl, 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.

EIS data Table, 3 shows that the Rct values increase and the Cdl 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 Rct values, are generally associated with slower corroding system. The decrease in the Cdl can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer, suggested that the inhibitor molecules function by adsorption 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)

Intermodulation spectra obtained from EFM measurements are presented in Figure, 5 as examples of steel in 3.5% NaCl + 16 ppm Na_2S containing different concentrations of curcum 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 + 16 ppm Na_2S alone and with different concentrations of the investigated inhibitor at 25°C (i_{corr}, βa, βc, 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. The obtained results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and EFM methods.

Biological Effect of Curcum on *Escherichia coli*

After the bacterial agriculture of *Escherichia coli*

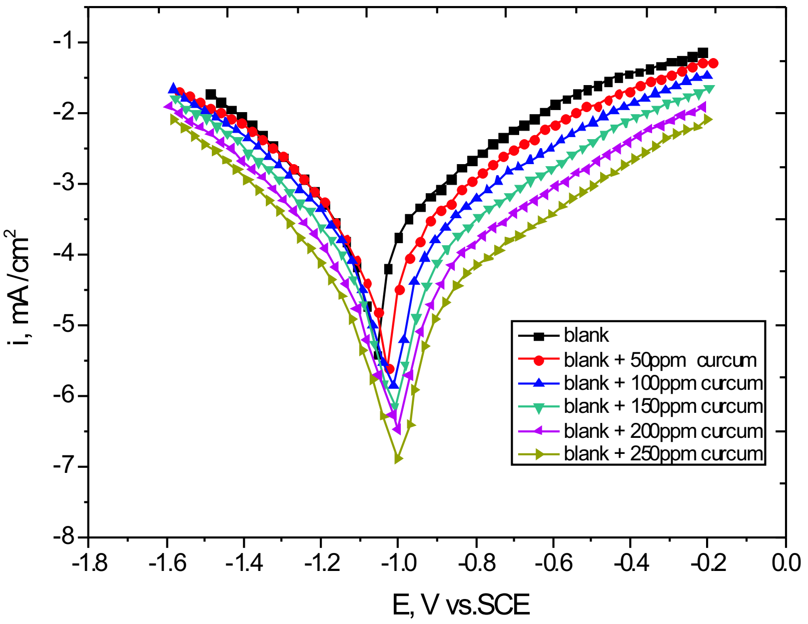

Figure 1 : Potentiodynamic polarization curves for the corrosion of steel in 3.5% NaCl + 16 ppm Na_2S in the absence and presence of different concentrations of *Curcum* at 25°C

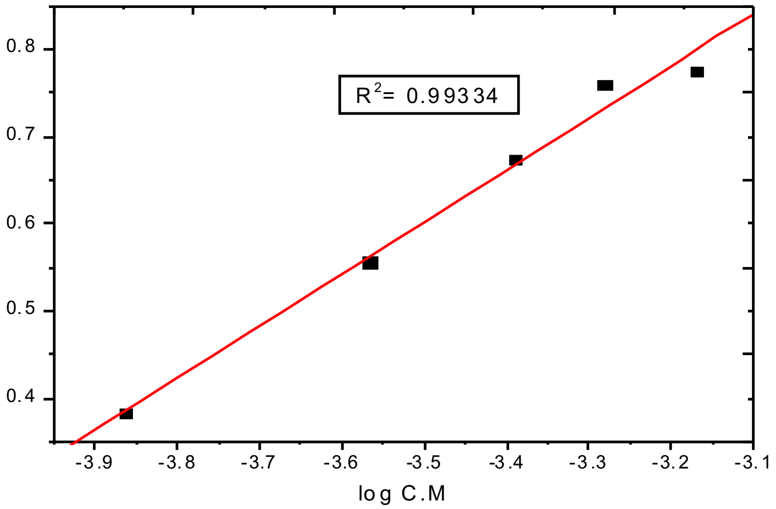

Figure 2 : Temkin adsorption isotherm plotted as θ vs. log C of *Curcum* for the corrosion of steel in sulfide polluted salt water

in the presence and absence of the inhibitor we found a little effect on the bacterial activity of *Escherichia coli* according to Table 5 and Figure, 6. *Curcum* 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 isotherm depicted in Figure, 2 characterizes the spontaneous physisorption of phytochemical composition of *Curcum* extract on heterogeneous surfaces32. Thus, the mechanism of corrosion inhibition of steel in NaCl polluted solution by the phytochemical compounds of the extract can be explained on the basis of adsorption on the metal surface. This indicates that the

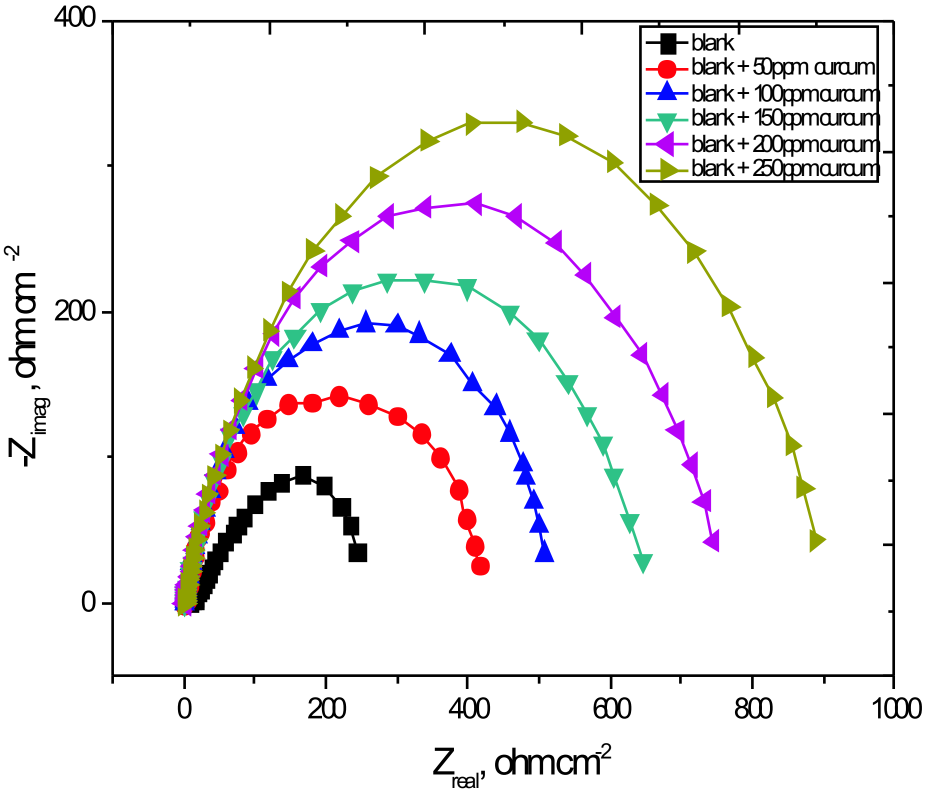

Figure 3 : Nyquist plots recorded for steel in 3.5% NaCl + 16ppm Na_2S with and without different concentrations of *Curcum* at 25°C

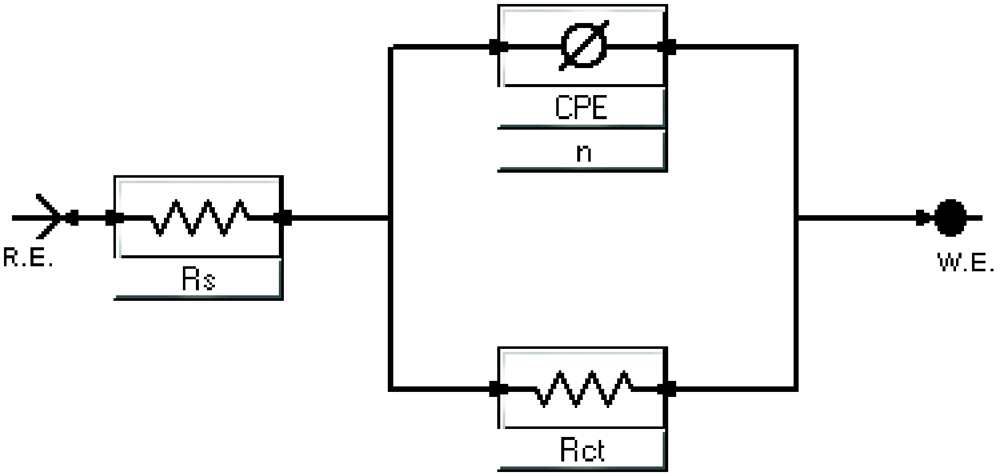

Figure 4 : Electrical Equivalent Circuit Used to Fit Impedance Data

inhibition efficiency of the extract is due to the presence of some or all of the above listed phytochemical constituents. The adsorption of the inhibitor molecules on the steel surface is due to the donor - acceptor interaction between π electrons of donor atoms and aromatic rings of inhibitors and the acceptor, i.e., vacant d orbital of iron surface atoms. 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 extract concentration. As reported before, sapponins,

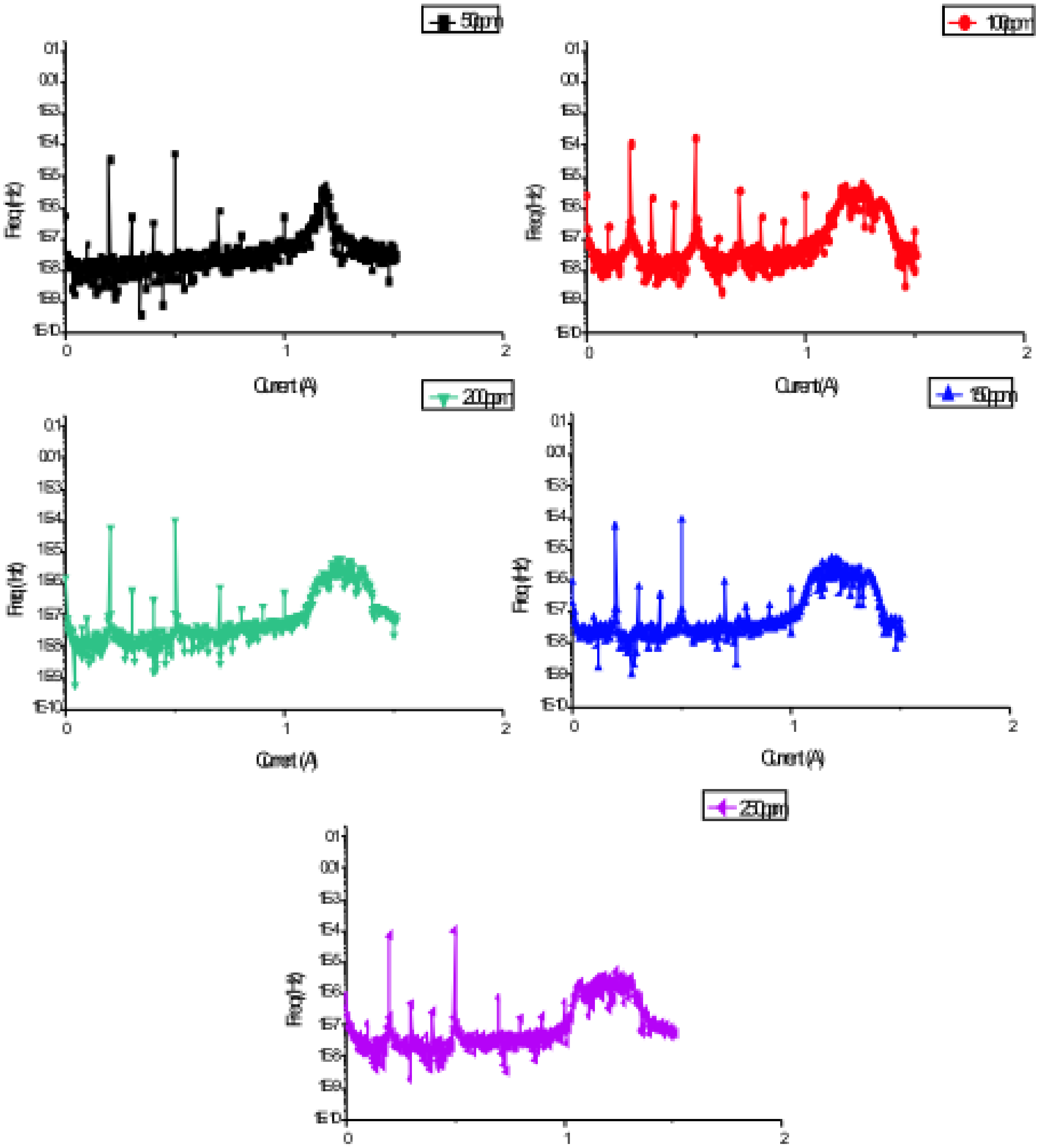

Figure 5 : Intermodulation Spectrum for Steel in 3.5 % NaCl + 16 ppm Na_2S With Various Concentrations of *Curcum* at 25°C

tannins and alkaloids are active constituents of most green inhibitors.

CONCLUSION

Based on the above results, the following conclusion can be drawn:

- Methanolic extract of *Curcum* plant was found to be an efficient inhibitor for the corrosion of steel in NaCl polluted solutions.
- Inhibition efficiency increased with an increase in curcum extract content.
- The corrosion process is inhibited by adsorption of the curcum extract on the steel surface following the Temkin adsorption isotherm. This indicates that the inhibition effect of the extract is due to adsorption of some or all the listed phytochemical constituents.

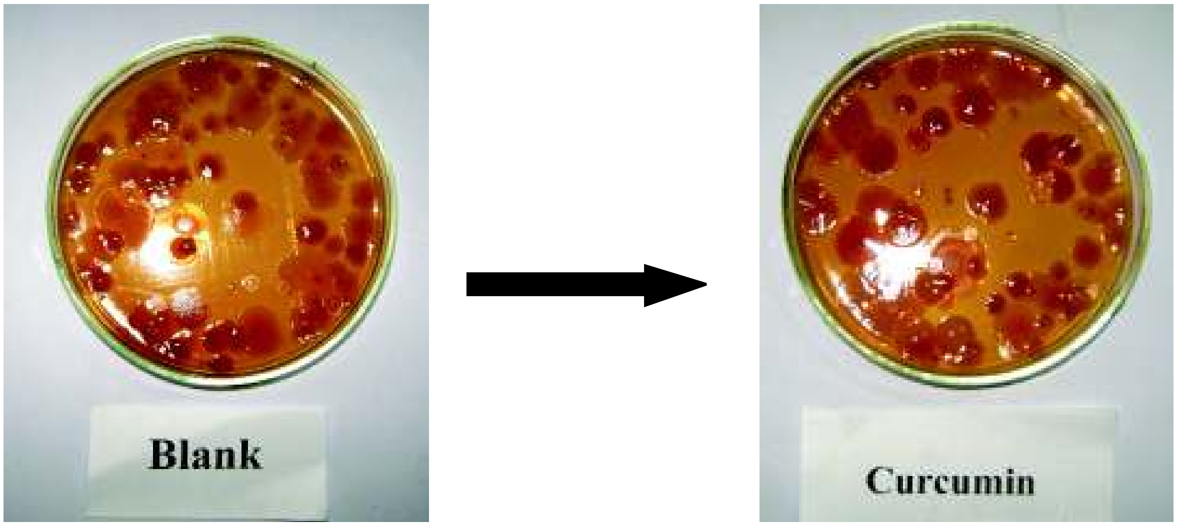

Figure 6 : Bacterial Agriculture in the Absence And Presence of Plant Extract Inhibitor

- Adsorption of methanolic extract of *Curcum* extract on the surface of the steel is spontaneous and occurs by physical adsorption.
- The negative free energy (-ΔG°ads) of adsorption indicates strong and spontaneous adsorption of the *Curcum* extract on the steel surface.
- Values of Tafel constant βa and βc confirm that the *Curcum* extract acts like mixed type inhibitor.
- Increase in R_p and R_{ct} values and decrease in i_{corr} and C_{dl} values confirm that the *Curcum* extract is adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption.
- The inhibition efficiencies determined by different electrochemical methods are in reasonable good agreement.
- Thus the *Curcum* extract was proved to be an effective eco friendly and low cost inhibitor.
- This inhibitor has no effect on the biological activity of *Escherichia coli*, and can be applying safety on sanitation plants.

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