

Abd El-Aziz S.Fouda<sup>1\*</sup>, Ayman Y. El-Khateeb<sup>2</sup>,  
Nabila M. Elbahrawi<sup>1</sup>

<sup>1</sup>El-Mansoura University, Department of Chemistry, Faculty of Science, El-Mansoura, Egypt, <sup>2</sup>Mansoura University, Department of Agric. Chemistry, Faculty of Agriculture, Mansoura, Egypt

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## Cupressus sempervirens extract as green inhibitor for corrosion of carbon steel in hydrochloric acid solutions

### ABSTRACT

The effect of an aqueous extract of *Cupressus sempervirens* on the corrosion manner of carbon steel in 1M hydrochloric acid solution has been measured by mass reduction, hydrogen evolution, electrochemical frequency modulation (EFM), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The efficiency of *Cupressus sempervirens* extract was examined with increasing dose of the extract and the temperature. The parameters of thermodynamic of corrosion and adsorption processes were measured and discussed. The extract was adsorbed on surface of metal chemically and was obtain obey Temkin isotherm. The potentiodynamic polarization resulted lead to the extract is mixed inhibitor type. The results given from the various methods were in best agreement.

**Keywords:** *Cupressus sempervirens*, corrosion inhibition, carbon steel, adsorption, HCl.

### 1. INTRODUCTION

Hydrochloric acid solution in oil fields is recommended as the low cost way to calcium carbonate dissolved, CaCO<sub>3</sub>, diagram in the pipelines under most system. Accordingly, corrosion inhibitors must be added with the solution of hydrochloric acid to prevent the destructive effect of acid on the surface of the pipelines [1]. Carbon steel has been best way for employed as a construction material for pipe study in the gas and oil production such as flow lines and transmission pipelines and down-hole tubular [2]. Several workers have been obtained on the utilized of natural organic products as corrosion inhibitors in various medium [3-12]. Most of the natural organic products are biodegradable, nontoxic and readily obtain in adequate quantities. Different section of the seeds of plants [13,14]. Fruits [15], leave [16] and flowers were extracted and used as corrosion inhibitors [17-22].

The aim for this paper is to obtain a naturally occurring, and low cost environmentally safe substance that could be utilized for corrosion inhibiting of metal surface. The utilized of such extract will simultaneously establish environmental and economic goals. In this piece of research, we report the inhibition action of *Cupressus sempervirens* extract against the corrosion of carbon steel in hydrochloric acid solutions.

\*Corresponding author: Abd El-Aziz S. Fouda

E-mail: asfouda@hotmail.com

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### 2. EXPERIMENTAL

#### 2.1. Weight loss measurements

Coupons were obtain from carbon steel sheet with a composition (in weight %) of C0.20, Mn 0.35, P 0.024, Si 0.003 and Fe is the rest. Specimens divided into 2.0 cm x 2.0 cm x 0.2 cm dimensions were used for weight loss measurements. The electrolyte was 1 M HCl solution prepared utilized bidistilled water. All chemicals reagents were analytical-grade. The extract was given by water infusion: A 5 g of dried and crushed leaves was added to a beaker with 100 mL of bidistilled water that was freshly heated then to sit for 30 min off the heat. After extraction, the sample was filtered with filter paper, the amount was lyophilized, and the plant extract was stored to the time for analysis. The experiments were obtained under naturally aerated and non-stirred conditions. The dose range of the *Cupressus sempervirens* extract utilized was varied from 50 to 300 ppm, and 100 mL of electrolyte was utilized for each run. After various time immersion half hours to three hours, the carbon steel samples were obtain and washed with bidistilled water then dried. The mass reduction was done on an analytical balance with a precision of 0.1 mg. The mass reduction data are used to measure the corrosion rate (CR) in millimeter per year (mmy<sup>-1</sup>) by the relation:

$$CR = \frac{K \times \Delta W}{D \times A \times t} \quad (1)$$

Where, K is a constant and equals to 8.76X10<sup>4</sup>, ΔW is the weight loss (mg), D is the mild steel

density ( $\text{g/cm}^3$ ),  $A$  is the exposure area of the specimen ( $\text{cm}^2$ ). Also, the degree of surface coverage ( $\theta$ ) and the surface Inhibition efficiency (%IE) was calculated from:

$$\%IE = 100 \times \theta = 100 \times [(W_0 - W) / W_0] \quad (2)$$

Where  $W_0$  and  $W$  are the data of the average mass loss with and without various extract, respectively.

## 2.2. Hydrogen evolution

Carbon steel sample with size  $2 \times 2 \times 0.2$  cm were utilized for the experiments of hydrogen evolution. Prior to each experiment, the surface of carbon sample were abraded with various grades of emery papers degreased with acetone and rinsed by bidistilled water. The specimen was inserted in a beaker having a capacity of 100 ml. evolved hydrogen gas was collected. It allowed measurement of the variation of the volume of hydrogen evolved during dissolution of the metal as a function of time. The experiments were done in presence and absence of the various doses of the extract. The corrosion rate ( $r$ ) was taken as the slope of straight line obtained from the relation between volume of evolved hydrogen and time.

## 2.3. Electrochemical methods

Electrochemical measurements were done by utilized a conventional three-electrode cylindrical glass cell at a temperature of  $25^\circ\text{C}$ . The working electrode was a carbon steel of above composition of  $1 \text{ cm}^2$  area and the rest being wrapped by utilized commercially obtainable epoxy resin.

EFM performed utilized two frequencies 20 and 50 mHz. The base frequency was 10 mHz. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 2 and 5 Hz.

(EIS) Electrochemical impedance method was carried out utilized signals AC of 1 V amplitude peak-to-peak in the range of frequency of 100 kHz to 5 mHz. The impedance curves are obtain in the Bode and Nyquist representation.

The cathodic and anodic polarization plots were given separately from -70 to 70 mV at a scan rate  $1 \text{ mVs}^{-1}$ . The above procedures were repeated for each dose of the extract. The electrochemical study were done by utilized a computer-controlled

instrument, The corrosion penetration rate (CR) in millimeter per year ( $\text{mm yr}^{-1}$ ) is calculated from the following equation [21]:

$$CR = [k \times a \times I / D \times V] \quad (3)$$

Where,  $k$  is a constant equals to 0.00327 when expressing corrosion penetration rate in millimeter per year ( $\text{mm yr}^{-1}$ ),  $a$  is the mass atomic of iron,  $I$  is the corrosion current density ( $\mu\text{A cm}^{-2}$ ),  $D$  is the carbon steel density ( $\text{g/cm}^3$ ), and  $V$  is the valence entered in the Tafel dialogue box. With:  $3270 = 10 \times [1 \text{ year (in seconds)} / 96497.8]$  and  $96497.8 = 1 \text{ Faraday in coulombs}$ . The % IE<sub>p</sub> was calculated from:

$$\%IE_p = 100 \times [1 - (I_{corr}^0 / I_{corr})] \quad (4)$$

Where,  $I_{corr}^0$  and  $I_{corr}$  are the current densities corrosion of without and with solution, respectively.

## 2.4. Surface examination

The surface morphology and vitality of energy dispersive X-ray (EDX) examination of carbon steel samples after weight reduction estimations in 1 M HCl in the nonattendance and nearness of 300 ppm Cupressus sempervirens concentrate were considered utilizing checking electron magnifying instrument (Jeol JSM-T20, Japan) outfitted with an Oxford Inca vitality scattering spectrometer framework. The working specimen was broke down at five distinct areas to guarantee reproducibility.

## 3. RESULTS AND DISCUSSION

### 3.1. Weight loss measurements

The weight loss of carbon steel specimens immersed into 1 M HCl, in absence and presence of different doses of Cupressus sempervirens extract, was investigated after different immersion times (30-180 min) at different temperature ( $25-45^\circ\text{C}$ ) only weight-loss curve at  $25^\circ\text{C}$  illustrated in Figure 1. The % IE values at different temperatures are shown in Table 1. The results showed that the presence of Cupressus plant extract suppresses the corrosion rate of the carbon steel specimens in 1M HCl solution. It was noted that the % IE rise with the rising of plant extract doses.

Table 1 Effect of various doses of Cupressus extract on the corrosion rate coverage surface ( $\theta$ ) and (%IE) inhibition efficiency of metal in 1M hydrochloric acid solution at different temperatures

Tabela 1. Uticaj različitih doza ekstrakta Cupressus na brzinu korozije pokrivene površine ( $\theta$ ) i (% IE) efikasnost inhibicije metala u 1M rastvora hlorovodonične kiseline na različitim temperaturama

[inh] ppm	25°C		35°C		45°C	
	$\theta$	%IE	$\theta$	%IE	$\theta$	%IE
0.0	---	---	---	---	---	---
50	0.525	52.5	0.570	57.0	0.624	62.4
100	0.604	60.4	0.648	64.8	0.698	69.8
150	0.664	66.4	0.706	70.6	0.752	75.2
200	0.700	70.00	0.747	74.7	0.795	79.5
250	0.739	73.9	0.776	77.6	0.826	82.6
300	0.765	76.5	0.806	80.6	0.845	84.5

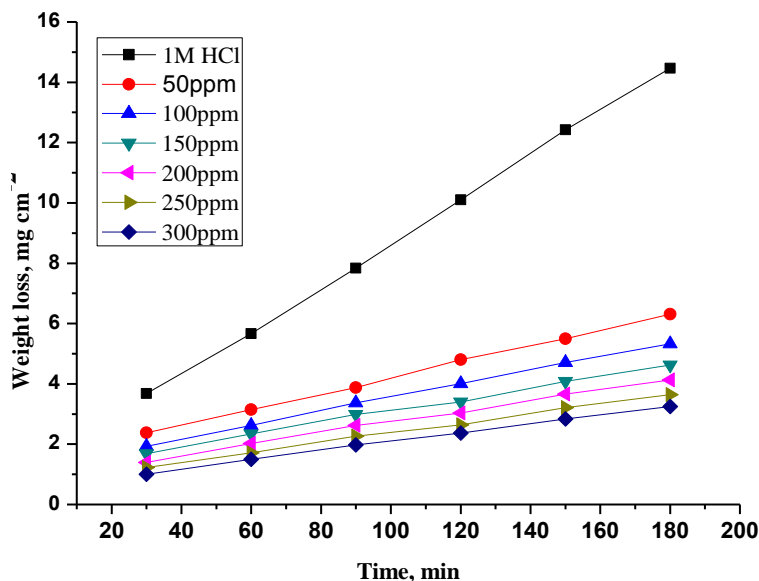
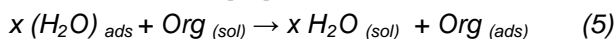


Figure 1. Time mass reduction curves for the dissolution of carbon steel in without and with various doses of Cupressus extract at 25°C

Slika 1. Krive rastvaranja ugljeničnog čelika bez i sa različitim dozama ekstrakta Cupressus na 25°C

3.1.1. Adsorption isotherms

The estimations of surface coverage  $\theta$  for various doses of the concentrated on extract at various temperatures have been utilized to illustrate the best isotherm to decide the adsorption procedure. The adsorption of extract particles on the surface of carbon steel electrode is viewed as substitutional adsorption process between the natural organic compound in aqueous phase ( $Org_{aq}$ ) and the  $H_2O$  molecules adsorbed on the aluminum surface [23]:



where,  $x$  = the ratio of size proportion, that is, the quantity of  $H_2O$  particles supplanted by one inhibitor atom. Endeavors were made to fit  $\theta$  qualities to different isotherms including Frumkin, Langmuir, Temkin and Freundlich isotherms.

By a wide margin the result were best fitted by Temkin adsorption isotherm. Plotting  $\theta$  Vs.  $\log C$  gave a line straight with unit slope data (Figure 2) lead to that the adsorption of extract atoms on surface of carbon steel obeys Temkin adsorption isotherm. From these outcomes one can hypothesizes that there is no cooperation between the adsorbed species.

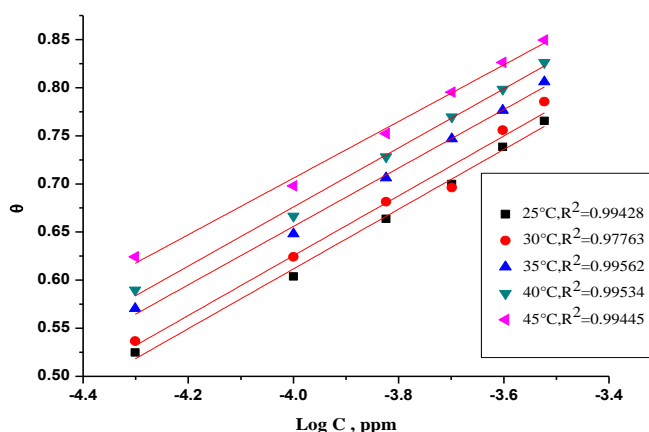


Figure 2. Curve fitting of corrosion data obtained from weight loss method for carbon steel without and with various doses of the investigated Cupressus extract to Temkin adsorption isotherm at different temperatures

Slika 2. Fitovane krive korozije dobijene iz postupka smanjenja težine ugljeničnog čelika, bez i sa različitim dozama ispitivanog ekstrakta Cupressus za Temkinove adsorpcione izoterme na različitim temperaturama

### 3.1.2. Temperature Effect

The clear energy of activation  $E_a^*$ , the enthalpy of activation  $\Delta H^*$  and the entropy  $\Delta S^*$  for the consumption of carbon steel in HCl arrangement in the nonattendance and nearness of various groupings of plants concentrates of plants extracts can be obtained from the following equations:

$$\text{Rate or } (k_{\text{corr}}) = A e^{(-E_a^*/RT)} \quad (6)$$

Equation for Transition-state:

$$\text{Rate or } (k_{\text{corr}}) = [RT/Nh e^{(\Delta S^*/R)} \exp^{(-\Delta H^*/RT)}] \quad (7)$$

Where, A = the frequency factor, h = the Planck's constant and N = Avogadro's number. A plot of  $\log k_{\text{corr}}$  against  $1/T$  and  $\log (k_{\text{corr}}/T)$  versus  $(1/T)$  obtain lines straight with a slope of  $(-\Delta H^*/2.303R)$  and  $(-E_a^*/2.303R)$ , respectively. The intercepts will be  $(\log R/Nh + \Delta S^*/2.303R)$  and A for Arrhenius and transition state equations, respectively.

The test results can be deciphered as interpreted as follows:

- Figure 3 speaks to  $\log$  rate versus  $1/T$  plots and Figure 4 speaks to  $\log (\text{rate}/T)$  versus  $1/T$  curves. The got estimations of activation energy,  $E_a^*$ , entropies,  $\Delta S^*$  and enthalpies,  $\Delta H^*$  are arranged in Tables 2.
- The lower in  $E_a^*$  with rise extract concentration in Table 2 is typical of chemisorption. The activation energy is lower in the presence of

Cupressus sempervirens extract than in its absence, this was due to lower rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at temperatures higher according to Hoar and Holliday [24]. But, Riggs and Hurd [25] explained that the lower in the activation energy of corrosion at levels higher of inhibition arises from a shift of the net corrosion reaction from the uncovered part of the metal surface to the covered one. Schmid and Huang [26] found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but the reaction rate on the covered area is substantially less than on the uncovered area similar to the present study.

- The signs +ve of the enthalpies ( $\Delta H^*$ ) reflect the endothermic nature of the steel dissolution process.
- The entropy of activation in presence and nonappearance of the inhibitor was extensive and negative. This infers the activated complex in the rate determining step represents association rather than dissociation, indicating that a decrease in disorder takes place, going from reactant to the activated complex [27].

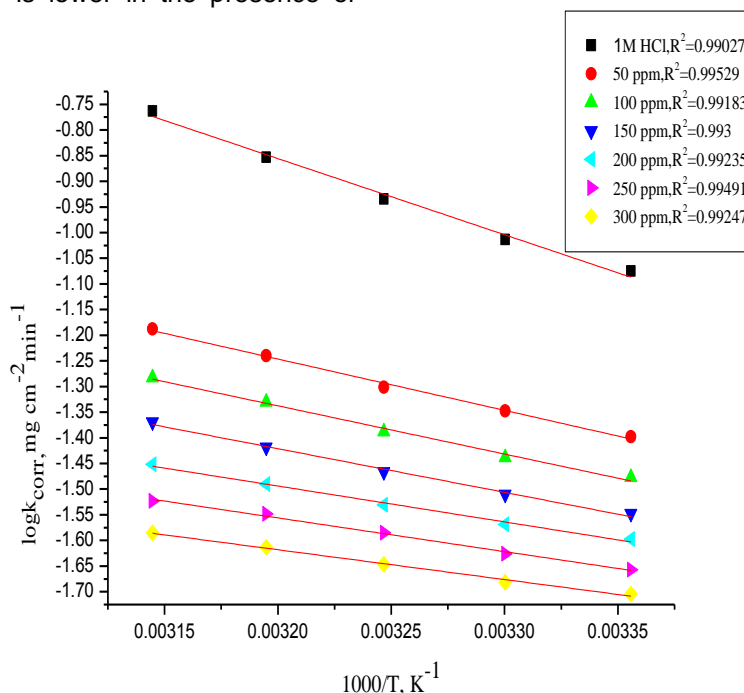


Figure 3: Arrhenius diagram for corrosion rates ( $k_{\text{corr}}$ ) for carbon steel without and with various doses of the investigated Cupressus extract in 1M HCl

Slika 3. Arrhenius dijagram za brzinu korozije ugljeničnog čelika, bez i sa različitim dozama ispitivanog ekstrakta Cupressus u 1M HCl

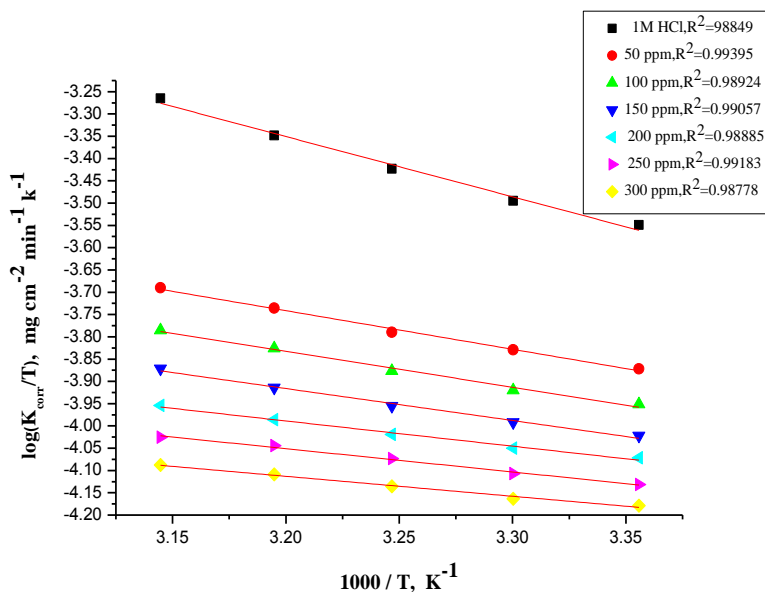


Figure 4:  $\log(k_{corr}/T)$  versus  $(1000/T)$  transition diagram of carbon steel without and with various doses of the investigated Cupressus extract in 1M HCl

Slika 4.  $\log(k_{corr}/T)$  prema  $(1000/T)$  prelazni dijagram ugljeničnog čelika, bez i sa različitim dozama ispitivanog ekstrakta Cupressus u 1M HCl

Table 2: Activation parameters for carbon steel without and with various doses of the investigated Cupressus extract in 1M HCl

Tabela 2. Parametri aktivacije za ugljenični čelik, bez i sa različitim dozama ispitivanog ekstrakta Cupressus u 1M HCl

[inh] ppm	Activation parameters			
	$A \times 10^3$ mg cm <sup>-2</sup> min <sup>-1</sup>	$E_a^*$ kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>
0.0	292.8	38.1	15.4	148.8
50	0.090	19.1	6.6	220.6
100	0.046	18.0	6.1	225.8
150	0.02	16.3	5.6	230.9
200	0.0055	13.4	5.2	235.4
250	0.0035	12.6	4.5	241.7
300	0.0017	11.1	3.9	241.7

3.2. Gasometric method

The disintegration response of carbon steel in 1M HCl without and containing distinctive doses of Cupressus sempervirens was contemplated utilizing hydrogen development strategy. The relationship between the volume of hydrogen developed amid the corrosion response and the reaction time is spoken to in Figure 5.

Investigation of the figure uncovers that, there is a straight connection between hydrogen volume and time. The rate of hydrogen liberated is little

toward the start of the response then after certain time it increments notably. The initial time interval, through which the rate of response is little, is the hatching time frame. During this incubation period, the breakdown of the pre-inundated oxide film on the metal surface happens before the begin of metal assault. Since carbon steel is promptly dissolvable in fluid acidic arrangements with the freedom of hydrogen the rate of hydrogen evolved compares to carbon steel corrosion rate. Along these slope lines, the slope of the straight portion of the diagram, after the incubation time period, were taken as calculate of the corrosion rates of carbon steel in free and inhibited acid solutions. Assessment of the bends of Figure 5 uncovers that the expansion of Cupressus sempervirens decreases the rate of hydrogen released as the Cupressus fixation is expanded.

Table 3. Inhibition efficiencies as revealed from hydrogen evolution measurements at 25° C.

Tabela 3. Efikasnost inhibicije izmereno pri izdvajanju vodonika na 25° C.

[inh] ppm	Corrosion rate(ml/min)	%IE
Blank (1M HCl)	27.9	----
50	9.4	66.3
100	8	71.3
150	7.4	73.5
200	6.2	77.8
250	4.9	82.4
300	3.8	86.4

The estimations of inhibition effectiveness of various concentrations of extract are given in Table 3. These qualities demonstrate that the IEs of the

Cupressus sempervirens are high at high concentrated and practically identical with those got from weight reduction method [28].

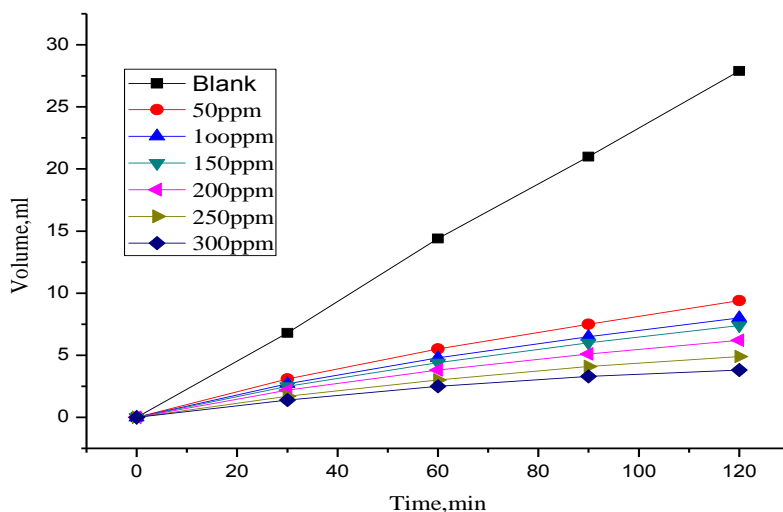


Figure 5: Evolution of Hydrogen during corrosion of carbon steel without and with various doses of the investigated Cupressus extract in 1M HCl

Slika 5. Izdvajanje vodonika tokom korozije ugljeničnog čelika, bez i sa različitim dozama ispitivanog ekstrakta Cupressus u 1M HCl

### 3.3. Potentiodynamic polarization technique

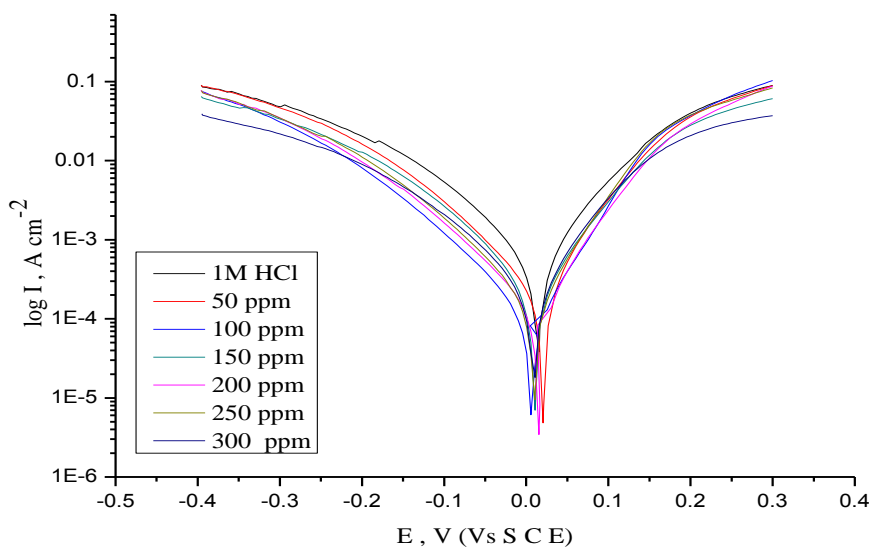


Figure 6. Shows normal anodic and cathodic Tafel polarization bends for carbon steel in 1 M HCl in absence and presence of different doses of Cupressus sempervirens.

Slika 6. Anodne i katodne Tafelove polarizacione krive za ugljenični čelik u 1M HCl, bez i sa različitim dozama ispitivanog ekstrakta Cupressus

The estimations of cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) Tafel constants were figured from the direct region of the polarization bends. The corrosion density current ( $I_{corr}$ ) was resolved from the crossing point of the straight parts of the cathodic bends with the stationary consumption potential ( $E_{corr}$ ). The

percentage inhibition efficiency (%IE) was calculated using the following equation:

$$IE\% = 100 \times [1 - (I_{corr,add}/I_{corr,free})] \tag{8}$$

Where,  $I_{corr,free}$  and  $I_{corr,add}$  are the current densities in the absence and presence of inhibitors,

respectively. Table 4 shows the impact of the inhibitor focuses on the activation energy parameters, for example,  $\beta_a$ ,  $\beta_c$ ,  $E_{corr}$ ,  $I_{corr}$  and % IE from the outcomes given in Table 4 the accompanying perception could be drawn:

(a) The Tafel lines are moved to more positive and negative potential for anodic and cathodic processes, respectively, in respect to the clear bend. This implies the plant influence both cathodic

and anodic processes. However the data suggested that the plant extract acts as chemical type inhibitor [29] (b) the estimations of  $E_{corr}$  change gradually to less negative qualities (i.e. nearly remain constant) and the estimations of  $I_{corr}$  decrease. (c) The inhibitor particles found in the aqueous extract block the corrosion sites. (d) The estimation of IEs increments indicating the inhibiting effect of the extract.

Table 4. The effect of various doses of Cupressus sempervirens extract on the free corrosion potential  $E_{corr}$ , corrosion current density,  $I_{corr}$ , Tafel slopes ( $\beta_a$ ,  $\beta_c$ ), Inhibition efficiency %IE and corrosion rate  $k_{corr}$  for the corrosion of carbon steel in 1 M HCl

Tabela 4. Efekat različitih doza ekstrakta Cupressus na korozioni potencijal  $E_{corr}$ , koroziju gustine struje,  $I_{corr}$ , Tafelove nagibe ( $\beta_a$ ,  $\beta_c$ ), efikasnost inhibicije % IE i brzinu koroziju  $k_{corr}$  za koroziju ugljeničnog čelika u 1M HCl

[inh] ppm	$-E_{corr.}$ mV vs. SCE	$i_{corr.}$ $\mu A cm^{-2}$	$\beta_c$ , mV dec <sup>-1</sup>	$\beta_a$ , mV dec <sup>-1</sup>	$k_{corr}$ , mpy	$\theta$	% IE
0.0	516	550	115	85	251.4	-	-
50	506	258	112	84	117.9	0.530	53.0
100	501	230	106	100	104.9	0.582	58.2
150	491	179	110	70	81.74	0.675	67.5
200	489	149	113	71	67.99	0.729	72.9
250	495	127	112	65	57.94	0.769	76.9
300	455	81	116	111	37.26	0.852	85.2

### 3.4. EIS tests

The equivalent electrical circuit model utilized for this system is shown below Figures 7 where  $R_{ct}$  = charge transfer resistance,  $R_s$  = resistor and  $R_s$ =resistance of solution, and  $C_{dl}$  represents the double layer capacitance [30]. The protection efficiency (%  $\eta_{EIS}$ ) and ( $\theta$ ) of the extract have been obtaining from the resistance of charge transfer data utilized the following equation:

$$\% \eta_{EIS} = \theta \times 100 = 100 \times [(R_{ct} - R_{ct}^*) / R_{ct}^*] \quad (9)$$

Where  $R_{ct}^0$  is the charge transfer resistance in the HCl, and  $R_{ct}$  is the charge transfer resistance in the presence of the extract. The interfacial double layer capacitance ( $C_{dl}$ ) values were computed from the impedance value and the higher ( $R_{ct}$ ) values, are generally associated with slower corroding system [31,32] by the following equation:

$$C_{dl} = 1 / 2\pi R_{ct} f_{max} \quad (10)$$

where  $f_{max}$  = maximum frequency (Hz)

EIS method was utilized to decide and to give us kinetic information and important mechanistic for the examined electrochemical system. Nyquist and Bode Figure 8 and Figure 9 impedance curves given form the C-steel electrode in acid solution at room temperature in vicinity and absence of different doses of Cupressus sempervirens extract. The presence of single capacitive loop both in the

presence and absence of extract. The Nyquist of extract curves from different semicircles is non-perfect as expected from the EIS theory which due to disappear of frequency [33], impurities, electrode heterogeneity resulting from surface from inhibitor adsorption, roughness of surface, dislocations, formation of grain boundaries and porous layers. Impedance values were calculated utilizing the circuit in Figure 7, in which  $R_{ct}$  = the charge transfer resistance,  $R_s$  = the electrolyte resistance.

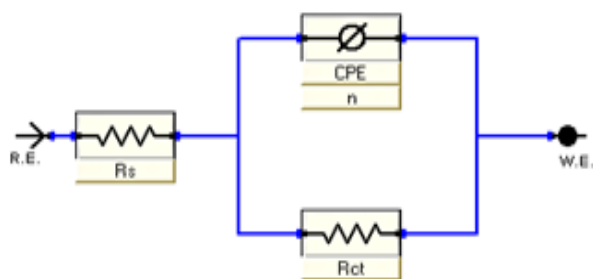


Figure 7. Equivalent circuit model utilized to fit the spectra of impedance

Slika 7. Model ekvivalentne šeme korišćen da odgovara spektru impedancije

The information acquired from spectra fitted is written in Table 5. The data in Table 5 demonstrates that the estimations of  $R_{ct}$  increment and the estimations of  $C_{dl}$  decrease with raise the doses of extract.

Table 5. Resulted from electrochemical impedance measurements for corrosion of carbon steel in 1M HCl solutions at various concentrations of Cupressus sempervirens at 25°C

Tabela 5. Rezultat elektrohemijske impedance za koroziju ugljeničnog čelika u 1M HCl pri različitim koncentracijama ekstrakta Cupressus na 25°C

[inh]. ppm	$C_{dl}$ $\mu F cm^{-2}$	$R_{ct}$ $\Omega cm^2$	$\theta$	% $\eta$
0.0	720.40	13.62	-	-
50	203.20	22.29	0.389	38.9
100	192.10	29.55	0.539	53.9
150	188.50	40.17	0.661	66.1
200	164.20	43.91	0.689	68.9
250	162.30	63.99	0.787	78.7
300	90.10	139.20	0.902	90.2

Diminish in  $C_{dl}$  and increment in  $R_{ct}$  data due to the decreased on dielectric constant (because of the continuous replacement of water molecules by the surfactant molecules on the steel surface) [34]. The %  $\eta_{EIS}$  given by EIS estimations are in great agreement with that given from potentiostatic polarization tests. The difference of efficiency for inhibition by two methods may be related to the variation in electrode surface status in different methods.

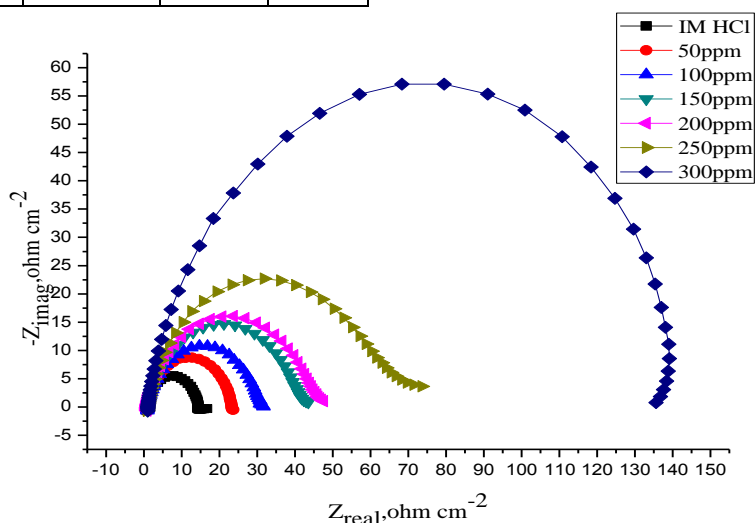


Figure 8. Nyquist plots showing effect of increments concentration of Cupressus extract on corrosion of carbon steel in 1M HCl solutions

Slika 8. Nyquist krive pokazuju efekat povećanja koncentracije Cupressus ekstrakt na koroziju ugljeničnog čelika u 1M HCl

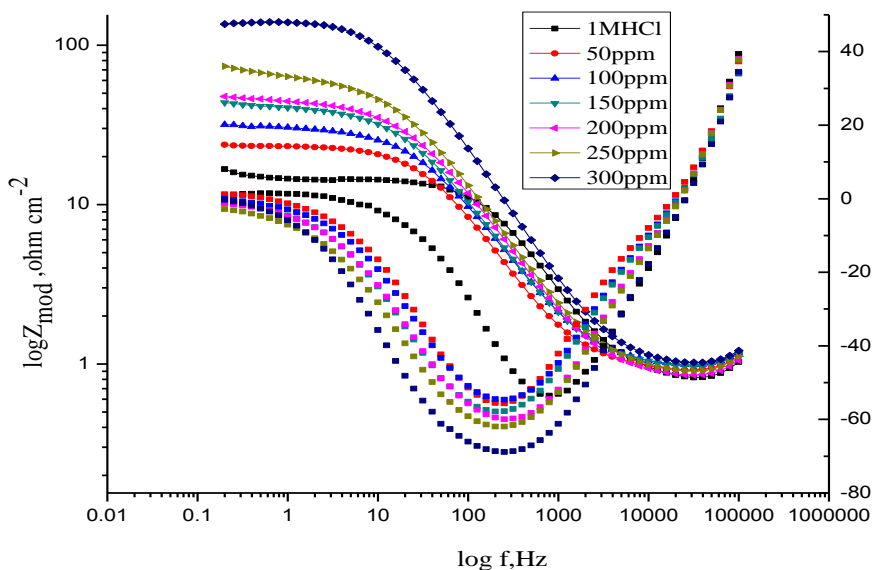


Figure 9. Bode plot for corrosion of carbon steel in 1M HCl without and with various dose of Cupressus extract at 25°C

Slika 9. Krive korozije ugljeničnog čelika u 1M HCl bez i sa različitim dozama ekstrakta Cupressus na 25°C



3.5. EFM test

EFM can be utilized as a fast and non-destructive experimental for rate of corrosion technique without prior knowledge of Tafel constants [35]. The %  $\eta_{EFM}$  was calculated using the equation

$$\% \eta_{EFM} = 100 \times [1 - (i_{corr} / i_{corr}^0)] \quad (11)$$

Where,  $i_{corr}^0$  and  $i_{corr}$  are corrosion current densities in the absence and presence of the inhibitor, respectively. The good EFM strength is causality factors, which act as an internal check on the validity of the EFM tests". The parameters of kinetic from EFM such as the (CF-2 and CF-3) causality factors, the ( $i_{corr}$ ) corrosion density current and ( $\beta_a$  and  $\beta_c$ ) Tafel slopes are given in Table 6. The protection efficiency %  $\eta_{EFM}$  increases by

increasing the doses of investigated extract. The causality factors CF-2 and CF-3 are near to their theoretical data [36], showing that the calculated data are quality good. The measured protection efficiency given from mass reduction, EIS and potentiostatic polarization methods are great concurrence with that acquired from EFM technique. Figures 10 and 11 show representative examples for the spectra of intermodulation obtained from EFM tests without and with various doses of the Cupressus sempervirens extract. Each EFM spectrum is a current response as a function of frequency. It is necessary to note that between the peaks the current response is very little [35,36]. Corrosion kinetic parameters are listed in Table 6.

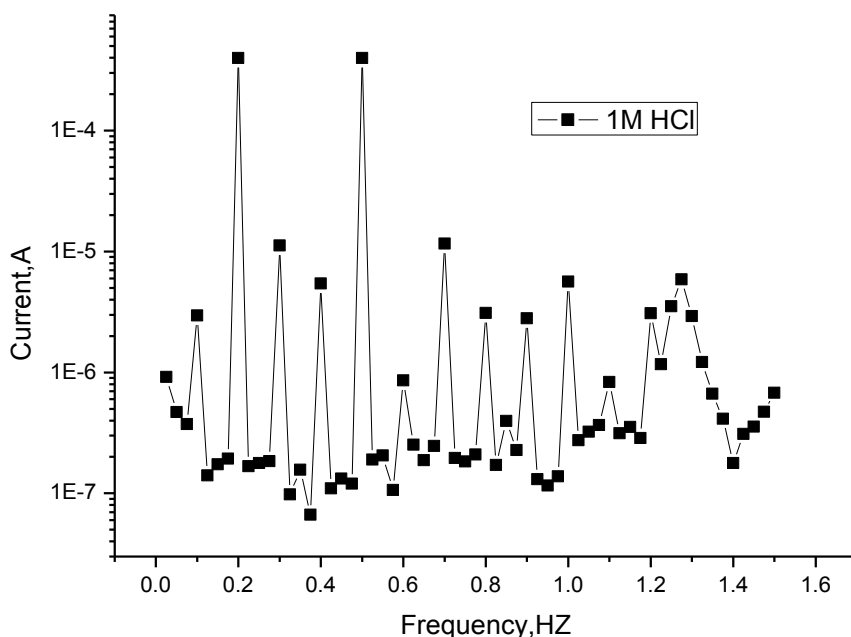


Figure 10. Intermodulation spectrum recorded for carbon steel in 1M HCl at 25°C  
Slika 10. Intermodulacijski spektar za ugljenični čelik u 1M HCl na 25°C

Table 6. Electrochemical kinetic parameters obtained by EFM technique for carbon steel in 1M HCl solutions containing various doses from the Cupressus sempervirens extract at 25°C

Tabela 6. Elektrohemijski kinetički parametri dobijeni EFM tehnikom za ugljenični čelik u 1M HCl sa različitim dozama ekstrakta Cupressus na 25°C

[inh]. ppm	$i_{corr}$ $\mu Acm^{-2}$	$\beta_a$ mVdec <sup>-1</sup>	$\beta_c$ mVdec <sup>-1</sup>	CF 2	CF 3	C.R mpy	$\theta$	% IE
0.0	809.7	109	142	1.3	2.8	370.0	-	-
50	409.1	82	96	1.7	2.9	186.9	0.495	49.5
100	278.6	84	101	1.8	3.1	127.3	0.656	65.6
150	261.4	91	100	1.4	3.2	119.4	0.677	67.7
200	246.9	77	94	1.7	3.1	112.8	0.695	69.5
250	233.2	75	89	1.9	3.4	106.6	0.712	71.2
300	203.2	92	98	1.6	2.6	92.8	0.749	74.9

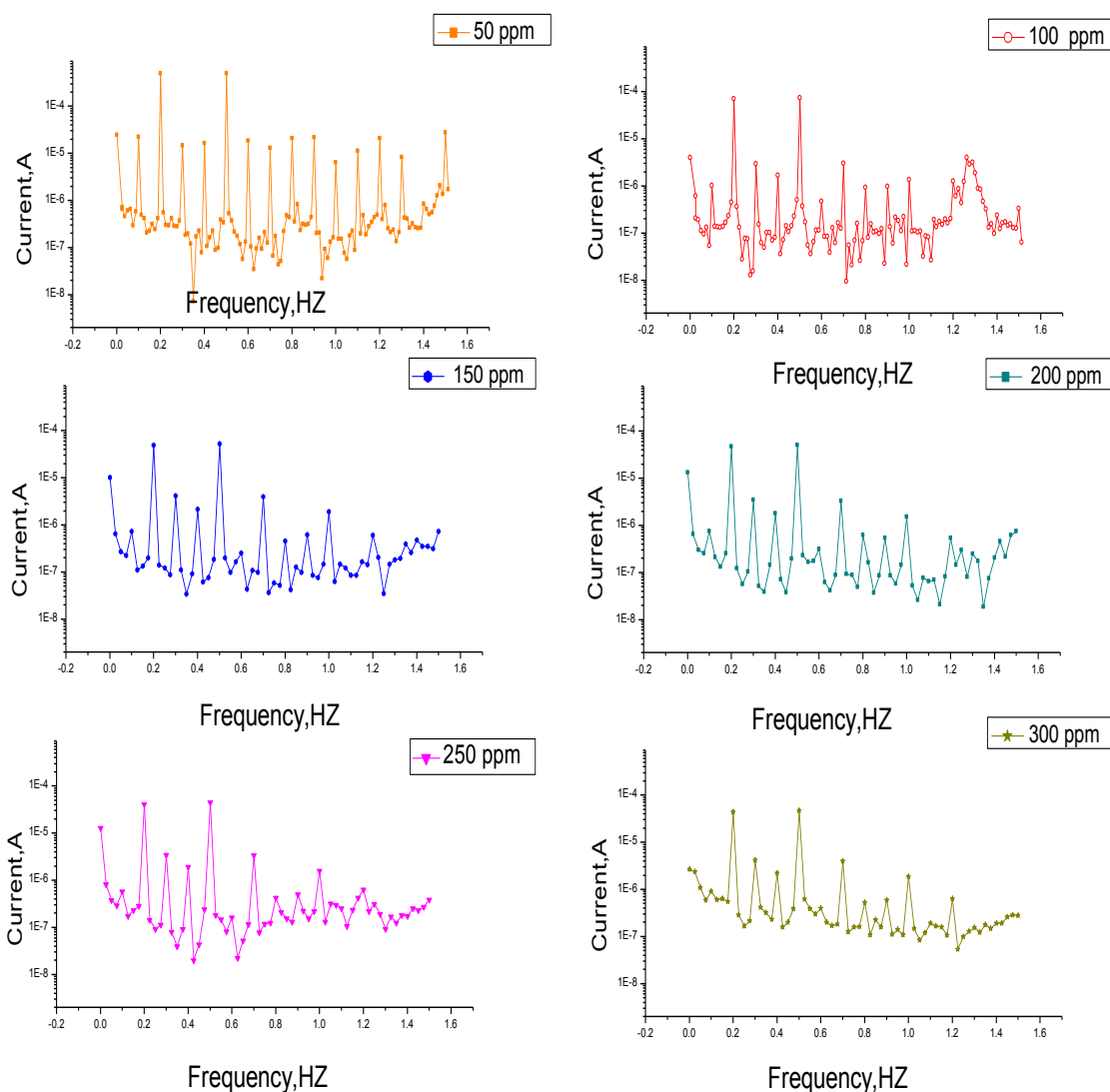


Figure 11. Intermodulation spectrums for recorded for carbon steel in 1M HCl in the without and with various doses (50-300 ppm) of Cupressus sempervirens extract at 25°C  
 Slika 11. Intermodulacijski spektri za ugljenični čelik u 1M HCl, bez i sa različitim dozama (50-300 ppm) ekstrakta Cupressus na 25°C

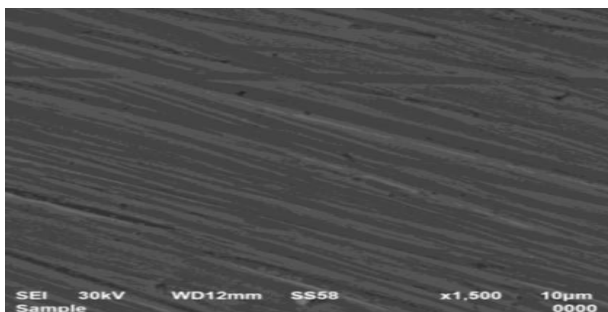
### 3.6. Scanning electron microscopy measurements

The morphology of the surface of the corroded carbon steel specimens was studied utilizing SEM after dipped in 1M HCl for 12 h. Figure 12-a shows the surface of pure carbon steel. Figure 12b-c represents the micrographs of carbon steel in 1M HCl in nonattendance and nearness of 300 ppm of Cupressus sempervirens extract. From Figure 12-b, the micrographs demonstrate a broad scratching made out of dark ranges. While with 300 ppm of the investigated extract, a protective film is formed on the surface of carbon steel as shown in Figure 12-c. This film gives off smooth and covers the whole surface of the sample without minor flaw. These features confirm the rise %IE given form Cupressus sempervirens extract.

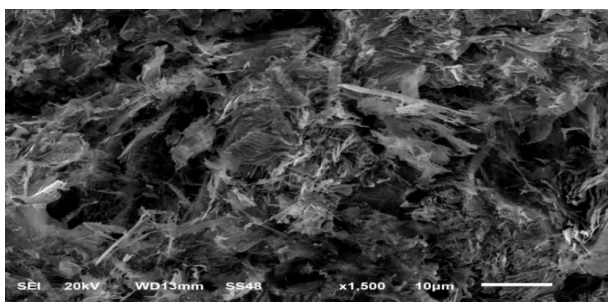
### 3.7. Energy dispersion spectroscopy (EDX) studies

“The goal of this section was to confirm the results obtained from chemical and electrochemical measurements that a protective surface film of inhibitor is formed on the electrode surface, the EDX spectra were employed to determine the elements on the surface of carbon steel after 12 hours immersion in test solution of 1M HCl without and with 300 ppm of extract, the EDX analysis in Figure 13-a shows the composition of pure surface of carbon steel specimen without any exposure to the acid and inhibitor treatment”. The component covered on the surface was observed by utilizing EDX spectra. Figure 13-b,c demonstrates the EDX investigation of metal steel in presence of inhibitor treatment and one molar hydrochloric acid. EDX

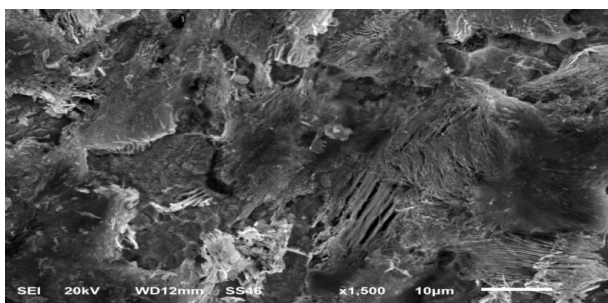
investigation demonstrates that just O and Fe were identified, which observed the presence of  $\text{Fe}_2\text{O}_3$  on passive film and depicts the EDX examination of steel in HCl just and with 300 ppm of Cupressus sempervirens extract. The additional new lines were observed from spectra, indicating the C presence (attributable to the carbon particles with Cupressus sempervirens extract).



a) Pure carbon steel  
a) Čist ugljeni čelik



b) 1M HCl



c) 1M HCl +300 ppm Cupressus sempervirens extract  
c) 1M HCl +300 ppm ekstrakt Cupressus

Figure 12. SEM micrographs for carbon steel in absence and presence of 300 ppm of Cupressus sempervirens extract

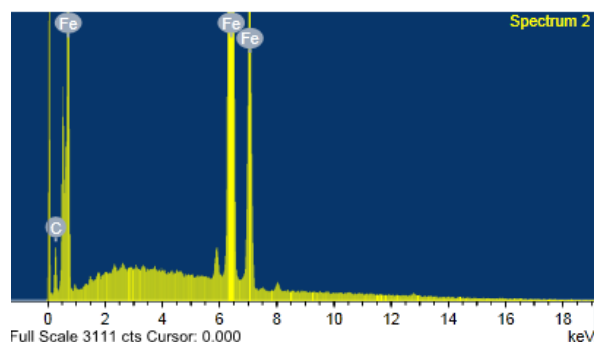
Slika 12. SEM mikrofotografije za ugljeni čelik u odsustvu i prisustvu 300 ppm ekstrakta Cupressus

These results confirm those from polarization tests which suggest that a surface film inhibited the metal dissolution, and hence retarded the evolution of hydrogen reaction. This surface film also raises the charge-transfer resistance of the anodic dissolution of carbon steel, as present as before. A comparable elemental distribution is shown in Table 7.

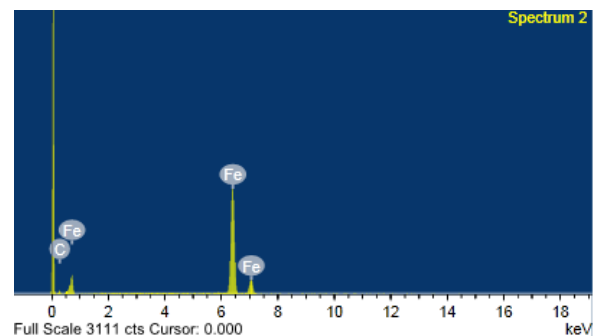
Table 7: Surface composition (weight %) of carbon steel after 12 hours immersion in HCl without and with 300 ppm of Cupressus sempervirens extract

Tabela 7. Površinski sastav (tež. %) ugljeničnog čelika nakon 12 sati potapanja u 1M HCl bez i sa 300 ppm ekstrakta Cupressus

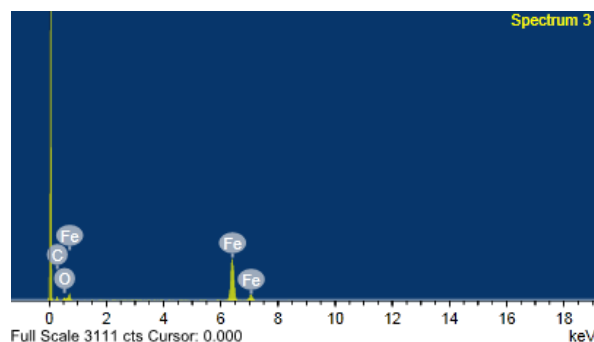
Mass %	Fe	C	O
Pure	86.18	13.82	-----
Blank	80.78	19.22	-----
300 ppm	52.56	34.29	13.15



a) Pure carbon steel surface  
a) Površina čistog ugljeničnog čelika



b) After 12 hours immersion in 1M HCl  
b) Posle 12 sati potapanja u 1M HCl



c) EDX spectra of carbon steel surface after treatment with 300 ppm of Cupressus sempervirens extract  
c) EDX spektar površine ugljeničnog čelika posle tretmana sa 300ppm u ekstraktu Cupressus  
Figure 13. EDX analysis on carbon steel in without and with of 300 ppm of the Cupressus sempervirens extract after 12 hours immersion in 1M HCl.  
Slika 13. EDX analiza ugljeničnog čelika bez i sa 300 ppm ekstrakta Cupressus posle 12 sati potapanja u 1M HCl.

#### 4. CONCLUSIONS

Weight reduction, EFM polarization, and impedance were utilized to consider the corrosion inhibition of mild steel in solution of 1 M HCl utilizing doses of Cupressus sempervirens as an earth safe inhibitor. The guideline conclusions are:

1. The corrosive medium of carbon steel is diminished upon the addition of Cupressus sempervirens concentrate and inhibition efficiency increments with raising the concentration of plant extract.
2. A surface film of extract on the electrode surface is obtain via sharing or transferring charge from the inhibitor molecules into the vacant orbitals on the metal surface (chemisorption).
3. EDX results of the electrode surface illustrated that a surface film of the extract is covered on the surface of electrode. This film retarded the reduction of H<sup>+</sup> ions and inhibited metal dissolution in hydrochloric acid solutions.
4. Chemisorption is proposed as the mechanism for inhibition of corrosion.
5. The inhibition efficiencies got from weight reduction information are practically identical with those got from polarization, EIS and EFM estimations.

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## IZVOD

### EKSTRAKT CUPRESSUS SEMPERVIRENS KAO ZELENI INHIBITOR ZA KOROZIJU UGLJENIČNOG ČELIKA U RASTVORU HLOROVODONIČNE KISELINE

*Efekat vodenog ekstrakta Cupressus sempervirens na način korozije ugljeničnog čelika u rastvoru 1M hlorovodonične kiseline je određivana promenom mase pri redukciji, izdvajanjem vodonika i metodama - elektrohemijском frekvencijskom modulacijom (EFM), potenciodinamičkom polarizacijom i merenjem impedanse (EIS). Efikasnost ekstrakta Cupressus sempervirens je ispitivana sa povećanjem doze ekstrakta i temperature. Termodinamički parametri procesa korozije i adsorpcije su mereni i diskutovani. Ekstrakt Cupressus se adsorbuje na površini metala hemijski i prati Temkinovu izotermu. Rezultat potenciodinamičke polarizacije je doveo do zaključka da ekstrakt pripada mešovitom tipu inhibitora. Navedeni rezultati dobijeni pri različitim metodama ispitivanja bili su u najboljoj korelaciji.*

**Ključne reči:** cupressus sempervirens, zeleni inhibitor, ugljenični čelik, adsorpcija, HCl.

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