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Inhibiting Corrosion Process of Carbon Steel in Sodium Chloride Aqueous Solution by Capsaicin Extract

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Abstract: In the present study the possibility of using Capsaicin extract from chili pepper as corrosion inhibitor for carbon steel in sodium chloride aqueous solution was investigated. The inhibitory effect was studied by several methods of investigation: weight loss, linear polarization, Tafel method for determining of the kinetic parameters and scanning electron microscopy, all of them providing complete information about the inhibiting mechanism. The diminution of corrosion rate in the presence of Capsaicin can be attributed to the adsorption of inhibitor molecules on the sample surface and blocking the active sites, or depositing corrosion products on the metal surface.

Keywords: capsaicin, natural plant extract, corrosion inhibitor, linear polarization, inhibitor efficiency.

1. Introduction

Carbon steel is used to make a wide range of equipment and metallic structures due to its low cost and good mechanical strength. Atmospheric corrosion is a major problem for the application of iron and its alloys in many types of service [1]. For this reason, the consumption of inhibitors to reduce corrosion has increased in the last few years. The corrosion control by inhibitors is one of the most common, effective, and economic methods to protect metals in all aggressive environments [2]. Most of the used inhibitors are organic compounds containing heteroatoms, such as oxygen, nitrogen, or sulfur, and multiple bonds, which allow the adsorption on the metal surface. The adsorption of inhibitors depends on the nature of the functional groups and electron density at the donor atom [2-4]. However, most of them are highly toxic to both human beings and environment. Several researchers have studied the effect of natural products as corrosion inhibitors in different media [5].

Recently, plant extracts have proved important as an environmentally acceptable source, readily available and renewable for a wide range of corrosion inhibitors. Extracts of plants are regarded as an incredibly rich source of naturally synthesized chemical compounds that can be recovered by simple methods with low costs [6].Such extracts contain mixtures of compounds and are biodegradable in nature. A significant number of papers were published having the intention to develop "green" corrosion inhibitors [7]. As well has researches intensified on natural products such as plant extracts and essential oils to obtain environmentally friendly corrosion inhibitors [8].

Until now, there are some known plant extracts used as corrosion inhibitors for carbon steel in acid medium: *Zenthoxylumalatum* [9], *Papaya, Poinciana pulcherrima, Cassia occidentalis, Daturastramonium, Tobacco, Black pepper* and *Soya been* [10], etc. The efficiency of these natural compounds mainly depends on their abilities to be adsorbed on the metal surface with the polar groups acting as the reactive centers [11].

Capsaicin with systematic (IUPAC) name N-[(4-hydroxy-3-methoxyphenyl)methyl]-8-methylnon-6-enamide is an active component of chili peppers, which are plants belonging to the genus *Capsicum* [12]. The extract is currently used for the treatment of diabetic neuropathy, osteoarthritis, post-herpetic neuralgia, and psoriasis [13], as well as there are many patents on insecticides, insect or animal repellents, and pesticides containing capsaicinoids [14].

The substitutional adsorption of an inhibitor towards adsorbed water molecules ($H_2O_{(ads)}$) may be represented by the following equation [15]:

$$\text{Capsaicin}_{(sol)} + nH_2O_{(ads)} \rightarrow \text{Capsaicin}_{(ads)} + nH_2O_{(sol)} \quad (1)$$

where, $\text{Capsaicin}_{(sol)}$ and $\text{Capsaicin}_{(ads)}$ are the Capsaicin molecules in aqueous solution and in the adsorbed state, respectively, *n* is the number of water molecules replaced by one inhibitor molecule.

The objective of the present work is to investigate the inhibitor effects of capsaicin extract on carbon steel corrosion in 3.5% sodium chloride (NaCl) using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electronic microscope (SEM).

2. Experimental

2.1. Materials

The working electrode was a cylindrical disc cut from a carbon steel sample. To determine the inhibitor effect of capsaicin on the corrosion rate of carbon steel in sodium chloride aqueous solution different concentration of the

Capsaicin have been used: 0.8, 2, 4, 10, 20 mg L^{-1} in the test solutions. The corrosive medium was prepared from sodium chloride (Merck, 99.9%). The chemical structure of Capsaicin ($C_{18}H_{27}NO_3$) is presented in figure 1 [16].

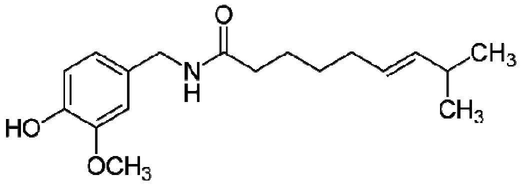


Figure 1. Chemical structures of Capsaicin [16]

2.2. Methods

The cyclic voltammetry, linear polarization, electrochemical impedance spectroscopy and weight loss methods were used in order to notice the inhibitive properties of Capsaicin extract on the carbon steel corrosion process. The surface morphology of corrosion samples has been characterized by scanning electron microscopy (SEM) using a FEI INSPECT S microscope, before and after corrosion tests.

The electrochemical measurements were performed in a 100 mL typical glass cell consisting ofa carbon steel specimen with 0.8 cm^2 exposed area as a working electrode (WE), two graphite counter electrodes (CE), and a Ag/AgCl electrode as reference.

The electrochemical studies were carried out using an BioLogics SP150 potentiostat/galvanostat. All potentials were referred to the saturated Ag/AgCl reference electrode. Carbon steel electrode was abraded with different grit emery papers, cleaned in ultrasonic bath, washed with distilled water and finally dried. The electrode potential was allowed to stabilize 60 min before starting the measurements.

3. Results and Discussion

3.1. Cyclic voltammetry method

The preliminary information about how Capsaicin extract can influence the corrosion process of carbon steel is pointed by its electrochemical behavior in the sodium chloride solution studied by cyclic voltammetry. In figures 2 ($dE/dt = 500$ mV s^{-1}) and3 ($dE/dt = 5$ mV s^{-1}) are shown the cyclic curves recorded on Pt as working electrode, in 3.5% NaCl (blank) solutions without and with different concentrations of Capsaicin.

The voltammogram recorded in blank solution presents the characteristics of polarization curves drawn in sodium chloride solutions. On anodic branch there are distinct the plateau corresponding to chlorine evolution reaction and the plateau characteristic for oxygen release. On the CV backward scan a cathodic peak at 1.0 V/AgAgCl, associated with the oxidation of superficial remanent oxygen, is highlighted. Also, on cathodic branch at more negative potentials then -1.0 V/AgAgCl only hydrogen evolution reaction is observed.

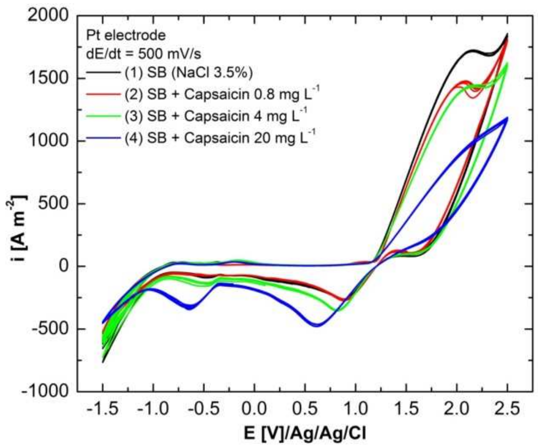


Figure 2. Cyclic voltammograms (5 cycles) in absence and presence of different concentrations of the extract, scan rate 500 mV s^{-1}

If organic compound is added in basic solution, new specific peaks can be noted. On anodic branch (figure 2), a low intensity oxidation peak, around potential -0.25 V/Ag/AgCl, is observed; similarly, on cathode curves reduction peaks appear at -0.7 V/Ag/AgCl. This means that Capsaicin added in the saline electrolyte are processed oxidated/reduced onto the platinum electrode surface.

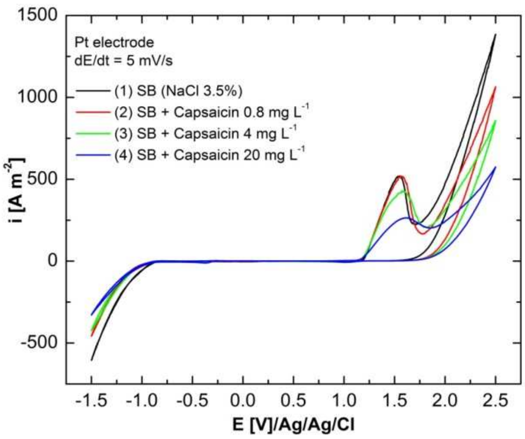


Figure 3. Cyclic voltammograms (5 cycles) in absence and presence of different concentrations of the extract, scan rate 5 mV s^{-1}

In order to identify how Capsaicin influences the electrode processes, polarization curves where recorded separately at higher sensitivity, in cathodic domain as well as in anodic one.

On cyclic voltammograms plotted for the anode branch (figure 4) in the potential range between +0.5 and 2.0 V/Ag/AgCl a pronounced oxidation peak can be seen, which was initially assigned to chloride ions oxidation from NaCl solution.

Correlating literature data [17-19] with the voltammetric results shown in Figure 5a and b, obtained for sodium chloride solution without and with addition of inhibitor at maximum concentration used in experimental studies (20 mgL^{-1}), it can be assigned that the oxidation peak appearing on the anodic branch corresponds to the organic compound oxidation. Also, the oxygen evolution reactions in 3.5% sodium chloride solution in the presence of Capsaicin are inhibited.

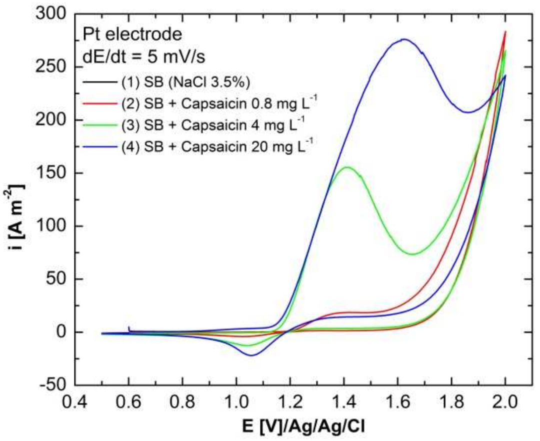
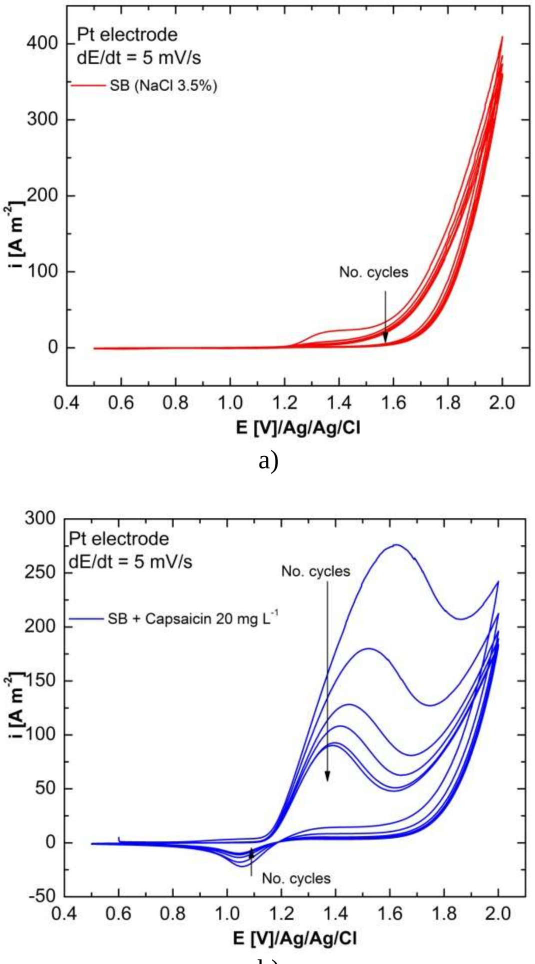


Figure 4. Cyclic voltammograms on Pt electrode for anodic polarization in 3.5% NaCl in the absence/presence of Capsaicin, scan rate 5 mV s^{-1}

Electrochemical oxidation of Capsaicin in neutral solution consists of two steps (figure 6) [17-19]. In the first stage, two electrons are discarded from neutral Capsaicin molecule in an irreversible anodic oxidation reaction forming phenoxoniumcation of capsaicinoids. Second stage consists of hydrolysis of the 2-methoxy group to form o-benzoquinone unit in the structure of Capsaicin by losing a proton and methanol [17-19].



a)

b)

Figure 5. Cyclic voltammograms (6 cycles) on Pt electrode for anodic polarizationin 3.5% NaCl in the absence (a) and presence of 20 mg L^{-1} Capsaicin, scan rate 5 mV s^{-1}

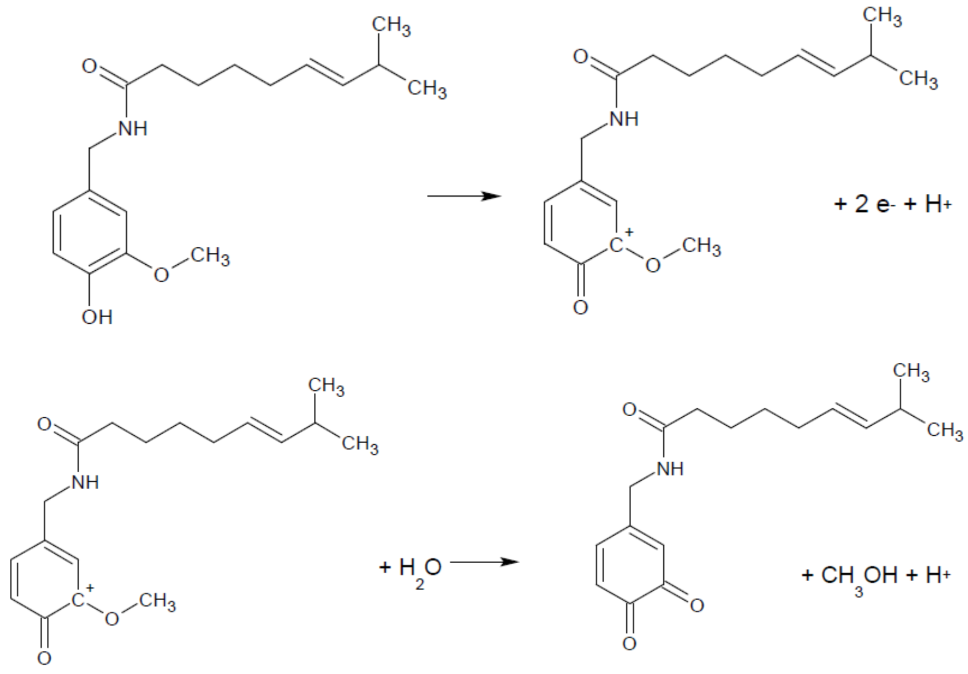


Figure 6. Capsaicin anodic electrooxidation mechanism [17-19]

Cyclic voltammograms drawn in cathodic domain on electrode platinum in test solutions used in corrosion studies are presented in figure 7. When Capsaicin extract was added in solutions around -0.40 V potential value a cathodic peak is observed whose correspond to backwards scan an oxidation peak at -0.30V potential value.

Also, the hydrogen evolution reactions in 3.5% sodium chloride solution in the presence of Capsaicin are inhibited due to the adsorption on platinum electrode surface of Capsaicin molecules or electrochemical oxidation or reduction Capsaicin products.

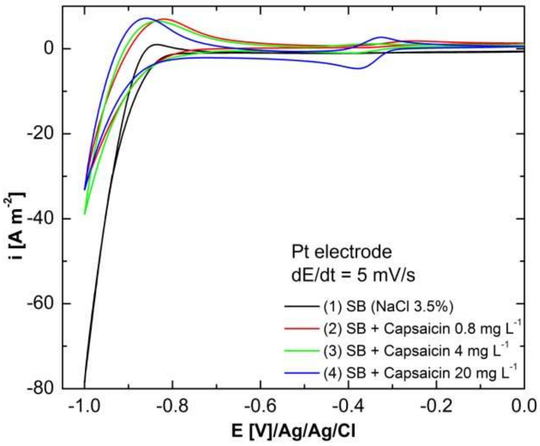


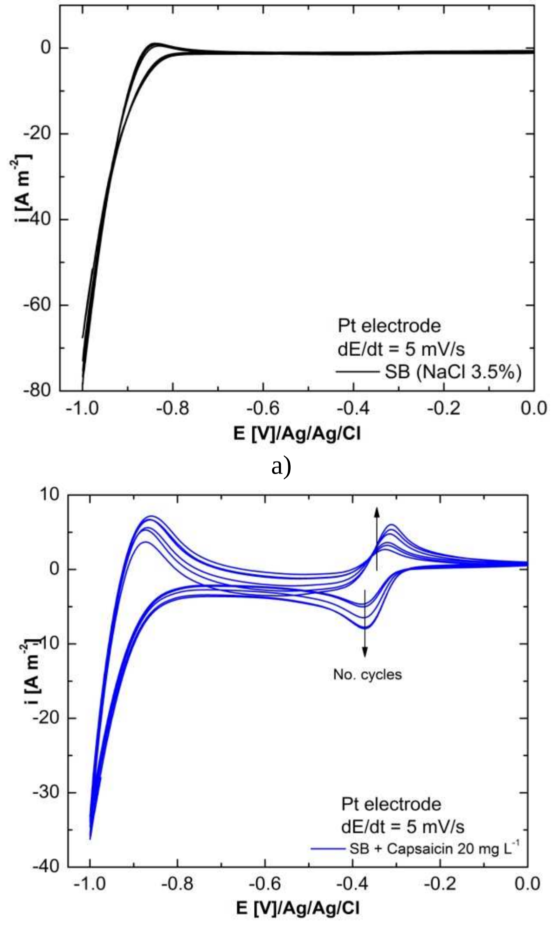
Figure 7. Cyclic voltammograms on Pt electrode for anodic polarization in 3.5% NaCl in the absence/presence of Capsaicin, scan rate 5 mV s^{-1}

Cyclic cathodic curves (5 cycles) recorded in 3.5% NaCl solutions without and with the highest concentration used in corrosion tests (20 mg L^{-1}) are shown in figures 8a and b.

Analyzing figure 8b it can be noticed that the intensity of peaks corresponding to Capsaicin transformations in the cathodic domain, increases with the number of cycles plotted.

The electrochemical redox process corresponding to these peaks can be described by equilibrium shown in figure 9. o-Benzoquinone structure of Capsaicin obtained by electrochemical oxidation reaction are reduced to o-hydro xyphenol (catechol) part of capsaicinoids [17-19].

Capsaicin effect on corrosion of carbon steel was studied in 3.5% NaCl corrosive environment by applying successive investigation methods presented above. These were applied after about 1 hour, sufficient time to install an electrode equilibrium or quasi-equilibrium state, as shown in figure 10.



a)

b)

Figure 8. Cyclic voltammograms (5cycles) on Pt electrode for anodic polarization in 3.5% NaCl in the absence (a) and presence of 20 mg L^{-1} Capsaicin, scan rate 5 mV s^{-1}

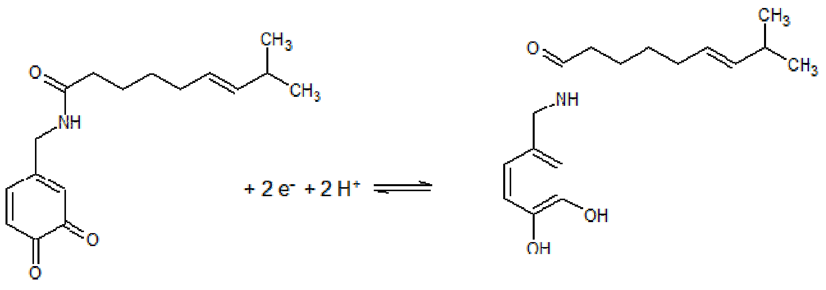


Figure 9. Capsaicin redox mechanism in potential range between 0 and -0.5V/Ag/AgCl [17-19]

TABLE 1. E_{OCP} values at 25˚C

Electrode	Capsaicin concentration[mg L^{-1}]	T[˚C]	E_{OCP} [V]/Ag/AgCl
Carbon steel	SB	25	-0.578
	0.8		-0.582
	2		-0.586
	4		-0.595
	10		-0.613
	20		-0.630

TABLE 2. Polarization parameters for carbon steel corrosion in 3.5% NaCl in the absence/presence of Capsaicin inhibitor

Capsaicin concentration [mg L^{-1}]	T [˚C]	i_{corr} [μA cm^{-2}]	E_{corr} [mV]	$-b_c$ [mV dec^{-1}]	b_a [mV dec^{-1}]	R_p [Ω]	v_{corr} [mm an^{-1}]	IE [%]	θ
SB	25	39.14	-601.1	294.0	77.1	276	1.15	-	-
0,8		28.98	-605.3	280.6	76.7	328	0.91	25.96	0.26
2		21.46	-612.5	275.5	75.5	345	0.806	45.17	0.45
4		10.74	-630.0	272.5	74.4	573	0.433	62.94	0.63
10		8.63	-643.1	268.3	72.9	712	0.459	77.95	0.78
20		3.45	-657.3	258.7	66.8	1228	0.219	91.19	0.91

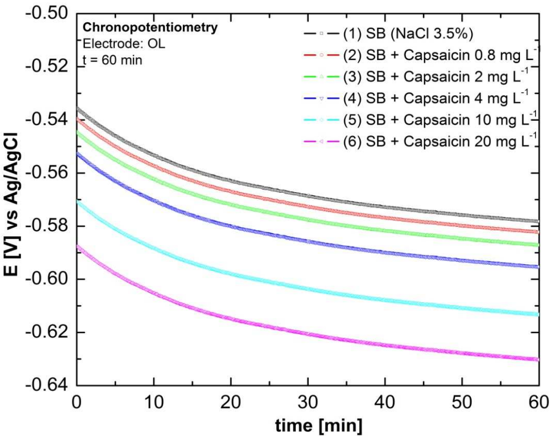


Figure 10. Open circuit potential for carbon steel electrode in 3.5% NaCl in the absence/presence of Capsaicin

The equilibrium potential values derived from the Figure 10 are shown in Table 1 as a function on the inhibitor concentration added in the corrosive environment. According with diagram depicted in figure 10 and E_{OCP} data from table 1 it can conclude that after 1 hour, in test solutions with different concentrations of inhibitor, carbon steel electrode equilibrium potential is shifted to more negative values, a phenomenon that can be attributed to the adsorption of Capsaicin molecules or corrosion products deposition on the electrode surface.

The manner in which Capsaicin acts as corrosion inhibitor for carbon steel in sodium chloride solution and its effect on the corrosion rate can be estimated by Tafel polarization method. The potentiodynamic polarization curves recorded at 25°C with 1 mV s^{-1} scan rate in test solutions without and with various concentrations of natural extract are presented in figure 11.

The potentiodynamic diagrams were recorded after removing the dissolved oxygen from solution to avoid any secondary reactions that may occur on electrode surface and after installing in the electrode a quasi-equilibrium state in electrolyte solutions.

The fitting values of the corrosion current density (i_{corr}), the corrosion potential (E_{corr}), the anodic (b_a) and the cathodic (b_c) Tafel slopes, the polarization resistance (R_p) and the corrosion rate (v_{corr}), with various concentrations of the Capsaicin extract as inhibitor were obtained from polarization profiles by extrapolating potentiodynamic curves using BioLogics 150N software. All obtained values are presented in Table 2.

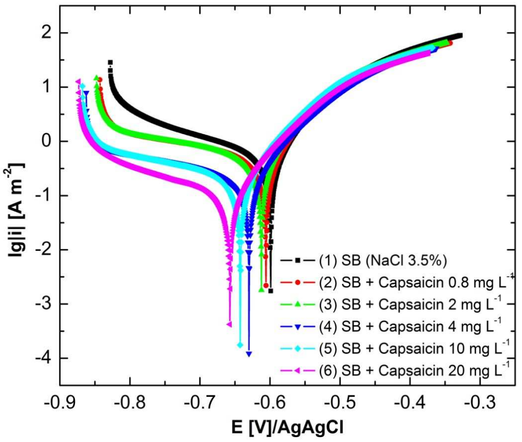


Figure11. Linear polarization curves on carbon steel electrode for anodic polarization in 3.5% NaCl without and with different concentration of Capsaicin at 25°C, scan rate 1 mV s^{-1}

From the results presented in Table 2, it can be seen that by increasing the inhibitor concentration, the corrosion rate is decreased in sodium chloride solution and inhibition efficiency increased. Also, the polarization resistance are increase with Capsaicin concentration added in test solution.

At lowest inhibitor concentrations in solution, it can be concluded that they impede the corrosion by merely blocking the reaction sites on carbon steel surface without interfering the anodic and cathodic reactions. This inhibitor cause no significant changes in the anodic and cathodic Tafel slopes. This suggest that Capsaicin behave as a mixed-type inhibitor and can be classified as adsorptive-type.

3.2. Weight loss method

Gravimetric measurements of carbon steel discs samples immersed in 100 mL 3.5% NaCl in the absence and presence of different Capsaicin concentrations after 240 hours of immersion time at 298 K, were chosen to compare inhibition efficiency at selected concentrations. As expected, weight loss of carbon steel samples are decreased in the present of expired drug with increase of the concentration. This means that Capsaicin acts as an efficient inhibitor.

The corrosion rate of carbon steel (W_{corr}) was determined using the relation (4) and the inhibition efficiency (*IE*) and surface coverage (θ) with equations (5) and (6):

$$W_{CORR} = \frac{W_1 - W_2}{S \times t} \quad (4)$$

where W_1 and W_2 are the initial and final mass of the samples in mg, *S* is the total surface area in cm^2 and *t* is the exposure time in h.

$$IE(\%) = (1 - \frac{W_{corr}}{W_{corr}^0}) \times 100 \quad (5)$$

$$\theta = 1 - \frac{W_{corr}}{W_{corr}^0} \quad (6)$$

where W_{corr} and W^0_{corr} are the weight loss in the presence and the absence of inhibitor, respectively.

From the results shown in Table 3, it can be seen that by increasing the inhibitor concentration the inhibition efficiency increased. Also, Capsaicin inhibition efficiency had almost the same high values as those obtained by linear polarization method.

3.3. Surface analysis

SEM analysis was performed to investigate the surface morphology of the carbon steel after immersion in 3.5% NaCl in the absence and the presence of 4 mg L^{-1} and 20 mg L^{-1} Capsaicin (figure 12) for 240 h at 298 K. Damaged surface was observed in the absence of inhibitor due to high dissolution rate of iron in NaCl solution.

The samples surface was protected by adsorption of inhibitor molecules that form a protective film, or due to complex compounds between iron and Capsaicin molecules. The comparing of micrographs recorded at same magnification for both samples suggest that corrosion process of carbon steel is inhibited which is confirmed by the weight loss measurement, cyclic voltammetry and polarization results.

The average compositions of the electrodes were evaluated by EDX microanalysis, whose results are given in Table 4 and in figure 13.

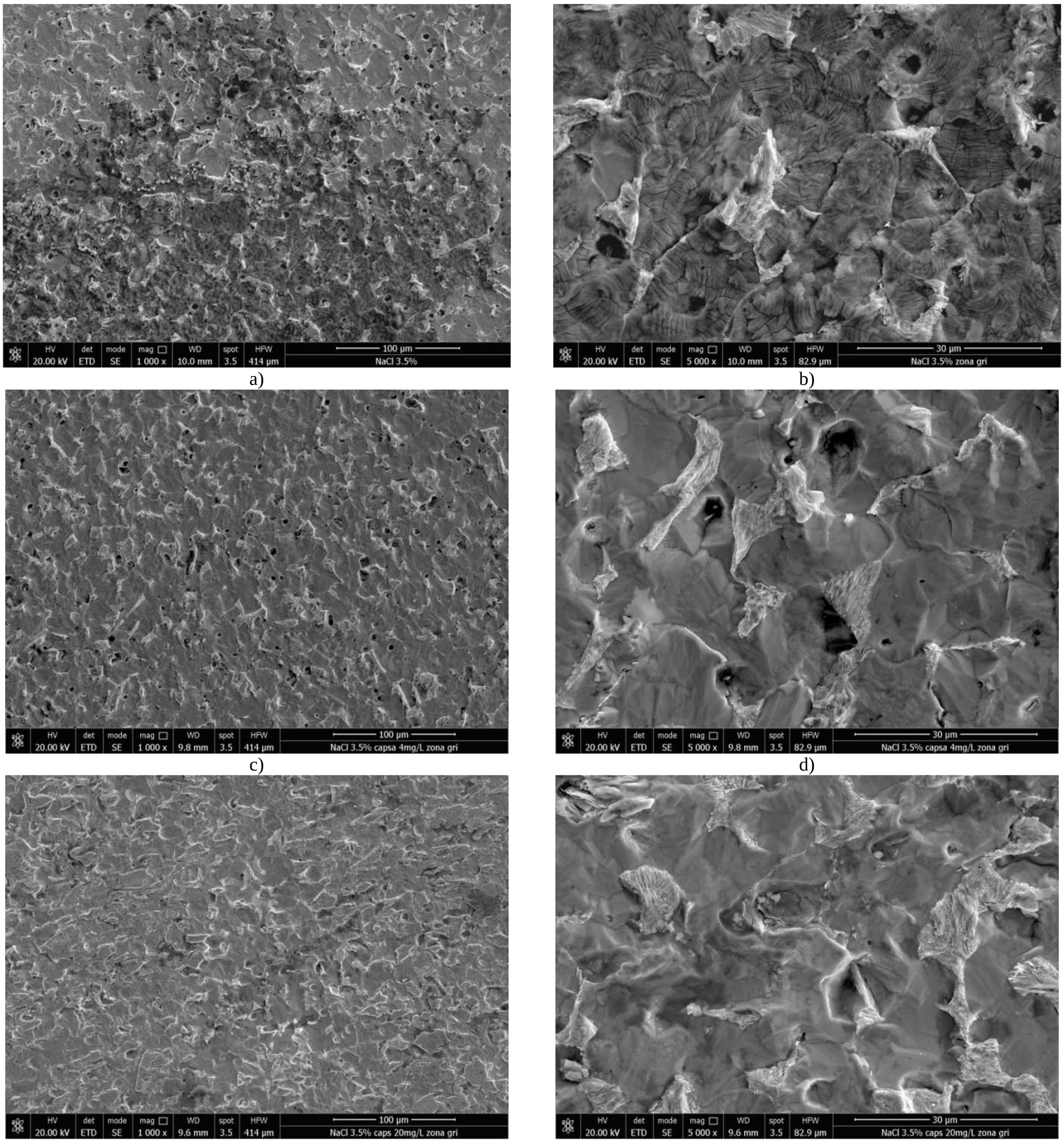
EDX microanalysis results confirm the Capsaicin inhibitory effect for carbon steel corrosion in NaCl 3.5%. The oxygen amount determined by this method is an important indicator for the quantity of iron oxides formed in carbon steel corrosion process using the test solutions with or without Capsaicin extract as inhibitor.

TABLE.3. The inhibition efficiency and surface coverage obtained by weight loss method

Capsaicin concentration [mg L^{-1}]	W_{corr} [mg cm^{-2} h^{-1}]	*IE* [%]	θ
SB	0.033	-	
0.8	0.025	25.65	0.26
2	0.018	47.12	0.47
4	0.009	64.79	0.65
10	0.003	81.19	0.81
20	0.001	92.16	0.92

TABLE 4. Chemical composition of test carbon steel electrodes after weight loss method

Element (wt%)	Test solution		
	NaCl 3.5% (SB)	BS + 4 mg L^{-1} Capsaicin	BS + 20 mg L^{-1} Capsaicin
Fe	37.44	53.97	71.66
O	48.62	32.71	12.38
Si	2.02	1.86	1.68
C	11.92	11.46	14.28
Total	100%	100%	100%



a) b)

c) d)

e) f)

Figure 12. SEM images obtained on carbon steel after 10 days immersion time in NaCl 3.5% without (a,b) and with Capsaicin 4 mg L^{-1} (c,d) and 20 mg L^{-1}(e,f) at different magnifications

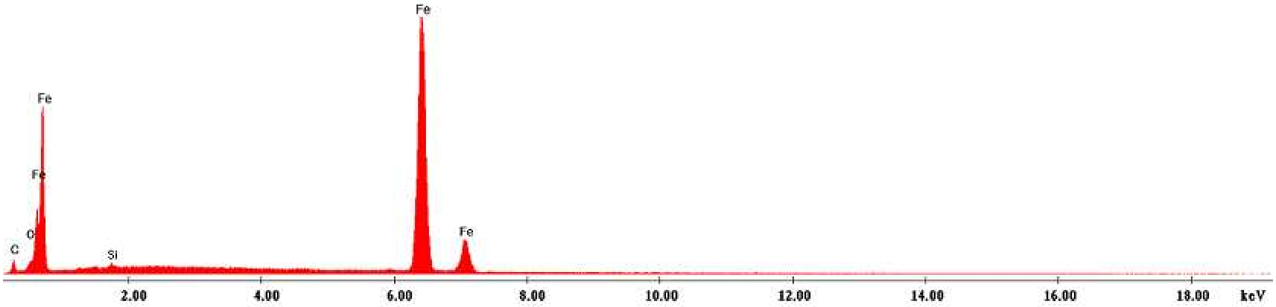


Figure 13. EDX on carbon steel samples after 10 days of immersion in NaCl 3.5% with 20 mg L^{-1} Capsaicin

4. Conclusions

Inhibition efficiency of the Capsaicin extract has been studied by two different methods: weight loss and linear polarization, all giving comparable results. This compound exhibited excellent inhibition performance as a mixed-type inhibitor for carbon steel in sodium chloride solutions at concentrations bigger than 4 mg L^{-1}.

Capsaicin extract act as efficient corrosion inhibitors in 3.5% NaCl solution and it exhibit a maximum inhibition efficiency of 92%. SEM micrographs showed that the inhibitor molecules or electrochemical oxidation-reduction Capsaicin product form a good protective film on the carbon steel surface.

The good inhibition efficiencies obtained in sodium chloride solution makes them a suitable alternative as plant extracts corrosion inhibitors in corrosion media in which the main ingredient is sodium chloride. Also, Capsaicin extract can be added to the list of non-toxic, cheap and effective green corrosion inhibitors from renewable sources.

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