

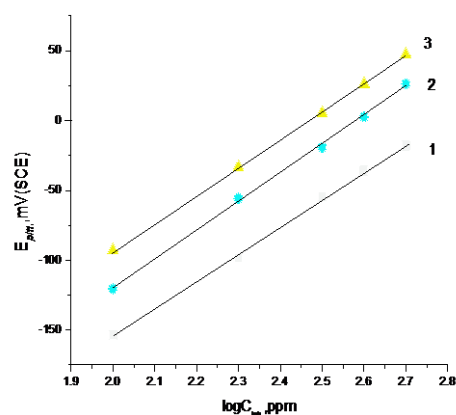
Research Article

Ginger, Garlic and Cinnamon Oils as Inhibitors for Corrosion of Carbon Steel in NaOH Solution

Abdallah.M^{*1,2}, Zaafarany I.A², Etre A.Y¹ and kamar A. M¹¹Department of Chemistry, Faculty of Science, Benha University, Benha, Egypt²Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukaramah, Saudi Arabia**Abstract**

Some natural oils, namely, ginger, garlic and cinnamon are used to inhibit the corrosion of carbon steel (G-1018) in 0.5 M NaOH solution was evaluated using galvanostatic and potentiodynamic anodic polarization techniques. The inhibition efficiency of these natural oils increases with increasing of its concentration. The inhibitory action of these oils is discussed in view of the adsorption of its the main component in the chemical structure of each oil on the steel surface. The adsorption process obeys Langmuir adsorption isotherm. Galvanostatic polarization measurements showed that these oils are of mixed type inhibitors. It was found that the addition of the chloride ions accelerates the pitting corrosion of carbon steel in 0.5 M NaOH solution by shifting the pitting potential to more negative values. The addition of these oils protects the carbon steel against pitting corrosion in chloride containing solutions by shifting the pitting potential to more positive values.

Keywords: Ginger oil, Garlic oil, Cinnamon oil, Corrosion Inhibitors, Carbon Steel, Pitting Corrosion

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Introduction

The study of carbon steel corrosion has become important, particularly in alkaline media because of the increased industrial application, especially in the petrochemical industry [1]. Corrosion problem is receiving more and more attention due to their damage to material. The use of inhibitors is one of the most practical methods for corrosion protection. Many researchers have devoted themselves to researching the inorganic and organic inhibitors, however, the biological toxicity of inhibitors, especially some inorganic salts such as chromate [2] and some organic compounds [3] were documented because of environmental harmful characteristics [4].

Organic compounds containing hetero atoms are commonly used to reduce the corrosion attack on the steel in aqueous solutions due to the higher basicity and electron density and thus assist in corrosion inhibition [5]. Although some of these compounds show good anticorrosive action, most of them are highly toxic to both human beings and the environment. These inhibitors may cause temporary or permanent damage to organ system such as the kidneys or liver, or to disturb a biochemical process or to disturb an enzyme system at some site in the body [11]. The toxicity may manifest either during the synthesis of the compound or during its applications. These lead investigations to focus on the use of naturally occurring substance in order to find environmentally friendly, inexpensive, readily available, non-hazardous and renewable sources of materials [12].

Several plant extracts and some essential oils have been reported as an inhibitor for different metals in alkaline or acidic solutions [13-14]. Previous work examined extract of henna (*Lawsonia*) as a corrosion inhibitor of carbon steel, nickel and zinc in different media [15]. Natural honey [16] and guar gum [17] was used to inhibit the dissolution of carbon steel in acidic solutions. Also, natural oils e.g. clove and black cumin oils were used as an inhibitor for corrosion of nickel, Inconel 600 and Inconel 690 in HCl solution [18-19]. Parsley, lettuce and radish oils are used to inhibit the corrosion of carbon steel in NaOH solution [20]. Rosemary oil was used as an inhibitor for corrosion of carbon steel in sulfuric acid solutions [21]. This work is devoted to examining some natural oils e.g. ginger, garlic and cinnamon oils as corrosion inhibitors for dissolution of carbon steel (G-1018) used in manufacture of Egyptian petroleum pipelines in 0.5 M NaOH solution using galvanostatic and potentiodynamic anodic polarization at voltage scan rate of 50 mVsec⁻¹. Also, these oils were used as inhibitors for pitting corrosion of C-steel in chloride containing solution using potentiodynamic anodic polarization technique at voltage scan rate 1 mVsec⁻¹.

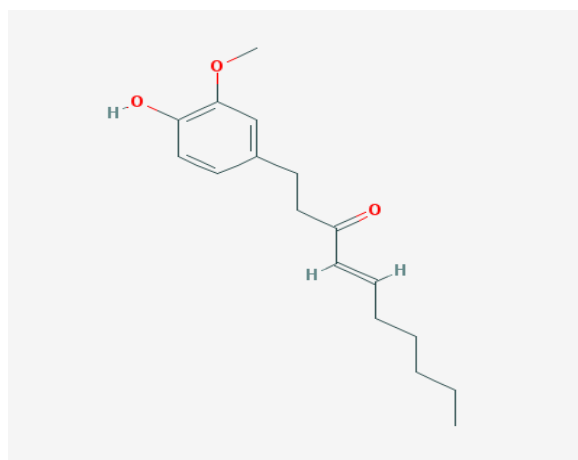
Experimental procedure

Carbon steel of type G-1018 used in this study has the following chemical composition (weight %) C (0.14), Mn (0.6), p (0.04), S (0.05) and Fe balance. Galvanostatic and potentiodynamic polarization measurement. Cylindrical rod embedded in Araldite with exposed surface area of 1cm² was used. The electrode was polished with different grades of emery paper, degreased with acetone and rinsed with distilled water. BDH grade NaOH was used for the preparation of the test solutions. The experiments were carried out at the 25±1°C using air thermostat.

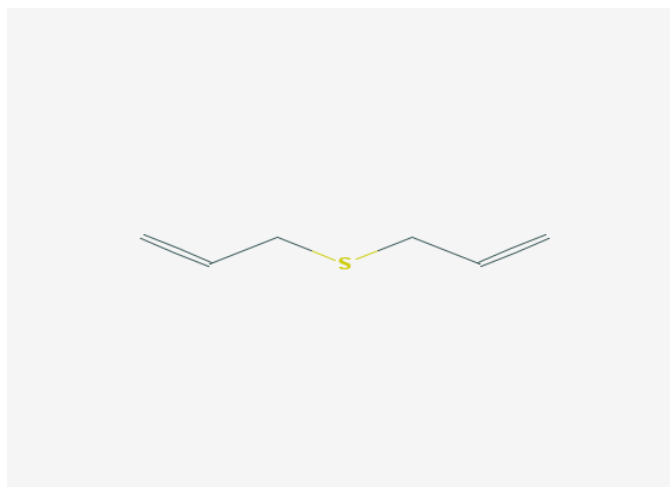
The galvanostatic and potentiodynamic anodic polarization experiments were carried out using a PS remote potentiostat with PS6 software for calculation of some corrosion parameters, e.g. corrosion current density (I_{corr}), corrosion potential (E_{corr}) and anodic and cathodic Tafel constants (b_a and b_c). The corrosion parameters were calculated from the intercept of the anodic and cathodic Tafel lines. The potentiodynamic anodic polarization curves were carried out at a scan rate of 50mVs⁻¹ and 1mVs⁻¹ respectively. A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used.

Three essential oils, namely, ginger, garlic and cinnamon oils were used in this study. The initial inhibitory solution is prepared from the dissolution of the natural oils in 0.5M NaOH solution. This later is obtained elsewhere [24].

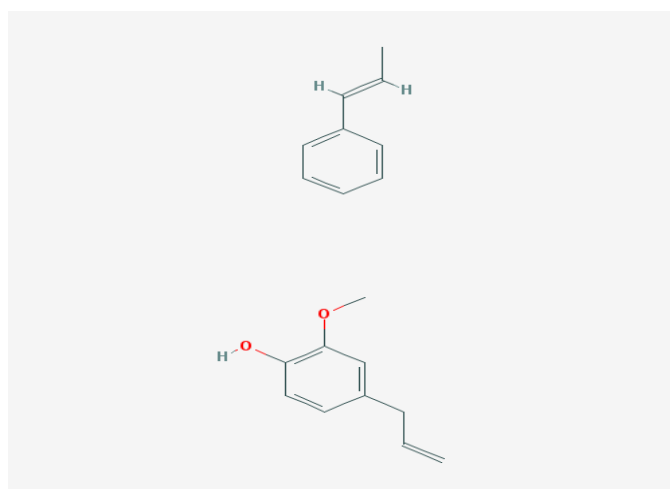
The main of chemical structure of these oils are as follows



Ginger oil



Garlic oil



Cinnamom oil

Results and Discussion

Galvanostatic polarization

Fig.1 represents the anodic and cathodic polarization curves of C-steel electrode in 0.5 M NaOH solution devoid of and containing different concentrations of ginger oil. Similar curves were obtained for the other two oils (not shown) but their corrosion parameter given in Table 1. The inhibition efficiency IE and surface coverage (θ) was calculated using the equation

$$I.E = (I_{free} - I_{add} / I_{free}) \times 100 \quad (1)$$

$$\theta = (I_{free} - I_{add} / I_{free}) \quad (2)$$

where, I_{free} and I_{add} are the corrosion current densities in free and inhibited solution, respectively.

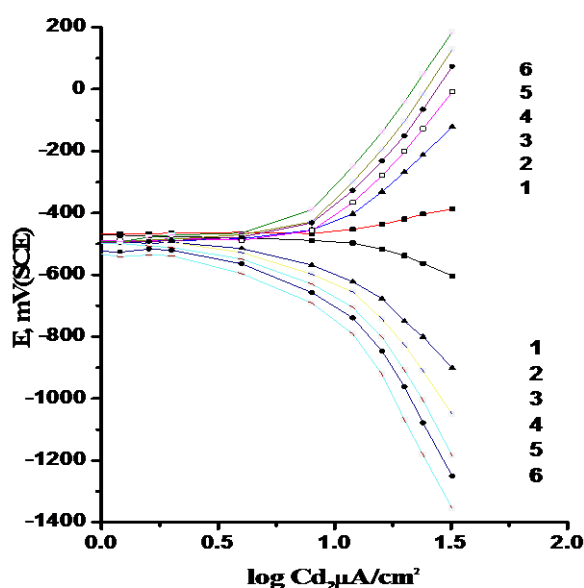


Figure 1 Galvanostatic polarization curves of carbon steel in 0.5M NaOH solution containing different concentrations of ginger oil (1) 0.00 (2) 100 (3) 200 (4) 300 (5) 400 (6) 500 ppm

Inspection of Fig (1) reveals that the polarization curves shift toward more negative potential and lower current density values upon the addition of the oil. This behavior reflects the inhibiting action of the oil. Inspection of the data in Table 1 reveals that, as the concentration of oils increases the values of anodic (b_a) and cathodic (b_c) Tafel slopes are changed slightly suggesting the inhibitory action of these compounds by adsorption at the metal surface according to blocking adsorption mechanism [25]. Also, these oils act mainly as a mixed type inhibitor. The values of E_{corr} are shifted toward a more negative direction, I_{corr} decrease and hence IE increases. This indicates that the inhibiting effect of these oils and the values of IE increase with increasing oil concentrations.

Table 1 Corrosion parameter obtained from galvanostatic polarization measurements of carbon steel in 0.5M NaOH solution containing different concentrations of some natural oils

Inhibitors	Conc. (M)	b_a mV dec^{-1}	b_c mV dec^{-1}	$-E_{\text{corr}}$ mV (SCE)	I_{corr} (mA cm^{-2})	% I.E	
Free	0.0	69.5	91	-478	0.655	-----	
	100	141	165	-511	0.350	46.56	
	200	148	157	-522	0.280	60.30	
	Ginger-Oil	300	157	178	-537	0.186	72.51
		400	165	183	-538	0.131	80.15
		500	175	193	-541	0.950	85.49
Garlic-Oil	100	143	141	-533	0.365	44.27	
	200	164	176	-537	0.280	57.25	
	300	168	181	-541	0.171	73.89	
	400	177	188	-543	0.124	81.06	
Cinnamon-	500	190	196	-548	0.116	82.29	
	100	153	152	-522	0.423	35.87	

Oil	200	156	170	-541	0.310	52.67
	300	173	180	-544	0.250	61.83
	400	180	188	-543	0.165	74.80
	500	193	200	-551	0.145	77.86

Adsorption isotherm

Organic inhibitors establish their inhibition via the adsorption of the inhibitor onto the metal surface. The adsorption processes of inhibitors are influenced by the chemical structures of compounds, the nature and surface charge of metal, the distribution of charge in the molecule and the type of corrosive media [26]. The inhibition efficiency of these natural oils is determined by its molecular adsorbability of its main component in each oil on the steel surface.

The degree of surface coverage θ corresponding to different concentrations of oils have been used to explain the best isotherm to determine the adsorption process. The adsorption of an oil adsorbate at a metal solution interface can be represented as a substitution adsorption process between the oil compound in the aqueous phase (oil)_{sol} and water molecules adsorbed on the steel surface (H₂O)_{ads}.



where, Oil_(sol) and Oil_{ads} are the oil compounds in the aqueous solution and adsorbed on the metallic surface, respectively, H₂O_(ads) is the water molecules on the metallic surface, X is the size ratio representing the numbers of water molecules replaced by one molecule of oil adsorbate.

The degree of surface coverage (θ) was found to increase with increasing the concentrations of these oils. This indicates that the inhibiting action of these oils toward the corrosion of carbon steel in 0.5 M NaOH solution by adsorption on the surface of steel. The adsorbed layer acts as a barrier between the metal surface and aggressive solution, leading to decrease of corrosion rate.

Attempts were made to fit θ values to various isotherms including Frumkin, Freundlich, Langmuir, Temkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm according to the following equation:

$$C/\theta = 1/K_{\text{ads}} + C \quad (4)$$

where, K_{ads} and C are the equilibrium constants of the adsorption process and additive concentration, respectively.

The plotting of C/ θ against C gives straight lines with unit slope (Fig. 2). This indicates that the adsorption of oils on the surface of carbon steel follows Langmuir adsorption isotherm, and, consequently, there is no interaction between the molecule adsorbed at the metal surface.

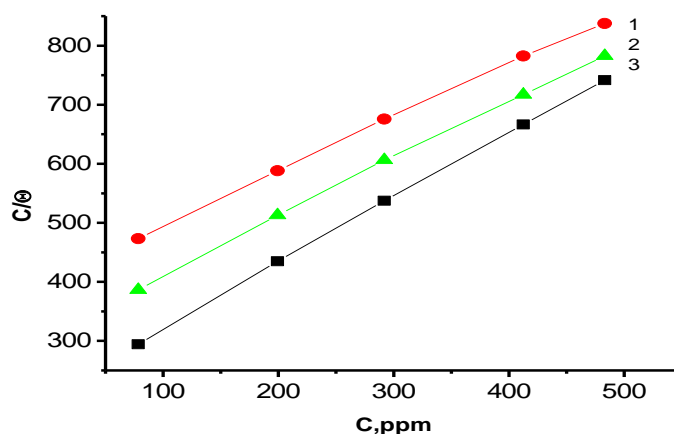


Figure 2 Langmuir adsorption isotherm for: (1) Ginger oil (2) Garlic oil (3) Cinnamon oil

Potentiodynamic anodic polarization measurements

The effect of addition of increasing concentrations of some natural oils e.g. ginger, garlic and cinnamon oils on the potentiodynamic anodic polarization curves of carbon steel electrode in 0.5 M NaOH solution at a scan rate 50 mVs^{-1} was studied.

Fig.3. shows typical potentiodynamic anodic polarization curves of carbon steel electrode in 0.5 M NaOH solution devoid of and containing increasing concentrations of ginger oil at a scan rate of 50 mVs^{-1} . Similar curves (not shown) were also obtained from other two oils.

Inspection of the curves of Fig 3 reveals that there is only one anodic peak, which is due the oxidation of Fe to $\text{Fe}(\text{OH})_2$ according to the following equation:



Increasing the concentration of these oils decreases the corrosion current peak (I_p) which suggests the inhibiting effect of these oils [27].

The inhibition efficiency (IE) was calculated using the following equation

$$\text{IE} = 100 \left(1 - \frac{I_{p(\text{add})}}{I_{p(\text{free})}} \right) \quad (6)$$

where, $I_{p(\text{add})}$ and $I_{p(\text{free})}$ is the anodic peak current densities in the presence and absence of oils. The values of peak current density and IE are listed in Table 2. From these values, it is clear that, as the concentration of additives increases the values of E_p shifted to more negative value and the value of I_p decreases, while the value of IE increases indicating the inhibiting effect of these compounds.

The order of percentage inhibition efficiency decreases in the following order.

Ginger oil > garlic oil > cinnamon oil

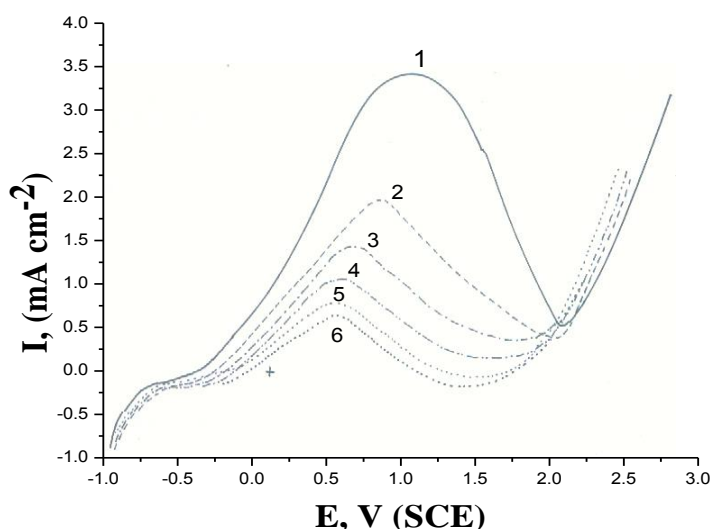


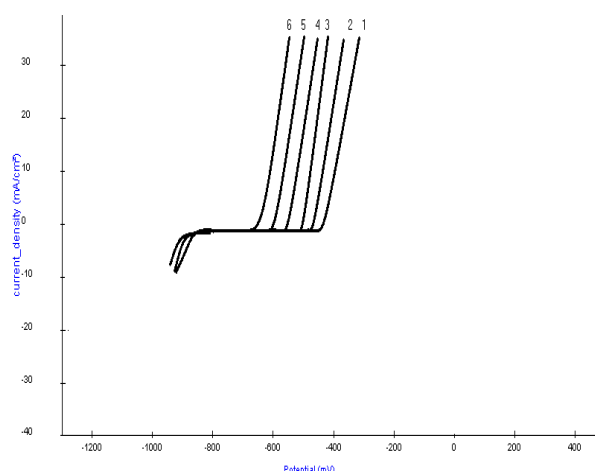
Figure 3 Potentiodynamic anodic polarization curves of carbon steel in 0.5 M NaOH solution containing different concentrations of ginger oil at scan rate of 50 mVs^{-1} : (1) 0.00ppm (2) 100ppm (3) 200ppm (4) 300ppm (5) 400ppm (6) 500ppm

Table 2 Corrosion parameters obtained from potentiodynamic anodic polarization measurements at scan rate 50mVs⁻¹ of carbon steel in 0.5M NaOH solution containing different concentrations of some natural oils

Inhibitor system	Conc. (M)	I _p , (mA cm ⁻²)	-E _p V(SCE)	%I.E
Free	0.0	3.47	0.91	-----
	100	1.98	0.86	42.9
	200	1.44	0.69	58.5
Ginger-Oil	300	1.07	0.60	69.1
	400	0.79	0.56	77.2
	500	0.65	0.54	81.2
Garlic-Oil	100	2.11	0.88	39.1
	200	1.60	0.78	53.8
	300	1.07	0.63	69.1
Cinnamon-Oil	400	0.82	0.53	76.3
	500	0.71	0.51	79.5
	100	2.42	0.86	30.2
Cinnamon-Oil	200	1.78	0.71	48.7
	300	1.44	0.61	58.5
	400	1.02	0.54	70.6
	500	0.92	0.43	73.4

Pitting Corrosion

Fig 4 shows the potentiodynamic anodic polarization curves of carbon steel electrode in different concentrations of NaCl solutions at a scan rate of 1mVs⁻¹. The slow scan rate allows the pitting initiation to occur at less positive potential [28]. Inspection of the curves in figure 4 reveals that, in the concentration range of NaCl studied the metal does not exhibit any anodic peak. However, an increasing the concentration of Cl⁻ ion, this is a sudden and marked increase of current density at a definite potential indicating the passivity breakdown and initiation of pitting corrosion [29]. The potential at which the sudden rise takes place is defined as the pitting potential (E_{pitt}). The higher concentration of Cl⁻ ion, the higher is the shift of pitting potential toward the active direction. The breakdown of passivity could be attributed to the adsorption of chloride ions on the passive film / solution interface [30-31]. Thus, when the electrostatic field reaches a certain value, the adsorbed anions begin to penetrate into the passive film and the pitting corrosion is initiated.

**Figure 3.1** Potentiodynamic anodic polarization curves of carbon steel in 0.5 M H₂SO₄ solution containing different concentrations of NaCl solutions at a scan rate 1mVsec⁻¹ (1) 0.00 (2) 0.1M (3) 0.2M (4) 0.3M (5) 0.4M (6) 0.5M NaCl

The dependence of E_{pitt} with the concentration of Cl^- ion is shown in Fig 5. The straight line relationship is obtained that obeys the equation [30-31].

$$E_{\text{pitt}} = a_1 - b_1 \log C_{\text{Cl}^-} \quad (7)$$

where a_1 and b_1 are constant that depend on the nature of metal used and the type of the aggressive ions, Inspection of (Fig.5), it is clear that as the concentration of Cl^- is increasing the pitting potential shifts to more negative values. This is attributed to the propagation of pitting corrosion.

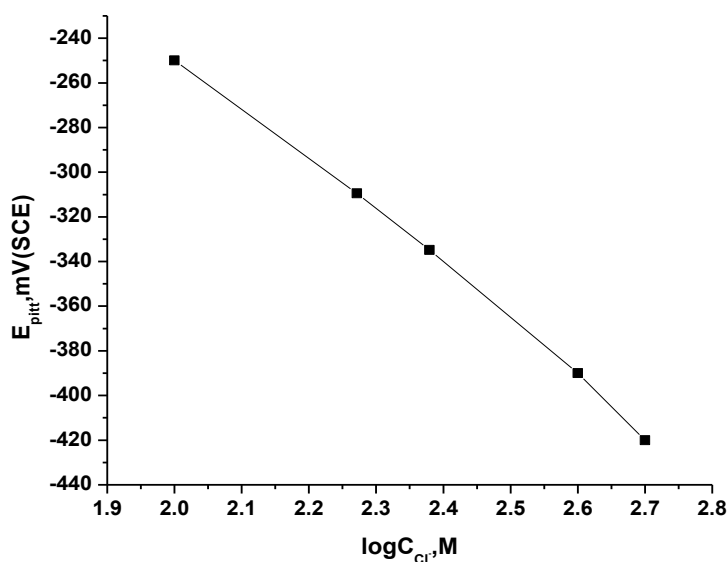


Figure 5 Potentiodynamic anodic polarization curves of carbon steel electrode in 0.5 M NaOH solution and different concentrations of NaCl at scan rate 1 mV sec^{-1} (1) 0.0M NaCl (2) 0.1M NaCl (3) 0.2M NaCl (4) 0.3M NaCl (5) 0.4M NaCl (6) 0.5 M NaCl

Inhibition of pitting corrosion

The effect of the increasing addition of the studied natural oils on the potentiodynamic anodic polarization curves of carbon steel in 0.5 M NaOH+0.5 M NaCl was studied at a scan rate of 1 mVs^{-1} . Similar curves (not shown) to those of Fig 4 were obtained in the presence of these oils. In their presence, the pitting potential was shifted toward a more positive direction this indicates the inhibiting effect of these oils for pitting corrosion.

Figure 6 represents the relationship between E_{pitt} and $\log C_{\text{inh}}$. From the curves of this figure, it is clear that, as the concentration of oils increases the pit is shifted to a more positive direction in accordance with the following equation [32].

$$E_{\text{pitt}} = a_2 + b_2 \log C_{\text{inh}} \quad (8)$$

where a_2 and b_2 are constants which depend on the type of additive and the nature of the electrode.

Inhibition afforded by these oils decreases in the following order:

Ginger oil > Garlic oil > Cinnamon oil

This order is a good agreement with the results obtained from other two techniques used.

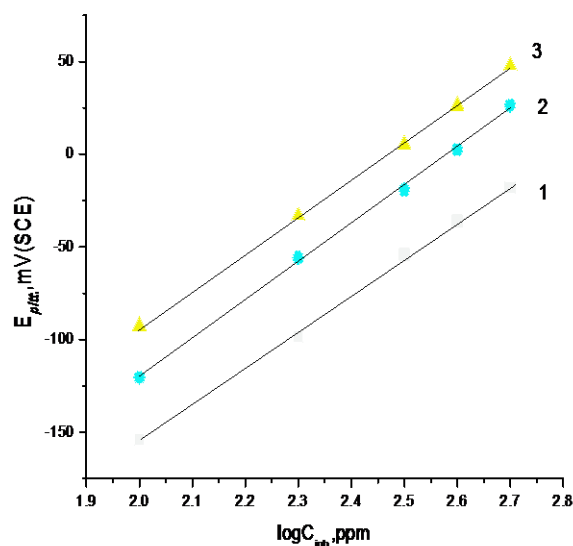


Figure 6 The relationship between pitting potential of C-steel and logarithm the concentration of natural oils (1) Ginger oil (2) Garlic oil (3) Cinnamon oil in the presence of 0.5 M NaOH solution

Inhibition mechanism

Inhibition the general and pitting corrosion of carbon steel in 0.5M NaOH solution by some natural oils, namely, ginger, garlic and cinnamon were investigated using galvanostatic and potentiodynamic anodic polarization techniques. There are some kinetic corrosion parameters were calculated. As the concentration of these oils increases led to decrease of weight loss, increase of surface coverage, decrease of peak current density, decrease of the corrosion current density and increase of inhibition efficiency.

The inhibiting effect of the natural oils could be explained to the adsorption of its component on the metal surface. The adsorbed layer act as a barrier between the metal surface and aggressive solution leading to decrease in the corrosion rate [33]. The adsorption process of these oils on the steel surface depends on many factors, including molecular size, charge density, presence of active centers on the chemical structure of inhibitor and ability to form complexes [34]. The inhibition efficiency is determined by molecular adsorption of the basic component of the oils such as aromatic rings on the surface of the steel.

Conclusions

1. Natural oils e.g. ginger, garlic and cinnamon inhibits the corrosion of carbon steel (G-1018) in 0.5M NaOH solution.
2. The inhibition efficiency increases with increasing the concentration of these oils.
3. The inhibition of this oil is due to the adsorption of the main component in the chemical structure of each oil on the surface of C-Steel.
4. The adsorption of these natural oils on the surface of C-Steel follows Langmuir adsorption isotherm.
5. These oils inhibit the pitting corrosion C-Steel in chloride containing solution.
6. The percentage inhibition efficiency obtained from the used techniques we're in a good agreement with each other.

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