



Turmeric and ginger as green inhibitors of mild steel corrosion in acidic medium

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Abstract

Extracts of turmeric and ginger rhizomes were separately studied as inhibitors of mild steel corrosion in 1 M HCl. The corrosion inhibition efficiency (IE) was investigated using weight loss method and potentiodynamic polarization measurements. Weight loss measurements were carried out at 25, 45, and 65°C for 1 h immersion time. The topography of the mild steel surface was analyzed using field emission scanning electron microscopy (FESEM). The results show that both inhibitors inhibit the mild steel corrosion and act as mixed type inhibitors. The IE increases with the increase in the inhibitors concentrations to attain 92 and 91% at 10 g/L of turmeric and ginger, respectively. At high concentrations of the inhibitors (i.e. 7.5 and 10 g/L), turmeric and ginger show their higher inhibition efficiencies at 45°C and 25°C, respectively. The adsorption of the inhibitors on mild steel surface obeys the Langmuir adsorption isotherm. Based on the obtained results, turmeric acts as a better corrosion inhibitor compared to ginger.

Keywords: Adsorption isotherms; Weight loss; Polarization; FESEM; Acid corrosion

1. Introduction

Metal corrosion is a serious issue since it causes a waste in resources and reduces equipment lifetime especially in acid solutions [1]. Therefore, the prevention of metal corrosion or the reduction of its rate has been given considerable effort. Corrosion inhibition of iron and mild steel in acid solutions has been extensively studied [2-4]. The use of corrosion inhibitors is one of the most practical and economic methods in corrosion inhibition studies. Organic compounds with heteroatoms such as oxygen, nitrogen, sulfur and phosphorus are the most reported inhibitors for the metal corrosion. Organic inhibitors act by the adsorption on the metal surface to form a layer and decrease the corrosion rate [5-7].

Organic compounds with low environmental impact are the most favorable corrosion inhibitors. Unlike synthetic corrosion inhibitors, plants extracts are eco-friendly, nontoxic, renewable, inexpensive and readily available. Many plants extracts have been studied and reported as effective inhibitors of iron and steel corrosion in acid solutions [8-10].

Turmeric and ginger rhizomes plants belong to Zingiberaceae family that is distributed mostly in tropical and subtropical areas. Zingiberaceae species have common uses in the Southeast Asian countries such as food flavor, traditional medicine, and source for certain dyes [11-13].

Turmeric rhizomes consist of volatile and non-volatile constituents. The non-volatile constituents are rich with phenolic compounds such as curcumin and other curcumin's derivatives. The corrosion inhibition effect of turmeric is attributed to the adsorption of phenolic constituents onto metal surface [14].

Corrosion inhibition performance of the ginger rhizomes is attributed mainly to the existence of 6-gingerol compound as a major component and other phenylpropanoid. These compounds possess an oxygen atom (heteroatom) at different functional groups. The presence of the oxygen atom and π -electrons of the aromatic ring is responsible for the inhibition performance of ginger extract [15].

In the present study, turmeric and ginger rhizomes were investigated and compared as green inhibitors of mild steel corrosion in 1 M HCl using weight loss, potentiodynamic polarization measurements and field emission scanning electron microscope (FESEM). The adsorption isotherm was also studied.

2. Materials and methods

2.1. Preparation of the test solution and inhibiting solution

The test solution (1 M HCl) was prepared by diluting analytical grade hydrochloric acid (37 wt. %) using distilled deionized water. The initial inhibiting solutions were prepared according to previously described procedure by Bouyanzer and Hammouti [16]. Ginger and turmeric rhizomes were separately crushed in 1 M HCl solution and were left for a period of four days.

2.2. Specimen preparation

The composition of the used mild steel was as follows (wt%): 0.305% C, 0.700% Mn, 0.016% P, 0.275% Si, 0.024% Cu, 0.075% Ni, 0.043% Cr, 0.012% Ti, 0.038% Al, 0.068% Zr, 0.021% Sn, and Fe balance. Mild steel specimens were abraded using 240, 320, 400, 600 and 1500 grades of sand papers. The specimens were well cleaned using distilled deionized water and then again by acetone.

2.3. Weight loss measurements

Weight loss was measured using specimens of apparent surface area of 4 cm². Mild steel specimens were immersed in 60 ml of 1 M HCl without and with various concentrations of the ginger and turmeric, separately. The measurements were carried out at 25, 45, and 65°C for 1 h immersion time. Each reported value was a mean of the duplicate experiments results for each case.

2.4. Potentiodynamic polarization measurements

The Autolab Potentiostat/Galvanostat instrument was used for the potentiodynamic polarization measurements by recording Tafel polarization curve. The measurements were carried out at room temperature (25±1°C) using 250 ml of 1 M HCl electrolyte without and with addition of the inhibitors. Polarization curves were recorded at a scan rate of 1 mV/s with scan range from -0.25 to +0.25 V with respect to open circuit potential (OCP). The measurements were conducted using a three-electrode cell assembly that contained a 1 cm² specimen of a mild steel embedded in specimen holder. Mild steel specimen acted as a working electrode (WE). Platinum electrode was used as a counter electrode (CE). The used reference electrode (RE) was a saturated calomel electrode (SCE).

2.5. Surface analysis

Mild steel surface was analyzed using a field emission scanning electron microscope (FESEM). The FESEM images were recorded for the samples after 2 h immersion time in the test solution at 25°C in the absence and presence of 7.5 g/L of the inhibitors.

3. Results and Discussion

3.1. Weight loss measurements

Corrosion rate (CR), in millimeter per year (mm/y), of mild steel in 1 M HCl without and with different concentrations of ginger and turmeric was calculated at different temperatures using Eq. 1 [17]:

$$CR \text{ (mm/year)} = \frac{87.6w}{AtD} \quad (1)$$

where w is the weight loss of mild steel (mg), A is the area of the specimen, t is the immersion time (h) and D is the density of mild steel (gcm⁻³).

The IE of the inhibitors was calculated using Eq. 2 [6]:

$$IE(\%) = \frac{W^{\circ} - W}{W^{\circ}} \times 100 \quad (2)$$

where W° and W are the corrosion rate of mild steel without and with the inhibitors, respectively. The values of CR and IE are given in Table 1.

Table 1 shows that the inhibitors reduce the corrosion rate of mild steel in 1 M HCl at all studied temperatures. The IE increases with the increase in the inhibitors concentrations. The inhibitory solutions of the ginger and turmeric consist of a mixture of compounds with heterocyclic structures that possess oxygen atom at different functional groups [14,15,18-20]. Therefore, the inhibition effect is due to the adsorption of the heterocyclic compounds onto the metal surface. According to the IE values, turmeric is more efficient inhibitor compared to ginger at most of the studied temperatures and concentrations.

As shown in Table 1, at high concentrations (i.e. 7.5 and 10 g/L), ginger shows its higher IE at 25°C. The IE of ginger decreases at the temperature of 45°C, and increases again at 65°C. The lower IE at 45°C can be explained by an increase of a desorption rate of the inhibitor's molecules from the steel surface. The higher IE

at 65°C is explained in terms of a specific interaction between the mild steel surface and the inhibitor at high temperature [16].

Turmeric shows the highest IE at a temperature of 45°C to attain 89 and 92% at 7.5 and 10 g/L, respectively. The IE of turmeric inhibitor increases with the increase of the temperature from 25°C to 45°C, and decreases at 65°C. This result can be explained by an increase in a desorption rate of the inhibitor at higher temperature.

Table 1: Corrosion rate (CR) and inhibition efficiency (IE) of ginger and turmeric at different temperatures.

T (°C)	Blank		2.5 g/L		5 g/L		7.5 g/L		10 g/L	
	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)
Ginger										
25	27.33	-	9.48	65.30	8.36	69.38	6.13	77.55	2.23	91.83
45	48.82	-	27.61	43.42	17.01	65.14	15.06	69.14	12.27	74.85
65	101.82	-	30.40	70.13	29.85	70.68	25.66	74.79	18.96	81.37
Turmeric										
25	27.33	-	8.08	70.41	6.69	75.51	5.85	78.57	5.02	81.63
45	48.82	-	9.76	80.00	6.69	86.28	5.29	89.14	3.90	92.00
65	101.82	-	31.24	69.31	22.31	78.08	19.80	80.54	16.17	84.11

3.2. Adsorption isotherms

Adsorption isotherms provide information about the interaction between corrosion inhibitors and metal surface. The experimental data which obtained from weight loss measurements were used to perform the adsorption isotherms study. Langmuir [21,22], Temkin [22], Frumkin [23] and Flory-Huggins [24] adsorption isotherms were applied.

$$\text{Langmuir: } \frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

$$\text{Temkin: } -2a\theta = \ln KC \quad (4)$$

$$\text{Frumkin: } \log \frac{\theta}{C(1-\theta)} = \log K + g\theta \quad (5)$$

$$\text{Flory-Huggins: } \log\left(\frac{\theta}{C}\right) = \log K + x\log(1 - \theta) \quad (6)$$

where K , ($L.g^{-1}$) is the equilibrium constant of adsorption, C is the inhibitor concentration in ($g.L^{-1}$), a is the molecular interaction parameter, g is the adsorbate parameter, and θ is the surface coverage. Surface coverage (θ) of the metal surface was calculated from weight loss data using Eq. 7:

$$\theta = \frac{IE(\%)}{100} \quad (7)$$

The obtained correlation coefficients (R^2) and lines' slopes are listed in Table 2.

Table 2: Correlation coefficients (R^2) and lines' slopes of several isotherms for ginger and turmeric adsorption on mild steel surface at different temperatures.

T (°C)	Langmuir		Temkin		Frumkin		Flory-Huggins	
	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
Ginger								
25	0.946	0.9594	0.1753	0.8105	0.9454	0.3418	0.5331	0.5592
45	1.04	0.9921	0.2234	0.9559	-0.0101	0.0009	1.0342	0.9153
65	1.1644	0.9908	0.0739	0.7337	-1.9128	0.3409	1.9882	0.6388
Turmeric								
25	1.1608	0.9992	0.0794	0.9944	-3.0367	0.971	2.6283	0.9769
45	1.0336	0.9996	0.0853	0.9975	-1.3348	0.8754	1.3852	0.9787
65	1.11	0.9994	0.1041	0.9844	-1.6469	0.9271	1.8662	0.9829

As shown in Table 2, Langmuir isotherm shows the best correlation (highest R^2) with the data of ginger and turmeric inhibitors. This explains the formation of monolayer of the inhibitors on mild steel surface and there is no interaction between the adsorbed molecules [23,25]. Flory-Huggins isotherm shows lower fit to the data of the inhibitors compared to Langmuir isotherm. Frumkin isotherm includes several cases which are attraction, repulsion, or no interaction between the adsorbed species. Frumkin isotherm becomes equivalent to the Langmuir isotherm when there is no interaction between the adsorbed species. The data of ginger inhibitor are not fitted to Frumkin isotherm. In addition, Frumkin isotherm show lower fit to turmeric data compared to Langmuir isotherm. Therefore, it can be concluded that the interaction between the adsorbed species which assumed by Frumkin isotherm is not expected [26]. The R^2 values obtained by Langmuir isotherm are higher and closer to one, compared to Temkin isotherm. Therefore, it can be concluded that there is no strong evidence for chemisorption of uncharged molecules on heterogeneous surface [27]. Furthermore, the slopes of the plots of Temkin, Frumkin, and Flory-Huggins show deviations from unity. The slopes of Langmuir's plots are almost unity, indicating that the adsorption of ginger and turmeric inhibitors onto mild steel obeys Langmuir isotherm [1,28-30].

Based on the discussion above, Langmuir isotherm shows the best correlation with the data of ginger and turmeric. Therefore, further details are discussed based on Langmuir isotherm. When (C/θ) was plotted versus the inhibitors concentration (C), a straight lines were obtained as shown in Figures 1 and 2.

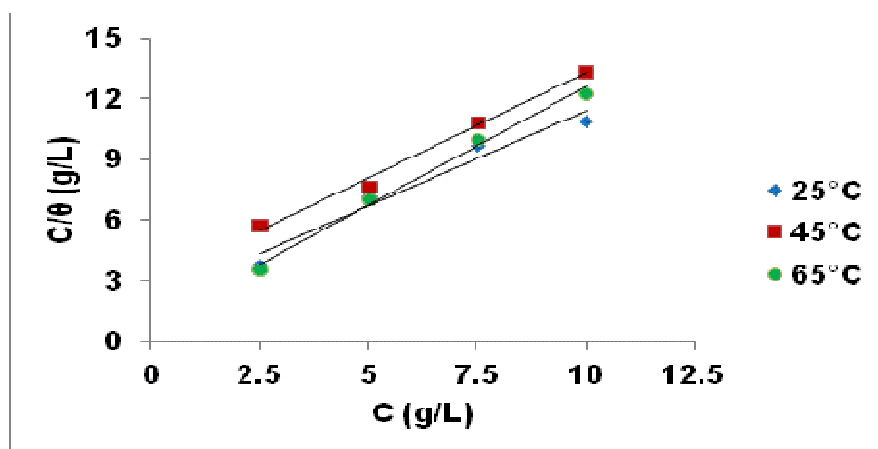


Figure 1: Langmuir adsorption isotherm of ginger on the mild steel surface in 1 M HCl at different temperatures.

According to the correlation coefficient (R^2) values (Table 2), Langmuir isotherm shows the best fit to turmeric data than the obtained fit to ginger data. The values of the equilibrium constant (K) are given in Table 3.

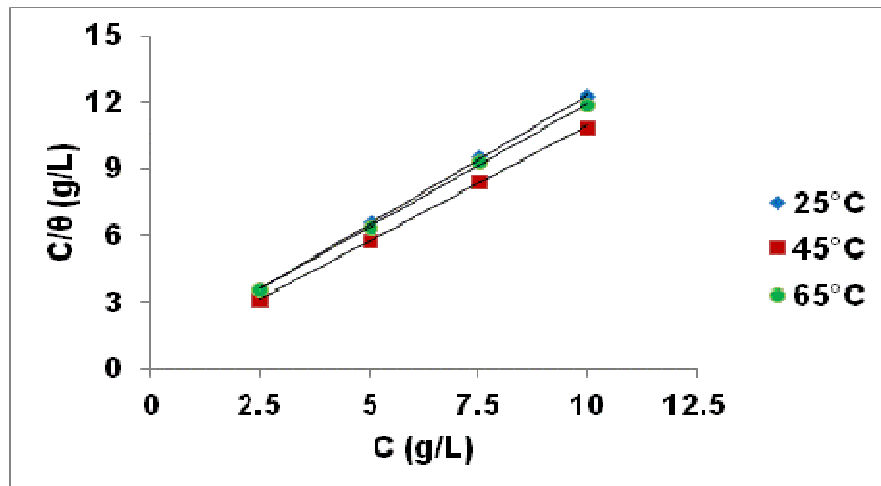


Figure 2: Langmuir adsorption isotherm of turmeric on the mild steel surface in 1 M HCl at different temperatures.

Table 3: Equilibrium constant (K) obtained by Langmuir isotherm for ginger and turmeric on mild steel surface at different temperatures.

T (°C)	Ginger		Turmeric	
	Intercept	K	Intercept	K
25	1.98	0.50505	0.735	1.36054
45	2.905	0.34423	0.585	1.70940
65	0.955	1.04712	0.86	1.16279

The higher value of K indicates stronger adsorption of the inhibitor on the mild steel surface and higher inhibiting effect [25]. Based on the values of the IE (Table 1) and K values of ginger inhibitor (Table 3), the lower values of K are at 45°C which show the lowest IE at all studied concentrations. The higher values of K are at 65°C which show higher IE especially at low concentrations (i.e. 2.5 and 5g/L). This result matches the findings obtained by Bouyanzer and Hammouti [16]. In addition, turmeric shows higher values of K at 45°C with higher IE at all studied concentrations. The lower K values are shown to be at 65°C. This indicates lower interaction between turmeric inhibitor and mild steel surface at 65°C compared to that at 45°C. This can be explained by the decrease of the strength of the interaction bonds at higher temperature.

3.3. Potentiodynamic polarization measurements

Figures 3 and 4 show the cathodic and anodic Tafel polarization curves of mild steel in 1 M HCl without and with different concentrations of ginger and turmeric, respectively. Tafel extrapolations of the anodic and cathodic lines of the polarization curves were used to determine various electrochemical parameters such as anodic and cathodic Tafel slopes (b_a and b_c), potential (E_{corr}), and current density of corrosion (i_{corr}) as given in Table 4. The IE was calculated using Eq. 8 [31,32]:

$$IE(\%) = \frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \times 100 \quad (8)$$

where i_{corr}° and i_{corr} are corrosion current densities in the absence and presence of the inhibitors, respectively. Table 4 shows a decrease in corrosion current density (i_{corr}) with the addition of the inhibitors. The value of i_{corr} decreases with increasing inhibitors concentrations. As shown by Figures 3 and 4, the addition of the inhibitors affects both the cathodic and anodic parts of the Tafel curves, and decreases both the cathodic and anodic current densities. Therefore, the presence of the inhibitors inhibits the hydrogen evolution and the anodic dissolution processes [15,33]. This result indicates that the inhibitors act as mixed type corrosion inhibitors. In addition, the maximum displacement in E_{corr} was 27mV and 38mV for ginger and turmeric, respectively. These results show that both inhibitors act as mixed type inhibitors since the displacement of $E_{corr} < 85mV$ [23,25,34].

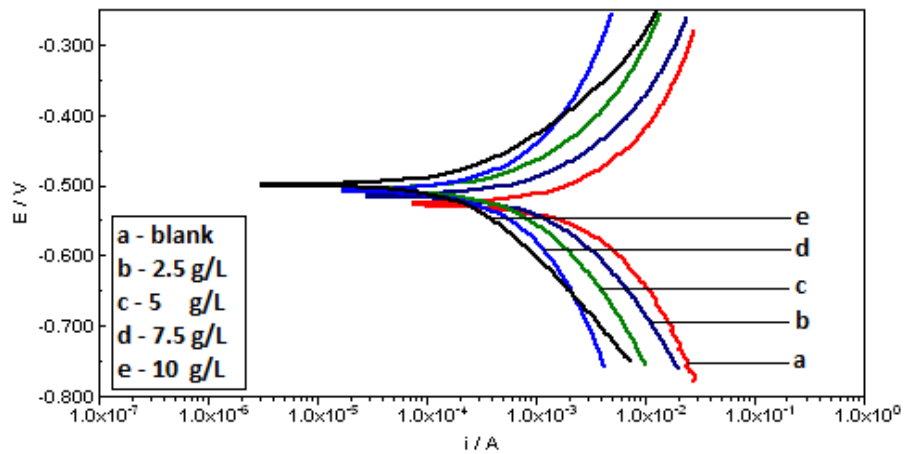


Figure 3: Polarization curves of mild steel in 1 M HCl without and with various concentrations of ginger at 25°C.

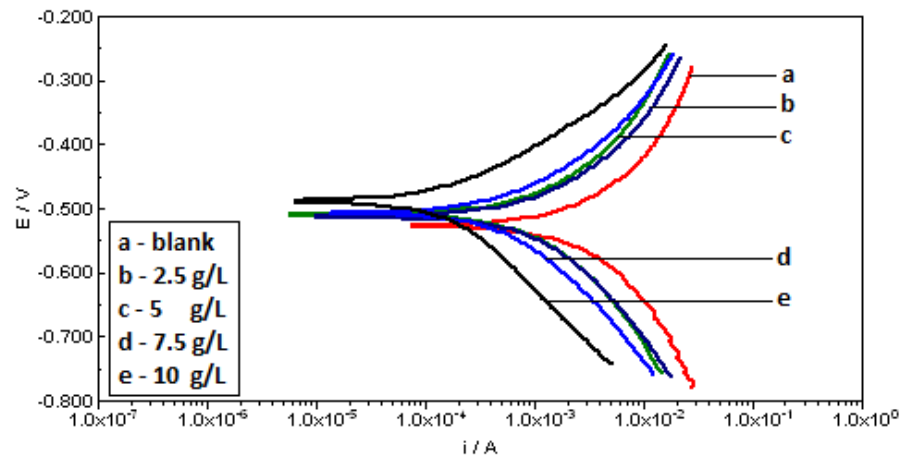


Figure 4: Polarization curves of mild steel in 1 M HCl without and with various concentrations of turmeric at 25°C.

Furthermore, the presence of the inhibitors changes the values of both anodic (b_a) and cathodic (b_c) Tafel constants (Table 4). This also confirms the mixed type inhibition mechanism of the inhibitors. The results obtained by potentiodynamic polarization measurements show that ginger and turmeric are effective inhibitors against mild steel corrosion in 1 M HCl. The IE increases with the increase in the inhibitors concentrations to attain 89 and 92% at 10 g/L of ginger and turmeric, respectively. The results indicate slightly better inhibition performance of turmeric compared to that of ginger. These results are in good agreement with the weight loss findings.

Table 4: Polarization parameters of mild steel in 1 M HCl without and with different concentrations of ginger and turmeric at 25°C.

Inhibitors	C (g/L)	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	E_{corr} (mV)	I_{corr} (μA cm ⁻²)	IE (%)
1 M HCl	0	134	128	-526	1587.0	-
Ginger	2.5	137	124	-513	844.6	46.78
	5	141	115	-506	444.9	71.96
	7.5	176	164	-507	376.5	76.27
	10	120	104	-499	165.3	89.58
Turmeric	2.5	129	119	-508	589.7	62.84
	5	133	101	-511	569.3	64.12
	7.5	137	113	-506	392.5	75.26
	10	133	96	-488	113.1	92.87

3.4. Surface analysis

Figure 5a and b shows FESEM images of polished mild steel surface and immersed samples for 2 h in the test solution (1 M HCl), respectively. The images show that the immersed mild steel surface is rough and highly corroded due to the acid attack. Figure 5c and d shows FESEM images of mild steel samples exposed for 2 h to the test solution containing 7.5 g/L of ginger and turmeric, respectively. The images show that mild steel surface is smooth in the presence of the inhibitors due to the formation of a protective layer onto the mild steel surface. The layer inhibits mild steel corrosion in acidic media.

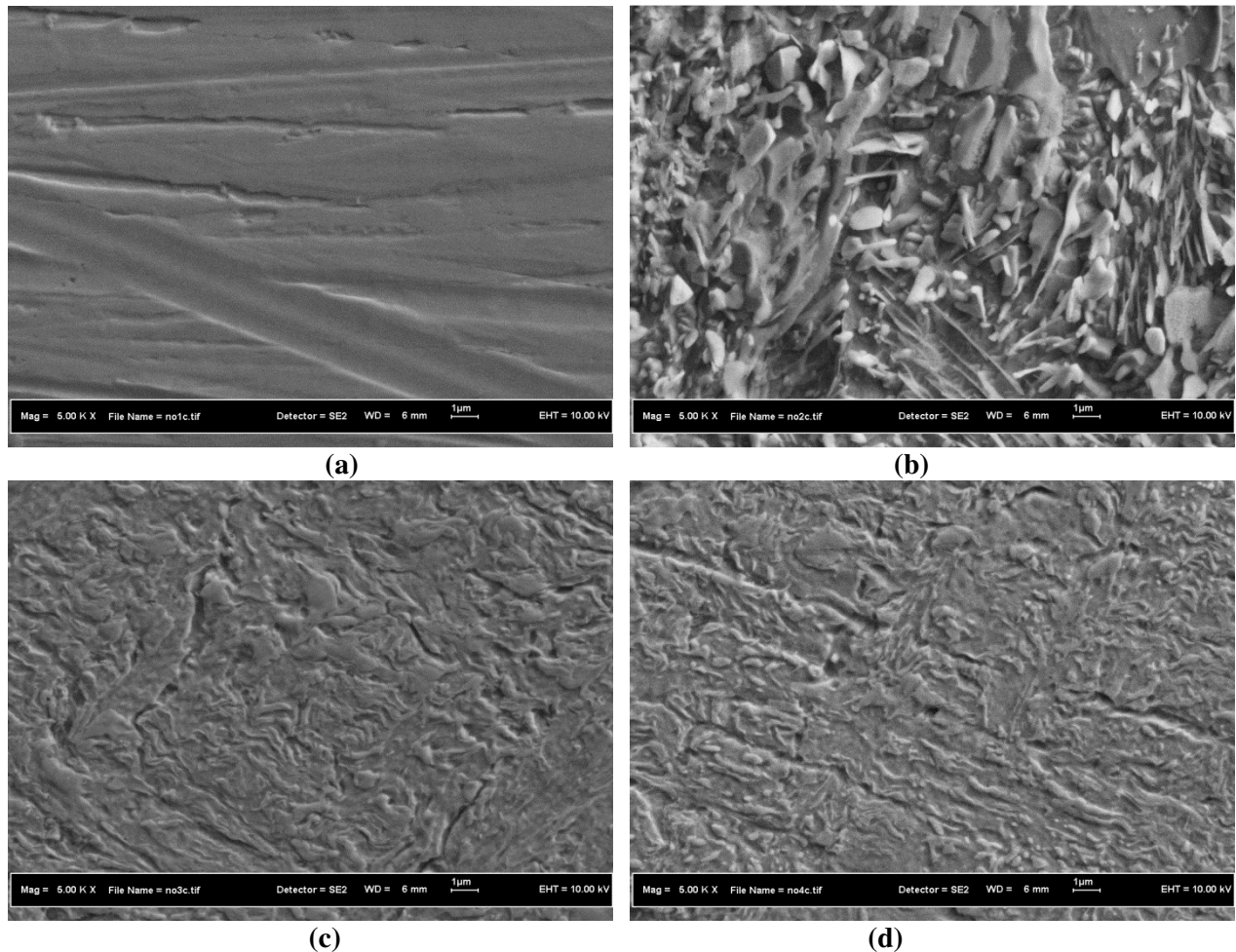


Figure 5: FESEM images of mild steel surface: (a) polished, (b) immersed in 1 M HCl for 2 h, (c) immersed in 1 M HCl with ginger for 2 h, (d) immersed in 1 M HCl with turmeric for 2 h.

Conclusion

Weight loss method, potentiodynamic polarization and field emission scanning electron microscopy (FESEM) were used to study the inhibition effect of turmeric and ginger extracts on the corrosion of mild steel in 1 M HCl. Turmeric and ginger showed good abilities to be effective inhibitors. The inhibition efficiencies determined by weight loss and potentiodynamic polarization methods are in good agreement. The corrosion inhibitory effect of both inhibitors occurs via adsorption of the extracts constituents onto the mild steel surface. The adsorption was found to follow Langmuir adsorption isotherm. There is no definite trend for the change of the inhibition efficiencies with temperature for both inhibitors. The FESEM images show that the mild steel surface is seriously corroded in the acidic medium without inhibitors. Mild steel surface is smooth in the presence of the inhibitors due to the formation of a protective film. The results show that turmeric performs as a better corrosion inhibitor with higher efficiencies at most of the studied temperatures and concentrations.

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