

Methanol Extract of *Rumex Vesicarius* L. as Eco-Friendly Corrosion Inhibitor for Carbon Steel in Sulfuric Acid Solution

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Abstract: The inhibiting effect of *Rumex vesicarius* L. extract on the carbon steel corrosion in H₂SO₄ was studied by weight loss, potentiodynamic polarization, electrochemical frequency modulation and electrochemical impedance techniques. The efficiency of the extract increased with increasing the extract concentration and with rising the temperature. The E_a^{*} (activation energy) and other parameters for the corrosion procedure have also been measured and discussed. potentiodynamic polarization measurements specified that this extract acts as mixed type inhibitor and chemically adsorbed on carbon steel surface following the Temkin isotherm. The data from different tests are in excellent agreement.

Keywords: *Rumex vesicarius* extract, EIS, EFM, SEM, Potentiodynamic polarization

Introduction

Carbon steel is the greatest useful substance which utilized as a material constructional in several productions and this is due to its outstanding mechanical properties and little price. Acidic solutions are utilized in several procedures such as; pickling of metals to eliminate scale, oil refinery by chemical procedures, components in rocket tools *etc.*,¹⁻⁴. Corrosion is the demolition of alloys and metals by electrochemical and chemical reactions with its environment. This phenomenon can be controlled and prevented using several methods^{5,6}. Corrosion inhibitors are widely used in industry for protecting a metal against Corrosion. There are several research have been distributed on the utilized of nature produces as corrosion protection⁷⁻²¹. Plant extracts utilized as corrosion protection are safe environment and economic. A lot of plant extracts employed as effect as corrosion protection for carbon steel in solution of acid²²⁻²⁴. The plant under studied is *Rumex vesicarius* which are edible. The leaves of greatest kinds include tannin and oxalic acid and many have slightly and astringent purgative potentials. This plant belongs to the family of Polygonaceae. In this paper the inhibiting effect of *Rumex vesicarius* L. extract on the carbon steel (CS) corrosion in H₂SO₄ was studied by using weight loss (WL), potentiodynamic polarization (PP), electrochemical frequency modulation (EFM) and electrochemical impedance (EIS) techniques. Morphology of surface was measured using SEM.

Experimental

Composition of CS sample is: 0.060% P, 0.0260% S, 0.10% C, 0.40% Mn and Fe rest. The coupons measure 2.0x2.0x0.2 cm were abraded to finish a mirror with help of emery paper of different grades and washed with second distilled water and dried utilizing filter papers.

Preparation of plant extracts

Plant material *Rumex vesicarius* were dried in the shade at room temperature, ground using electrical mill into fine powder and extracted by soaking in methanol. The solvent from extracts was removed and dried under vacuum at 60-65 °C using a rotary evaporator. The solid of the extract was liquefied in second distilled water (1 g /L). The crude extracts were preserved under refrigeration until use²⁵.

Weight loss method

The specimens were abraded with emery paper, cleaned by second distilled water and lastly dried between two filter papers and weighed. The samples were dipped in 100 mL of 0.5 M of H₂SO₄ in existence and nonexistence of various concentration of the extract. The concentration range of *Rumex vesicarius* extract used was varied from 50 to 300 ppm. The immersion time intervals from 30 to 180 min. After specified periods of time, the coins were weighed again. The corrosion rates (CR) of the metal specimens were measured using the following relationship²⁶:

$$CR = \Delta W / At \quad (1)$$

CR= corrosion rate, ΔW =reduction in mass (mg), A= surface area (cm²), t= time (min) . The protection efficiency (IE%) was obtained from Eq.2.

$$IE\% = 100 \times [1 - (\Delta W_1 / \Delta W_2)] \quad (2)$$

Where, ΔW_2 and ΔW_1 are the weight losses in nonexistence and existence of the extract, respectively.

Electrochemical techniques

A three electrode cell assembly was used for electrochemical measurements. They were arranged in a glass cell. (SCE) saturated calomel electrode as a reference electrode, a platinum counter electrode as auxiliary electrode and CS as a working electrode. The working electrode was made of square specimen of CS with area 1 cm². The electrode surface was treated in the same manner as in the weight loss test. All tests were performed at temperature (25.0 °C). Before starting the measurements, the potential of electrode was studied for 25 min. Measurements were performed by Gamry apparatus (PCI4/750) with Gamry classification depends on the ESA 400 and computer frame works software DC 105 for PP tests, software EFM140 for EFM and software EIS 300 for EIS.

Electrochemical frequency modulation measurements

Two frequencies 2, 5 Hz were used as potential perturbation²⁷, with frequency = 0.1 Hz was used for EFM test. The (CF-2 and CF-3) causality factors, (i_{corr}) and β_a and β_c were calculated by using the biggest peaks²⁸.

Electrochemical impedance measurements

Open circuit potential (OCP) has been used and current signals in frequency range from 100 kHz to 10 Hz for impedance measurements. The θ and %IE were calculated using the following Eq.3

$$IE\% = 100 \times [1 - R_{ct (free)} / R_{ct (inh)}] \quad (3)$$

Where $R_{ct (free)}$ and $R_{ct (inh)}$ are the resistances without and with inhibitors individually.

Potentiodynamic polarization tests

Potentiodynamic polarization scan used to obtain Tafel curves by sweeping the working potential from -700 to 700 mV at scan rate 1 mVs⁻¹. i_{corr} was calculated by extrapolation of cathodic and anodic Tafel lines to gives $\log i_{\text{corr}}$ and E_{corr} . θ and %IE were given from the EIS results using the below Eq 4.

$$\text{IE}\% = 100 \times [1 - i_{\text{corr}}(\text{inh}) / i_{\text{corr}}(\text{free})] = \theta \times 100 \quad (4)$$

Where $i_{\text{corr}}(\text{inh})$ and $i_{\text{corr}}(\text{free})$ are the currents for corrosion in the absence and presence of *Rumex vesicarius* extract, respectively.

Results and Discussion

The data of CR, θ and IE% of CS in H₂SO₄ (0.5 M) solution in the various concentration of *Rumex vesicarius* extract are given in Table 1. The weight loss of CS in acidic solution in the absence and presence of various concentration of extract after various immersion time (30-180 min) at 25.0 °C are given in Figure 1. %IE improved with increase the concentration of *Rumex vesicarius* and with increase in temperature. The %IE is due to the adsorbed *Rumex vesicarius* extract on the CS and formation of a layer from adsorbed molecules on CS surface which isolates the surface of CS from acidic solution and blocking the sites of corrosion²⁹.

Table 1. Effect of different concentration of *Rumex vesicarius* extract on CR and IE% of CS in H₂SO₄ at various temperatures

Conc., of Extract ppm	25 °C		30 °C		35 °C		40 °C		45 °C	
	CR mg cm ⁻² min ⁻¹	IE%	CR mg cm ⁻² min ⁻¹	IE%	CR mg cm ⁻² min ⁻¹	IE%	CR mg cm ⁻² min ⁻¹	IE%	CR mg cm ⁻² min ⁻¹	IE%
0	0.0428	-	0.0715	-	0.1085	-	0.1979	-	0.2789	-
50	0.0138	67.7	0.0198	72.3	0.0263	75.8	0.0406	79.5	0.0541	80.6
100	0.0116	72.8	0.0161	77.5	0.178	83.6	0.0287	85.5	0.0354	87.3
150	0.0100	76.6	0.0139	80.5	0.0152	86.0	0.212	89.3	0.027	90.3
200	0.0090	78.5	0.0123	82.8	0.0137	87.4	0.0181	90.9	0.0221	92.1
250	0.0084	80.4	0.0107	84.9	0.0116	89.3	0.0154	92.2	0.0182	93.5
300	0.0077	82.1	0.0095	86.8	0.0102	90.6	0.0125	93.7	0.0143	94.9

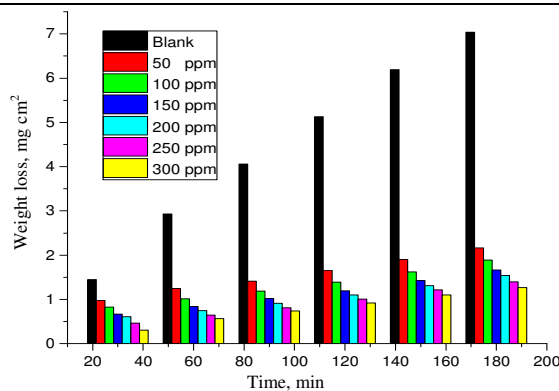


Figure 1. Weight loss of CS in acidic solution in the *Rumex vesicarius* extract at different concentration

Adsorption isotherms

Rumex vesicarius extract is adsorbed on the CS surface due to that the interaction energy among the CS surface and the extract is more than that between H₂O molecules and metal^{30,31}. From the data the Temkin model adsorption isotherms fit in the excellent manner (Figure 2). The Temkin adsorption isotherm may be expressed by:

$$a\theta = \ln K_{\text{ads}} C \quad (5)$$

Where C = concentration of the extract

Table 2. Thermodynamic adsorption parameters

T, K	log K _{ads}	−ΔG [°] _{ads} , kJ mol ^{−1}	ΔH [°] _{ads} , kJ mol ^{−1}	ΔS [°] _{ads} , J mol ^{−1} K ^{−1}
298	4.96	38.3		407.7
303	5.23	40.5		408.1
308	5.51	42.8	83.2	409.0
313	5.71	44.7		408.2
318	5.88	46.4		407.6

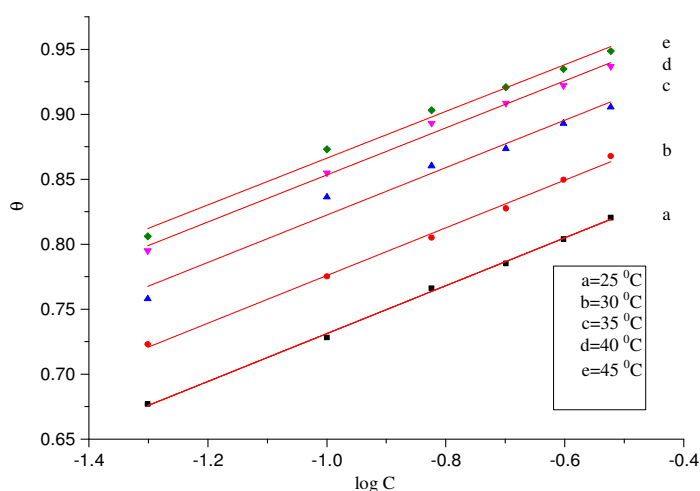


Figure 2. Temkin adsorption model of *Rumex vesicarius* extract on the CS surface at different temperatures

Thermodynamic parameters

The thermodynamic parameters such as; ΔG° , ΔS° , ΔH° and E_a° were calculated³²⁻³⁴ from the corrosion rate data obtained from weight loss experiments using the equation 6 and listed in the Table 2. E_a° was estimated from Arrhenius equation 7:³⁵

$$\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - T\Delta S^{\circ}_{\text{ads}} \quad K_{\text{ads}} = (1/55.5) \exp(-\Delta G^{\circ}_{\text{ads}}/RT) \quad (6)$$

$$k = A \exp(-E_a^{\circ}/RT) \quad (7)$$

Where A = Arrhenius constant, R=gas constant and k=rate of corrosion. Figure 3 was plotted between $\log k_{\text{corr}}$ vs. $1/T$ for various concentration of *Rumex vesicarius* extract. From the figure the E_a° value can be calculated from the slope of the line. The ΔH° and the ΔS° can be computed using another formula of transition state expression:

$$k = (RT/Nh) \exp(\Delta S^{\circ}/R) \exp(\Delta H^{\circ}/RT) \quad (8)$$

Where, h = Planck's constant and N = Avogadro's number. The data of ΔH^* and ΔS^* can be measured by plotting $\log(k_{\text{corr}}/T)$ vs. $1/T$ (Figure 4). The data of E_a , ΔS^* and ΔH^* are shown in Table 3.

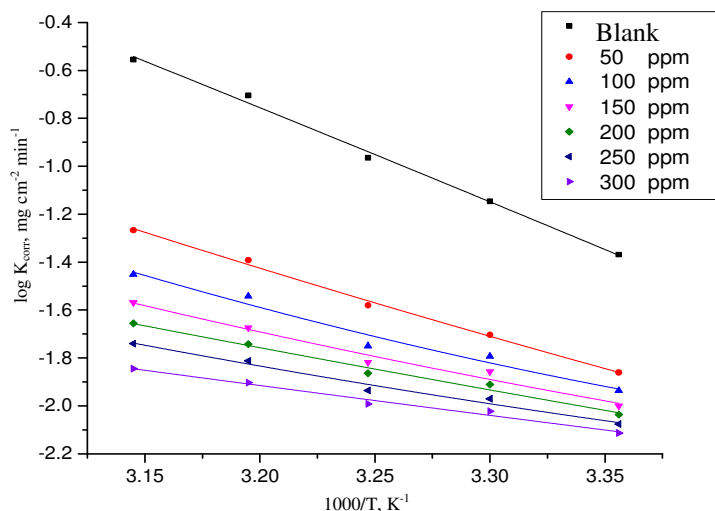


Figure 3. $\log k_{\text{corr}}$ vs. $1/T$ curves for various concentration of *Rumex vesicarius* extract

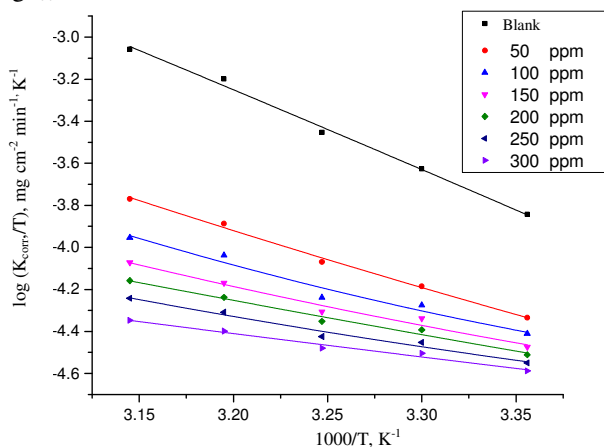


Figure 4. $\log (k_{\text{corr}}/T)$ vs. $1/T$ diagram for various concentration of *Rumex vesicarius* extract

Table 3. Thermodynamic parameters for corrosion of CS at different concentration of *Rumex vesicarius* extract in 0.5 M H_2SO_4 solution

C_{inh} , ppm	E_a^* , kJ mol^{-1}	ΔH^* , kJ mol^{-1}	$-\Delta S^*$, $\text{J mol}^{-1}\text{K}^{-1}$
0	75.2	31.6	27.3
50	54.4	22.5	106.6
100	44.3	18.1	142.1
150	37.9	15.4	164.3
200	33.8	13.6	179.1
250	30.1	11.9	192.2
300	23.9	9.3	213.8

Potentiodynamic polarization measurements

The potentiodynamic polarization curves for CS in the various concentration of *Rumex vesicarius* extract at 25 °C are shown in Figure 5. From the figure, one can noted that both (discharge hydrogen) cathodic and (CS dissolution) anodic reactions were inhibited by adding various concentration of *Rumex vesicarius* extract. Both β_a and β_c were moved to positive and negative directions, respectively. The electrochemical parameters, E_{corr} , β_a and β_c , θ , IE% and i_{corr} were measured and given in Table 4. Data shows that by addition of extract the values of i_{corr} were lowered while the values of E_{corr} and β_a and β_c had no significant change. So the *Rumex vesicarius* extract performance as mixed type inhibitor.

Table 4. Electrochemical parameter, i_{corr} , E_{corr} , β_a , β_c , k_{corr} , θ and IE% of CS in 0.5 M H_2SO_4 in the various concentration of *Rumex vesicarius* extract

C_{inh} , ppm	i_{corr} , $\mu\text{A cm}^{-2}$	$-E_{\text{corr}}$, mV v.s. SCE	β_a , mV dec $^{-1}$	β_c , mV dec $^{-1}$	k_{corr} , mpy	θ	IE%
0	1350	448	81.6	144.2	616.7	-	-
50	100	487	53.6	179.3	45.9	0.926	92.6
100	92.5	485	48	148.4	42.3	0.931	93.1
150	79.9	477	48.8	189	36.5	0.941	94.1
200	76.1	482	52.2	174	34.8	0.944	94.4
250	72.5	476	41.2	156	33.2	0.946	94.6
300	59.7	475	49.6	169	27.3	0.958	95.8

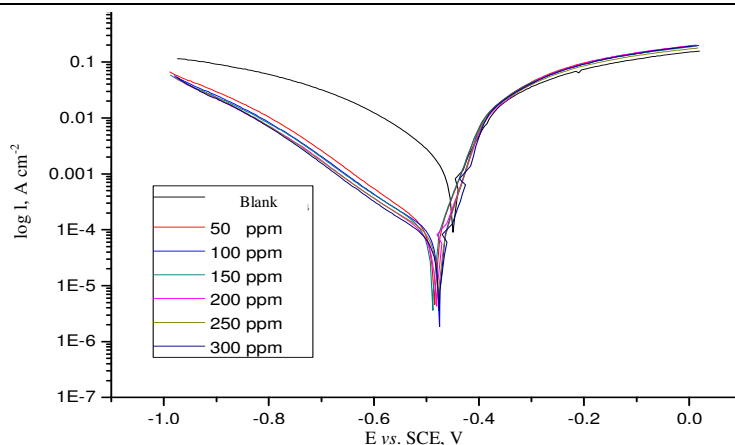


Figure 5. Potentiodynamic polarization diagram for CS in 0.5 M H_2SO_4 in the various concentration of *Rumex vesicarius* extract at 25 °C

EFM Tests

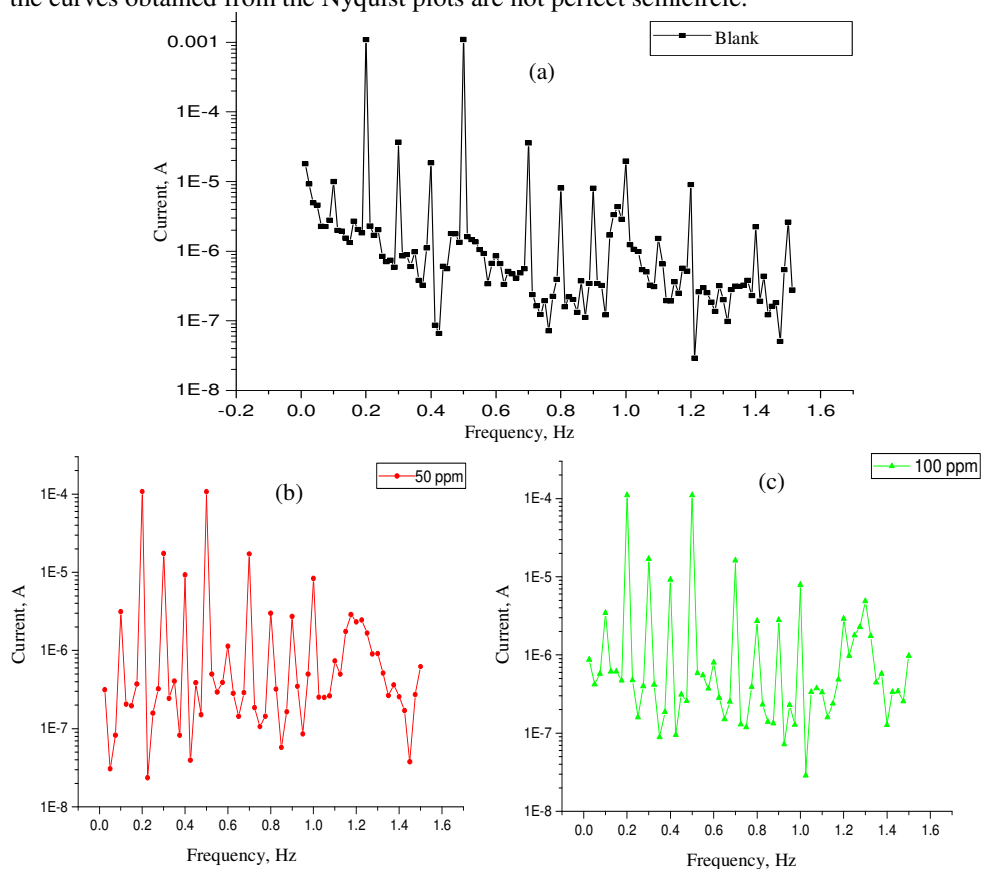
The data obtained from EFM for CS in 0.5 M H_2SO_4 at various concentration of *Rumex vesicarius* extract at 25 °C were measured and are listed in Table 5. The data observed that, the corrosion current densities decrease by increasing the concentration of *Rumex vesicarius* extract while the inhibition efficiency (IE%) increases. The causality factors are close to their theoretical values. The values of i_{corr} can be obtained directly from EFM measurements and independent of the knowledge of Tafel constants. The IE% can be calculated as in Eq. 4. The intermodulation spectra obtained from EFM in absence and presence of different concentration of *Rumex vesicarius* extract are shown in Figure 6(a-g).

Table 5. EFM for CS in the various concentration of *Rumex vesicarius* extract at 25 °C

Conc., of Extract, ppm	$i_{\text{corr.}}$ $\mu\text{A cm}^{-2}$	β_a , mV dec^{-1}	β_c , mV dec^{-1}	CF-2	CF-3	$k_{\text{corr.}}$ mpy	θ	IE%
0	2217	116.3	152.4	1.91	5.06	1.01	-	-
50	148.9	62.4	162.8	1.97	3.18	68.1	0.933	93.3
100	144.8	61.1	139.7	1.95	3.34	66.2	0.935	93.5
150	137.3	59.5	187.7	1.92	3.03	62.7	0.938	93.8
200	132.9	59.7	157.9	1.96	2.90	60.7	0.940	94.0
250	120.9	57.5	157.8	1.97	3.51	55.2	0.954	95.4
300	107.8	59.0	157.5	1.90	3.62	49.3	0.951	95.1

EIS measurements

The EIS of CS in the various concentration of *Rumex vesicarius* extract are shown in Figures 7(a-b) where Figure 7(a) is Nyquist plots and Figure 7(b) is Bode plots. The curves shows that there are gradual increases in the shape of each semicircle of the Nyquist curves by increasing the concentration of the extract. The obtained EIS parameters (R_{ct}), the double layer capacitance (C_{dl}) and the (IE%) are listed in Table 6. These data shows there is an increase in (R_{ct}) while the (C_{dl}) decreased. Due to electrode surface homogeneities and the roughness, the curves obtained from the Nyquist plots are not perfect semicircle.



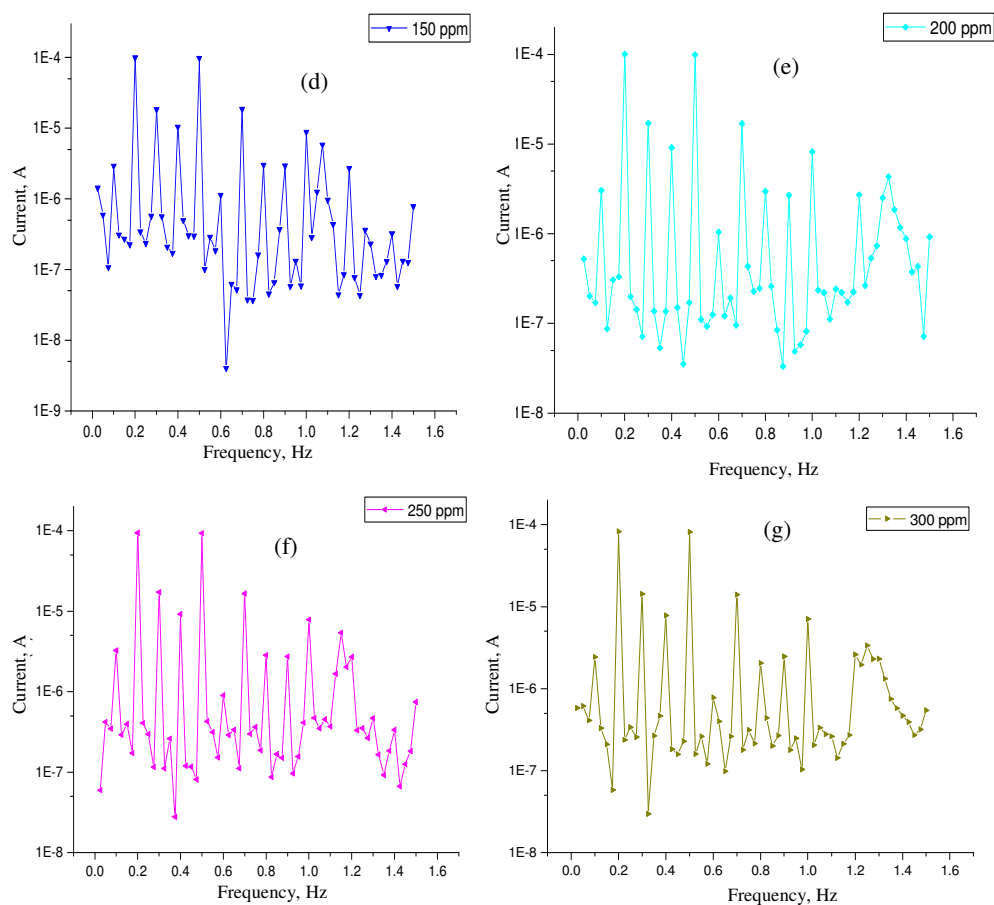


Figure 6. Intermodulation spectrum for CS in 0.5 M H_2SO_4 in the various concentration of *Rumex vesicarius* extract

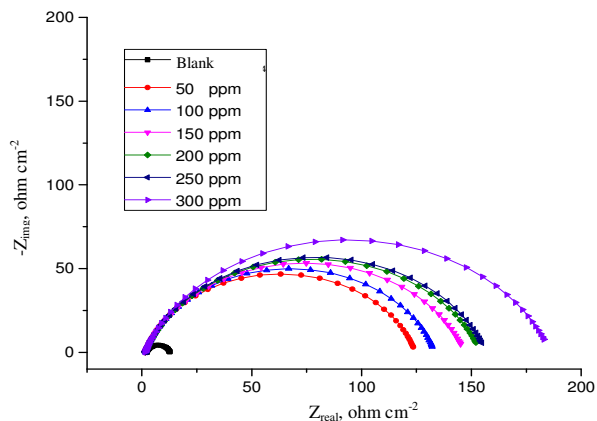


Figure 7(a). Nyquist diagrams for CS in the various concentration of *Rumex vesicarius* extract

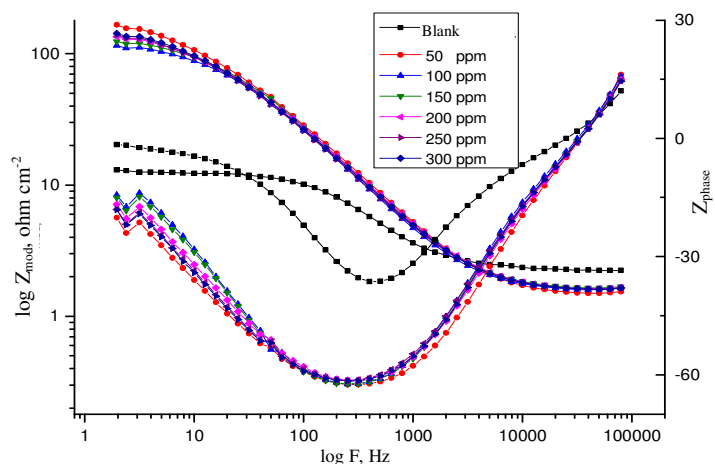


Figure 7(b). Bode curves for CS in 0.5 M H_2SO_4 for various concentration of *Rumex vesicarius* extract

Table 6. Data from EIS measurements for CS corrosion in the existence and nonexistence of various concentration of *Rumex vesicarius* extract at 25 °C

Conc., ppm	R_{ct} , Ωcm^2	C_{dl} , $\mu\text{F cm}^{-2}$	θ	IE%
0	10.36	96.1	-	-
50	122.80	92.3	0.916	91.6
100	131.7	90.1	0.921	92.1
150	145.2	89.6	0.929	92.9
200	153.0	86.3	0.932	93.2
250	155.2	81.6	0.934	93.4
300	184.7	77.6	0.944	94.4

SEM analysis

The CS morphology surface was analyzed using SEM experiments after immersion in 0.5 M H_2SO_4 in the absence and presence of 300 ppm of *Rumex vesicarius* extract for 24 h immersion. Figure 8(a) shows the clear CS surface, Figure 8(b) gives the surface of the metal was damaged by H_2SO_4 and Figure 8(c) shows the surface of the metal in presence of 300 ppm of *Rumex vesicarius* which does not affected by corrosion.

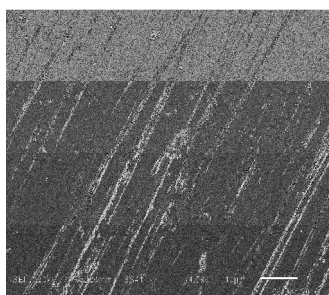


Figure 8(a). SEM of Pure metal

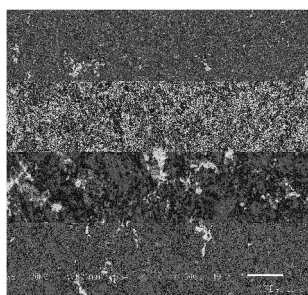


Figure 8(b). SEM of Metal + H_2SO_4

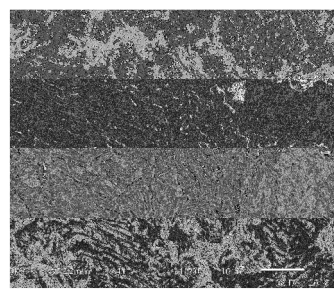


Figure 8(c). SEM of Metal + H_2SO_4 + 300 ppm of *Rumex vesicarius*

Explanation for inhibition

This plant mainly contains anthraquinones, flavonoids, polyphenols lipids and sterols³⁶. The adsorption on the CS surface (via the chemisorptions), include the movement of molecules of water from the CS surface and sharing of electrons among the iron and oxygen or *Rumex vesicarius* adsorb by donor-acceptor connections among vacant d orbitals of iron and π -electrons of the aromatic rings. In the acid medium steel surface bear's positive charge, so it is difficult to the protonated molecules to adsorb on the CS surface due to the electrostatic repulsion. Cl^- ions get adsorbed on CS surface create an excess negative charge toward the solution and favor more adsorption for the cations³⁷. Owing to the electrons lone-pair of O and N atoms in *Rumex vesicarius* molecules or the protonated molecules may association with freshly produced Fe^{2+} ions on the CS surface forming CS inhibitor complexes. These complexes adsorbed onto the CS by force (Van Der Waals) to form protecting cover to prevent CS from corrosion.

Conclusion

The inhibiting effect of *Rumex vesicarius* L. extract on the carbon steel corrosion in H_2SO_4 was studied. The inhibition efficiency increases with the increase in the concentration of *Rumex vesicarius* extract. The *Rumex vesicarius* was adsorbed chemically and physically on the CS obeying Temkin isotherm. Results obtained from potentiodynamic polarization measurement indicate that this extract acts on both cathodic and anodic reactions (*i.e.* mixed type inhibitor). Results obtained from weight loss measurements and electrochemical tests are in excellent agreement.

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