Effect of Almudinah Almonawarah Soil Solution on the Corrosion of Steel in Acidic Media

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The effect of Almadinah Almonawarah soil solution on the corrosion of steel in 2 M H_2SO_4 was studied using chemical (gravimetric and gasometric) techniques at 30 and 60° C and electrochemical (impedance and polarization) techniques at 30 ° C. The results revealed that the studied soil solution inhibits the corrosion of steel in acid media and the inhibition efficiency increase with increasing concentration of soil solution but decrease with rising temperature. Polarization showed that Almadinah Almonawarah soil solution acts as mixed type inhibitor. The experimental data were corroborated with the Freundlish as well as Langmuir adsorption isotherms. The values of activation energy suggest that the inhibition process is activation controlled.

Keywords: Acid solutions, Sulphuric acid, Steel, Electrochemical impedance spectroscopy, Polarization, Acid corrosion, Acid inhibition.

INTRODUCTION

Corrosion in an aqueous environment and in an atmospheric environment (which also involves thin aqueous layers) is an electrochemical process because corrosion involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. It results from the tendency of metals to react electrochemically with oxygen, water and other substances in the aqueous environment. Most useful metals react with the environment to form more or less protective films of corrosion reaction products that prevent the metals from going into solution as ions[1]. Electrochemical corrosion occurring under such conditions is a major destructive process that results in such costly, unsightly and destructive effects as the formation of rust and other corrosion products, the creation of the gaping holes or cracks in aircraft, automobiles, boats, gutters, screens, plumbing and many other items constructed of every metal except gold[2].

Soil corrosion is a complex phenomenon, with a multitude of variables involved. Chemical reactions involving almost each of the existing elements are known to take place in soils. The relative importance of variables changes for different materials, making a universal guide to corrosion impossible[3].

The response of steel to soil corrosion depends primarily on the nature of the soil and certain other environmental factors, such as the availability to moisture and oxygen. These factors can lead to extreme variations in the rate of the attack[4]. Some general rules can be formulated. Soils with high moisture content, high electrical conductivity, high acidity and high dissolved salts will be most corrosive. The effect of aeration on soils differs from the effect of aeration in water because poorly aerated conditions in water can lead to accelerated attack by sulfate-reducing an aerobic bacteria[4].

Steel is widely used in various industries as a structural material, and is one of the most significant compounds in the world for the industrial purposes. Categorically, sulfuric acid is extremely corrosive and is classified as hazardous chemical[4].

The known hazard effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Plant extracts and soil solutions have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extract are viewed as safe and an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost[5-23]. Many reports were done on the corrosion behaviour of metals in soil solution[24-32].

The current research work is an attempt to give some light on the effect of soil solution of Almadinah Almonawarah city in Saudi Arabia on the corrosion of steel in sulphuric acid as safe inhibitor.

EXPERIMENTAL

The experiments were performed with steel sample from Shaban company of weight percentage composition as in Table-1.

All chemicals used were of analytic grade. The blank corroding solution was 2.0 M H_2SO_4 (PAI-Panreac).

TABLE-1 CHEMICAL COMPOSITION OF STEEL								
Element	C	Cr	Mo	S	P	Si	Mn	Fe
Amount (%)	0.28	0.9	0.05	0.03	0.025	0.41	0.52	97.88

Preparation of soil solution (inhibitor): Soil was collected from underground of the middle of Almadinah Almonawarah city. The preparation of soil solution was carried out as follows:

A total of 600 g of dry soil were boiled with 600 mL de-ionized water with timely shaking and stirring for 1 day. The obtained extract was filtered by using Whatmann filter paper and placed in a measuring flask and completed to 250 mL by de-ionized water.

These measurements were carried out by two methods; hydrogen evolution method (HEM) and mass-loss method (MLM).

(a) Hydrogen evolution measurements: A clean weighed rod of 5 cm in length and 0.6 cm in diameter was polished by emery papers starting with 100 to1200 then it was immersed in the test solution and immediately the volume of the evolved hydrogen gas was measured as a function of time as described elsewhere[14,32]. In each new study the measurements of the sample area were checked and the change in volume of hydrogen gas was recorded every 5 min for 60 min.

(b) Mass loss measurements: The clean weighed rod of steel was suspended in the test solution and at the end of each experiment of HE measurements, the sample was withdrawn from the test solution, washed thoroughly with de-ionized water followed by ethanol and dried with a stream of air and reweighed.

Electrochemical techniques

(a) Electrochemical impedance spectroscopy measurements: Electrochemical impedance spectroscopy measurements were carried out using an impedance spectrum analyzer (ACM Gill AC) connected to a Samsung computer (Bridge DVD ASUS 8X max). All experiments were in the frequency range between 30 kHz and 0.5 Hz. The input signal amplitude was 10 mV peak to peak in both high and low frequency ranges.

(b) Potentiodynamic polarization measurements : The polarization curves were determined over a wide range of electrode potentials using AMEL-potentiostat Mod. 533 Italy, using the usual electrolytic cell as described elsewhere[33,34].

RESULTS AND DISCUSSION

The chemical measurements were carried out using hydrogen evolution (HE) and mass loss (ML) methods. Figs. 1 and 2 show the plots of hydrogen volume with time curves for steel in 2 M H_2SO_4 in the absence and presence of different concentrations of Almadinah Almonawarah soil solution at 30 and 60 °C, respectively. The corrosion rates (R and R') are given in Tables 2 and 3, respectively.

The inhibition percentages were calculated from hydrogen evolution (Inh.$_{HE}$%) and mass-loss (Inh.$_{ML}$%) measurements using the following two eqns. 1 and 2 [17,35]:

$$\text{Inh.\%}_{HE} = 100 \ (1 - R \ / \ R°) \qquad (1)$$
$$\text{Inh.\%}_{ML} = 100 \ (1 - R` \ / \ R`°) \qquad (2)$$

where R°, R, R`°and R` represent the corrosion rates from hydrogen evolution and mass-loss in the absence and presence of studied extract, respectively.
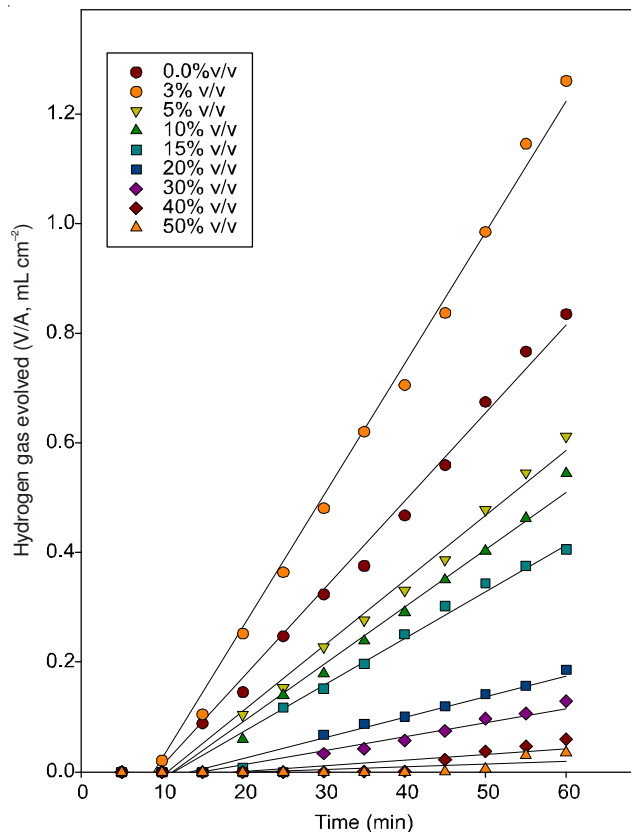

Fig. 1.   Hydrogen gas/time curves for steel corrosion in 2 M H_2SO_4 in presence of different concentrationsof Almadinah Almonawarah soil solution at 30 °C
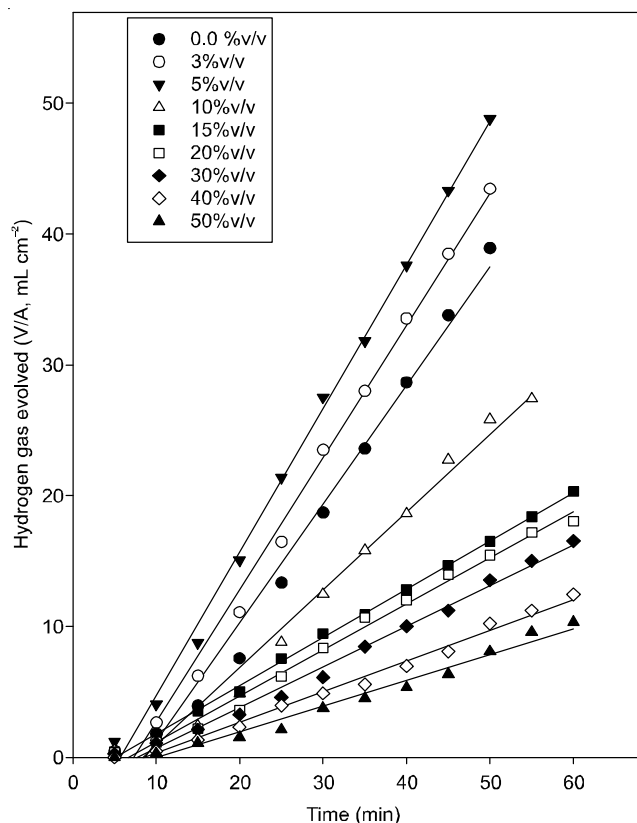

Fig. 2.   Hydrogen gas/time curves for steel corrosion in 2 M H_2SO_4 in presence of different concentrations of Almadinah Almonawarah soil solution at 60 °C

TABLE-2
RESULTS OBTAINED FROM MASS LOSS AND HYDROGEN
EVOLUTION METHODS FOR STEEL CORROSION IN 2 M
H_2SO_4 IN PRESENCE OF DIFFERENT CONCENTRATIONS OF
ALMADINAH ALMONAWARAH SOIL SOLUTION At 30° C

$c_{inh.}$	$R' \times 10^5$	$R \times 10^2$	$Inh._{ML}$	$Inh._{HE}$
0	3.644	1.606	–	–
3	6.134	2.394	-68.33	-49.06
5	2.5189	1.087	30.88	32.32
10	2.2725	0.945	37.64	41.16
15	1.5968	0.651	56.18	60.78
20	1.0047	0.376	72.43	76.59
30	0.61222	0.253	83.20	84.25
40	0.34223	0.101	90.61	93.71
50	0.15667	0.048	95.70	97.00t

TABLE-3
RESULTS OBTAINED FROM MASS LOSS AND HYDROGEN
EVOLUTION METHODS FOR STEEL CORROSION IN 2 M
H_2SO_4 IN PRESENCE OF DIFFERENT CONCENTRATIONS OF
ALMADINAH ALMONAWARAH SOIL SOLUTION AT 60° C

c_{inh}	$R_{ML} \times 10^3$	$R_{HE} \times 10^1$	$Inh._{ML}\%$	$Inh._{HE}\%$
0	1.5797	9.0679	–	–
3	2.3835	10.9613	-50.88	-20.88
5	2.0196	10.0871	-27.85	-11.24
10	1.9894	36.6449	25.94	26.66
15	0.6886	4.8819	45.00	46.16
20	0.55140	3.5186	65.10	61.20
30	0.52126	3.0971	67.00	65.85
40	0.26987	2.3399	77.85	74.20
50	0.27023	1.9636	82.89	78.35

The Figures and Tables show that, the rate of steel corrosion decreases as the concentration of Almadinah Almonawarah soil solution is increased (increase the inhibition efficiency), except at low concentration (3 % v/v) it gives a dual behaviour, this can be attributed to the formation of soluble compounds[36,37]. Similar results were obtained from mass loss measurements.

Figs. 3 and 4 represent the variation of inhibition efficiency with concentration of Almadinah Almonawarah soil solution from both mass loss measurement and hydrogen evolution measurement, respectively. The results revealed that Almadinah Almonawarah soil solution acts as an inhibitor for steel corrosion in acidic solution and it can suggest that the inhibitor molecules are adsorbed on the steel/solution interface where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent. The increase in the inhibition efficiency observed at high concentration of soil solution indicates that more inhibitor molecules are adsorbed on the metal surface thus providing wider surface coverage.

It is obvious that the rate of steel corrosion in the absence and presence of Almadinah Almonawarah soil solution increases with rising temperature from 30 to 60° C. Figs. 5 and 6 show the plots of logarithm of Theta (log Θ) (surface coverage) *versus* logarithm of inhibitor concentration at 30° C and 60° C to be linear from both hydrogen evolution and mass loss methods, respectively. This indicates that the experimental data fits freundlish isotherm at studied temperatures. Figs. 7 and 8 also show the plots of C/Θ *versus* C, the linear plots obtained indicate that the experimental data also obey Langmuir adsorption isotherm.
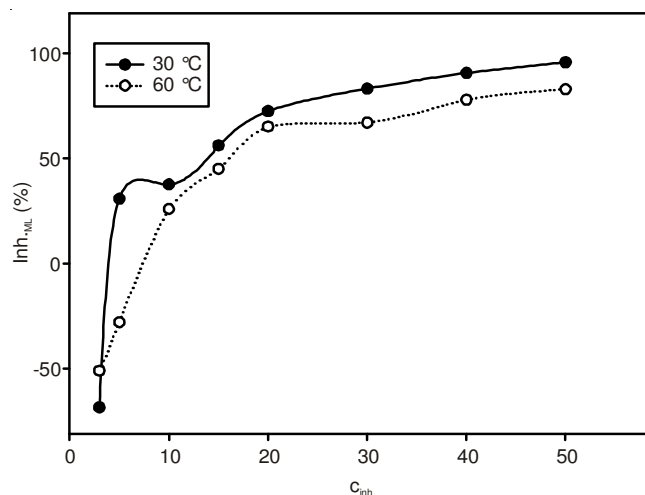

Fig. 3. Variation of inhibition efficiency with C_{inh} at 30 °C and 60 °C from mass loss method
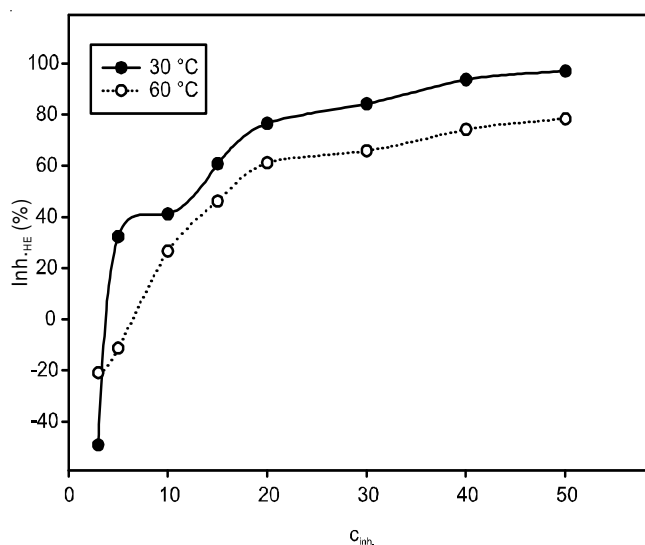

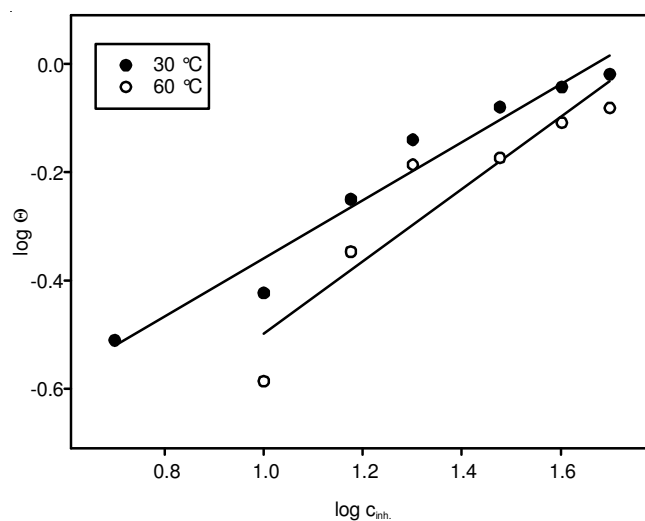Fig. 4. Variation of inhibition efficiency with C_{inh} at 30 °C and 60 °C from hydrogen evolution method

Fig. 5. Plots of logarithm surface coverage (log Θ) *vs*. logarithm C_{inh} at 30 °C and 60 °C from mass loss method
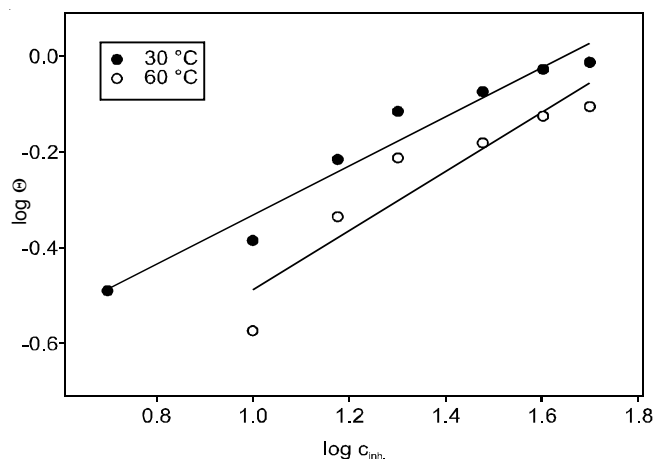
Fig. 6. Plots of logarithm surface coverage (log Θ) vs. logarithm C_{inh} at 30 °C and 60 °C from hydrogen evolution method
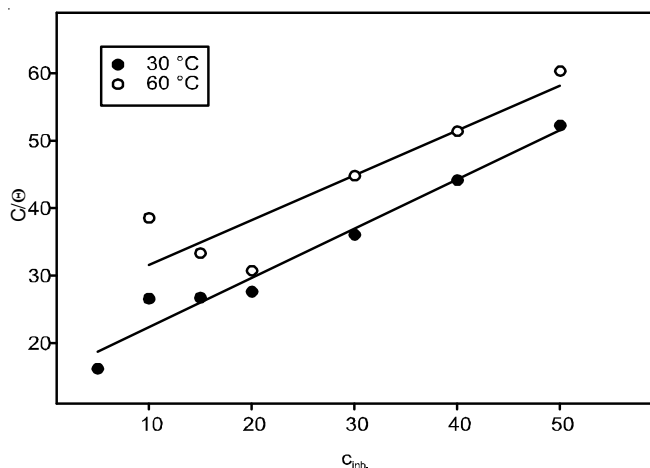

Fig. 7. Langmuir isotherm for adsorption of Almadinah Almonawarah soil solution in 2.0 M H_2SO_4 at 30 °C and 60 °C from mass loss method
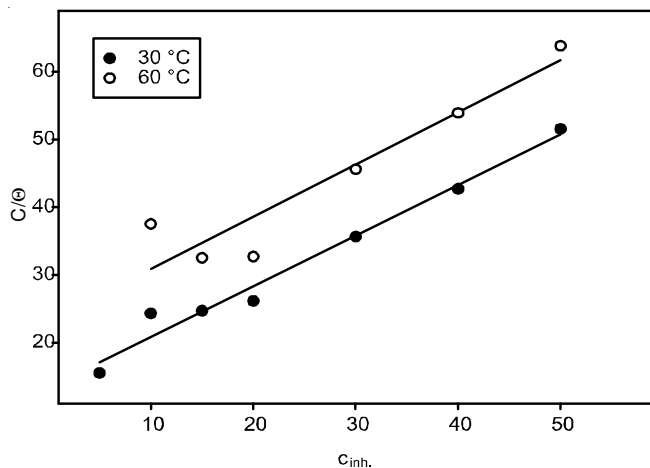

Fig. 8. Langmuir isotherm for adsorption of Almadinah Almonawarah soil solution in 2.0 M H_2SO_4 at 30 °C and 60 °C from hydrogen evolution method

Electrochemical study

Electrochemical impedance spectroscopy measurements: The corrosion behaviour of steel sample in 2 M H_2SO_4 solution in the absence and presence of Almadinah Almonawarah soil solution was investigated by the EIS method at 30 °C. The

obtained Nyquist plots of the studied extract are shown in Fig. 9. It can be seen that the obtained impedance diagrams show almost a semicircle for the free acid and in the presence of Almadinah Almonawarah soil solution extract. The semicircle appearance indicates that the corrosion of steel is mainly controlled by the charge transfer process and the presence of Almadinah Almonawarah soil solution extract do not alter the mechanism of dissolution on steel surface in acidic solution[13,15].
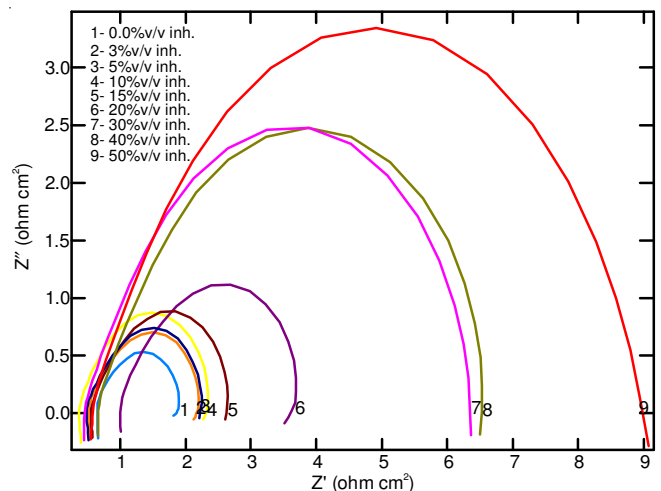

Fig. 9. Nyquist plots for steel corrosion in 2 M H_2SO_4 in the absence and presence of different concentrations of inhibitor extract at 30 °C

Inhibition percentage efficiencies obtained from EIS measurements are calculated from the following eqns. 3 and 4[38-42]:

$$Inh \cdot R_{ct}\% = \left(R_{cto}^{-1} - R_{ct}^{-1} / R_{cto}^{-1}\right) \times 100 \qquad (3)$$

$$Inh \cdot C_{dl}\% = (C_{dlo} - C_{dl}/C_{dlo}) \times 100 \qquad (4)$$

where R_{cto}^{-1} and R_{ct}^{-1} are the values of charge transfer resistance and C_{dlo} and C_{dl} are the double layer for steel in 2 M H_2SO_4 solution without and with the soil solution, respectively. The values of inhibition efficiency calculated from eqns. 3 and 4 are listed in Table-4.

TABLE-4
ELECTROCHEMICAL PARAMETERS AND INHIBITION
EFFICIENCIES FROM IMPEDANCE MEASUREMENTS FOR THE
CORROSION OF STEEL IN THE ABSENCE AND PRESENCE OF
DIFFERENT CONCENTRATIONS OF INHIBITOR AT 30° C

C% (v/v)	R_{sol}.(cm²)	R_{ct}(cm²)	C_{dl}(F)	Inh.R_{ct}(%)	Inh.C_{dl}(%)
0.0	0.6546	1.321	8.581	–	–
3.0	0.5349	1.011	9.951	-30.66	-15.97
5.0	0.5043	1.866	6.160	29.21	28.21
10.0	0.3917	2.092	5.527	36.86	35.59
15.0	0.5737	2.246	4.907	41.18	49.82
20.0	0.6008	3.003	3.911	56.01	54.42
30.0	0.4609	6.135	3.257	78.47	62.04
40.0	0.6707	6.165	2.757	78.57	67.87
50.0	0.5766	8.345	1.726	84.17	79.89

Potentiodynamic polarization measurements: The potentiodynamic polarization curves for steel corrosion in 2 M H_2SO_4 in the absence and presence of different concentrations of Almadinah Almonawarah soil solution extract at 30° C are shown in Fig. 10. The electrochemical parameters (corrosion

potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) and the inhibition percentages (Inh·$_P$ %) for Almadinah Almonawarah soil solution are recorded in Table-5.
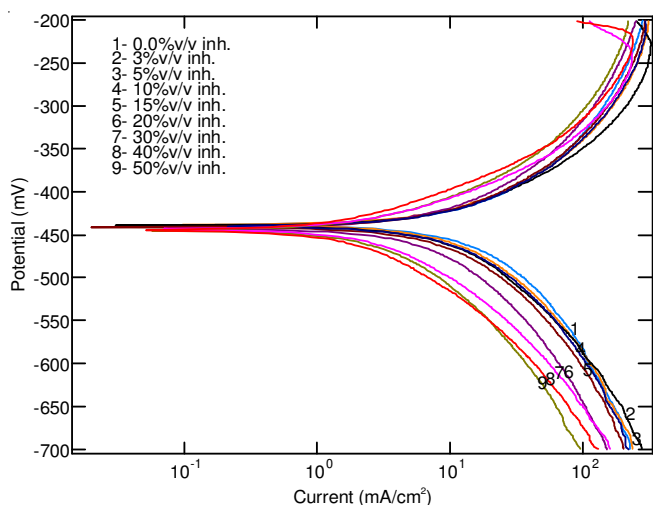

Fig. 10. Polarization curves for steel corrosion in 2 M H_2SO_4 in the absence and presence of different concentrations of inhibitor at 30 °C

TABLE-5
ELECTROCHEMICAL PARAMETERS AND INHIBITION EFFICIENCIES FROM POLARIZATION MEASUREMENTS FOR THE CORROSION OF STEEL IN THE ABSENCE AND PRESENCE OF DIFFERENT CONCENTRATIONS OF INHIBITOR AT 30 °C

C % (v/v)	-$E_{corr.}$(mV)	$I_{corr.}$(mA/cm^2)	b_a	b_c	Inh·$_{icorr.}$ (%)
0.0	438.70	30.959	116.78	140.00	–
3.0	438.92	24.809	101.65	145.04	19.87
5.0	439.80	23.699	85.607	134.27	23.45
10.0	443.19	20.393	87.375	135.78	34.13
15.0	441.75	18.978	95.106	137.38	38.70
20.0	440.03	15.170	98.014	142.85	51.00
30.0	445.77	11.694	86.304	150.52	62.23
40.0	443.81	9.1230	71.884	122.68	70.33
50.0	444.88	5.6930	67.653	106.00	81.61

Fig. 10 shows that Almadinah Almonawarah soil solution extract retards both cathodic and anodic processes (metal dissolving and hydrogen evolution). This appears in the displacement of Tafel lines (cathodic and anodic), *i.e.*, these soil solution extract acts as mixed type inhibitor. The values of b_a and b_c are varied in irregular shape. This behaviour was previously observed in many others studies[43-45].

As can be seen from Table-5 that there is irregular displacement in the corrosion potential ($E_{corr.}$) values to less negative (more positive) values with regard to the free acid solution and decrease of I_{corr} values was associated with a shift in the corrosion potential E_{corr} to less negative values especially at high concentrations.

The values of Inh.% were determined from polarization measurements according to the following equation:

$$\text{Inh·}_p \% = \left(1 - I_{corr} / I_{corr}^0\right) \times 100 \qquad (5)$$

where I_{corr}^0 and I_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively.

Fig. 11 shows the plots of Inh.% against inhibitor concentration from the above four methods for steel in 2 M H_2SO_4. It can be seen that with increasing the concentration of Almadinah Almonawarah soil solution, there is an increase in inhibition efficiency at all experimental techniques.
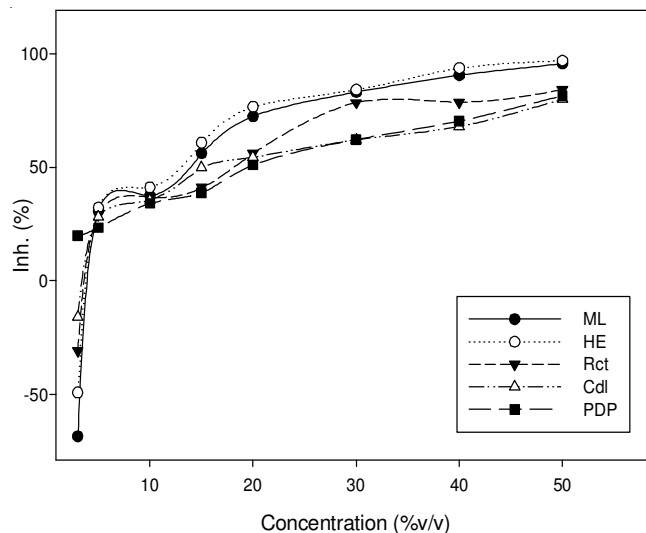

Fig. 11. Variation of inhibition efficiency with C_{inh} at 30 °C from four methods

Fig. 12 also shows the plots of logarithm of inhibitor surface coverage *versus* logarithm of inhibitor concentration at 30 °C to be linear. This indicates that the experimental data fits Freundlish isotherm.
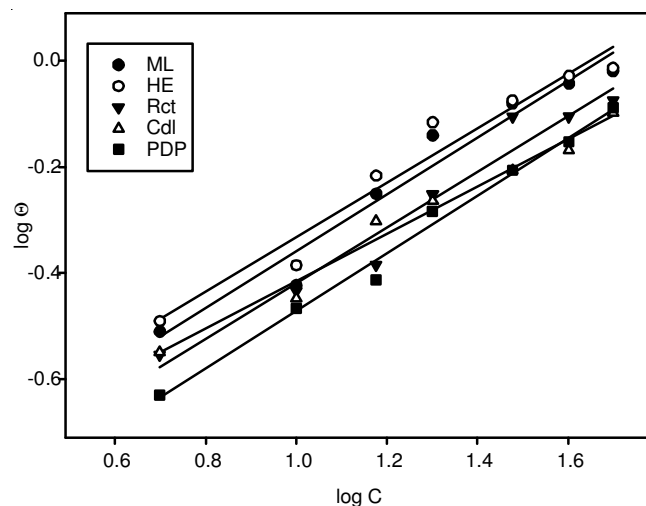
Fig. 12. Plots of logarithm surface coverage *vs.* logarithm C_{inh} at 30 °C from four methods

A large number of experimental adsorption isotherm fit Langmuir equation reasonably well. The values of surface coverage calculated from all methods were used in the plots of C/Θ *versus* C in Fig. 13. Although the linear plots obtained indicate that the experimental data obey the Langmuir adsorption isotherm given by Farooqi *et al.*[46]:

$$C/\Theta = 1/b + C \qquad (6)$$

where C is the inhibitor concentration, none of the plots have slope equal to unity. Such deviations from unity may be attribute to interaction between the adsorbed molecules on the metal surface[33].
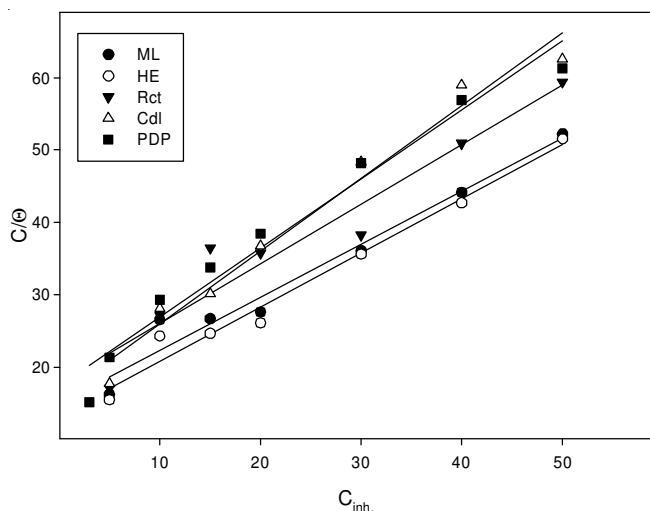

Fig. 13. Langmuir isotherm for adsorption of Almadinah Almonawarah soil solution in 2 M H_2SO_4 at 30 °C from four methods

Kinetic consideration: The activation energy E_a for the dissolution of steel in 2 M H_2SO_4 solution between 30 and 60 °C in the absence and presence of Almadinah Almonawarah soil solution were calculated from the Arrhenius equation[47,48]:

$$\log R_2/R_1 = Ea/2.303R (1/T_1 - 1/T_2) \tag{7}$$

where R_1 and R_2 are the corrosion rates at temperatures T_1 and T_2, respectively. The values of heat of adsorption Q_{ads} were calculated using the equation[47]:

$$Q_{ads}\cdot(kJmol^{-1}) = 2.303R[\log(\Theta_2/1-\Theta_2) \\ - \log (\Theta_1/1-\Theta_1)\times T_1T_2/T_2-T_1] \tag{8}$$

where Θ_1 and Θ_2 are the degrees of surface coverage at temperatures T_1 and T_2.

The calculated values of activation energy E_a and heat of adsorption Q_{ads} are given in Tables 6 and 7. These data revealed that the heats of adsorption were all negative and ranged from -9.582 to -42.64 kJ mol^{-1} from mass loss method and from -16.55 to -61.25 kJ mol^{-1} from hydrogen evolution method. The negative Q_{ads} values indicates that the adsorption and hence the inhibition efficiency decreases with rising temperature[47]. The activation energy values of 105.48 and 112.88 kJ mol^{-1} obtained from mass loss and hydrogen evolution respectively, in the absence of inhibitor is less than the mean values of 120.64 and 131.98 kJ mol^{-1}, respectively, in inhibited system containing Almadinah Almonawarah soil solution extract.This type of behaviour indicates that the inhibitor retards corrosion at ordinary temperature while the inhibition efficiency is considerably diminished at higher temperatures[34,49]. Since corrosion primarily occurs at surface sites free of adsorbed inhibitor molecules, the higher activation energies in the presence of Almadinah Almonawarah soil solution can be attributed to the decrease in surface area available for corrosion. The observed variation of activation energy with inhibition efficiency suggests that the inhibition process is activation controlled.

TABLE-6
CALCULATED VALUES OF ACTIVATION ENERGY E_a (kJ mol^1) AND HEAT OF ADSORPTION Q_{ads} (kJ mol^1) FOR STEEL CORROSION IN 2 M H_2SO_4 WITH ALMADINAH ALMONWARAH SOIL SOLUTION EXTRACT FROM ML METHOD

System	Activation energy E_a (kJ mol^1)	Heat of adsorption Q_{ads} (kJ mol^1)
2 M H_2SO_4	105.48	–
3 %v/v	102.42	–
5 %v/v	122.69	22.53
10 %v/v	125.15	-15.22
15 %v/v	111.84	-12.56
20 %v/v	112.08	-9.582
30 %v/v	124.37	-24.93
40 %v/v	122.22	-28.24
50 %v/v	144.13	-42.64

TABLE-7
CALCULATED VALUES OF ACTIVATION ENERGY E_a (kJ mol^1) AND HEAT OF ADSORPTION Q_{ads} (kJ mol^1) FOR STEEL CORROSION IN 2 M H_2SO_4 WITH ALMADINAH ALMONWARAH SOIL SOLUTION EXTRACT FROM HYDROGEN EVOLUTION METHOD

System	Activation energy E_a (kJ mol^1)	Heat of adsorption Q_{ads} (kJ mol^1)
2 M H_2SO_4	112.88	–
3 %v/v	107.01	–
5 %v/v	126.78	20.67
10 %v/v	119.02	-18.31
15 %v/v	120.82	-16.55
20 %v/v	127.02	-28.16
30 %v/v	134.53	-28.53
40 %v/v	152.39	-46.00
50 %v/v	168.30	-61.25

Conclusions

(1) The extract of Almadina Almunwarh soil solution acts as a good inhibitor for corrosion of steel in 2 M H_2SO_4 solution.

(2) The inhibition efficiency increases with increasing inhibitor concentration but decreases with rising temperature.The maximum efficiency 87.67 % was found for 50 % v/v at 1 h of an immersion time.

(3) The inhibition action is performed *via* adsorption of the extract compounds on steel surface. The adsorption process is spontaneous and follows Fruendlich and Langmuir adsorption isotherms.

(4) The Nyquist diagrams consisted of a capacitive semi-circle at all frequencies.

(5) Polarization revealed that Almadinah Almonawarah soil solution extract is a mixed inhibitor and the molecules are adsorbed on both anodic and cathodic sites at the metal surface.

(6) The inhibition is due to the adsorption of Almadinah Almonawarah soil solution compounds on steel surface and blocking is active sites.

(7) The observed variation of activation energy with inhibition efficiency suggests that the inhibition process is activation controlled.

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