Int. J. Electrochem. Sci., 16 **(2021)** Article Number: 211118, doi: 10.20964/2021.11.40

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Inhibition Effects of Citrulline and Glutamine for Mild Steel Corrosion in Sulfuric Acid Environment: Thermodynamic and Kinetic Aspects

Arafat Toghan[1,2], *Ahmed Fawzy*[3,4,*], *Nada Alqarni*[5], *Adel Abdelkader*[2], *Abbas I. Alakhras*[1]

[1] Chemistry Department, College of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh 11623, Saudi Arabia
[2] Chemistry Department, Faculty of Science, South Valley University, Qena 83523, Egypt
[3] Chemistry Department, College of Applied Sciences, Umm Al-Qura University, Makkah 21955, Saudi Arabia
[4] Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt
[5] Chemistry Department, College of Science, University of Bisha, Bisha 61922, Saudi Arabia
[*]E-mail: afsaad13@yahoo.com

Received: 8 Augst 2021 / *Accepted:* 15 September 2021 / *Published:* 10 October 2021

The inhibition of mild steel corrosion in sulfuric acid environment was evaluated by citrulline and glutamine at fixed temperatures. The tools used for this evaluation were potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and mass loss (ML) measurements. Also, the morphology of mild steel surfaces was examined prior to and after corrosion adding the tested inhibitors by scanning electron microscopy (SEM). The evaluated inhibition efficiencies (% IEs) of the tested inhibitors increased with their concentrations but decreased with increasing sulfuric acid concentration. Results of PDP technique indicated that the examined compounds behaved as mixed inhibitors with cathodic majority. ML studies revealed that % IEs reduced with increasing temperature. The investigational results acquired from all utilized techniques are agreeable with each others which disclosed that the %IEs of citrulline were higher than glutamine under comparable conditions. The acquired great % IEs of the tested inhibitors was understood on the basis of strong adsorption of amino acids on mild steel surface creating a defensive layer and this adsorption was noticed to accord with Langmuir isotherm. Thermodynamic and kinetic parameters were computed and discussed which confirm the physical adsorption mechanism of the examined inhibitors. The kinetics of the corrosion inhibition by such compounds revealed negative first order of corrosion inhibition process demonstrating the acquired great % IEs of the investigated compounds.

Keywords: Mild steel, Amino acids, Corrosion inhibitors, Fuel cell, Thermodynamic & kinetic aspects

1. INTRODUCTION

Corrosion is a naturally occurring electrochemical process that results in a weakening of important properties of metals and alloys ensuing a serious complications for the economy and integrity [1-3]. Rust of iron and iron alloys, in particular, is deliberated as a dangerous industrial challenge especially in acidic environments [4-9]. Also, metal corrosion occurred in fuel cells is considered as a multi-factorial phenomenon and persists a fundamental subject in furthermost research and development activities of both public and private institutions. Acidic solutions are extensively used in various purposes such as fuel cells, industrial cleaning, pickling of steel, acid discaling and petroleum processes. Though, because of the aggressiveness of the acidic solutions, the metal vessels employed in these purposes are susceptible to corrosion. Consequently, it was essential to safeguard metals from the dangerous impacts of corrosion in various media [10-15].

Employing corrosion inhibitors is regarded as the preeminent approach to resist corrosion of the surfaces of metals and alloys due to the facility of their use and low cost. Corrosion inhibitors are materials utilized to inhibit corrosion phenomenon of the metallic surfaces [16-19]. Supreme of the proficient corrosion inhibitors are organic compounds having heteroatoms, conjugated π-bond systems, polar groups and aromatic rings [20-22]. The proficiencies of the organic inhibitors were set to be dependent on their abilities for adsorption on the surface of metal by replacing H_2O molecule on the surface [23-26]. One of the significant category of compounds employing as corrosion inhibitors is the amino acids that are the constructing blocks of proteins and numerous important substances such as hormones, nucleic acids, etc. [27]. They are regarded as proficient and green corrosion inhibitors because they are environmentally friendly compounds, relatively cheap, wholly soluble in aqueous solutions and manufactured with extreme purity [28,29]. Certain investigations inferring amino acids on the corrosion of various metals and alloys like iron [30], bronze [31], carbon steel [32], zinc [33], copper [34], aluminum [35] and tin [36] were stated. Amino acids acted as proficient corrosion inhibitors because of the presence of π-electrons, heteroatoms in their structures through which they are either strongly adsorbed or construct metal complexes at the metallic surfaces resulting in the protection of these surfaces from the aggressiveness of the corrosive solutions [37]. The principal aims of the present investigation were to determine the inhibition effectiveness of two amino acids, viz. citrulline and glutamine (their structures are illustrated in Figure 1) that play roles in a variety of biochemical functions and are environmentally friendly for mild steel corrosion in 0.5 M H_2SO_4 environment utilizing several techniques. Also, thermodynamic and kinetic features were investigated.

Citrulline Glutamine

Figure 1. Structures of Citrulline (Cit) and Glutamine (Gln).

2. EXPERIMENTAL

2.1. Material

The solutions utilized in this investigation were made from analytical grade chemicals. The solvent employed was double distilled water. The main corrosive environment used in all investigations was 0.5 M H_2SO_4, which prepared by diluting a 99% H_2SO_4 in double distilled water. Solutions of the amino acids citrulline (2-Amino-5-(carbamoylamino)pentanoic acid) and glutamine (2,5-Diamino-5-oxopentanoic acid) were prepared using bidistilled water and they utilized in the range of concentrations: 100 to 500 ppm (mg/l). Additional solutions were made by dissolving the requisite quantities of the chemicals in double distilled water and the preferred concentrations were acquired by proper dilution. Experiments were carried out on mild steel specimens (SABIC Company, Saudi Arabia) with a composition (wt. %): 0.076 C, 0.125 Mn, 0.0126 Cr, 0.034 Cu, 0.012 Si, 0.008 S, 0.009 P, 0.003 Mo, 0.027 Ni and the rest is iron. Every experimental run was repeated about 3 times under similar circumstances to test the reproducibility, and the mean of the three replicated values was utilized and inserted in the tables.

2.2. Methods

PDP and EIS tests were conveyed out on a thermostated PGSTAT30 potentiostat /galvanostat. Prior to each test, Sabic steel electrode (working electrode) was prepared as reported [6,7] and was directly inserted into the 0.5 M H_2SO_4 solution (corrosive medium) and / or pre-requisite amino acid quantity at OCP (open circuit potential) which attained after almost 30 min. of insertion. In PDP, the potential was automatically changed in the range of: -200 to + 200 mV vs. OCP with a scan rate of 1.0 mV/s. The values of % IE of the examined amino acids can be computed from Eq. 1 [38]:

$$\%\ \mathrm{IE} = \theta \times 100 = \left[1 - \frac{i_{corr\,(inh)}}{i_{corr}}\right] \mathrm{x}\ 100 \qquad (1)$$

where, i_{corr} and $i_{\mathrm{corr(inh)}}$ are corrosion current densities before and after adding the inhibitor, respectively.

In EIS, the frequency range was: 100 kHz to 0.1 Hz, and the amplitude was 4.0 mV (peak to peak) using AC signals at OCP. Also, % IE values were computed using the equation [39]:

$$\%\ \mathrm{IE} = \left[1 - \frac{R_{ct}}{R_{ct\,(inh)}}\right] \mathrm{x}\ 100 \qquad (2)$$

where R_{ct} and $R_{\mathrm{ct(inh)}}$ are the charge transfer resistance values before and after adding the inhibitor, correspondingly.

ML tests were done in vessels with a temperature-controlled. The mild steel specimens were cylinder-shaped rods (almost 14 cm^2 area). Steel specimens were also prepared for these tests as stated earlier [6,7]. The corrosion rate (CR) was determined in mpy (mils penetration per year) from the equation [40]:

$$\mathrm{CR\ (mpy)} = \frac{KW}{Atd} \qquad (3)$$

where K is a constant (3.45 x 10^6), W is the ML in grams, A is the steel sample area in cm^2, t is the time in hour and d is the density of steel (7.86 g/cm^3). The % IE values were computed from Eq. 4 [38]:

$$\% \text{ IE} = \theta \text{ x } 100 = \left[1 - \frac{CR_{inh}}{CR}\right] \text{ x } 100 \qquad (4)$$

where CR and CR_{inh} are corrosion rate values without and with inhibitor, respectively.

Surface morphology of the surfaces of mild steel samples was explored before and after adding a 500 ppm of the investigated amino acids using JEOL Scanning Electron Microscope model T-200 with a repeat voltage of 10.0 kV. First, the surfaces of the Sabic steel specimens were scratched with diverse emery papers up to a grade of 1200 then washed with double distilled water. Before examination, the tested steel specimens were putted in the tested solution for 24 h.

3. RESULTS AND DISCUSSION

3.1. PDP Measurements

3.1.1. Effect of H_2SO_4 Concentration on the Corrosion Rate of Sabic Steel

PDP measurements for the corrosion of mild steel in H_2SO_4 solutions in the concentration range: 0.1 to 1.0 M at 303 K were conveyed out and the Tafel plots were recorded from which the corrosion parameters, viz, corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c, β_a) were determined and recorded in Table 1. The results revealed that the value of i_{corr} of mild steel augmented with rising [H_2SO_4], demonstrating an augmentation of mild steel corrosion with rising H_2SO_4 concentration.

Table 1. PDP results for mild steel corrosion in various concentrations of H_2SO_4 solutions at 303 K.

[H_2SO_4] (mol dm^{-3})	**-E_{corr} (mV(SCE))**	**β_a (mV/decade)**	**-β_c (mV/decade)**	**i_{corr} (μA/cm^2)**
0.1	437	102	77	143
0.3	448	97	81	165
0.5	**466**	**83**	**75**	**196**
0.7	464	85	73	215
1.0	471	78	71	239

3.1.2. Effect of Added Amino Acids on the Corrosion Rate

The PDP curves for mild steel in 0.5 M H_2SO_4 solution before and after addition of the amino acids are shown in Figure 2 (a) and (b). Values of E_{corr}), i_{corr} , β_c , β_a , % IE and θ were computed from PDP curves and inserted in Table 2. From Figure 2 and the results inserted in Table 2, it can be seen that, addition of the amino acids to the corrosive environment moved the PDP curves recorded for the pure

H_2SO_4 solution to lesser current densities signifying inhibition of mild steel corrosion. Values of % IE increased with rising the amino acids' concentrations and the order of % IE was: Cit > Gln.

The higher values of % IEs could be elucidated in the light of strong adsorption of the amino acid molecules on the steel surface, which delays both metal dissolution and hydrogen evolution, and therefore, reduces the corrosion rate [41]. Due to the amino acid inhibitors showed observable anodic and cathodic inhibition impacts with obviously moving E_{corr} to more cathodic potentials in comparison with that observed for the pure corrosive medium, it could be established that the examined amino acids behaved as mixed-type inhibitors with cathodic majority.

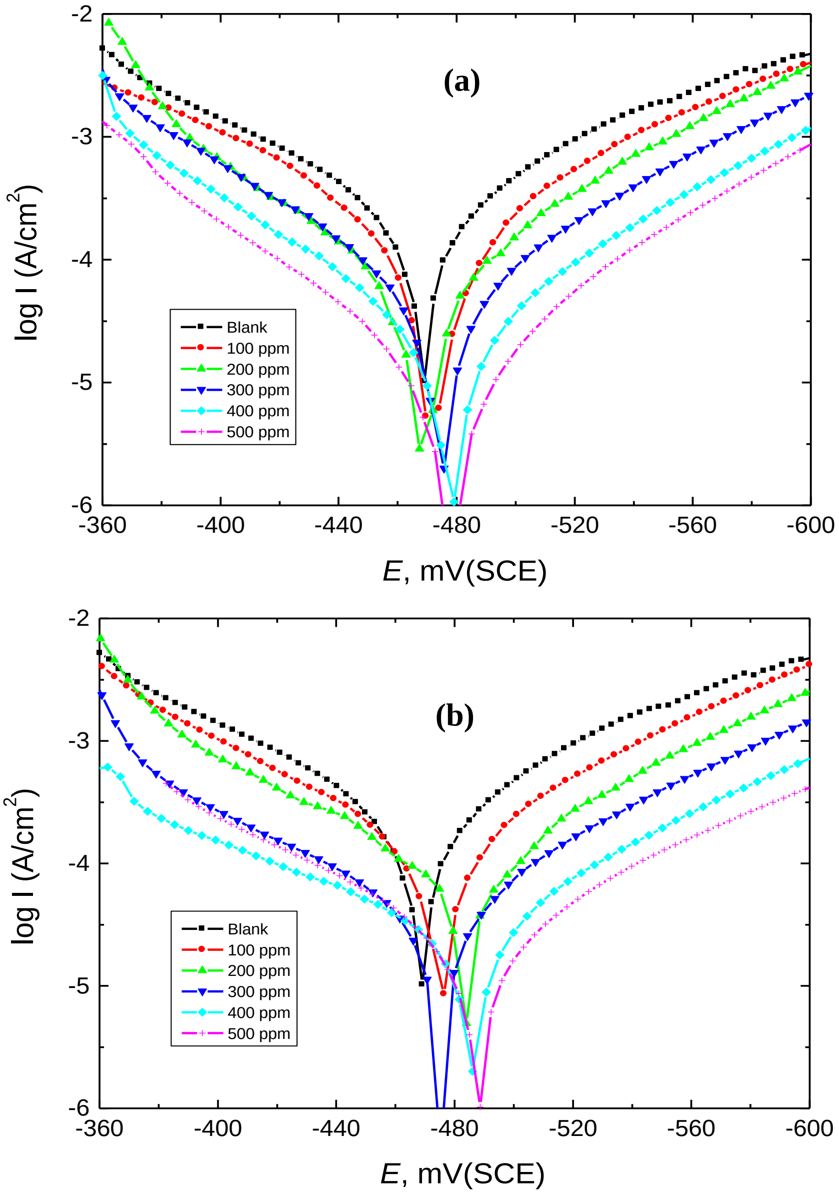


Figure 2. PDP curves for mild steel corrosion in 0.5 M H_2SO_4 solution before and after addition of: (a) citrulline, and (b) glutamine, at 303 K.

Table 2. PDP results for mild steel corrosion in 0.5 M H_2SO_4 solution before and after addition of citrulline (Cit) and glutamine (Gln) at 303 K.

Inh.	**Inh. conc. (ppm)**	**-E_{corr} (mV(SCE))**	**β_a (mV/dec.)**	**-β_c (mV/dec.)**	**i_{corr} (μA/cm^2)**	**% IE**	**θ**
	0	**466**	**83**	**75**	**196**	**--**	**--**
Cit	**100**	470	56	71	80	59	0.59
	200	465	65	70	47	76	0.76
	300	476	66	68	31	84	0.84
	400	479	64	64	24	88	0.88
	500	482	60	63	18	91	0.91
Gln	**100**	475	81	73	96	51	0.51
	200	483	86	74	57	71	0.71
	300	474	80	73	39	80	0.80
	400	486	103	75	25	87	0.87
	500	488	80	73	22	89	0.89

3.2. EIS Measurements

The corrosion performance of mild steel in 0.5 M H_2SO_4 solution was studied before and after adding the examined amino acids at 303 K and after immersion of mild steel electrode in the corrosive solution for about 30 min. by EIS technique. Figure 3 illustrates: (a) Nyquist plots, (b) Bode magnitude plots, and (c) Bode phase plots for the corrosion of mild steel corrosion in H_2SO_4 solution without and with numerous concentrations of the amino acids.

It was seen from the Nyquist and Bode plots that the obtained impedance spectra contained of only depressed capacitive loops and one-time constants, respectively, signifying that adsorption of the examined amino acids occurs throughout covering the metal surface and the corrosion is achieved by charge transfer process [42]. Also, the general shape of the curves is the same without or with amino acids demonstrating that there was no change in the Sabic iron corrosion mechanism [43]. It was realized from the Nyquist plots that the size of the capacitive semicircle increased with increasing the concentration of the added amino acids revealing reduction of the corrosion rate and enhance of the % IEs. Additionally, the Bode phase plots manifested that the phase angle was augmented with rising the amino acids' concentrations. This indicated that the Sabic steel surface was significantly altered to smooth due to construction of a protecting layer of the inhibitors' molecules on the mild steel surface leading to a reduction in the corrosion rate [44].

The obtained impedance spectra were analyzed using the equivalent circuit model presented in Figure 4. Impedance parameters kike solution resistance (R_s), charge transfer resistance (R_{ct}) and constant phase element (CPE) were calculated from the impedance spectra and are inserted in Table 3. The obtained outcomes signified that adding the examined amino acids to the corrosive medium resulted in increasing the R_{ct} value and this action was enhanced with rising amino acids' concentrations.

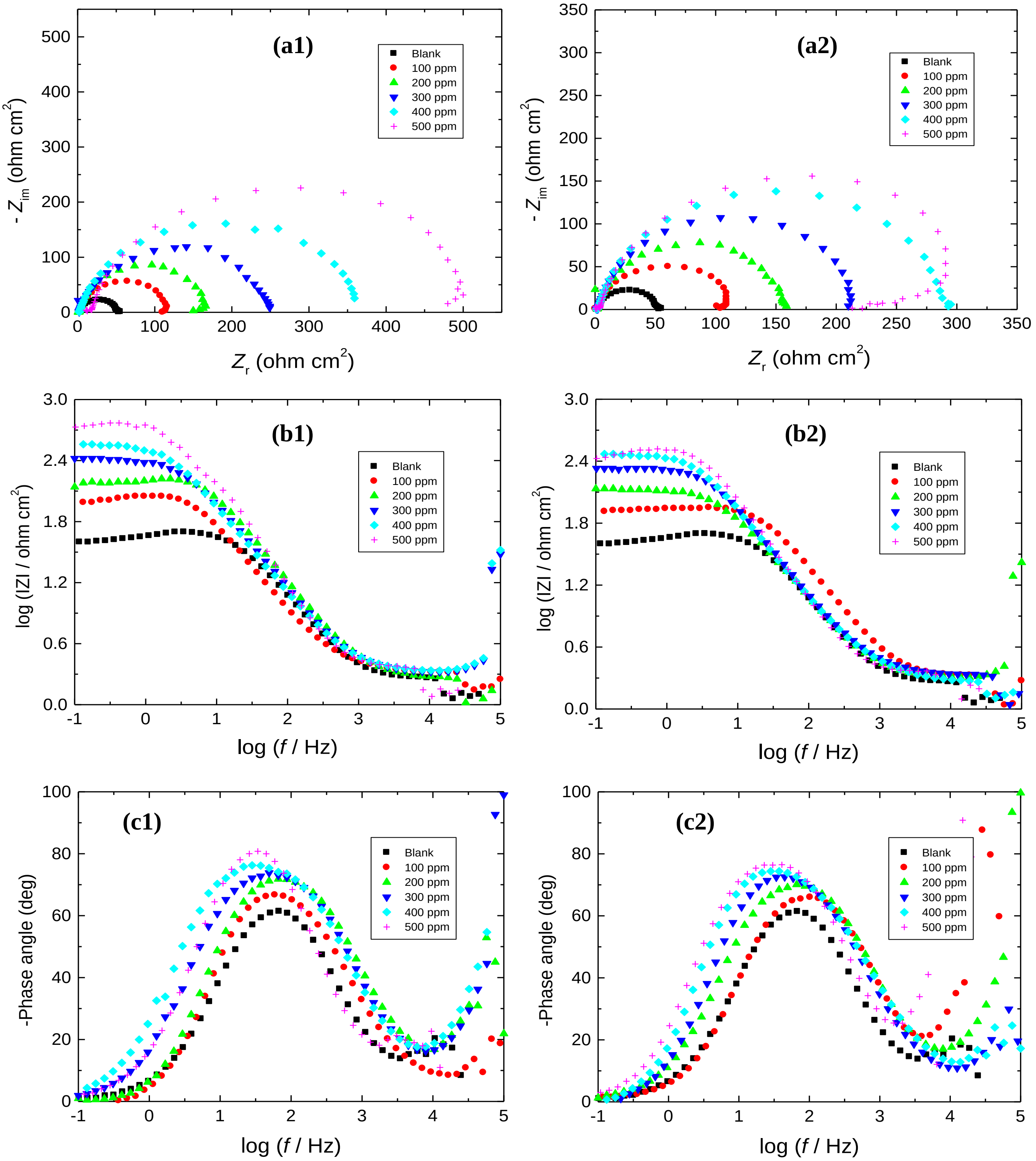


Figure 3. (a) Nyquist, (b) Bode magnitude plot, and (c) Bode phase plot for the corrosion of mild steel in 0.5 M H_2SO_4 solution at 303 K in the absence and presence of: (1) citrulline, and (2) glutamine, at 303 K.

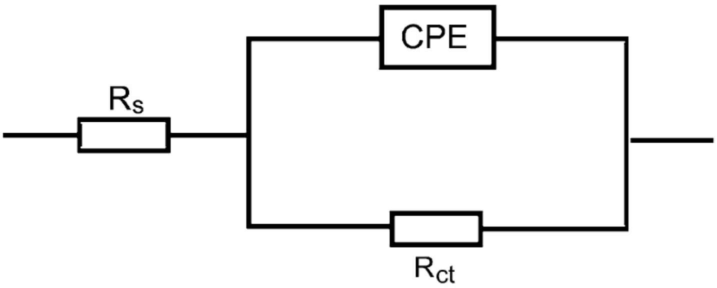


Figure 4. Electrochemical equivalent circuit utilized to analyze the EIS results for the corrosion of mild steel in 0.5 M H_2SO_4 solution before and after addition of the examined amino acids.

Table 3. EIS results for the corrosion of mild steel in 0.5 M H_2SO_4 solution before and after addition of citrulline (Cit) and glutamine (Gln) at 303 K.

Inhibitor	**Inh. conc. (ppm)**	**R_s (ohm cm^2)**	**R_{ct} (ohm cm^2)**	**10^{-2} CPE (μF/cm^2)**	**% IE**	**θ**
	0	**1.23**	**55**	**28.86**	--	--
Cit	**100**	0.74	117	15.07	53	0.53
	200	1.08	167	11.88	67	0.67
	300	1.75	251	9.07	78	0.78
	400	3.87	366	7.23	85	0.85
	500	11.49	503	6.31	89	0.89
Gln	**100**	1.02	108	16.33	49	0.49
	200	2.17	162	12.24	66	0.66
	300	1.95	221	10.26	75	0.75
	400	2.71	290	9.12	81	0.81
	500	3.95	305	10.40	82	0.82

This behavior was attributed to adsorption of the investigated amino acids' molecules on the steel/solution interface [45] leading to the protection of the Sabic steel surface. The values of % IEs were augmented with rising the concentration of the tested amino acids indicating that these compounds are efficient inhibitors for the corrosion of mild steel in H_2SO_4 solution.

3.3. ML Measurements

3.3.1. Effect of Added Amino Acids on the Corrosion Rate

WL experiments of mild steel in 0.5 M H_2SO_4 solution were conveyed out before and after addition of various concentrations of citrulline and glutamine (100 – 500 ppm) at various temperatures (293 – 323 K); only the ML vs. time plots gained at 303 K are illustrated here, Figure 5(a) and (b). Values of CR, θ and % IE of the amino acids are calculated and listed in Table 4. The Table indicates that for the examined amino acids, CR values get reduced and % IE enhanced with their concentrations.

These outcomes resulted in the conclusion that these amino acids are proficient as inhibitors for mild steel corrosion in 0.5 M H_2SO_4 medium. In consistence with the previous employed techniques (PDP and EIS), the order of % IEs is: Cit > Gln.

3.3.2. Effect of Temperature

With increasing temperature, the rate of corrosion was increased and correspondingly the values of % IEs of the examined amino acids were decreased as inserted also in Table 4. The observed decrease in the values of % IEs as the temperature rises proposes that the adsorption mechanism of the tested amino acid was physical [46]. Commonly, in acidic medium, rising temperature accelerates H_2 evolution and reduces the adsorption of the inhibitor, thus increase of the rate of corrosion of metallic surface [47].

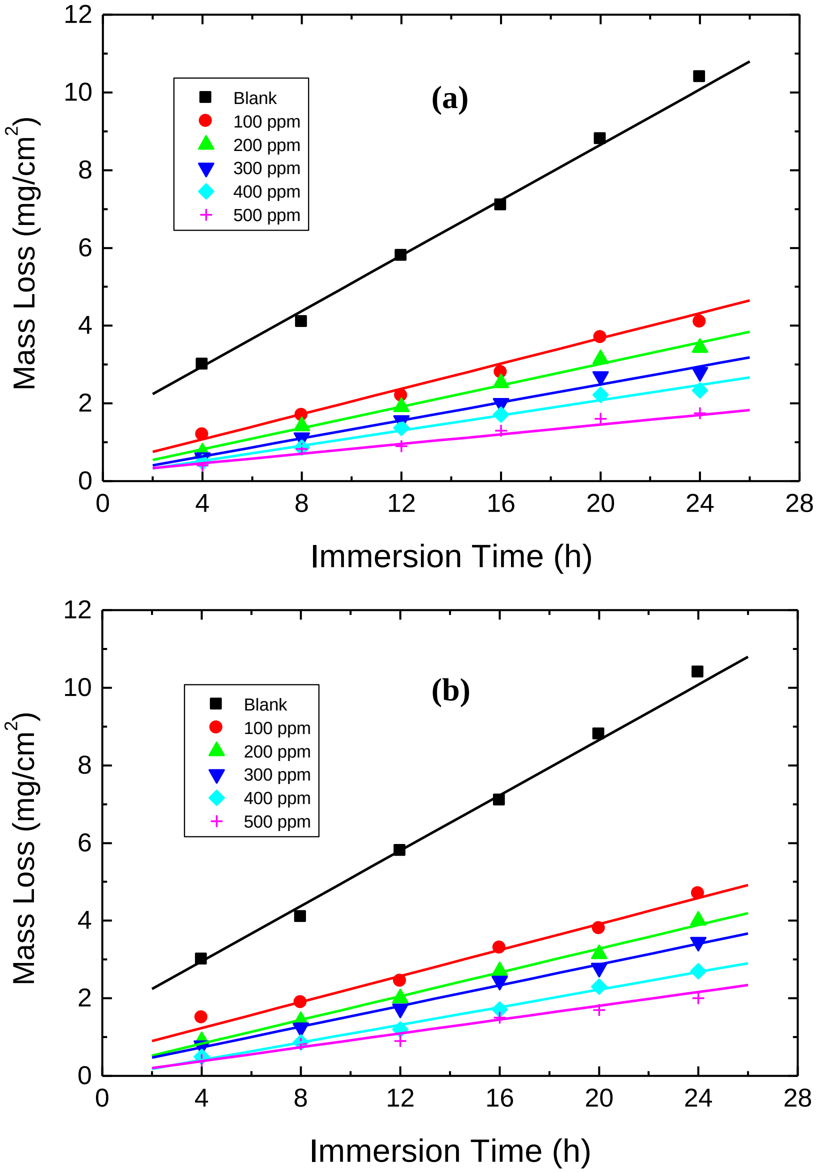


Figure 5. Plots of mass loss versus immersion time for mild steel in 0.5 M H_2SO_4 solution before and after addition of: (a) citrulline, and (b) glutamine, at 303 K.

Table 4. Average values of corrosion rates (CR) of mild steel in 0.5 M H_2SO_4 solution before and after addition of citrulline (Cit) and glutamine (Gln) at different temperatures.

Inh.	**Inh. conc. (ppm)**	**Temperature (K)**											
		293			**303**			**313**			**323**		
		CR	**% IE**	**θ**	**CR**	**% IE**	**θ**	**CR**	**% IE**	**θ**	**CR**	**% IE**	**θ**
	0	**116**	--	--	**132**	--	--	**146**	--	--	**155**	--	--
Cit	**100**	42	64	0.64	51	61	0.61	57	61	0.61	67	57	0.57
	200	27	77	0.77	34	74	0.74	41	72	0.72	45	71	0.71
	300	20	83	0.83	28	79	0.79	35	76	0.76	39	75	0.75
	400	15	87	0.87	22	83	0.83	26	82	0.82	31	80	0.80
	500	13	89	0.89	21	84	0.84	25	83	0.83	26	83	0.83
Gln	**100**	46	60	0.60	57	57	0.57	64	56	0.56	73	53	0.53
	200	31	73	0.73	41	69	0.69	47	68	0.68	53	66	0.66
	300	24	79	0.79	30	77	0.77	37	75	0.75	39	75	0.75
	400	17	85	0.85	25	81	0.81	32	78	0.78	36	77	0.77
	500	16	86	0.86	22	83	0.83	28	81	0.81	31	80	0.80

3.3.3. Effect of Immersion Time on % IE

The effect of immersion time on the values of % IE for a 500 ppm of the amino acids in 0.5 M H_2SO_4 solution was investigated for 4 to 30 h at 303 K and is shown in Figure 6.

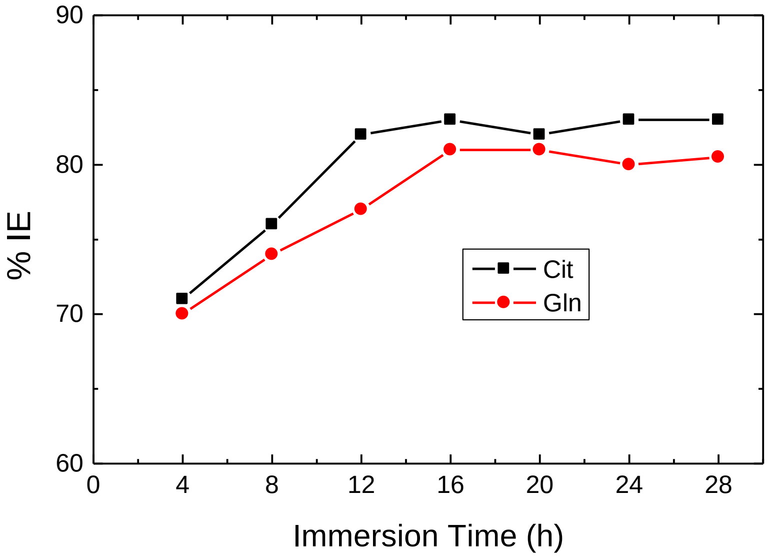


Figure 6. Variation of % IE with immersion time for mild steel in 0.5 M H_2SO_4 containing 500 ppm of the examined amino acids at 303 K.

The figure indicates that the values % IE rise significantly with increasing the immersion time up to about 12 and 16 h for Cit. and Gln, respectively, then reduce faintly with small lapse of time and lastly reach fixed values. Increasing % IE with immersion time at first stages can be ascribed to adsorption of multilayers of the amino acid molecules on the surface of Sabic steel resulting in additional % IE values. After about 20 h, % IE reach fixed values indicating that the adsorbed layers become more compact and more stable on the steel surface [48,49]. This specifies that the amino acids are proficient inhibitors for mild steel corrosion in 0.5 M H_2SO_4.

3.3.4. Adsorption Consideration

As discussed in the earlier sections, the gained % IEs of the examined amino acids were related to the strong adsorption of these compounds on the steel surface. There are two suggested styles of adsorption: physical and chemical adsorption [50]. Foe examining the adsorption style of the examined inhibitors, corrosion tests were carried out to suit experimental results with different adsorption isotherms like Langmuir, Temkin, Freundlich, Frumkin, Flory–Huggins, etc. So that, the plots of the fractional surface coverage (C_{inh}/θ) vs. the inhibitor concentration (C_{inh}) at different temperatures were drawn. The plots gave straight lines with approximately unit slopes as shown in Figure 7(a) and (b) designating that the adsorption corresponds to Langmuir isotherm which is described by the equation [51]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (5)$$

where K_{ads} is the adsorptive equilibrium constant which calculated and listed in Table 5.

3.3.5. Thermodynamic Parameters

The determined thermodynamic parameters of the adsorption process, standard free energy ($\Delta G^{o}_{\mathrm{ads}}$), standard heat ($\Delta H^{o}_{\mathrm{ads}}$) and standard entropy ($\Delta S^{o}_{\mathrm{ads}}$), can give noteworthy knowledge about the corrosion inhibition mechanism. The values of $\Delta G^{o}_{\mathrm{ads}}$ (introduced in Table 5) were calculated at different temperatures by Eq. 6 [52],

$$\Delta G^{o}_{\mathrm{ads}} = -RT \ln(55.5\, K_{\mathrm{ads}}) \qquad (6)$$

Table 5 showed that $\Delta G^{o}_{\mathrm{ads}}$ values acquired for citrulline were greater than those obtained for glutamine indicating that citrulline was more strongly adsorbed on the surface of Sabic steel in the corrosive medium than glutamine. This is in a good accord with % IEs of the tested amino acids acquired from all utilized methods. The acquired $\Delta G^{o}_{\mathrm{ads}}$ values designated that the adsorption mechanism of the amino acids on mild steel in 0.5 M H_2SO_4 solution may be a mixed from physical and chemical adsorption [53].

The $\Delta H^{o}_{\mathrm{ads}}$ values were computed using Van't Hoff equation [54]:

$$\ln K_{\mathrm{ads}} = \frac{-\Delta H^{o}_{ads}}{RT} + \text{Constant} \qquad (7)$$

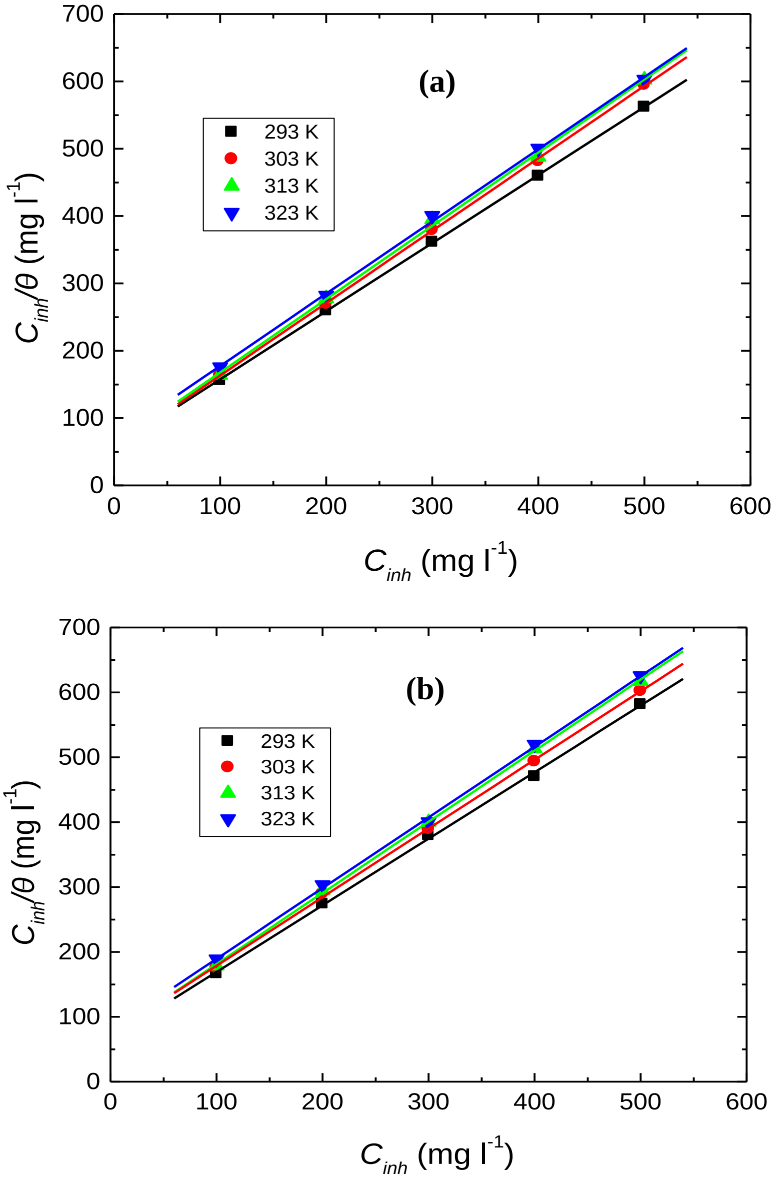


Figure 7. Langmuir adsorption isotherms for: (a) citrulline, and (b) glutamine, adsorbed on mild steel surface in 0.5 M H_2SO_4 solution at different temperatures.

Plots of ln K_{ads} vs. 1/T were linear as illustrated in Figure 8, therefore, the values of $-\Delta H^o_{ads}$ were computed and inserted in Table 5. The acquired negative values of ΔH^o_{ads} indicated that the adsorption of amino acids' molecules on the Sabic steel surfaces was an exothermic process with a physical nature (physisorption) [53,55].

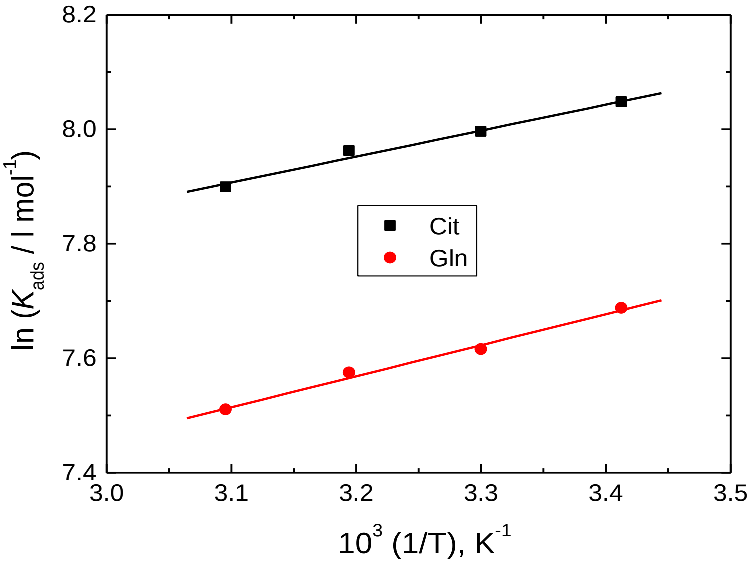


Figure 8. Van't Hoff plots for citrulline (Cit) and glutamine (Gln) adsorbed on mild steel surfaces in 0.5 M H_2SO_4 solution.

Table 5. Values of K_{ads} and thermodynamic parameters for the corrosion of mild steel in 0.5 M H_2SO_4 solution in the presence of different concentrations of citrulline (Cit) and glutamine (Gln) at different temperatures.

Inhibitor	**Temp. (K)**	**10^{-3} K_{ads} l mol^{-1}**	**ΔG^o_{ads} kJ mol^{-1}**	**ΔH^o_{ads} kJ mol^{-1}**	**ΔS^o_{ads} J mol^{-1} K^{-1}**
Cit	**293**	3.13	-29.39	-3.77	95.92
	303	2.97	-30.26		95.41
	313	2.86	-31.17		94.12
	323	2.69	-31.98		93.54
Gln	**288**	2.18	-28.51	-4.51	65.98
	298	2.03	-29.30		66.91
	308	1.95	-30.16		67.80
	318	1.83	-30.95		68.48

Also, values of ΔS^o_{ads} were calculated from the equation:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \quad (8)$$

The calculated values of ΔS^o_{ads} are inserted in Table 5. The acquired + values of ΔS^o_{ads} revealed increasing the randomness at the steel/solution interface throughout the adsorption of amino acid molecules on the steel surface. This may be due to more water molecules were desorbed from the metal surface by inhibitors' molecules [56].

3.3.6. Kinetic Parameters

The activation energy (E_a^*) was determined using Arrhenius equation [57]:

$$\ln \mathrm{CR} = \ln \mathrm{A} - \frac{E_a^*}{RT} \qquad (9)$$

Figure 9 shows the Arrhenius plots (ln CR vs. 1/*T*) for mild steel in 0.5 M H_2SO_4 before and after addition of diverse concentrations of the examined amino acids, from which the values of E_a^* were calculated and are inserted in Table 6.

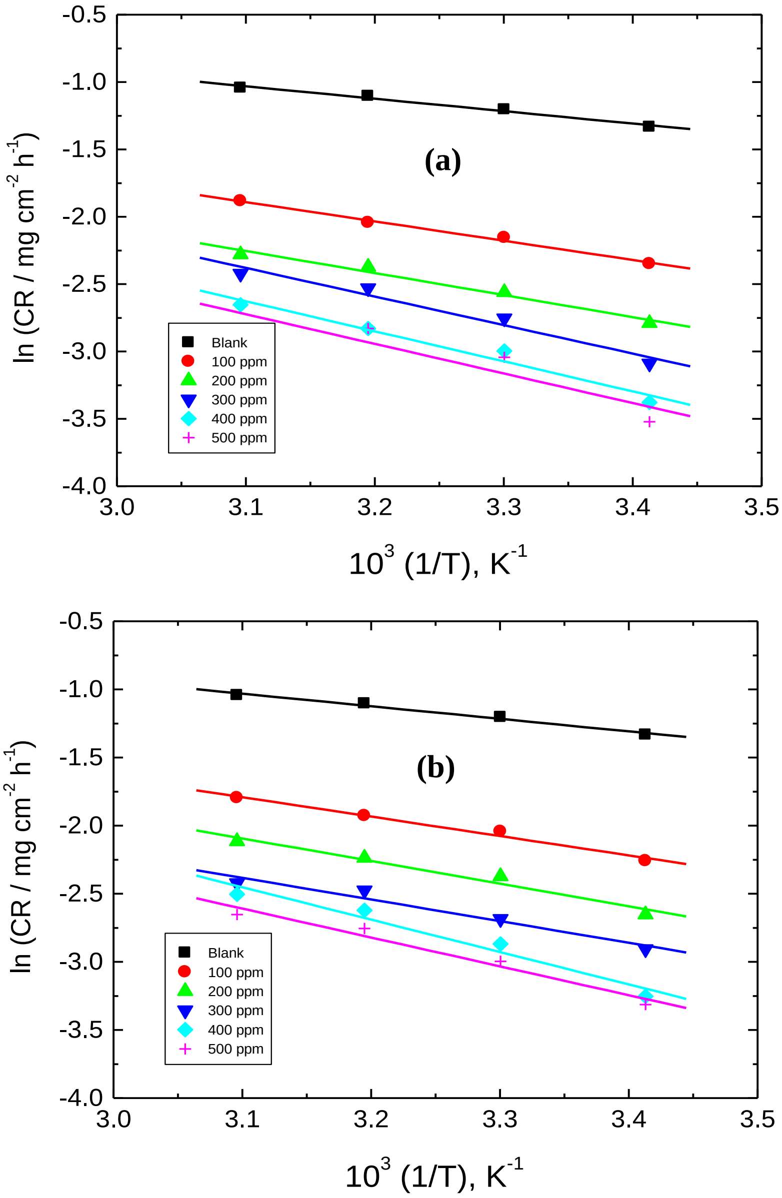


Figure 9. Arrhenius plots for the corrosion of mild steel in 0.5 M H_2SO_4 solution before and after addition of different concentrations of: (a) citrulline, and (b) glutamine.

The obtained values of E_a^* with amino acids were larger than that in the corrosive medium proving that the amino acids' molecules are adsorbed on the steel surface forming a barrier amongst the steel surface and the corrosive medium [58,59]. Moreover, the range of the obtained E_a^* values were found to be 11.89 – 18.21 kJ mol^{-1} which are lower than 80 kJ mol^{-1}, needed for chemical adsorption, indicating that the mechanism of adsorption of the amino acids in the present investigation was physical [60,61]. These observations are consistent with those based on the values of both ΔG^o_{ads} and ΔH^o_{ads} authorizing the rationality of the gained outcomes.

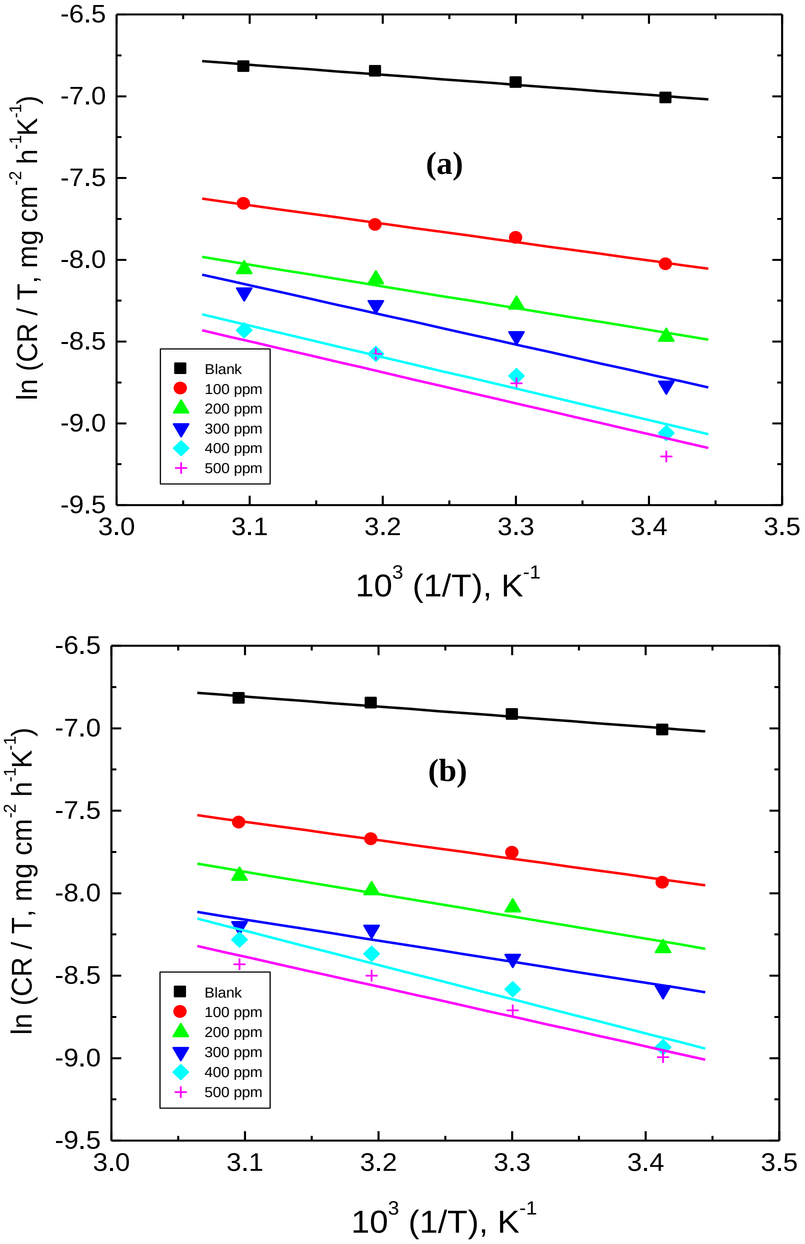


Figure 10. Transition state plots for the corrosion of mild steel in 0.5 M H_2SO_4 solution before and after addition of different concentrations of: (a) citrulline, and (b) glutamine.

The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) of metal corrosion have been evaluated from transition state equation [62],

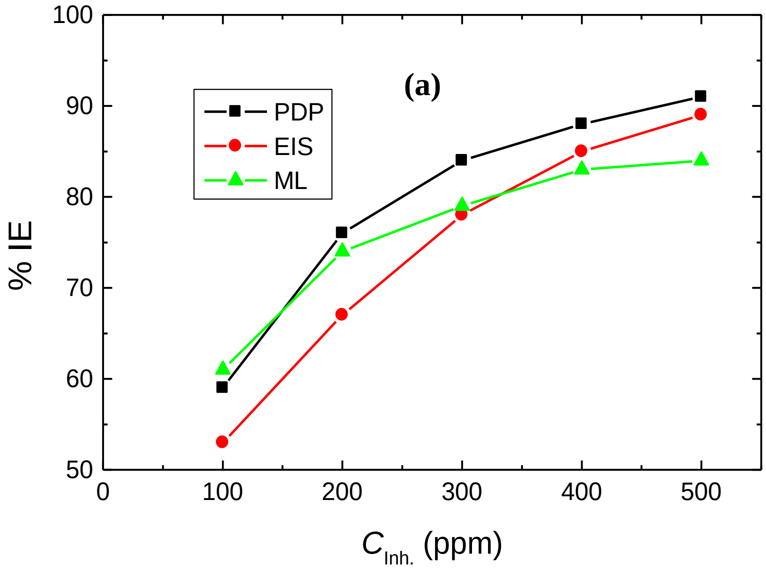
$$\ln\left(\frac{CR}{T}\right) = \left(\ln\frac{R}{Nh} + \frac{\Delta S^*}{R}\right) - \frac{\Delta H^*}{R}\frac{1}{T} \qquad (9)$$

where, N is Avogadro's number and h is Planck's constant.

The plots of ln(CR/T) vs. 1/T were set be linear as shown in Figure 10. The computed ΔH^* and ΔS^* values are listed in Table 6. The positive sign of ΔH^* recommends that the corrosion process was endothermic. Also, the high and negative values of ΔS^* before and after addition of amino acids inferring that the activated complexes constructed in the rate-determining step denotes an association rather than dissociation causing in a reduce in the disorder [63].

Table 6. Activation parameters for the corrosion of mild steel in 0.5 M H_2SO_4 solution before and after addition of different concentrations of citrulline (Cit) and glutamine (Gln).

Inhibitor	**Inh. conc. (ppm)**	E_a^* **kJ mol^{-1}**	ΔH^* **kJ mol^{-1}**	ΔS^* **J mol^{-1} K^{-1}**
	0	7.66	**5.12**	**-40.78**
Cit	**100**	11.91	9.37	-34.71
	200	13.55	11.03	-32.46
	300	17.58	15.07	-20.81
	400	18.54	15.98	-19.98
	500	18.21	15.15	-21.64
Gln	**100**	11.89	9.23	-34.13
	200	13.85	11.24	-30.80
	300	13.14	10.57	-34.96
	400	19.70	17.23	-14.98
	500	17.58	15.07	-23.31



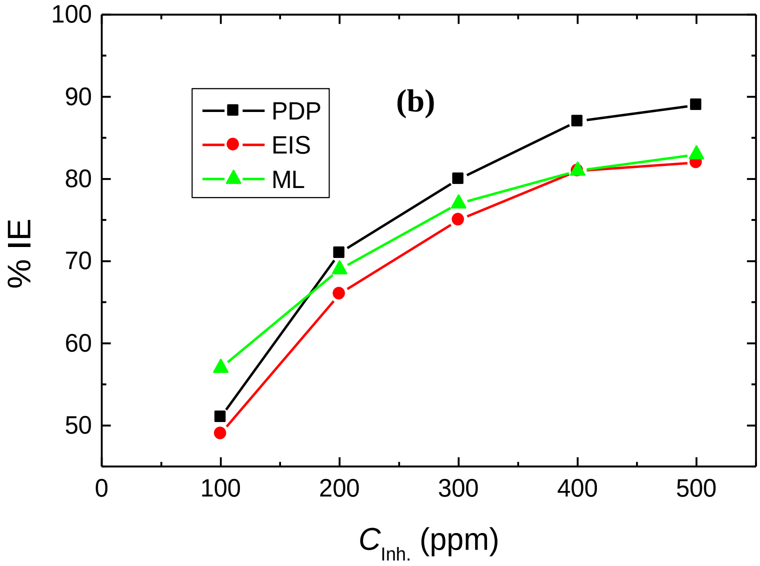


Figure 11. Variation of % IEs of: (a) citrulline, and (b) glutamine, with their concentrations in the corrosion of mild steel in 0.5 M H_2SO_4 solution at 303 K using PDP, EIS and ML techniques.

Figure 11 illustrates the comparing the change in % IEs of the examined amino acids with their concentrations in the corrosion inhibition of Sabic steel in 0.5 M H_2SO_4 solution at 303 K, gained from all employed techniques, PDP, EIS and ML. The figure demonstrates that the investigational outcomes obtained from all used techniques were in a great accord with each other's authorizing the rationality of the gained outcomes.

3.6. Kinetics of Corrosion Inhibition

The kinetics of corrosion inhibition of mild steel in 0.5 M H_2SO_4 solution before and after adding numerous concentrations of the examined amino acids, $\boldsymbol{C_{inh.}}$, can be brightened by the equation [64],

$$CR = k\, C_{inh.}^{n} \qquad (10)$$

where ***k*** is the specific rate constant with the same unit of the corrosion rate (mg cm^{-2} h^{-1}), and **n** signifies the order of corrosion inhibition reaction. The plots of log **CR** vs. log $\boldsymbol{C}_{inh}$ for both amino acids is shown in Figure 12.

The values of **n** and ***k*** were calculated from the slopes and intercepts of such plots. Values of **n** were found to be -1.09 and -1.05 where those of ***k*** were 1.421 x 10^{-4} and 8.76 x 10^{-5} mg cm^{-2} h^{-1} for Cit. and Gln, respectively. The obtained values of **n** indicated that the corrosion inhibition by the examined amino acids were approximately negative first order reactions. The inverse proportionality of the corrosion rates with the inhibitors' concentrations and the negative sign of **n** values refer to good % IEs of the examined amino acids [65].

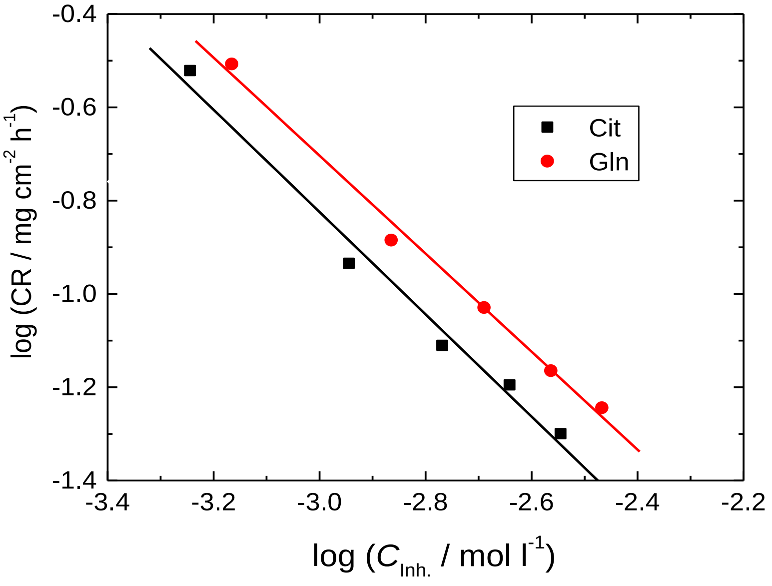
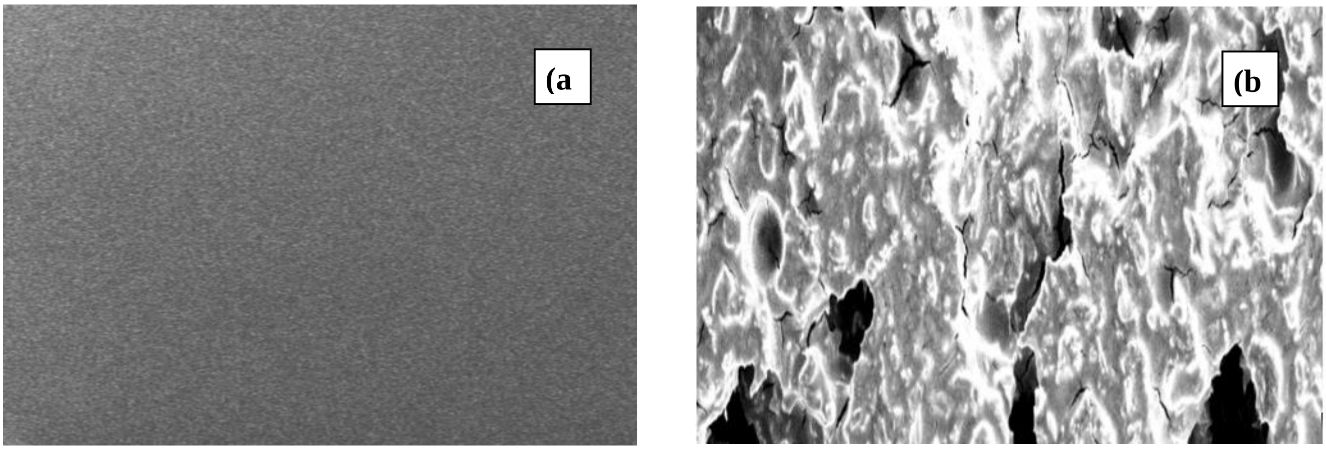


Figure 12. log CR vs. log C_{inh} for the inhibition of mild steel corrosion in 0.5 M H_2SO_4 solution by the examined amino acids at 303 K.

3.8. Surface Investigation

SEM micrographs of the surfaces of mild steel specimens in the tested corrosive medium and in the presence of a 500 ppm of the tested amino acids are shown in Figure 13(a–e). Figure 13 (a) and (b) shows a polished mild steel surfaces before and after 24 h immersion in the corrosive medium, correspondingly. Figure 13(b) manifests a great damage of Sabic steel surface including large and deep holes. Figure 13 (c) and (d) show SEM micrographs after adding a 500 ppm of citrulline and glutamine, correspondingly, to the examined medium. It can be manifest that, the great damage observed in the steel surface was vanished and the surfaces of mild steel were largely covered with the amino acid molecules, which due to strong adsorption of such compounds on the surfaces, results in protecting steel surfaces, thus exhibiting an excellent corrosion inhibition properties [66-68].



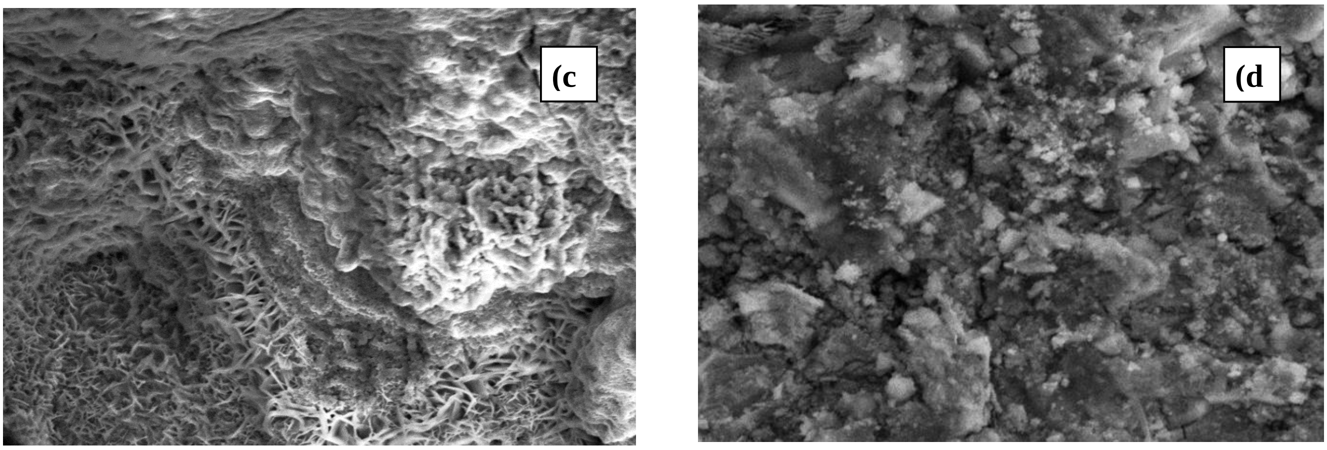


Figure 13. SEM micrographs (x 5000) of the surfaces of mild steel samples; (a) before dipping, (b) after dipping in 0.5 M H_2SO_4 solution for 24 h, (c, d) after 24 h dipping in 0.5 M H_2SO_4 with 500 ppm of citrulline and glutamine, respectively.

4. CONCLUSIONS

1) The inhibition of mild steel corrosion in sulfuric acid solutions was examined by citrulline and glutamine at fixed temperatures using various tools.

2) The examined amino acids were proficient inhibitors for the corrosion of mild steel in H_2SO_4 solutions.

3) Results of PDP technique indicated that the tested compounds act as mixed inhibitors with cathodic majority.

4) The acquired great % IEs of the tested inhibitors was understood in the light of strong adsorption of the amino acid molecules on the steel surface creating a protective film.

5) The adsorption of the amino acid molecules was found to accord with Langmuir isotherm.

6) Thermodynamic and kinetic parameters were computed and discussed which confirm the physical adsorption mechanism of the examined inhibitors.

7) The kinetics of the corrosion inhibition by such compounds revealed negative first order of corrosion inhibition process demonstrating the acquired great % IEs of the investigated compounds.

8) The investigational outcomes acquired from all utilized techniques are agreeable with each others which disclosed that the %IEs of citrulline were higher than glutamine under comparable conditions.

ACKNOWLEDGMENTS

This research was supported by the Deanship of Scientific Research, Imam Mohammad Ibn Saud Islamic University, Saudi Arabia, Grant No. (19-12-12-003).

References

1. A. Fawzy, H.A. El-Ghamry, T.A. Farghaly and T.M. Bawazeer, *J. Mol. Str.,* 1203 (2019) 1203.
2. T. M. Bawazeer, H.A. El-Ghamry, T.A. Farghaly and A. Fawzy, *J. Inorg. Organomet. Polym. Mater.,* 30 (2020) 1609.
3. M. Alfakeer, M. Abdallah and A. Fawzy, *Int. J. Electrochem. Sci.,* 15 (2020) 3283.
4. M. Abdallah, B.A. Al Jahdaly, M.M. Salem, A. Fawzy and A.A. Abdel Fattah, *J. Mater. Env. Sci.,* 8 (2017) 2599.
5. M. Abdallah, M.M. Salem, I.A. Zaafarany, A. Fawzy and A.A. Abdel Fattah, *Orient. J. Chem.,* 33 (2017) 2875.
6. A. Fawzy, M. Abdallah, M. Alfakeer, H.M. Altass, I.I. Althagafi and Y. A. El Ossaily, *Green Chem. Lett. Rev.,* 14 (2021) 488.
7. M. Alfakeer, M. Abdallah and A. Fawzy, *Green Chem. Lett. Rev.,* 14 (2021) 509.
8. M. Abdallah, A. Fawzy and A. Al Bahir, *Int. J. Electrochem. Sci.,* 15 (2020) 4739.
9. M. Abdallah, A. Fawzy and H. Hawsawi, *Int. J. Electrochem. Sci.,* 15 (2020) 5650.
10. F. Faisal, A. Toghan, M. Vorokhta, I. Khalakan, V. Matolin and J. Libuda, *App. Sur. Sci.,* 350 (2015) 142.
11. A. Toghan, M.M. Abou-krisha, F.H. Assaf and F. El-Sheref, *Int. J. Electrochem. Sci.,* 16 (2021) 151044.
12. K.M. Takroni, H.A. El-Ghamry and A. Fawzy, *J. Inorg. Organomet. Polym. Mater.,* 29 (2019) 1927.
13. M. Abdallah, A. Al-Bahir, H.M. Altass, A. Fawzy, N. ElGuesmi, A.S.A. Gorair, F. Benhiba, I. Warad and A. Zarrouk, *J. Mol. Liq.,* 330 (2021) 115702.
14. M. Abdallah, A. Fawzy, H. Hawsawi, R.S.A. Hameed and S.S. Al-Juaid, *Int. J. Electrochem. Sci.,* 15 (2020) 8129.
15. M. Amin, M.A. Ahmed, H.A. Arida, F. Kandemirili, M. Saracoglu, T. Arsland and H.A. Basaram, *Corros. Sci.,* 53 (2011) 1895.
16. A. Toghan, M. Gouda, K. Shalabi and H.M. Abd El-Lateef, *Polymers,* 13 (2021) 2275.
17. M. Abdallah, A. Fawzy and M. Alfakeer, *Int. J. Electrochem. Sci.,* 15 (2020) 10289.
18. A. Fawzy, T. Farghaly, A.A. Al Bahir, A.M. Hameed, A. El-Harbi and Y.A. El-Ossaily, *J. Mol. Str.,* 1223 (2021) 129318.
19. M. Abdallah, A. Fawzy and A. Al Bahir, *Chem. Eng. Commun.,* (2020) 1852220.
20. A. Fawzy and A. Toghan, *ACS Omega*, 6 (2021) 4051.
21. M. Abdallah, I. Zaafarany, A. Fawzy, M.A. Radwan and E. Abdfattah, *J. Am. Sci.,* 9 (2013) 580.
22. M. Abdallah, O.A. Hazazi, A. Fawzy, S. El-Shafei and A.S. Fouda, *Prot. Met. Phys. Chem. Surf.,* 50 (2014) 659.
23. A.S. Fouda and A.S. Ellithy, *Corros. Sci.,* 51 (2009) 875.
24. O.A. Hazazi, A. Fawzy, M.R. Shaaban and M.I. Awad, *Int. J. Electrochem. Sci.,* 9 (2014) 1378.
25. A. Toghan, H.S. Gadow, H. M. Dardeer, and H.M. Elabbasy, *J. Mol. Liq.*, 325 (2021) 115136.
26. O.A. Hazazi, A. Fawzy and M.R. Shaaban, *Int. J. Electrochem. Sci.,* 9 (2014) 4086.
27. G. Wu, *Amino Acids, Biochemistry and Nutrition*, CRC Press, Boca Raton, 2013.
28. A. Toghan, A. M. Abo-baker, H. M. Rageh and M. Abd-Elsabour, *RSC Advances,* 9 2019) 13145.
29. N.O. Eddy, *Mol. Simul.,* 36 (2010) 354; N.O. Eddy, *J. Adv. Res.,* 2 (2011) 35.
30. Z.S. Kandemirli and F. Bingul, *Prot. Met. Phys. Chem*., 45 (2009) 46.
31. T. Wang, J. Wang and Y. Wu, *Corros. Sci.,* 97 (2016) 89.
32. Z. Zhang, N. Tian, W. Zhang, X. Huang, L. Ruan and L. Wu, *Corros. Sci.*, 111 (2016) 675.
33. H. Nady, *Egypt. J. Pet.,* 26 (2017) 905.
34. M.A. Amin and K.F. Khaled, *Corros. Sci.,* 52 (2010) 1194.
35. D. Wang, L. Gao, D. Zhang, D. Yang, H. Wang and T. Lin, *Mater. Chem. Phys.*, 169 (2016) 142.
36. M.A. Quraish, F.A. Ansari, J. Jamal, D. Indian, *J. Chem. Technol.*, 11 (2004) 271.
37. A. M. Awad, N. A. Abdel Ghany, T. M. Dahy, *J. Appl. Surf. Sci.,* 256 (2010) 4370.

38. P. Manjula, S. Manonmani, P. Jayaram and S. Rajendran, *Anti-Corros. Methods Mater.*, 48 (2001) 319.
39. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li and D. Li, *J. Appl. Electrochem.*, 32 (2002) 65.
40. L.B. Tang, G.N. Mu and G.H. Liu, *Corros. Sci.,* 45 (2003) 2251.
41. G.N. Mu, X.H. Li, Q. Qu and J. Zhou, *Corros. Sci.,* 48 (2006) 445.
42. J.C. Bessone, K. Mayer, W. Tuttner and J. Lorenz, *Electrochim. Acta,* 28 (1983) 171.
43. F.M. Reis, H.G. De Melo and I. Costa, *Electrochim. Acta*, 51 (2006) 17.
44. A.M. Muhsen, A. El-Haddad, B. Radwan, M.H. Sliem, W.M.I. Hassan and A.M. Abdullah, *Sci. Reports,* 9 (2019) 3695.
45. S.Y. Sayed, M.S. El-Deab, B.E. El-Anadouli and B.G. Ateya, *J. Phys. Chem. B,* 107 (2003) 5575.
46. T.P. Zhao and G.N. Mu, *Corros. Sci.,* 41 (1999) 1937.
47. F. Touhami, A. Aouniti, Y. Abed, B. Hammouti, S. Kertit, A. Ramdani and K. Elkacemi, *Corros. Sci.,* 42 (2000) 929.
48. M. Bjelopavlic, J. Ralston and G. Reynolds, *J. Coll. Int. Sci.,* 208 (1998) 183.
49. M.A. Deyab, *Corros. Sci.,* 49 (2007) 2315.
50. A.H. Mehaute and G. Grepy, *Solid State Ionics*, 17 (1989) 9.
51. M. Christov and A. Popova, *Corros. Sci.,* 46 (2004) 1613.
52. S.K. Shukla and M.A. Quraishi, *Corros. Sci.,* 51 (2009) 1007.
53. F. Bentiss, M. Traisnel and M. Lagrenee, *Corros. Sci.,* 42 (2000) 127.
54. L.B. Tang, G.N. Mu and G.H. Liu, *Corros. Sci.,* 45 (2003) 2251.
55. K.F. Khaled, *J. Appl. Electrochem*., 39 (2009) 429
56. W. Durnie, R.D. Marco, A. Jefferson and B. Kinsella, *J. Electrochem Soc.,* 146 (1999) 1751.
57. M. Elachouri, M.S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert and E. Essassi, *Corrosion,* 52 (1996) 103.
58. R. Solmaz, *Corros Sci*., 79 (2014) 169.
59. X. Li, S. Deng, H. Fu and T. Li, *Electrochim. Acta*, 54 (2009) 4089.
60. B. Xu, Y. Liu, X. Yin, W. Yang and Y. Chen, *Corros. Sci.,* 74 (2013) 206.
61. A. Anejjar, A. Zarrouk, R. Salghi, H. Zarrok, D. Ben Hmamou, B. Hammouti, B. Elmahi and S.S. Al-Deyab, *J. Mater. Env. Sci.,* 4 (2013) 583.
62. J.O.M. Bockris and A.K.N. Reddy, *Modern Electrochemistry*, Vol. 2, Plenum Press, New York, 1977.
63. J. Marsh, *Advanced Organic Chemistry*, 3rd ed., Wiley, Eastern New Delhi, 1988.
64. E.A. Noor, *Corros. Sci.,* 47 (2005) 33.
65. S.B. Aoun, *Int. J. Electrochem. Sci.,* 8 (2013) 10788.
66. A. Fawzy, M. Abdallah, I.A. Zaafarany, S.A. Ahmed and I.I. Althagafi, *J. Mol. Liq.,* 265 (2018) 276.
67. A. Fawzy, I.A. Zaafarany, H.M. Ali and M. Abdallah, *Int. J. Electrochem. Sci.,* 13 (2018) 4575.
68. A. Fawzy, M. Abdallah, M. Alfakeer and H. M. Ali, *Int. J. Electrochem. Sci.,* 14 (2019) 2063.