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Experimental Study for The Carbon Steel Corrosion Mitigation Effect of the Prepared Trimeric Cationic Surfactant in 1M HCl

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Abstract

Newly synthesized trimeric cationic surfactant namely; N,N'-(((2-(2-((1-(dodecyldimethylammonio)propan-2-yl)oxy)-2-oxoethyl)-2-hydroxysuccinyl) bis(oxy))bis(propane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium) bromide; (ADPC$_{12}$) and its chemical structure has been certain by FTIR and 1HNMR spectroscopic analysistechniques. Gravimetric and electrochemical testes suggested the inhibition affinity of the prepared tested compound. Tafel curves suggested that the tested ADPC$_{12}$ acted as mixed-type effective inhibitor. The inhibitor efficiency increased by increasing the inhibitor concentration, reaching 90.03% at 1x10-4M. The inhibitor behavior study of ADPC$_{12}$ is returned in to its adsorption affinity and follows Langmuir adsorption isotherm. Surface morphology study verified the adsorption of ADPC$_{12}$ on X-65 steel surface. Thermodynamic activation parameters were calculated and discussed thoroughly.

KEYWORDS: Trimeric cationic surfactant; Efficiency; Langmuir adsorption isotherm; Tafel.

1. Introduction

Acid pickling process is a common industrial cleaning process in petrochemical production and oil-well practices to remove mineral oxides and mineral scale depositions, but this process must be controllable due to the highly destructive corrosion effect of mineral acid used HCl [1-3]. Eco-friendly organic inhibitors applications are emerged to touch the environmental restrictions demands. High inhibition efficacy, cheap production cost, low toxic effects, and easy manufacturing make surfactant compounds have merits over the other organic and inorganic inhibitors (such as Chromates, molybdates, phosphates, and nitrates). They have higher electron density active centers (N, S, O and π electrons) that aid them to adsorb over the metal surface and cover it away from the surrounding corrosive media [4-7]. Mechanical exceptional properties of carbon steel alloys and its low cost make it has potential application in many industrial fields. Unfortunately, carbon steel alloys should be protected during industrial process from aggressive media especially HCl due to carbon steel sensitivity [8-12].One of the popular and potential application methods to fight metal deterioration is inhibitors especially in acidic media [2, 13-16]. Based on the adsorption phenomena the surface-active agent adsorbs over metallic surface and form a protective layer which

shield the metal surface away from the surrounding aggressive media [17, 18].Trimeric cationic surfactants have high surface-active properties more than the other cationic surfactant types and subsequently has a several applications in industry especially petroleum fields [19-22]. Adsorption capability of cationic surfactants is referred to the highly adsorption properties of Nitrogen, Oxygen, aromatic ring and double bond that have active sites with high electron density, can produce shielded film on the metallic surface [23-28]. It can be noticed that, the chemical structure of the investigated compound ADPC$_{12}$, contains the three quaternarization centers with long chain aliphatic length that strength the adsorption attraction of the ADPC$_{12}$ on the carbon steel surface and then enhance its corrosion inhibition efficacy in the aggressive acidic medium. The aim of work here is the preparation of trimeric cationic surfactants ADPC$_{12}$ to study its corrosion resistance effect on X65 steel dissolution in acidic medium (1M HCl) by Weight loss as a chemical technique accompanied with electrochemical tests. SEM surface study confirms the obtained results.

2. Experimental
2.1 Synthesis

Esterification reaction of citric acid with N-(2-hydroxypropyl)-N, N-dimethyldodecan-1-aminium bromide [DPC$_{12}$] with molar ratio 1:3 and refluxed in 100 mL of xylene in the presence of p-toluene sulfonic acid (0.01 wt.%) as a dehydrating agent to yield N,N'-(((2-(2-((1-(dodecyldimethylammonio)propan-2-yl)oxy)-2-oxoethyl)-2-hydroxysuccinyl) bis (oxy)) bis(propane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium)bromide [ADPC$_{12}$]. The reaction mixture was refluxed with stirring continuously till remove water of azeotropic (0.27 mL) was collected using Dean-Stark

receiver trap. The reaction was completed when no more water was collected. The reaction mixture was distilled under a vacuum in order to eliminate unreacted excess, remaining materials and solvent completely. The achieved products were poured in diethyl ether (for purification) and acetone (for recrystallization) in order to gain the desired triquaternary ammonium trimeric cationic surfactants, and the chemical structure was represented in Scheme 1.
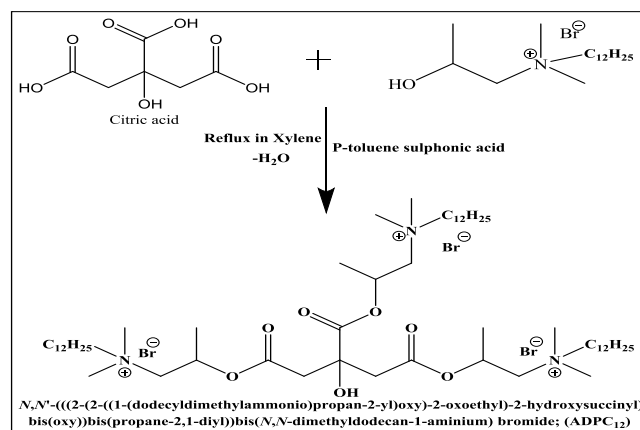
Scheme 1. Synthesis of the trimeric cationic surfactants (**ADPC$_{12}$**)

The chemical structures of the produced triquaternary ammonium trimeric cationic surfactants were confirmed according to the following:

a) Elemental analysis.

(ADPC$_{12}$) C$_{57}$H$_{116}$Br$_3$N$_3$O$_7$ (1195.28)

	%C	%H	%N	%Br
Calcd	57.28	9.78	3.52	20.05
Found	57.12	9.73	3.47	19.81

b) The IR spectrum presented in **Fig. 1** for ADPC$_{12}$ presented the following absorption bands: 3347 cm^{-1} correspond to (O–H group), 3023 cm^{-1} correspond to (C–N+), 2924 cm^{-1} and 2854 correspond to (C–H aliphatic asymmetric and

symmetric stretching respectively), 1735 cm−1 correspond to (C=O stretching of ester group), 1126 cm−1 correspond to (C–N+ stretching of aliphatic amine), 1182 cm−1 correspond to (C–O stretching of the ether linkage of ester). Also, showed complete disappear of the absorption band of both hydroxyl and carbonyl groups of carboxylic acid at 2500−3000 cm−1 and at 1710 cm−1 respectively, and the appearance of a different absorption peak at 1735 cm−1 reference to the formation of ester group of the synthesized tri-ester of trimeric cationic surfactants (ADPC$_{12}$) **Fig. 1**.
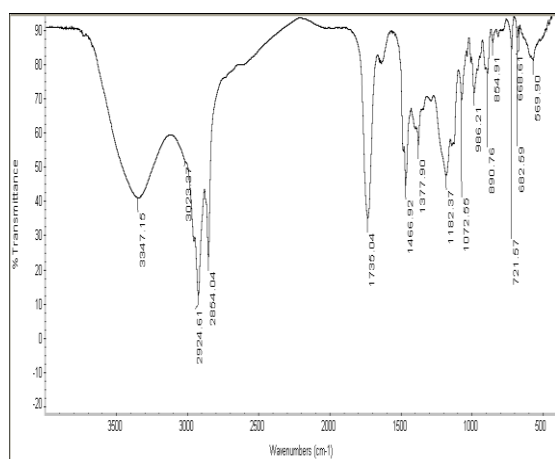

Fig. 1. IR spectrum of compound (ADPC$_{12}$)

c) ^{1}HNMR spectrum of compound (ADPC$_{12}$) in DMSO−d6 as representative sample for the prepared triquaternary ammonium trimeric cationic surfactants based on citric acid and 1-dimethylamino-2-propanol, Fig. 2} showed signals at: δ= 0.83-0.86 ppm [t, 9H, (CH3 CH2−)3], 1.24-1.28 ppm {m, 54H, [CH3(CH2)9]3}, 1.11 ppm {d, 9H, [OCH(CH3)CH2N+]3}, 1.61-1.70 ppm [m, 6H, (CH3(CH2)9CH2CH2N+)3], 2.78 ppm [s, 4H, (CH2C=O)2], 3.07 ppm {d, 6H, [OCH(CH3)CH2N]3},3.22-3.26 ppm [t, 6H, (CH3(CH2)9CH2CH2N+)3], 3.35 ppm {s, 18H, [−N(CH3)2]3}, 5.31 ppm {m, 3H,

[OCH(CH3)CH2N+]3}, 4.20 ppm [s, 1H, OH] (Fig. 2). The prepared compound (ADPC$_{12}$) was acquired as a pasty pale-yellow and water-soluble substance, product = 84%.
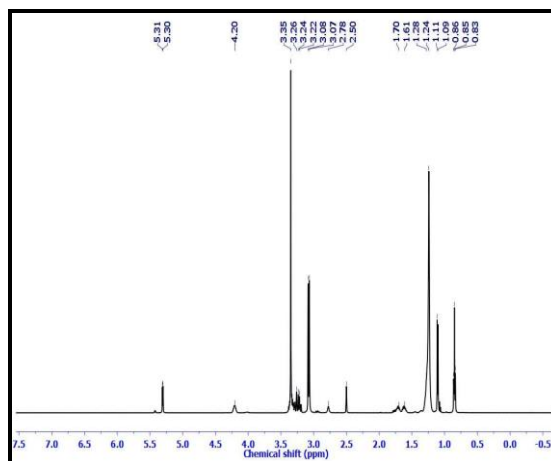

Fig. 2. 1HNMR spectrum of compound (ADPC$_{12}$)

2.2 corrosion tests

The sample was carbon steel electrode having the chemical structure wt. % was: 0.078 C; 0.751 Mn; 0.058 Si; 0.015 Cr; 0.005 P; and Fe balanced. Coupons with dimensions 5 cm x1.5 cm x 0.1cm were used for gravimetric test method. For electrochemical tests, the alloy surface was reformed to give cylindrical shape with the exposed surface area 0.384 cm^2. Prior to each run, the exposed surface is scraped with sequences of emery papers up to 2000 grad, then cleaned in acetone and distilled water. 1M HCl as a destructive medium prepared by 37% HCl (analytical grade) diluted with distilled water. The effective concentration range of the inhibitor was 1x10^{-6} 1x10^{-4}M in 1 M HCl. X65 carbon steel working electrode (WE), a platinum wire auxiliary electrode (CE), and a silver–silver chloride (Ag/AgCl 3M KCl) electrode as a reference electrode, was used for measurements. The electrochemical tests were performed using potentiostat, tacussel radiometer PGZ 402 (Volta lab 80). Immersion of X65 carbon

steel working electrode into the test prepared solution for thirty minutes to run an open circuit potential (Eocp) steady state [29].

Calculations of inhibition efficiency of ADPC₁₂:

The values of both corrosion current density and charge transfer resistance abbreviated as (Icorr) and (Rct) were obtained from Electrochemical impedance spectroscopy and Tafel methods respectively were taken as functions to calculate the inhibition efficiency values:

$$\eta_E\% = (1 - R_{ct(free)}/R_{ct(treated)}) \times 100 \qquad (1)$$

$$\eta_T\% = (I^\circ_{corr} - I_{corr}/I^\circ_{corr}) \times 100 \qquad (2)$$

Where:

Rct (free) and Rct (treated) are the charge transfer impedance of X-65 steel in free aggressive (1M HCl) solution and treated counterpart with ADPC₁₂ different concentration.

I°_{corr} and I_{corr} are the corrosion current denesity in both balnked aggressive 1M HCl and treated counterpart with different ADPC₁₂ concentrations [18, 30].

2.3 Surface morphology study

Morphological investigation study by immersion of carbon steel X65 slides surface in free 1M HCl for 6h at 25 ◦C and the other treated with 1x10⁻⁴ M of ADPC₁₂ has been executed by the scanning electron microscope (SEM) of QUANTA FEG 250 model.

3.   Results and discussion
3.1 Evaluation of synthesized inhibitor efficiency
3.3.1.   Impact of inhibitor dosage.

The weight loss method is considered as useful tool to monitor the corrosion and corrosion inhibition because of its accuracy and simply applied [31, 32]. The inhibition efficiency (ηw) values with different ADPC₁₂ concentrations in 1.0 M HCl at 25 ℃ is showed in **Fig.3** and the relevant obtained data are recorded in **Table 1**.
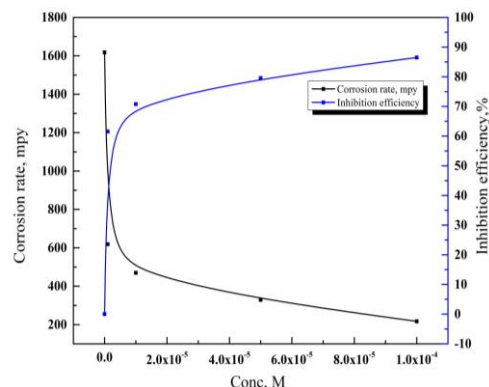
Fig. 3: Influence of the inhibitor dose on the rate of corrosion and the inhibition performance of the ADPC₁₂ inhibitor.

Table 1: Gravimetric results for carbon steel 1.0 M HCl with and without different concentrations of the synthesized trimeric cationic surfactant (ADPC₁₂) at room temperature.

Inh.	Conc, M	Weight loss (g)	CR mpy	Θ	IE%
Blank	0.00	0.643	1609.21	———	———
ADPC₁₂	1x10⁻⁶	0.706	618.626	0.6888	68.88
	1x10⁻⁵	0.67	469.842	0.7401	74.01
	5x10⁻⁵	0.641	328.89	0.8201	82.01
	1x10⁻⁴	0.925	217.302	0.8651	86.51

Data showed that, the corrosion rate (CR, mpy) decreased with increasing the concentration of the synthesized inhibitor (from 1x10⁻⁶ to 1x10⁻⁴ M), i.e. obvious improvement of the corrosion inhibition with the inhibitor concentration. This is due to the fact that the ADPC₁₂ inhibitor adsorption ability increased on X65 steel surface with its concentration, the corrosion rate, CR, (mpy), the % of inhibition performance ($\eta\%$) and degree of surface coverage (θ) were determined as follow [33, 34].

$$CR(mpy) = \frac{W*(3.45*10^6)}{(7.87)A*t} \qquad (3)$$

$$\eta\% = \theta * 100 = \left(\frac{\Delta W}{W_0}\right) * 100 \qquad (4)$$

Where,

1. A (cm2) is the X65 surface area.

2. t (h) is the immersion time.

3. $\Delta W = (W_0 - W)$ is the net weight loss without (W_0) and with (W) inhibitor, respectively.

3.3.2. Impact of temperature

The temperature influence on the rate of X65 corrosion in blanked 1M HCl and treated 1×10^{-4} M ADPC$_{12}$ inhibitor studied by weight loss technique and in 25–55 °C temperature range was shown in Table 2.

Table 2: Effect of temperature on the X-65 corrosion in 1M HCl in absence and presence of 1×10^{-4} M ADPC$_{12}$

		Blank	ADPC$_{12}$
Conc (M)		0.00	1×10^{-4}
25 °C	CR	1609.21	217.302
	IE, %	--	86.49
35 °C	CR	3453.341	447.1332
	IE, %	--	87.05
45 °C	CR	5403.18	675.006
	IE, %	--	87.50
55 °C	CR	8566.79	1010.949
	IE, %	--	88.19

The obtained data showed that the η_w slightly temperature range increase 25–55 °C. This behavior showed that the chemical adsorption of the prepared corrosion inhibitor (ADPC$_{12}$) on the surface of carbon steel in 1.0 M HCl solution. The activation energy (E_a) of the deterioration reaction in presence and absence of the synthesized nonionic surfactants is calculated using Arrhenius equation [35]:

$$CR = k\exp^{\left(\frac{-E_a}{RT}\right)} \qquad (5)$$

(R) and (k) are the universal gas and the Arrhenius constants, respectively. In **Fig.4**,
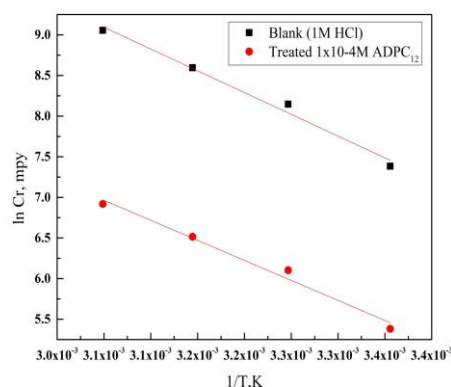

Fig.4: Arrhenius plots of the corrosion rate for carbon steel in 1.0M HCl in absence and presence of 1×10^{-4}M of trimeric cationic surfactant (ADPC$_{12}$).

The slope of *(lnCR) vs. (1/T)* relationship of highly regression coefficient gives the (E_a) values, recorded in **Table.3.**

Table.3: Thermodynamic activation data for X-65 steel corrosion in 1M HCl in absence and presence of 1×10^{-4} M ADPC$_{12}$

Solution	E_a (kJ.mol^{-1})	ΔH_a (kJ.mol^{-1})	ΔS_a (J.K^{-1}mol^{-1})
blank	44.53	41.93	91.6
1×10^{-4}M ADPC$_{12}$	40.96	38.37	63.17

According to the tabulated data in **Table.3**, the value of E_a decreases after adding the synthesized trimeric cationic surfactant (ADPC$_{12}$) at optimum concentration 1×10^{-4}M. According to Riggs and Hurd the reduction in E_a with concentration of the prepared cationic surfactant is typical of chemisorption., they illustrate the drop in E_a of corrosion process at higher inhibition levels comes from the corrosion reaction is shifted from the uncovered portion on the metal surface to the other covered area [36, 37]. And this is confirmed by Schmid and Huang postulated that the

partial reactions on anode and cathode is inhibited by organic molecules on the electrode surface and a parallel reaction occur on the covered area, but that the reaction rate of corrosion the shielded area is fewer than the other on naked area. According to the transition state equation (6), the values of apparent entropy of activation, (ΔS_a), and enthalpy of activation, (ΔH_a), for X-65 steel corrosion reaction in 1.0 M HCl were calculated from the corrosion rate values at different temperatures before and after adding of 1×10^{-4} M ADPC$_{12}$ [38, 39].

$$CR = \left(\frac{RT}{Nh}\right) exp^{\left(\frac{\Delta S_a}{R}\right)} exp^{\left(\frac{-\Delta H_a}{RT}\right)} \qquad (6)$$

Where, (h) is Planck's constant and N is Avogadro's number. Ln (CR/T) versus 1/T straight-line relation is shown in **Fig.5**.
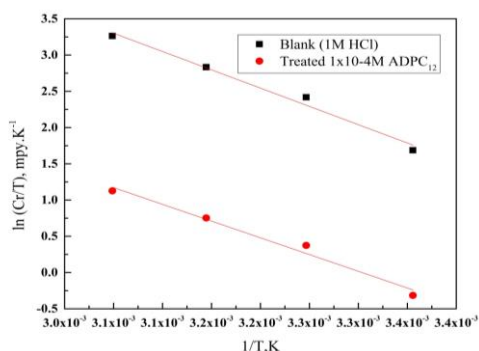

Fig. 5: Transition state plot of the corrosion rate for carbon steel in 1.0 M HCl in the 1×10^{-4}M of trimeric cationic surfactant (ADPC$_{12}$). The values of ΔH_a and ΔS_a calculated were tabulated in **Table.3**. Inspection of these data reveals that the activation parameters (ΔH_a and ΔS_a) of the dissolution reaction of carbon steel in 1.0 M HCl in the presence of the inhibitor are less than those in the free 1.0M HCl. These observations indicated to the prepared trimeric cationic surfactant (ADPC$_{12}$) are adsorbed over the X65 carbon steel surface instead of the adsorbed the water and/ or aggressive anions.

3.3.1.1. Electrochemical impedance spectroscopy (EIS)

EIS measurements are performed to prove the behavior of occurred corrosion reaction of X-65 steel surface in absence (HCl free) and after add of trimeric cationic surfactant (ADPC$_{12}$). EIS spectra after immersion of X65-steel 30 mints in 1M HCl in absence and addition of various concentration of insight trimeric cationic surfactant (ADPC$_{12}$), Nyquist and bode plots are presented as in **Fig. 6.a,b,c**.
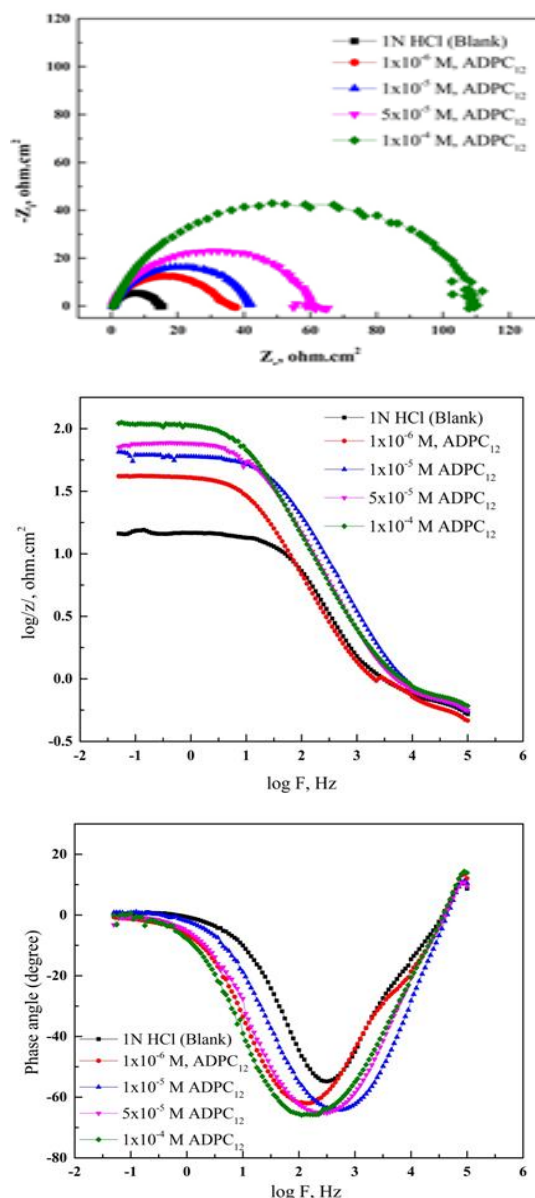

Fig.6 Nyquist (a), bode (b) and phase degree (c) diagrams for X-65 steel in 1 M HCl in absence and

presence of different concentration of trimeric cationic surfactant (ADPC$_{12}$) at 25 ∘C.

Nyquist plots shown in **Fig.6a,b,c** represent as one capacitive loop at high frequency (HF) region with one time constant. This indicates that mass transfer resistance control without changing X65-steel reaction mechanism [40]. The shape of Nyquist plots in the blank solution and after adding different concentrations of the trimeric cationic surfactant (ADPC$_{12}$) are the same without significant change unless the diameter values that increase with the addition of the tested compounds. This indicates the additives inhibition effect on the corrosion reaction of X-65 carbon steel without any change of X65-steel reaction mechanism in the aggressive acidic media [41]. Bode plots inspection indicates that, higher values of shifted impedance modulus /Z/ and the phase angle to -90° at frequency of lower and intermediate regions, respectively [42, 43]. Nyquist plot showed semicircle depressed curves as this is due to frequency dispersion phenomena [44]. **Fig. 7**
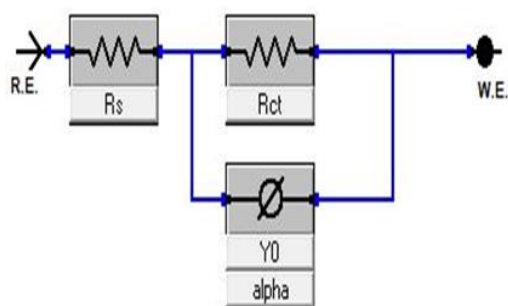

Fig. 7: The proposed equivalent circuit

Shows the proposed equivalent circuit which fit and simulate the EIS experimental data. It contains of the resistance of electrolyte (R$_s$) in series with the charge transfer resistance (R_{ct}) which in corresponding with constant phase element (CPE) in place of the model capacitor double layer (C$_{dl}$) to get a more confirmed representitave data. The electrochemical EIS

parameters resulted such as: inhibition efficiency $(\eta\%)$, R$_{ct}$, Rs, and CPE, and the calculations according to equation (1), where equation (7) refer to calculations of double-layer capacitance (C$_{dl}$) [45, 46] are recorded in **Table 4.**

Table 4: Electrochemical impedance spectroscopy parameters for X-65 in 1M HCl in absence and presence of different concentration of ADPC$_{12}$ at 298 K

Inh.	Conc, M	Rs, (Ω.c m2)	Rct, (Ω. cm2)	n	Cdl, (µF/ cm2)	Θ	IE%
Blank	0.00	0.643	14.02	0.725	237.3	----	------
ADPC$_{12}$	1x10^{-6}	0.706	35.65	0.782	175.2	0.6067	60.67
	1x10^{-5}	0.67	41.92	0.794	151.5	0.6655	66.55
	5x10^{-5}	0.641	58.62	0.824	128.5	0.7608	76.08
	1x10^{-4}	0.925	108.53	0.845	105.8	0.8708	87.08

$$C_{dl} = 1/(2\pi R_{ct} F_{img\rightarrow Max}) \tag{7}$$

Where, $F_{img\rightarrow Max}$, is the frequency at the maximum imaginary resistance.

accurate examination and discussion of the recorded results and obtained EIS data in **Table 4** showed that: by the addition of trimeric cationic surfactant (ADPC$_{12}$) the R$_{ct}$ values of the tested (X-65 steel increased compared to the counterpart blank and further concentration increased till the peak reach at 1x10^{-4} M. This is due to formation of protective layer X-65 steel surface which kept it away from the aggressive action of HCl and consequently decrease corrosion rate on X-65 steel [47]. In the other side, decreasing C$_{dl}$ values with increasing R$_{ct}$, where drop C$_{dl}$ value is occurred due to the replacement of water or/and aggressive ions with the adsorbed trimeric cationic surfactant (ADPC$_{12}$).

3.3.1.2. Electrochemical Potentiodynamic polarization measurements.

The electrochemical kinetic parameters of the corrosion and corrosion inhibition of X65 carbon steel have been obtained from Tafel polarization data in the absence and presence of several concentrations of the prepared trimeric cationic surfactant (ADPC$_{12}$) is exported from the **Fig. 8**.
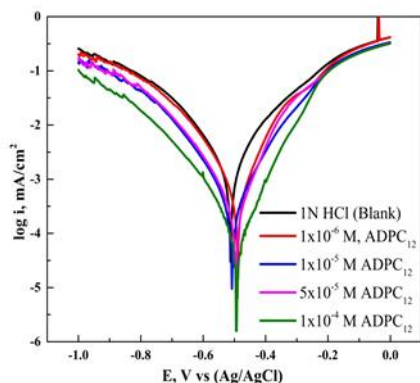

Fig.8: Tafel polarization curves obtained at 25℃ in 1 M HCl in the absence and presence of different concentrations of (ADPC$_{12}$).

From **Fig. 8,** it's obvious that by adding trimeric cationic surfactant (ADPC$_{12}$) shifts the anodic/cathodic polarization curves toward the noble direction, indicate to decreasing deterioration rate of the tested steel alloy [48]. Not to mention, the addition of the prepared inhibitors has no noticeable effect on the corrosion potential values where the corrosion potential changes over the inhibitor concentration range were within ±85 mV around blank one, and this indicates that the mixed type of inhibitor was [49]. The electrochemical parameters obtained from **Fig. 8**, such as i_{corr}, E_{corr}, β_a, and β_c, are tabulated in **Table 5**. In addition to that, the percentage of inhibition efficiency (*IE %*) are calculated according to Equation (2) and tabulated in **Table 5**.

Table 5: Tafel parameters for X-65 in 1M HCl in absence and presence of different concentration of ADPC$_{12}$ at 298 K

	Conc	$-E_{corr}$	I_{corr}	Ba	$-\beta c$	Rp	CR	Θ	IE
	M	mV	mA/cm^2	mV/dec	mV/dec	Ohm.cm2	mpy		%
Blank	0.00	514.8	1.6	122.5	129.2	17.06	732.37	-----	-----
ADPC$_1$	1x10^{-6}	492.3	0.623	91.6	114.3	35.44	285.16	0.610	61.06
	1x10^{-5}	509.7	0.514	120.8	107	47.93	235.27	0.678	67.87
	5x10^{-5}	498.4	0.3116	85.1	111.8	67.33	134.11	0.805	80.52
	1x10^{-4}	495.4	0.155	81	90	119.43	62.95	0.903	90.31

The inspection of **Table 5.** declares that the addition of inhibitors has a high effect on the corrosion current density and corrosion rate even in low concentrations. i_{corr} is dramatically decreased compared to the blank counterpart.

This refers to the adsorption ability of the prepared trimeric cationic surfactant (ADPC$_{12}$) inhibitor due to the presence of high electron density centers (O, N, and π electrons). Corrosion rate (*mpy*) can be calculated using the corrosion current density according to Equation (4):

$$CR = \frac{0.129 * Eq.Wt. * i_{corr}}{d} \tag{8}$$

Where; $Eq.Wt.$, d, and i_{corr} are the current equivalent weight, the iron density, and corrosion current density, respectively [50]. Furthermore, the corrosion current density and *CR* decrease with the concentrations of inhibitor. Furthermore, the polarization resistance calculated using the Stern-Geary Equation (9) and tabulated in **Table 5**:

$$R_p = \frac{[(\beta_a . \beta_c)/2.303(\beta_a + \beta_c)]}{I_{corr}} \tag{9}$$

Where, β$_a$ and β$_c$ are the slopes of the anodic and cathodic Tafel, respectively. The polarization resistance value is inversely proportional to the corrosion current density. So, the R$_p$ increases with increasing the concentration of the added inhibitor.

The potentiodynamic polarization values agree with R_{ct} values obtained from EIS that will be discussed above [51, 52]. It's quite obvious; the inhibition behaviour of trimeric cationic surfactant (ADPC$_{12}$) is the same like that deduced from the weight loss. This indicates that the obtained results from the electrochemical techniques (EIS& Tafel) are consent with chemical one (weight loss).

3.4. Adsorption Isotherm

Organic compounds suppress the corrosion reaction rate of carbon steel by adsorption on the metal-solution interface. The adsorbed molecules attraction between themselves in addition to their attraction with the electrode surface take place based on the adsorption phenomena [53, 54]. Several adsorption isotherm patterns should be utilized to can expect the more fitted one such as: Frumkin, Temkin, Freundlich, and Langmuir isotherms to give information about the kind of the adsorption process happen over the metallic surface. The synthesized trimeric cationic surfactant (ADPC12) inhibitor was extremely close to Langmuir isotherm pattern as presented in Fig. 9. [55,56].
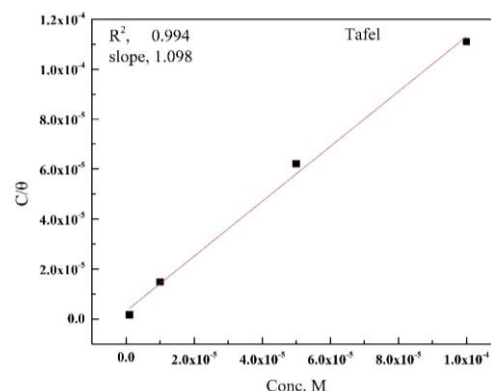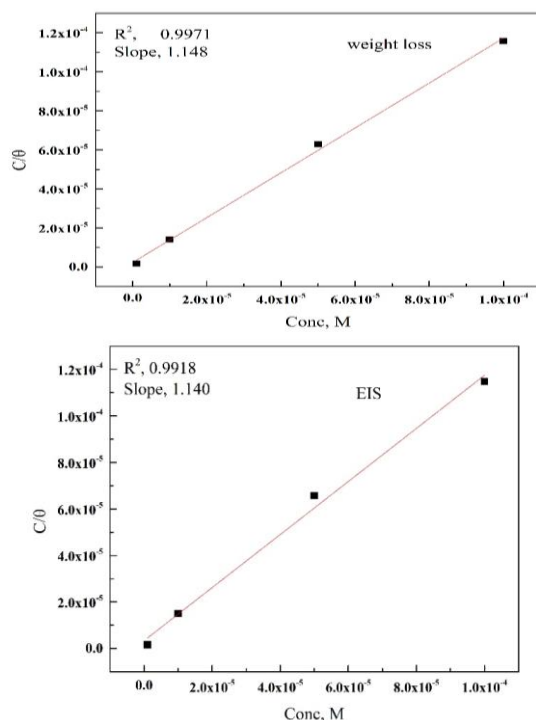

Fig. 9. Langmuir plots of (ADPC₁₂) using weight loss, EIS and Tafel data at 298K.

Depending on the results of surface coverage $(\theta = \frac{\eta}{100})$ found from the electrochemical experiments (weight loss, EIS & Tafel) using several concentrations of the synthesized trimeric cationic surfactant (ADPC$_{12}$), Langmuir adsorption isotherm model can be applied according to the following equation (10):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{10}$$

Where; Θ, the surface coverage; K$_{ads}$, adsorption constant; and C, inhibitor concentration. The inhibitor adsorption free energy (ΔG$_{ads}$) was calculated with the help of (K$_{ads}$) value according to Equation (11):

$$\Delta G_{ads} = (\frac{1}{55.5}) \, exp \, exp \, (\frac{-k_{ads}}{RT}) \tag{11}$$

Where, the molar concentration value of the water was 55.5; M, and (R) is fixed value of gas at the standard conditions. The results of ΔG$_{ads}$ and K$_{ads}$ are recorded in Table 6. K$_{ads}$ is directly proportional to the adsorption strength of inhibitor and the −ve sign of ΔG$_{ads}$ points to the spontaneously of the adsorption process. The higher ΔG$_{ads}$; more than -40kJmol^{-1}, values recorded in **Table 6**.

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Table 6: Langmiur isotherm parameters for the adsorption of the prepared ADPC₁₂ at 298K.

Isotherm	Parameter	Method		
		Tafel	EIS	Weight loss
ADPC₁₂	R^2	0.9944	0.9918	0.9971
	K, (L.mg^{-1}) x 10^4	31.72	29.49	43.02
	-$\Delta G_{ads.}$(kJmol^{-1})	41.34	41.16	42.09

Indicate that the chemical adsorption behavior of the prepared compound which occurs via the transfer of electrons from the free electron pairs from high electron centres to the vacant 3d orbital of Fe forming a covalent bond. This observation is matched with the activation thermodynamic parameters calculated before.

3.5.   Surface analysis SEM

SEM analysis technique gives a 2.D visual information about the performance of the insight the synthesized trimeric cationic surfactant (ADPC₁₂) inhibitor toward the metal corrosion. **Fig. 10.**
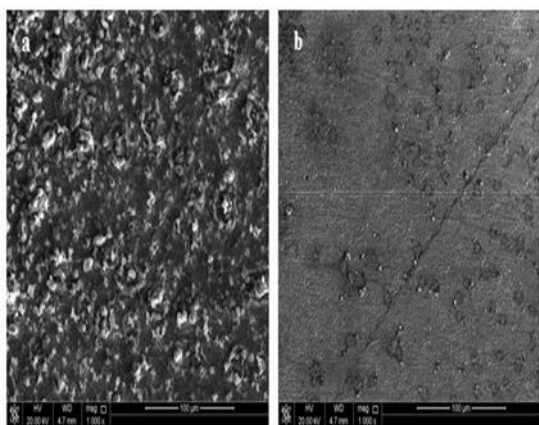

Fig.10. SEM images of mild steel exposed to 1.0 M HCL solution in the absence (a) and presence of 1X10^{-4} M trimeric cationic surfactant (ADPC₁₂)

represents the X65 slides in 1M HCl in the absence and by adding of the prepared the trimeric cationic surfactant (ADPC₁₂) inhibitor.

Form **Fig. 10**, It can be observed that the higher damage X65 surface fulfilled with corrosion product while, after adding the optimum concentration of 1x10^{-4}M of trimeric cationic surfactant (ADPC₁₂), the X65 surface becomes smoother and freer somewhat from corrosion product this inferred the inhibition action of ADPC₁₂via prevent the active centers on the metal surface [47, 57].

4. Conclusions

1- Trimeric cationic surfactant (ADPC₁₂) has been synthesized and its chemical structure is certain by FTIR and ^{1}HNMR spectroscopic analysis.

2- ADPC₁₂ existence decrease, corrosion current density (I_{corr}) and double layer capacitance (C_{dl}).

3- X65 carbon steel charge transfer resistance is enhanced to 108.5 ohm.cm^2 relative to blank one (14.05 ohm.cm^2).

4- The area covered with the ADPC₁₂ increased with ADPC₁₂ concentration and this led to rising the percentage of inhibition efficiency.

5- The adsorption process of ADPC₁₂ over x65 carbon steel surface follows Langmuir adsorption isotherm and mode was chemisorption such as ΔG_{ads} results was more fewer than -40 kJ/mol.

6- SEM study confirmed the performed tests of weight loss and electrochemical experiments via the observation of smooth surface and somewhat free from corrosion product on the metal surface.

7- The proposed cationic surfactant can be used as an alternative for commercial drilling fluid and that we work on.

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6. References

[1] M. Finšgar, J. Jackson, Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review, Corrosion science 86 (2014) 17-41.

[2] G. Schmitt, Application of inhibitors for acid media: report prepared for the European federation of corrosion working party on inhibitors, British Corrosion Journal 19(4) (1984) 165-176.

[3] K. Zohdy, R.M. El-Sherif, S. Ramkumar, A. El-Shamy, Quantum and electrochemical studies of the hydrogen evolution findings in corrosion reactions of mild steel in acidic medium, Upstream Oil and Gas Technology (2020) 100025.

[4] M. Migahed, A.A. Farag, S. Elsaed, R. Kamal, M. Mostfa, H. Abd El-Bary, Synthesis of a new family of Schiff base nonionic surfactants and evaluation of their corrosion inhibition effect on X-65 type tubing steel in deep oil wells formation water, Materials Chemistry and Physics 125(1-2) (2011) 125-135.

[5] M. Vinutha, T. Venkatesha, Review on mechanistic action of inhibitors on steel corrosion in acidic media, Portugaliae Electrochimica Acta 34(3) (2016) 157-184.

[6] M.H. Sliem, M. Afifi, A.B. Radwan, E.M. Fayyad, M.F. Shibl, F.E.-T. Heakal, A.M. Abdullah, AEO7 surfactant as an eco-friendly corrosion inhibitor for carbon steel in HCl solution, Scientific reports 9(1) (2019) 1-16.

[7] K. Zohdy, A. El-Shamy, A. Kalmouch, E.A. Gad, The corrosion inhibition of (2Z, 2′ Z)-4, 4′-(1, 2-phenylene bis (azanediyl)) bis (4-oxobut-2-enoic acid) for carbon steel in acidic media using DFT, Egyptian Journal of Petroleum 28(4) (2019) 355-359.

[8] E.A. Badr, Inhibition effect of synthesized cationic surfactant on the corrosion of carbon steel in 1 M HCl, Journal of Industrial and Engineering Chemistry 20(5) (2014) 3361-3366.

[9] A. El Bribri, M. Tabyaoui, B. Tabyaoui, H. El Attari, F. Bentiss, The use of Euphorbia falcata extract as eco-friendly corrosion inhibitor of carbon steel in hydrochloric acid solution, Materials Chemistry and Physics 141(1) (2013) 240-247.

[10] S.S. Prabha, R.J. Rathish, R. Dorothy, G. Brindha, M. Pandiarajan, A. Al-Hashem, S. Rajendran, Corrosion problems in petroleum industry and their solution, Eur. Chem. Bull 3(3) (2014) 300-307.

[11] F. Ropital, Current and future corrosion challenges for a reliable and sustainable development of the chemical, refinery, and petrochemical industries, Materials and corrosion 60(7) (2009) 495-500.

[12] E.-S.M. Sherif, A.T. Abbas, D. Gopi, A. El-Shamy, Corrosion and corrosion inhibition of high strength low alloy steel in 2.0 M sulfuric acid solutions by 3-amino-1, 2, 3-triazole as a corrosion inhibitor, Journal of Chemistry 2014 (2014).

[13] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Al Himidi, H. Hannache, 2, 3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1 M HCl, Materials chemistry and physics 105(1) (2007) 1-5.

[14] I. Ahamad, R. Prasad, M. Quraishi, Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steel in acidic media, Corrosion Science 52(4) (2010) 1472-1481.

[15] L. Chauhan, G. Gunasekaran, Corrosion inhibition of mild steel by plant extract in dilute HCl medium, Corrosion Science 49(3) (2007) 1143-1161.

[16] M.A. Malik, M.A. Hashim, F. Nabi, S.A. Al-Thabaiti, Z. Khan, Anti-corrosion ability of surfactants: a review, Int. J. Electrochem. Sci 6(6) (2011) 1927-1948.

[17] M. Solomon, S. Umoren, I. Udosoro, A. Udoh, Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid solution, Corrosion science 52(4) (2010) 1317-1325.

[18] A.E. El-Tabey, A.G. Bedir, E. Khamis, M. Abd-El-Raouf, F. Zahran, M.A. Yousef, A. Al-Sabbagh, Synthesis and Evaluation of New Poly Cationic Surfactants as Corrosion Inhibitors for Carbon Steel in Formation Water, Egyptian Journal of Chemistry 63(3) (2020) 833-850.

[19] Q. Zhao, Z. Gao, Synthesis and surface-active property of bis-quaternary ammonium-sodium sulfate Gemini surfactant, Frontiers of Chemistry in China 1(4) (2006) 434-437.

[20] M.E.S. Abdul-Raouf, A.R.M. Abdul-Raheim, N.E.S. Maysour, H. Mohamed, Synthesis, surface-active properties, and emulsification efficiency of trimeric-type nonionic surfactants derived from tris (2-aminoethyl) amine, Journal of Surfactants and Detergents 14(2) (2011) 185-193.

[21] A. Laschewsky, L. Wattebled, M. Arotçaréna, J.-L. Habib-Jiwan, R.H. Rakotoaly, Synthesis and

properties of cationic oligomeric surfactants, Langmuir 21(16) (2005) 7170-7179.

[22] A. El-Tabei, M. Hegazy, A. Bedair, M. Sadeq, Synthesis and inhibition effect of a novel Tri-cationic surfactant on carbon steel corrosion in 0.5 M H2SO4 solution, Journal of Surfactants and Detergents 17(2) (2014) 341-352.

[23] H.M. Abd El-Lateef, M.A. Abo-Riya, A.H. Tantawy, Empirical and quantum chemical studies on the corrosion inhibition performance of some novel synthesized cationic gemini surfactants on carbon steel pipelines in acid pickling processes, Corrosion Science 108 (2016) 94-110.

[24] M.A. Hegazy, A.S. El-Tabei, Synthesis, surface properties, synergism parameter and inhibitive performance of novel cationic gemini surfactant on carbon steel corrosion in 1 M HCl solution, Journal of Surfactants and Detergents 16(2) (2013) 221-232.

[25] M. Mobin, S. Masroor, Cationic gemini surfactants as novel corrosion inhibitor for mild steel in 1M HCl, Int. J. Electrochem. Sci 7 (2012) 6920-6940.

[26] M. Hegazy, A. El-Tabei, A. Bedair, M. Sadeq, Synthesis and inhibitive performance of novel cationic and gemini surfactants on carbon steel corrosion in 0.5 MH 2 SO 4 solution, RSC Advances 5(79) (2015) 64633-64650.

[27] D. Belanger, J. Pinson, Electrografting: a powerful method for surface modification, Chemical Society Reviews 40(7) (2011) 3995-4048.

[28] N. El Basiony, E.E. Badr, S.A. Baker, A. El-Tabei, Experimental and theoretical (DFT&MC) studies for the adsorption of the synthesized Gemini cationic surfactant based on hydrazide moiety as X-65 steel acid corrosion inhibitor, Applied Surface Science 539 (2021) 148246.

[29] M. Migahed, S. Rashwan, M. Kamel, R. Habib, Synthesized polyaspartic acid derivatives as corrosion and scale inhibitors in desalination operations, Cogent Engineering 4(1) (2017) 1366255.

[30] A. Al-Sabagh, M. Migahed, S. Sadeek, N. El Basiony, Inhibition of mild steel corrosion and calcium sulfate formation in highly saline synthetic water by a newly synthesized anionic carboxylated surfactant, Egyptian journal of petroleum 27(4) (2018) 811-821.

[31] H. Elmsellem, A. Aouniti, M. Khoutoul, A. Chetouani, B. Hammouti, N. Benchat, R. Touzani, M. Elazzouzi, Theoretical approach to the corrosion inhibition efficiency of some pyrimidine derivatives using DFT method of

mild steel in HCl solution, J Chem Pharm Res 6(4) (2014) 1216-1224.

[32] M.F. Zaky, I. Sabbah, N.A. Negm, M. Hendawy, Biocidal Activity and Corrosion Inhibition of Some Cationic Surfactants Derived from Thiol Polyurethane, Egyptian Journal of Chemistry 61(1) (2018) 45-60.

[33] N.E. Basiony, A. Elgendy, H. Nady, M. Migahed, E. Zaki, Adsorption characteristics and inhibition effect of two Schiff base compounds on corrosion of mild steel in 0.5 M HCl solution: experimental, DFT studies, and Monte Carlo simulation, RSC advances 9(19) (2019) 10473-10485.

[34] N. Ismail, H. Megahed, A. Ali, M.A. Eletre, Application of Theophylline Anhydrous as Inhibitor of Acid Corrosion of Aluminum, Egyptian Journal of Chemistry 60(1) (2017) 95-107.

[35] S. John, A. Joseph, Adsorption, Surface Morphological, and Electrochemical Studies on the Inhibitive Properties of 4-(N, N-dimethylaminobenzilidine)-3-mercapto-6-methyl-1, 2, 4-triazin (4H)-5-one (DAMMT) on Mild Steel in 0.5 N H2SO4, Journal of dispersion science and technology 33(8) (2012) 1097-1105.

[36] F. Bentiss, M. Lebrini, M. Lagrenée, Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2, 5-bis (n-thienyl)-1, 3, 4-thiadiazoles/hydrochloric acid system, Corrosion Science 47(12) (2005) 2915-2931.

[37] M. Hegazy, M. Zaky, Inhibition effect of novel nonionic surfactants on the corrosion of carbon steel in acidic medium, Corrosion science 52(4) (2010) 1333-1341.

[38] S.A. Umoren, M.J. Banera, T. Alonso-Garcia, C.A. Gervasi, M.V. Mirífico, Inhibition of mild steel corrosion in HCl solution using chitosan, Cellulose 20(5) (2013) 2529-2545.

[39] G. Schmid, H. Huang, Spectro-electrochemical studies of the inhibition effect of 4, 7-diphenyl-1, 10-phenanthroline on the corrosion of 304 stainless steel, corrosion science 20(8-9) (1980) 1041-1057.

[40] S. Abd El Wanees, N. ElBasiony, A. Al-Sabagh, M. Alsharif, S. Abd El Haleem, M. Migahed, Controlling of H2 gas production during Zn dissolution in HCl solutions, Journal of Molecular Liquids 248 (2017) 943-952.

[41] N. El Basiony, A. Elgendy, A.E. El-Tabey, A. Al-Sabagh, G.M. Abd El-Hafez, M. Abd El-raouf, M. Migahed, Synthesis, characterization, experimental and theoretical calculations (DFT and MC) of ethoxylated aminothiazole as

inhibitor for X65 steel corrosion in highly aggressive acidic media, Journal of Molecular Liquids 297 (2020) 111940.

[42] F. Mansfeld, L. Han, C. Lee, G. Zhang, Evaluation of corrosion protection by polymer coatings using electrochemical impedance spectroscopy and noise analysis, Electrochimica Acta 43(19-20) (1998) 2933-2945.

[43] E.M. Anwar, L.S. Kheiralla, R.H. Tammam, Effect of fluoride on the corrosion behavior of Ti and Ti6Al4V dental implants coupled with different superstructures, Journal of Oral Implantology 37(3) (2011) 309-317.

[44] M. Yadav, U. Sharma, P. Yadav, Isatin compounds as corrosion inhibitors for N80 steel in 15% HCl, Egyptian Journal of Petroleum 22(3) (2013) 335-344.

[45] K. Boumhara, M. Tabyaoui, C. Jama, F. Bentiss, Artemisia Mesatlantica essential oil as green inhibitor for carbon steel corrosion in 1 M HCl solution: Electrochemical and XPS investigations, Journal of Industrial and Engineering Chemistry 29 (2015) 146-155.

[46] A. Popova, M. Christov, A. Vasilev, Inhibitive properties of quaternary ammonium bromides of N-containing heterocycles on acid mild steel corrosion. Part II: EIS results, Corrosion Science 49(8) (2007) 3290-3302.

[47] A.A. Abd-Elaal, N. Elbasiony, S.M. Shaban, E. Zaki, Studying the corrosion inhibition of some prepared nonionic surfactants based on 3-(4-hydroxyphenyl) propanoic acid and estimating the influence of silver nanoparticles on the surface parameters, Journal of Molecular Liquids 249 (2018) 304-317.

[48] E. McCafferty, Validation of corrosion rates measured by the Tafel extrapolation method, Corrosion science 47(12) (2005) 3202-3215.

[49] M.A. Amin, S.S. Abd El Rehim, H.T. Abdel-Fatah, Electrochemical frequency modulation and inductively coupled plasma atomic emission spectroscopy methods for monitoring corrosion rates and inhibition of low alloy steel corrosion in HCl solutions and a test for validity of the Tafel extrapolation method, Corrosion Science 51(4) (2009) 882-894.

[50] S.D. Shetty, N. Shetty, F. Parvaz, K. Agnihotri, P. Mewawala, Investigating the Inhibiting Action of Thiourea Derivative on Mild Steel Corrosion in Acid Medium, International Journal of Applied Engineering Research 12(12) (2017) 3237-3242.

[51] N.F. Atta, A. Fekry, H.M. Hassaneen, Corrosion inhibition, hydrogen evolution and antibacterial properties of newly synthesized organic inhibitors on 316L stainless steel alloy in acid medium, international journal of hydrogen energy 36(11) (2011) 6462-6471.

[52] I. Epelboin, M. Keddam, H. Takenouti, Use of impedance measurements for the determination of the instant rate of metal corrosion, Journal of Applied Electrochemistry 2(1) (1972) 71-79.

[53] W. Durnie, R. De Marco, A. Jefferson, B. Kinsella, Development of a structure-activity relationship for oil field corrosion inhibitors, Journal of the Electrochemical Society 146(5) (1999) 1751.

[54] K. Ataka, J. Heberle, Functional vibrational spectroscopy of a cytochrome c monolayer: SEIDAS probes the interaction with different surface-modified electrodes, Journal of the American Chemical Society 126(30) (2004) 9445-9457.

[55] C.A. Başar, Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, Journal of Hazardous Materials 135(1-3) (2006) 232-241.

[56] E. Malkoc, Y. Nuhoglu, Determination of kinetic and equilibrium parameters of the batch adsorption of Cr (VI) onto waste acorn of Quercus ithaburensis, Chemical Engineering and Processing-Process Intensification 46(10) (2007) 1020-1029.

[57] D. Lopez, W.d. Schreiner, S. De Sánchez, S. Simison, The influence of carbon steel microstructure on corrosion layers: an XPS and SEM characterization, Applied Surface Science 207(1-4) (2003) 69-85.