

## Evaluation of protection performances of novel synthesized bis-oxindole-based derivatives for the corrosion of aluminum in acidic environment

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### ABSTRACT

Three bis(3-schiff base-indoline-2-one) derivatives, **3(a-c)**, and two bis-spirotriazole-indole derivatives, **5(a,b)**, were synthesized and were evaluated as inhibitors for the corrosion of Al in 1.0 M HCl at 303 K. Weight loss (WL) method was applied for evaluation of the inhibition efficiencies (% IEs) of all synthesized compounds while WL in addition to potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were employed in case of the compound that has the highest % IE values. The collected results illuminated that the synthesized compounds were discovered to be efficient inhibitors and their % IEs were set to vary with their concentrations, structures, and the corrosive medium concentration. WL outcomes revealed that, the order of % IEs of the synthesized compounds was: **5a**  $\approx$  **5b** > **3a** > **3b**  $\geq$  **3c**. The acquired high % IEs of such compounds were attributed to their potent adsorption on the Al surface and production of a protective film, and this adsorption was agreed with Langmuir adsorption isotherm. The kinetics of corrosion inhibition by the synthesized compounds appeared a negative-first order process confirming the gained higher values of % IEs of such compounds. PDP results indicated that the compound **5a** behaves as a mixed inhibitor with a cathodic majority. The results acquired from the three utilized tools were set to be in a good agreement with each other's confirming the validity of the obtained results.

### 1. Introduction

Aluminum is the second used metal in the world after steel, due to its lightness coupled with its strength, high electrical and thermal conductivities, low density, relatively low cost and high corrosion resistance [1–3]. Aluminum remarkably applied in industries as well as chemical industries such as air technology and desalination plants and food industry due to its comparatively proper availability for production of vessel [4]. It is considering a reaction metal reacts spontaneously with air and /or water [5]. Globally, corrosion is a problem that hinders economic development in both industrialize and developing nations,

because it has inverse effect which are not obvious, such the lack of productiveness, infrastructure deterioration and significant economic losses due to industrial equipment. Every year, the industrial companies containing, energy, chemical, food processing, transport and construction are suffering from corrosive environment which is leads losses of billions of dollars [6]. In aerated media, a protective oxide film is proposed to construct on the Al surface which is inert, steady and adherent that preserves the Al surface from additional corrosion [7–9]. However, this oxide film is broken in lower or higher pH media especially, in the presence of aggressive ions such as Cl<sup>-</sup> ions [10,11]. Because of the passivation, Al has the ability to resist corrosion to some level, but its

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corrosion mainly occurs in an aqueous acidic medium [4] especially in industrial area [4–6,12]. Hence, mineral acids and alkalis are very corrosive for Al. Acidic media such as HCl are usually used as a corrosive pickling and cleaning of Al. Various studies were performed regarding to the corrosion inhibition of Al in HCl solutions [13–17].

Inhibitors of corrosion are widely employed to decrease the corrosive attack on objects that include metal [18]. The type of acidic solution, temperature of the solution, concentration, presence of dissolved inorganic or organic elements, and the type of metallic materials should all be taken into consideration when selecting corrosion inhibitors. Corrosion inhibitors come in a wide variety of forms and formulations [6,12]. Addition of some organic and inorganic compounds was set to prevent corrosion of Al [5]. However, when compared organic inhibitors to the inorganic ones we are observed organic inhibitors less toxic [4]. The Most of organic compounds with various functional groups, heteroatoms including nitrogen, oxygen, sulfur, and phosphorus, multiple bonds, or aromatic rings, as well as multiple bonds or aromatic rings are regarded as organic inhibitors [18–23]. The performances of such inhibitors vary with their abilities for adsorption on the metallic surfaces [24–28]. Triazole is one of the heterocyclic moieties having three N atoms in its structure [29]. The triazoles displayed certain desirable characteristics such as metabolic degradation / resistance, reduction conditions, anti-oxidant [30], and high acid / base hydrolysis stability [31].

From all these finding in addition to our efforts in the synthesis of organic corrosion inhibitors for various metals in different media [32–36], the chief goals of the present study were to examine the inhibition effectiveness of five novel synthesized bis-oxindole-based derivatives for protection of Al from corrosion in 1.0 M HCl solution. Various tools were employed in this investigation as weight loss (WL), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS)). Also, the kinetics of corrosion of Al and its inhibition were investigated.

## 2. Experimental

### 2.1. Instruments for conformation of the structures of the examined compounds

Recording melting points	Gallenkamp apparatus
IR spectra	KBr / Pye-Unicam SP300 spectrophotometer
<sup>1</sup> H and <sup>13</sup> C NMR spectra	DMSO- <i>d</i> <sub>6</sub> / Varian Gemini 300 NMR spectrometer (300 MHz for <sup>1</sup> H NMR and 75 MHz for <sup>13</sup> C NMR)
Mass spectra	GCMS-Q1000-EX Shimadzu and GCMS 5988-A HP spectrometers

### 2.2. Synthesis of the examined compounds

#### 2.2.1. Reaction of bis-oxindole derivative 1 with aniline derivatives 2(a-c)

In a 50 mL round flask, we put a mixture of 2.5 mmols of each of bis-oxindole derivative 1 and the 5.0 mmols of the suitable aniline derivative 2 in 25 mL acetic acid glacial. The mixture was refluxed for 5 h then the solid formed was collected with filtration on hot. The solid was purified by crystallization from dioxane to afford 1,1'-(propane-1,3-diyl) bis(3-substitutedphenylimino-indoline-2-one) (3a-c).

#### 2.2.2. Cycloaddition reaction of compounds 3(b,c) with hydrazoneyl chloride 4

A mixture of 0.002 mole of compound 3 and 0.004 mole hydrazoneyl chloride 4 in 50 mL chloroform was refluxed for 10 h. The solvent was evaporated after the reaction mixture was completed (testing the progress of the reaction with TLC). The colored residue was triturated with methanol and filtered off and crystallized with dioxane to afford the series of bis spiro1,2,4-triazole-indoline-2-one derivatives 5(a,b).

## 2.3. Corrosion experiments

### 2.3.1. Materials and methods

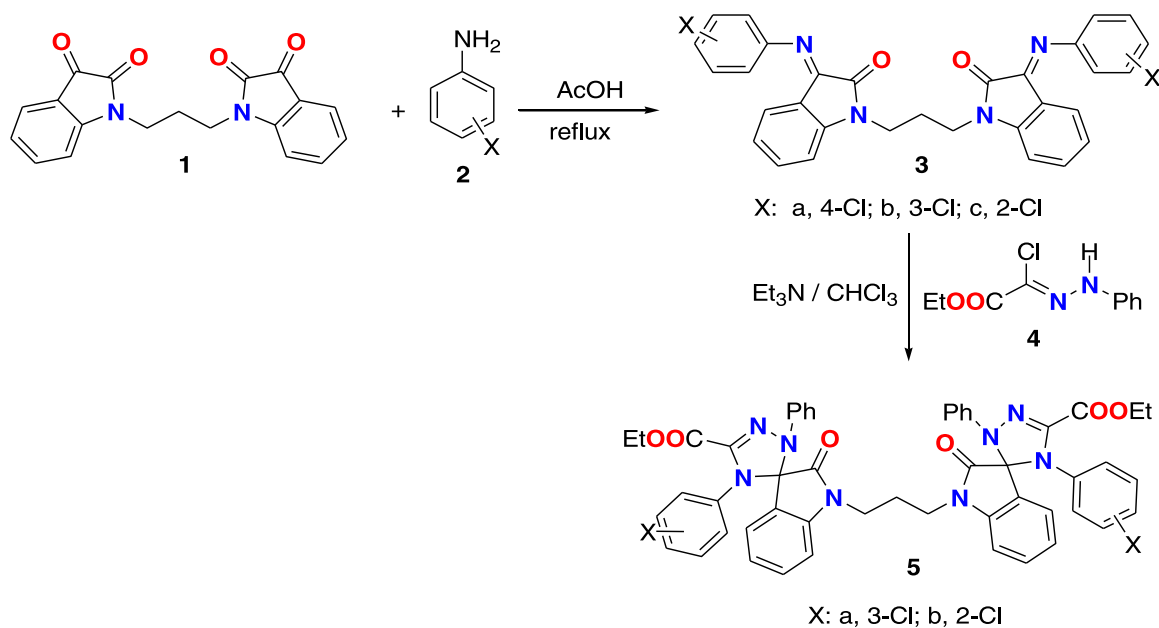
All chemicals used in this investigation were of analytical grade and the solvent used for the preparation of their solutions was double distilled water. The principal corrosive solution was 1.0 M HCl (Sigma-Aldrich). The tested concentrations of the examined compounds (inhibitors) were 40 to 200 mg/L. All corrosion tests were performed on the commercially pure aluminum samples (Saudi Arabia) with purity of 99.9% (0.1% Cu). Al sheets (with dimension of 4 × 2 × 0.2 cm<sup>3</sup>) were employed for WL method. For both PDP & EIS techniques, a cylinder-shaped rod with exposed area of 1.0 cm<sup>2</sup> was pressed into a Teflon holder.

Weight loss (WL) method as a chemical tool was used for investigation of the inhibition efficiencies (% IEs) of all examined compounds (inhibitors) while WL in addition to potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) as electrochemical techniques were used in case of the compound that has the highest% IE values. Prior to each corrosion test, the surface of Al specimen was degreased with different grades of emery paper, washed with double distilled water, rinsed with acetone and finally dried. In WL experiments, the polished cleaned aluminum sheets were inserted in a 100 ml of the examined corrosive solution for a fixed time. The average weight loss (mg/cm<sup>2</sup>) for at least two like experiments was taken. In both PDP and EIS measurements the aluminum electrode was treated as in WL measurements, then it was inserted immediately into the glass cell that contained 50 ml of the corrosive solution (1.0 M HCl) without and with the requested concentration of the examined compound. All experiments were recorded using thermostated PGSTAT30 potentiostat / galvanostat. The used cells contains: Al specimen as a working electrode (WE), a platinum sheet as a counter electrode, and calomel as a reference electrode. Prior to starting any experiment, the WE was immersed in the tested solution for 30–40 min. to achieve a stable open circuit potential (OCP). PDP experiments were performed in the potential range of about ± 250 mV vs. OCP at scan rate of 1.0 mV/s. In EIS studies, the frequency range was: 100 kHz to 0.1 Hz, and the amplitude was 5.0 mV (peak to peak) utilizing AC signals at OCP.

## 3. Results and discussion

### 3.1. Synthesis and conformation of the structures of the examined compounds

Our target compounds; three bis(3-schiff base-indoline-2-one) derivatives, 3(a-c), and two bis-spirotriazole-indole derivatives, 5(a,b), were synthesized as depicted in Scheme 1 [37]. Firstly, Schiff base of bis-oxindole derivative 1 [38] was achieved through condensation of compound 1 with the selected aniline derivatives 2 in acidic medium (AcOH). The structure of the synthesized three Schiff base derivatives of bis-oxindole 3(a-c) were assured using the available spectral data as for example, the mass spectra for all derivatives 3(a-c) were characterized with the appearance of the expected molecular ion peak for each derivative agree with its exact molecular weight as tabulated in Table 1. Furthermore, the <sup>1</sup>H NMR of the same derivatives 3(a-c) revealed one pentat signal at δ = 1.23–2.0 ppm for the middle CH<sub>2</sub> group of -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>- moiety in addition to the triplet signal for the two terminal equivalent CH<sub>2</sub> groups at δ = 3.72–3.78 ppm. Conversion of the two Schiff base moieties N=C of derivatives 3 to the spirotriazole in derivatives 5 were achieved via the cycloaddition of hydrazoneyl chloride 4 to Schiff base derivatives 3(b,c) in chloroform (Scheme 1). The IR and mass spectra of bis-spiro(triazole-oxindole) derivative 5b confirmed its formation as for example, the IR data showed two C=O absorption bands at 1705 and 1732 cm<sup>-1</sup> for the carbonyl of oxindole and ester-carbonyl of triazole ring, respectively. In addition, the mass spectra of the two bis(spirotriazoleoxindole) derivatives 5(a,b), showed the expected large molecular ion peak for each derivative in



Scheme 1. Synthesis of bis-oxindoles **3(a-c)** and bis-spiro(triazole-oxindole) derivatives **5(a,b)**.

agreement with its exact molecular weight as tabulated in Table 1.

## 3.2. Corrosion studies

### 3.2.1. WL measurements

**3.2.1.1. Effect of [HCl] on the CRs.** To investigate the impact of the corrosive medium concentration, [HCl], on the values of corrosion rates (CRs) of Al, WL experiments for Al sheets were performed in various concentrations of HCl solutions, namely, from 0.5 M to 2.0 M at 303 K. Values of CR expressed in mils penetration per year (mpy) were calculated from Eq. (1) [39]:

$$CR(\text{mpy}) = \frac{KW}{Atd} \quad (1)$$

where  $K$  is a constant ( $3.45 \times 10^6$ ),  $W$  is the WL in grams,  $A$  is the Al sheet area in  $\text{cm}^2$ ,  $t$  is the time in hour and  $d$  is the density of aluminum.

The calculated values of CRs of Al sheets were inserted in Table 2. The obtained values of CRs were increased with increasing the concentration of HCl solution. This is due to the increased concentration of the aggressive  $\text{Cl}^-$  ions with rising [HCl] resulting in acceleration of Al dissolution. It was suggested [40] that at low  $[\text{Cl}^-]$ , the constructed protective oxide film on the Al surface [7,41–44] was ruptured and healed spontaneously. Higher  $[\text{Cl}^-]$  prevented healing which results in a reduction in the passive region. At very high  $[\text{Cl}^-]$ , the passive regions are completely absent specifying direct attack of Al [45].

**3.2.1.2. Effect of inhibitors' concentrations.** WL experiments for aluminum sheets in 1.0 M HCl solution without and with different concentrations (40 – 200 mg/L) of the examined organic compounds symbolized: **3a**, **3b**, **3c**, **5a** and **5b**, were performed at 303 K. Fig. 1 shows only the plots of WL versus immersion time in the presence of the compound **5a** as a representative example. The values of both % IEs and degrees of surface coverage ( $\theta$ ) of the examined compounds were calculated from Eq. (2) [46]:

$$\% \text{IE} = \theta \times 100 = \left[ 1 - \frac{CR_{\text{inh}}}{CR} \right] \times 100 \quad (2)$$

where CR and  $CR_{\text{inh}}$  are the values of corrosion rates without and with the inhibitor, respectively.

The calculated values of the CRs of aluminum as well as the values of % IEs and  $\theta$ s of the examined compounds at 303 K are listed in Table 3. The results recorded in Table 3 signified that the values of the CRs of aluminum were reduced and the values of both % IEs and  $\theta$ s of the examined compounds were increased with increasing their concentrations (Fig. 2). This can be ascribed to the increased adsorption of the organic molecules on the aluminum surface with augmenting their concentrations resulting in a reduction of the values of CRs and, thus, increasing the values of both % IEs and  $\theta$ s. Hence, the examined compounds are considered as efficient inhibitors for the corrosion of aluminum in 1.0 M HCl solution. Also, the results revealed that, at similar concentrations, the values of % IEs increased as follows: **5a**  $\approx$  **5b** > **3a** > **3b**  $\geq$  **3c** (compound **5a** was found to have the highest % IE) as illuminated in Fig. 2. This trend can be described by the variance in the force of the adsorption of the tested compounds on the Al surface as a result of the difference in the chemical structures of the examined compounds associated with the electronic densities of the heteroatoms, conjugated  $\pi$ -bonds, polar groups, aromatic rings, etc. contained in these compounds.

**3.2.1.3. Adsorption isotherms.** To discuss the adsorption mechanism of the examined compounds on the Al surface in this present investigation, the values of degree of surface coverage ( $\theta$ ) of the synthesized compounds at different concentrations were inserted in different adsorption isotherms such as Langmuir, Frumkin, Temkin, Freundlich, etc. The gained results were discover to agree with Langmuir adsorption isotherm as shown in Fig. 3 and defined by Eq. (3) [47],

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (3)$$

where  $K_{\text{ads}}$  is the adsorption constant which their values were calculated from the intercepts of the linear plots in Fig. 3 and are listed in Table 4.

**3.2.1.4. Kinetics of aluminum corrosion and its inhibition.** The kinetics of the corrosion of Al in 1.0 M HCl solution and in the presence of the compound **5a** at 303 K was studied. The plots of  $-\ln(\text{WL})$  vs. time were linear as shown Fig. 4) illuminating that the kinetics of the corrosion of Al in 1.0 M HCl solution and its inhibition by the examined compound **5a** were negatively first order processes. The slopes of such plots refer to the first order rate constant values,  $k_1$  (in  $\text{h}^{-1}$ ), that are listed in Table 5.

**Table 1**  
Physical properties, EA and spectral data for derivatives **3(a-c)** and **5(a,b)**.

Compd. No.	Physical properties, EA and mass spectra.	IR and NMR data
<b>3a</b>	Dark red crystals, 78% Yield, mp. 242–244 °C. C <sub>31</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> (553.44): Calculated (Found)%: C, 67.28(67.14); H, 4.01(3.95); N, 10.12(10.01)%. MS: <i>m/z</i> : 77 (74), 114 (25), 186 (57), 245 (69), 268 (64), 323 (50), 361 (40), 398 (50), 476 (100), 495 (36), 533 (33), 553 (M <sup>+</sup> , 35), 554 (M <sup>+</sup> +1, 27).	IR spectrum, $\nu$ , cm <sup>-1</sup> : 1092, 1168, 1296, 1350, 1469, 1600 (C = N), 1724(C = O). <sup>1</sup> H NMR spectrum, $\delta$ , ppm: 1.23 (p, <i>J</i> = 8.5 Hz, 2H, CH <sub>2</sub> ), 3.72 (t, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 7.25–8.29 (m, 16H, Ar-H).
<b>3b</b>	Orange solid, 73% Yield, mp. 245–247 °C. C <sub>31</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> (553.44): Calculated (Found)%: C, 67.28(67.21); H, 4.01(3.97); N, 10.12(10.07)%. MS: <i>m/z</i> : 74 (100), 77 (92), 84 (12), 91 (13), 111 (24), 114 (15), 127 (15), 219 (23), 247 (55), 263 (21), 287 (12), 321 (15), 347 (18), 387 (11), 441 (23), 462 (17), 553 (M <sup>+</sup> , 18), 554 (M <sup>+</sup> +1, 3).	IR spectrum, $\nu$ , cm <sup>-1</sup> : 1091, 1168, 1192, 1296, 1350, 1469, 1604(C = N), 1724(C = O). <sup>1</sup> H NMR spectrum, $\delta$ , ppm: 2.0 (p, <i>J</i> = 8.5 Hz, 2H, CH <sub>2</sub> ), 3.78 (t, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 7.11–7.64 (m, 16H, Ar-H);
<b>3c</b>	Red solid, Yield 77%, mp. 214–216 °C. C <sub>31</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> (553.44): Calculated (Found)%: C, 67.28(67.19); H, 4.01(3.89); N, 10.12(10.02)%. MS: <i>m/z</i> : 77 (23), 85 (29), 121 (38), 236 (78), 252 (67), 259 (100), 292 (99), 300 (80), 355 (52), 363 (64), 391 (31), 403 (42), 431 (85), 447 (59), 494 (22), 547 (24), 553 (M <sup>+</sup> , 44).	IR spectrum, $\nu$ , cm <sup>-1</sup> : 2947 (sp <sup>3</sup> CH), 1732 (C = O), 1604 (C = N), 1465, 1350, 1292, 1219, 1087. <sup>1</sup> H NMR spectrum, $\delta$ , ppm: 1.90 (p, 2H, CH <sub>2</sub> ), 3.78 (t, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 6.73–7.64 (m, 16H, Ar-H); <sup>13</sup> C NMR spectrum, $\delta$ , ppm: 25.1 (CH <sub>2</sub> ), 37.9 (CH <sub>2</sub> ), 111.1, 115.7, 115.9, 118.0, 123.6, 124.8, 124.9, 127.9, 128.6, 144.9, 150.9, 158.7, 183.7 (C = O).
<b>5a</b>	Dark red solid, 59% Yield, mp. 259–261 °C. C <sub>51</sub> H <sub>42</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>6</sub> (933.84): Found,%: C, H, N, Calculated (Found)%: C, 65.59 (65.41); H, 4.53 (4.39); N, 12.00 (11.90). MS: <i>m/z</i> : 85 (36), 116 (57), 145 (44), 269 (44), 395 (57), 440 (54), 594 (57), 732 (81), 809 (100), 850 (48), 832 (59), 898 (49), 917 (32), 933 (M <sup>+</sup> , 36).	<sup>1</sup> H NMR spectrum, $\delta$ , ppm: 1.21 (t, <i>J</i> = 8.5 Hz, 6H, 2CH <sub>3</sub> ), 1.99 (p, <i>J</i> = 8.5 Hz, 2H, CH <sub>2</sub> ), 3.82 (t, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 4.31 (q, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 7.05–7.95 (m, 26H, Ar-H);
<b>5b</b>	Orange solid, 64% Yield, mp. > 300 °C. C <sub>51</sub> H <sub>42</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>6</sub> (933.84): Calculated (Found)%: C, 65.59 (65.38); H, 4.53(4.41); N, 12.00 (11.89). MS: <i>m/z</i> : 105 (45), 160 (48), 213 (57), 258 (63), 290 (99), 503 (70), 678 (100), 805 (75), 933 (M <sup>+</sup> , 30).	IR spectrum, $\nu$ , cm <sup>-1</sup> : 1083, 1155, 1289, 1335, 1458, 2956 (sp <sup>3</sup> CH), 1597 (C = N), 1705(C = O), 1732(C = O). <sup>1</sup> H NMR spectrum, $\delta$ , ppm: 1.27 (t, <i>J</i> = 8.5 Hz, 6H, 2CH <sub>3</sub> ), 2.06 (p, <i>J</i> = 8.5 Hz, 2H, CH <sub>2</sub> ), 3.74 (t, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 4.35 (q, <i>J</i> = 8.5 Hz, 4H, 2CH <sub>2</sub> ), 7.19–7.90 (m, 26H, Ar-H);

**Table 2**  
Values of corrosion rates (CR) of Al in diverse [HCl] solutions at 303 K.

[HCl], M	0.5	1.0	1.5	2.0
CR (mpy)	319	378	414	435

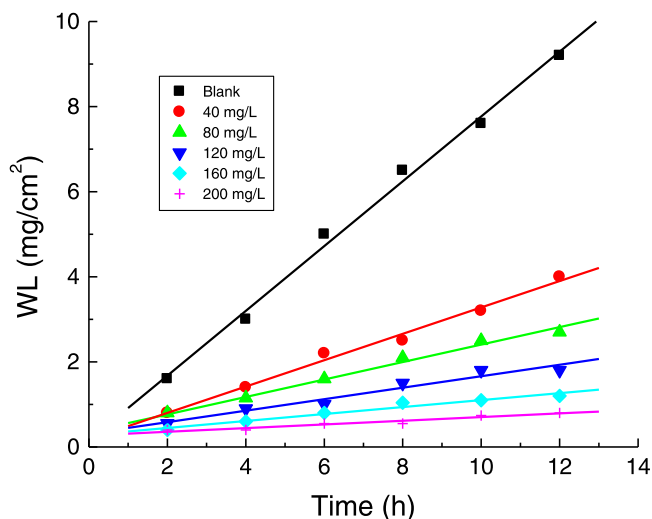
The values of half-life times ( $t_{1/2}$ , h) were computed from Eq. (4) [48] and are also included in Table 5,

$$t_{1/2} = \frac{0.693}{k_1} \quad (4)$$

The order ( $n$ ) of corrosion inhibition of Al with respect to the concentration of the examined compound **5a** ( $C_{inh}$ ) was computed using Eq. (5) [49],

$$\log CR = \log k + n \log C_{inh}. \quad (5)$$

where,  $k$  is the specific rate constant (mg/cm<sup>2</sup> h).



**Fig. 1.** WL versus immersion time for the corrosion of Al in 1.0 M HCl solution and with adding the compound **5a** at 303 K.

The plot of log CR versus log  $C_{inh}$  for the compound **5a** (as an example) was linear as shown in Fig. 5. The value of  $n$  was calculated from the slope of such plot and was found to be  $-0.93$ . The gained value of  $n$  illuminated that the corrosion inhibition process was negative fractional-first order reaction with respect to the inhibitor concentration. Besides, the negative sign of  $n$  as well as the reverse proportionality of the value of CR with the inhibitor concentration (Fig. 5) refers to a good% IE of the examined compound [50].

### 3.2.2. PDP measurements

Fig. 6 shows the PDP curves (Tafel plots) for Al corrosion in 1.0 M HCl solution, in the absence and presence of various concentrations (40 – 200 mg/L) of the examined compound **5a** at 303 K. The values of corrosion parameters acquired from these Tafel plots for the examined compound, viz. corrosion potential ( $E_{corr}$ ), anodic and cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ), corrosion current density ( $i_{corr}$ ), polarization resistance ( $R_p$ ) were calculated and are listed in Table 6. The values of% IEs of the synthesized compound **5a** were calculated via Eq. (6) and are also inserted in Table 6.

$$\% IE = \theta \times 100 = \left[ 1 - \frac{i_{corr(inh)}}{i_{corr}} \right] \times 100 \quad (6)$$

where,  $i_{corr}$  and  $i_{corr(inh)}$  are the values of corrosion current densities without and with the examined compound, respectively.

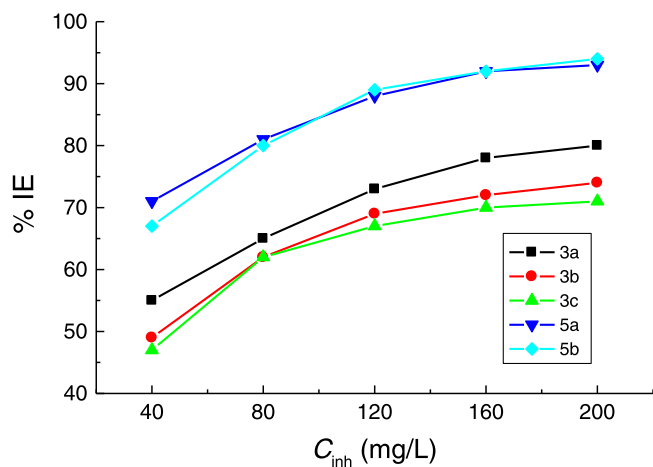
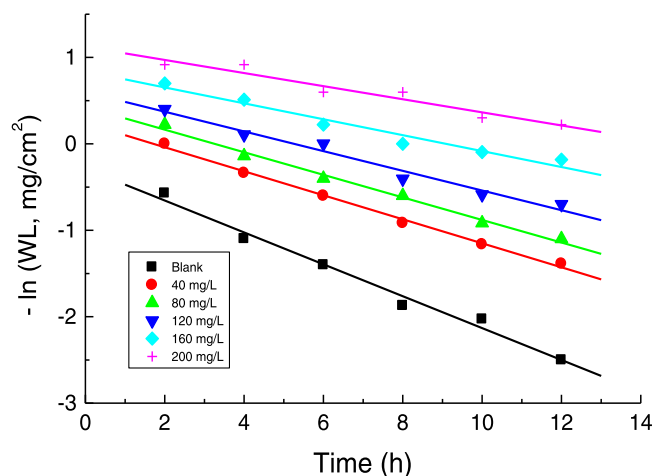
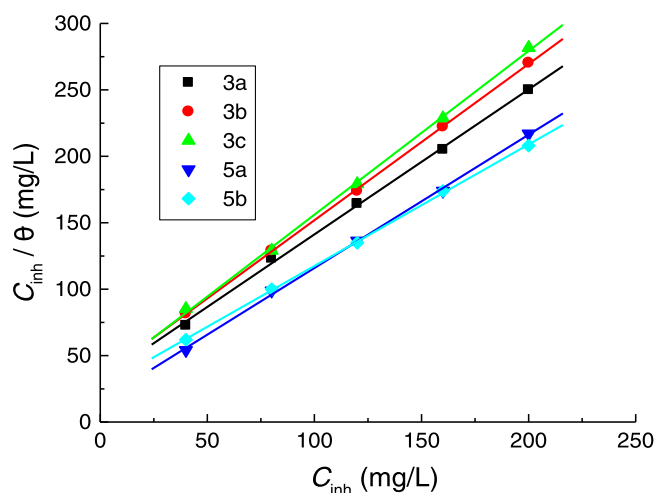
Fig. 6 showed that addition of the compound **5a** to the corrosive medium shifted the anodic and cathodic Tafel branches of PDP curve of Al with of the corrosive medium to less  $i_{corr}$  values. This behavior resulted in hindering both anodic and cathodic reactions and, thus, inhibits the corrosion of Al. The original value of  $E_{corr}$  for Al in the corrosive medium (blank) was shifted to negative or cathodic direction after addition of various concentrations of the compound **5a** signifying that such compound can be regarded as a mixed-type inhibitor with cathodic majority [51]. Also, both values of  $\beta_a$  and  $\beta_c$  were found to change on adding the examined compound confirming that such compound played as a mixed type inhibitor. The value of  $i_{corr}$  of Al in the corrosive solution was reduced with increasing the  $R_p$  value, and also% IE values upon rising the concentration of the examined compound.

### 3.2.3. EIS measurements

EIS measurements for Al corrosion in 1.0 M HCl solution and in the presence of different concentrations of the examined compound **5a** at 303 K are shown in Fig. 7. These spectra represented as Nyquist plots showed single depressed capacitive loops and one-time constants

**Table 3**Values of CRs of Al in 1.0 M HCl solution, % IEs and  $\theta$ s of the synthesized compounds at 303 K.

Compound	3a			3b			3c			5a			5b		
Conc. (mg/L)	CR	% IE	$\theta$	CR	% IE	$\theta$	CR	% IE	$\theta$	CR	% IE	$\theta$	CR	% IE	$\theta$
0 (Blank)	378	–	–	378	–	–	378	–	–	378	–	–	378	–	–
40	170	55	0.55	193	49	0.49	200	47	0.47	110	71	0.71	125	67	0.67
80	132	65	0.65	144	62	0.62	144	62	0.62	72	81	0.81	76	80	0.80
120	102	73	0.73	117	69	0.69	125	67	0.67	45	88	0.88	42	89	0.89
160	83	78	0.78	106	72	0.72	113	70	0.70	30	92	0.92	30	92	0.92
200	76	80	0.80	98	74	0.74	110	71	0.71	26	93	0.93	23	94	0.94

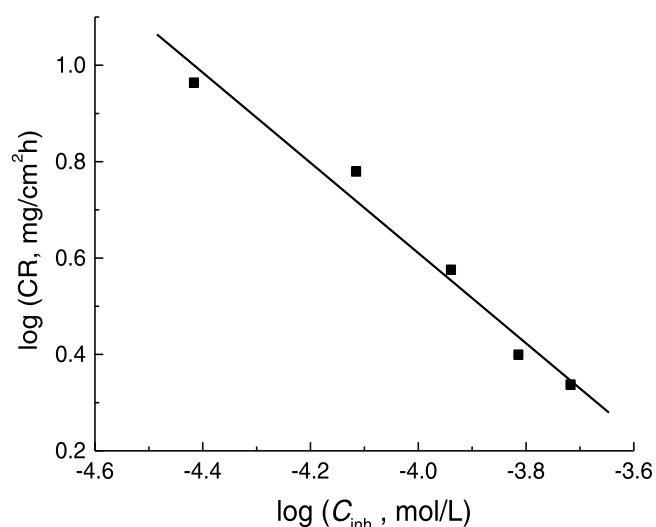
**Fig. 2.** Variation of % IEs of the synthesized compounds with their concentrations in the corrosion of Al in 1.0 M HCl solution at 303 K.**Fig. 4.** First-order rate constant plots in the corrosion of Al in 1.0 M HCl solution and with adding the compound 5a at 303 K.**Fig. 3.** Langmuir adsorption isotherms for the synthesized compounds adsorbed on the Al surface in 1.0 M HCl solution at 303 K.**Table 4**Values of the adsorption constant ( $K_{ads}$ ) in the corrosion of Al 1.0 M HCl solution without and with the synthesized compounds at 303 K.

Compound	3a	3b	3c	5a	5b
$10^{-3} K_{ads}$ (L/mol)	11.87	11.18	11.09	65.01	39.98

signifying that the corrosion of Al was controlled mainly by the charge-transfer process and double layer behavior [52]. Fig. 7 illuminated that the size of the capacitive loops of Al in the corrosive medium was increased gradually after addition of the examined compound 5a

**Table 5**Values of  $k_1$  and  $t_{1/2}$  for the corrosion of Al in 1.0 M HCl solution and with adding the compound 5a at 303 K.

Conc. (mg/L)	$k_1$ , $h^{-1}$	$t_{1/2}$ , h
0 (Blank)	0.184	3.77
40	0.138	5.02
80	0.130	5.33
120	0.117	5.92
160	0.092	7.53
200	0.075	9.24

**Fig. 5.** log CR vs. log  $C_{inh}$  for the inhibition of Al corrosion in 1.0 M HCl solution using the compound 5a at 303 K.

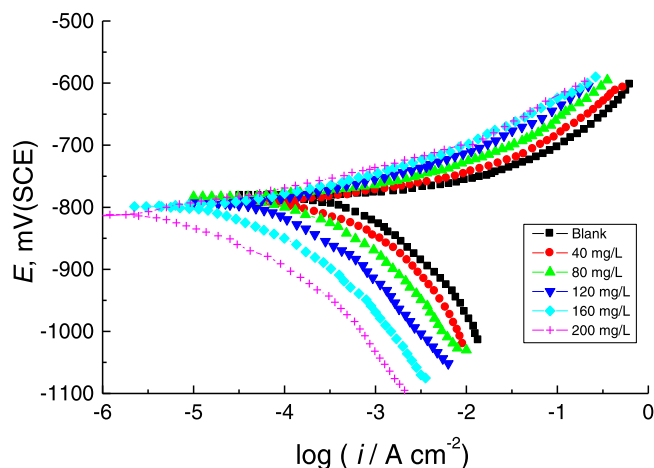


Fig. 6. PDP curves of the corrosion of Al in 1.0 M HCl solution and with adding the compound **5a** at 303 K.

Table 6

Polarization parameters for the corrosion of Al in 1.0 M HCl solution and with adding the compound **5a** at 303 K.

Conc. (mg/L)	$-E_{corr}$ (mV (SCE))	$\beta_a$ (mV/dec.)	$-\beta_c$ (mV/dec.)	$i_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_p$ (ohm $\text{cm}^2$ )	% IE	$\theta$
0 (Blank)	781	41	151	645	22	–	–
40	782	48	139	219	71	66	0.66
80	784	54	133	155	108	76	0.76
120	791	55	119	103	159	84	0.84
160	802	57	106	65	248	90	0.90
200	816	63	96	32	517	95	0.95

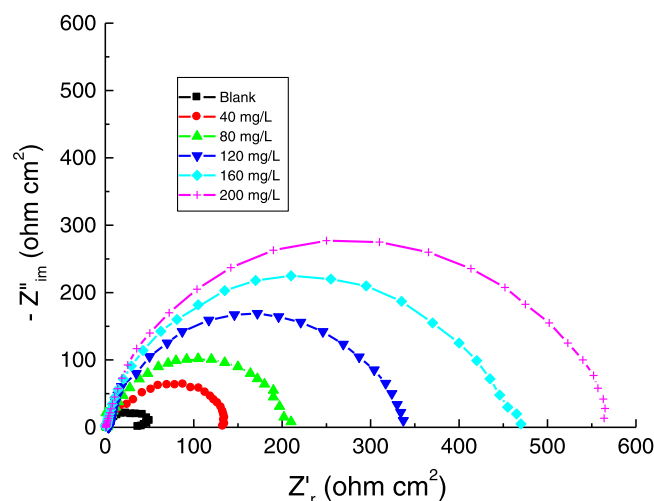


Fig. 7. Nyquist plots for the corrosion of Al in 1.0 M HCl solution and with adding the compound **5a** at 303 K.

indicating a decrease in the corrosion rate of Al, thus an increase in the % IE, and the latter was augmented with rising the concentration of the examined compound. The obtained EIS spectra were analyzed by matching to the equivalent circuit illustrated in Fig. 8. The values of solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ) and constant phase element (CPE) obtained from Nyquist plots were evaluated and are listed in Table 7. Also, the values of % IEs were calculated via Eq. (7) [41] and are included in Table 7,

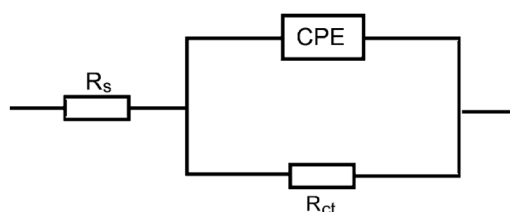


Fig. 8. Electrochemical equivalent circuit used to appropriate the EIS output data for the corrosion of Al in 1.0 M HCl solution and with the synthesized compounds.

Table 7

Impedance parameters for the corrosion of Al in 1.0 M HCl solution and with adding the compound **5a** at 303 K.

Conc. (mg/L)	$R_s$ (ohm $\text{cm}^2$ )	$R_{ct}$ (ohm $\text{cm}^2$ )	$X^2$	CPE ( $\mu\text{F}/\text{cm}^2$ )	% IE	$\theta$
0 (Blank)	0.7	51	0.46	281	–	–
40	1.6	138	0.73	113	63	0.63
80	2.1	204	1.23	87	75	0.75
120	1.7	340	1.98	58	85	0.85
160	2.3	464	2.42	40	89	0.89
200	2.9	567	2.18	31	91	0.91

$$\% \text{IE} = \left[ 1 - \frac{R_{ct}}{R_{ct(\text{inh})}} \right] \times 100 \quad (7)$$

where  $R_{ct}$  and  $R_{ct(\text{inh})}$  are the charge transfer resistances without and with the added drug, respectively.

The gained values of EIS parameters indicated that addition of the compound **5a** to the corrosive solution resulted in a rise in the value of  $R_{ct}$  with a reduce in the CPE value of the corrosive solution. This indicates that the added compound **5a** behaves as an inhibitor through its adsorption at the Al/solution interface resulting in shielding the Al surface from the corrosive medium and, thus enhancing the values of % IE [53,54].

Finally, the gained values of % IEs obtained from the different employed techniques (WL, PDP and EIS) for the compound **5a** were compared (Fig. 9) and designated a good agreement of all utilized techniques with each other's.

Fig. 10 represent the adsorption spirotriazole derivatives **5** on the aluminum surface in 1.0 M HCl solution.

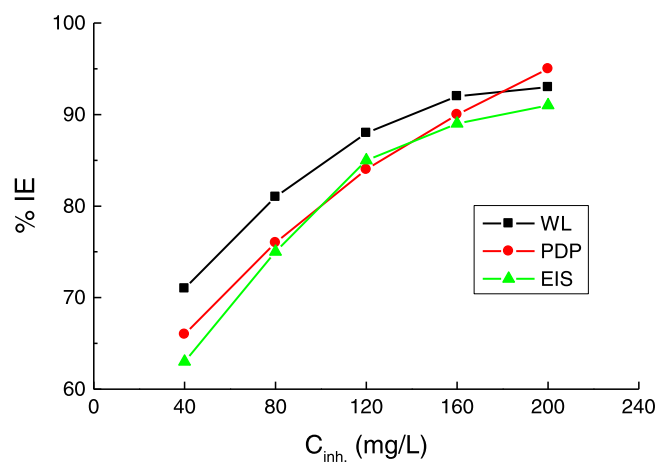


Fig. 9. Comparison between the techniques used with respect to the values of % IEs of the compound **5a** with its concentrations for the corrosion of Al in 1.0 M HCl solution at 303 K.

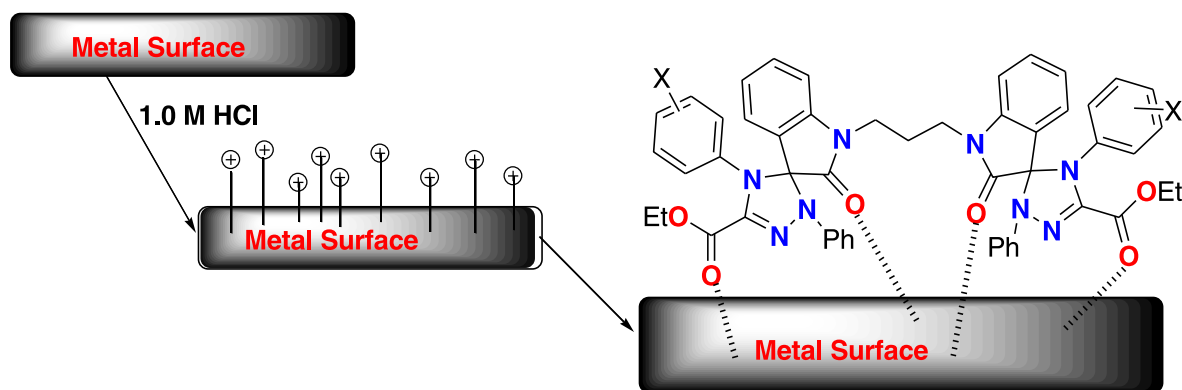


Fig. 10. The Schematic representation of the adsorption spirotriazole derivatives 5 on the aluminum surface in 1.0 M HCl solution.

#### 4. Conclusions

The synthesized compounds were discovered to be efficient inhibitors for the corrosion of aluminum in 1.0 M HCl at 303 K using different techniques. The % IEs were set to vary with their concentrations, structures and the corrosive medium concentration. Also, the order of the % IEs of the examined compounds was:  $5a \approx 5b > 3a > 3b \geq 3c$ . The adsorption of inhibitors was agreed with Langmuir adsorption isotherm. Moreover, the kinetics of corrosion inhibition by the examined compounds was discussed. PDP results indicated that the compound 5a behaves as a mixed inhibitor with a cathodic majority. The results acquired from the three utilized tools in case of the compound 5a were set to be in a good agreement with each other's confirming the validity of the obtained results. Finally, the synthesized corrosion inhibitors in this article were found effective to inhibition Al-corrosion with low cost.

#### Authors agreement

All authors agree to submit the article to publish in Journal of Molecular Structure.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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