ORIGINAL ARTICLE

# Synthesis and Evaluation of Some Triazole Derivatives as Corrosion Inhibitors and Biocides

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Abstract Three compounds namely; 5-(phenyl)-4H-1,2,4triazole-3-thiol, 3-(decylthio)-5-phenyl-1H-1,2,4-triazole and 3-(benzylthio)-5-phenyl-1H-1,2,4-triazole) were synthesized. The chemical structure of the prepared compounds was confirmed using FTIR and <sup>1</sup>H-NMR analysis. The compounds were tested as corrosion inhibitors against the corrosion of carbon steel in 1 M HCl using weight loss, polarization and electrochemical impedance methods. The results revealed that these compounds have significant inhibiting effects on the corrosion of carbon steel. Polarization studies showed that the compounds act as mixed-type inhibitors which retard the anodic and the cathodic reactions with a predominant effect towards the cathodic reaction. The prepared compounds were evaluated as antimicrobial agents against sulfate-reducing bacteria using the serial dilution method, which showed good biocidal action.

**Keywords** Triazole derivatives · Corrosion inhibition · Antimicrobial activity

### Introduction

Hydrochloric acid solution is commonly used for the removal of undesirable scale and rust in metalworking processes, cleaning of boilers, and heat exchangers [1, 2]. To prevent the

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Applied Surfactant Laboratory, Petrochemicals Department, Egyptian Petroleum Research Institute, El-Zhoor, Nasr City, Cairo 11727, Egypt e-mail: ali\_ashour5@yahoo.com metal dissolution and acid consumption during these processes, Inhibitors are often used [3–5]. The organic compounds containing O, S and/or N atoms act as effective inhibitors [6–8] throughout the adsorption on the metal surfaces and then decrease the corrosion process [9–12]. Triazole and triazole-type compounds containing sulfur, and heterocyclic species have attracted more attention because of their excellent corrosion inhibition performance [13–19]. Zhang et al. [20] studied the inhibiting action of oxadiazole–triazole derivatives against the corrosion of mild steel in sulfuric acid solution. The results indicated that the compounds are acted as efficient corrosion inhibitors in the acidic solution.

The strategies to control the effects of microbiologically influenced corrosion (MIC) in oil field companies include the reduction of the sulfate-reducing bacteria (SRB) using biocides; in order to: kill the organisms which enter the system, and reduce the growth rate of microorganisms within the biofilm. Microbiologically influenced souring (MIS) is the production of  $H_2S$  through the metabolic activities of the sulfate-reducing bacteria. A better chance of mitigating MIS in some down-hole environments is using biocides [21]. The objective of this work is to synthesize three triazole derivatives and to study their corrosion inhibition effect on carbon steel dissolution in acidic medium, and their biocidal activity against SRB.

#### **Materials and Methods**

Synthesis of 5-(phenyl)-4H-1,2,4-triazole-3-thiol (I)

A mixture of benzoic acid (12.2 g, 0.1 mol) and thiosemicarbazide (91.1 g, 0.1 mol) was heated under reflux at 140 °C in the presence of xylene as a solvent and *p*-toluene sulfonic acid as a dehydrating agent until the theoretical

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amount of water was collected in the dean stark trap [22]. The mixture was cooled and the product was filtered to obtain 1-(benzoyl)-thiosemicarbazide, which was refluxed for 3 h in 200 ml of NaOH solution (2 N), then cooled and acidified to pH 4. The precipitate was filtered off and recrystallized from methanol to yield 5-(phenyl)-4*H*-1,2,4-triazole-3-thiol (I) as shown in Scheme 1 [23].

Synthesis of 3-(decylthio)-5-phenyl-1*H*-1,2,4-triazole (II)

A mixture of 5-(phenyl)-4*H*-1,2,4-triazole-3-thiol (1.77 g, 0.1 mol) and 1-bromodecane (2.22 g, 0.01 mol) was refluxed in ethanolic alkali (0.08 g KOH in 20 ml ethanol) for 2 h and then cooled to precipitate compound (II) which was recrystallized from ethanol [24].

Synthesis of 3-(benzylthio)-5-phenyl-1*H*-1,2,4-triazole (III)

A mixture of 5-(phenyl)-4H-1,2,4-triazole-3-thiol (1.77 g, 0.01 mol) and benzyl chloride (1.26 g, 0.01 mol) was refluxed in ethanolic alkali (0.08 g KOH in 20 ml ethanol) for 2 h, and then cooled to precipitate compound (III) which was recrystallized from ethanol [24].

#### Analyses

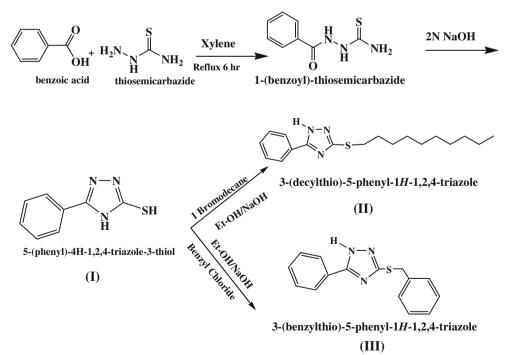
The chemical structures of the synthesized compounds (I, II, III) were confirmed by FTIR and <sup>1</sup>H-NMR

spectroscopy. FTIR spectra showed the following bands: at 940 cm<sup>-1</sup> (I), 926 cm<sup>-1</sup> (II), 924 cm<sup>-1</sup> (III) for (N-C-S), 1,299 cm<sup>-1</sup> (I), 1,312 cm<sup>-1</sup> (II), 1,309 cm<sup>-1</sup> (III) for (N-N-C), 3,365 cm<sup>-1</sup> (I), 3,432 cm<sup>-1</sup> (II), 3,395 cm<sup>-1</sup> (III) for (N-H), 681 cm<sup>-1</sup> (I), 682 cm<sup>-1</sup> (II), 682 cm<sup>-1</sup> (III) (C-S), 3,060 cm<sup>-1</sup> (I), 3,059 cm<sup>-1</sup> (II), 3,059 cm<sup>-1</sup> (III) for (Ar CH), 1,452 cm<sup>-1</sup> (I), 1,422 cm<sup>-1</sup> (II), 1,418 cm<sup>-1</sup> (III) for (C–N), 2,056 cm<sup>-1</sup> (I) for (SH), 2,924 cm<sup>-1</sup> (II), 2,935 cm<sup>-1</sup> (III) and 2,853 cm<sup>-1</sup> (II), 2,825 cm<sup>-1</sup> (III) for (CH<sub>2</sub> asym and sym). <sup>1</sup>H-NMR spectra of (I, II, III) showed peaks at:  $\delta = 7.75$  ppm (m, 5H, Ar–H),  $\delta = 3.25$  ppm (s, 1H, S–H) for compound (I);  $\delta = 7.84$  ppm (m, 5H, Ar–H),  $\delta = 3.38$  ppm (t, 2H, S–CH<sub>2</sub>),  $\delta = 1.45$  ppm (m, 16H, CH<sub>2</sub>),  $\delta = 0.81$  ppm (t, 3H, CH<sub>3</sub>) for compound (II);  $\delta = 7.86$  ppm, 7.24 ppm (m, 10H, Ar–H),  $\delta = 3.86$  ppm (t, 2H, S-CH<sub>2</sub>) for compound (III).

#### Corrosion Measurements

#### Weight Loss Measurements

The weight loss experiments were performed with carbon steel specimens having a composition of: 0.21 C, 0.025 Mn, 0.082 P and the remainder is Fe. The carbon steel sheet dimensions were 6 cm  $\times$  3.0 cm  $\times$  0.6 cm, the test was done according to ASTM G31-72 (re-approved 2004). The steel coupons were immersed in 1 M HCl with and without the inhibitors I, II and III at concentrations of 100, 200, 400, 600 ppm by weight for 24 h at different temperatures (25, 45 and 65 °C). Then coupons were washed,



Scheme 1 Illustrated the chemical structure of the synthesized triazole derivatives

dried and weighed accurately [25]. The test was repeated three times and the weight loss was their average. The corrosion rate (*R*) and the inhibition efficiency ( $\eta$  %) were calculated using Eqs. (1–2):

$$R = W/At \tag{1}$$

$$\eta \% = [(R_0 - R)/R_0] \times 100$$
(2)

where *W* is the average weight loss of three parallel carbon steel sheets, *A* is the total surface area of the specimen, *t* is the immersion time, *R* and  $R_0$  are the corrosion rate with and without the inhibitor, respectively [26, 27].

#### Polarization Measurements

The polarization measurements were carried out using a potentiostat (Volta lab 40 PGZ 301 in a conventional three electrode cell system, France). The working electrode was immersed in the test solution for 30 min until the open circuit potential (OCP) is reached. The working electrode was polarized in cathodic and anodic directions. The corrosion current densities ( $I_{corr}$ ) were calculated by extrapolation of Tafel lines to pre-determine the OCP [28]. A standard ASTM electrochemical glass cell was used and a platinum electrode was used as an auxiliary electrode. All potentials were measured against a saturated calomel electrode (SCE) as a reference electrode. The potential was increased with a rate of 30 mV/min started from 1,000 to 200 mV. The inhibition efficiency ( $\eta \%$ ) was calculated using Eq. (3):

$$\eta \% = [(I_0 - I)/I_0] \times 100 \tag{3}$$

where the I and  $I_0$  are the current density values with and without inhibitors.

# Electrochemical Impedance Technique

The Electrochemical Impedance Spectroscopy (EIS) measurements were carried out using alternating current (AC) signals of amplitude 10 mV peak to peak at the OCP in the frequency range of 100 kHz to 30 MHz using a potentiostat.

#### Antimicrobial Activity Measurements

The growth inhibition of the three prepared compounds on the SRB was measured using the serial dilution method. SRB-contaminated water was supplied from Qarun Petroleum Co. (Western Desert, Egypt). This water was used for the microbial inhibition test. The test was conducted according to ASTM D4412-84 [29]. The tested water was subjected to growth of about 1,000,000 bacteria cells/ml. The prepared compounds were tested as a biocide for the SRB by doses of (50, 100, 200 and 400 ppm). The system was incubated with a contact time of 3.0 h; each system was cultured in SRB specific media for 21 days at 37-40 °C.

#### **Biodegradation Test**

The biodegradability test in river water of the synthesized inhibitors I, II, and III was carried out using the surface tension method (Du-Noüy tensiometer, Krüss type K6, Germany) using a platinum ring [30, 31] at 1 % inhibitor concentration. Each inhibitor was dissolved in river water to a concentration of 100 ppm and incubated at 38 °C. A sample was withdrawn daily (for 7 days), filtered and the surface tension value was measured. The biodegradation percentage (D %) was calculated using Eq. (4):

$$D\% = (\gamma_{\rm t} - \gamma_{\rm o})/(\gamma_{\rm bt} - \gamma_{\rm o}) \times 100 \tag{4}$$

where:  $\gamma_t$  is the surface tension at time *t*,  $\gamma_o$  is the surface tension at time 0 (initial surface tension) and  $\gamma_{bt}$  is the surface tension of river water without addition of inhibitor at time *t*.

# **Results and Discussion**

Weight Loss Technique

#### Effect of Inhibitor Concentration

In a steel/water system, the steel surface is covered with a layer of FeOOH through which the interaction of surfactant molecules takes place. The OH groups on the solid surface are the most important sites for surface interactions; these groups can act as acids or bases. The adsorption process is highly dependent on various parameters such as pH and electrolyte content [32].

The corrosion inhibiting efficiencies  $(\eta)$  of the synthesized compounds of the carbon steel corrosion in 1 N HCl were measured. The test was done at different temperatures 30-60 °C. Different inhibitor concentrations (100, 200, 400, 600 ppm by weight) were used. The results were illustrated in Fig. (1), (Figs. 1-2, supplementary file) and listed in Table 1. It was found that the efficiency of synthesized triazole derivatives decreases the corrosion rates of the steel in testing solutions and its inhibition efficiencies are dependent on its concentration in the tested solution. Also, it is clear that gradual increasing the inhibitor concentration from 100 to 600 ppm decreases the steel corrosion rate. The increase of efficiency,  $\eta$  with increasing the inhibitor concentration is attributed to the adsorption of the inhibitor molecules on the steel surface and thus increases the metal surface coverage [33].

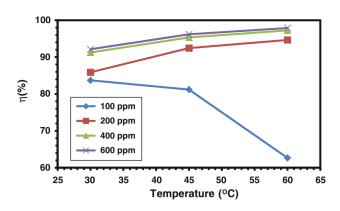


Fig. 1 Variation of  $\eta$  % against temperatures for inhibitor II

A visual examination was carried out after the weight loss measurements were over. It can be noted that, in the absence of inhibitor, a uniform corrosion attack was observed, while on the other hand in the presence of inhibitors, such an attack was not observed: therefore, the surface area was bright and did not present any corrosion form, which is indicative that no attack was occurring on the surface area.

# Effect of Temperature

To examine the action of inhibitors at elevated temperatures, mass loss experiments were carried out at different temperatures (30–60 °C). The results indicate that efficiency shows different trends for the testing compounds. It was noticed that at a lower concentration (100 ppm by weight) all compounds show a decrease in efficiency with increasing solution-temperature of all the testing compounds I, II and III. The same trend was obtained for higher concentrations of compound I. Meanwhile at higher concentrations of the solutions (200 to 600 ppm by weight) of compounds II and III, the efficiency increases with increasing the temperature from 30 to 60 °C [33]. At any temperature, the inhibition efficiency with the increases in temperature. This is attributed to physical adsorption. At higher temperatures, the physical adsorption was less. The time gap between the process of adsorption and desorption of inhibitor molecules over the metal surface becomes shorter with an increase in the temperature. Hence, the metal surface remains exposed to the acid environment for a longer period, therefore the inhibition efficiency falls at elevated temperatures [33]. A slight increase or constancy in  $\eta$  with the increase in temperature at higher concentrations for (II, III) may be due to the chemical adsorption alone or due to the combination of physical and chemical adsorption [34]. The mass loss experiment showed a rapid increase in weight loss at elevated temperature in the absence of inhibitor. This shows that the tested inhibitor molecules are good corrosion inhibitors for steel in 1 N HCl in the range of temperatures studied.

# Apparent Activation Energy $(E_a)$ and Pre-exponential Factor (A)

The activation parameters for the corrosion process were calculated from the Arrhenius Eq. (5), and transition state Eq. (6).

$$\ln K = \left(\frac{-E_{\rm a}}{RT}\right) + \ln A \tag{5}$$

$$\ln\left(\frac{K}{T}\right) = \left(\ln\left(\frac{R}{N_{\rm A}h}\right) + \left(\frac{\Delta S^*}{R}\right)\right) - \frac{\Delta H^*}{RT} \tag{6}$$

where: k is the corrosion rate, A is the pre-exponential factor (Arrhenius constant), R is the gas constant and T is the absolute temperature. h is the Plank constant,  $N_A$  is the Avogadro number,  $\Delta S$  is the entropy of activation,  $\Delta H$  is the enthalpy of activation.

The activation corrosion energy ( $E_a$ ) for different concentration of compounds (I, II and III) was calculated by linear regression between ln (K) and 1,000/T as shown in Fig. 2, (Fig. 3, supplementary file) and the results are shown in Table 2. Inspection of Table 2 shows that values of  $E_a$ obtained in solutions containing triazole derivative compounds (II and III) are lower than those in the inhibitor-free acid solutions at high concentrations (400–600 ppm by

 Table 1
 Weight loss, corrosion rate, surface coverage and corrosion inhibition efficiency in the absence and presence of 600 (ppm by weight) of compounds I, II and III at different temperatures

Inhibitor name	Blank			Ι			II			III		
Temp. (°C)	30	45	60	30	45	60	30	45	60	30	45	60
Weight loss (mg)	344.6	1,013.2	2,400	58.2	233.8	661.3	27.1	38.6	50.5	27.5	42.1	55.2
Corrosion rate (mg/cm <sup>2</sup> h)	0.306	0.902	2.136	0.051	0.208	0.588	0.024	0.034	0.044	0.024	0.037	0.049
$\theta$	_	-	-	0.831	0.769	0.724	0.921	0.961	0.978	0.921	0.95	0.977
ηw (%)	_	_	-	83.1	76.9	72.4	92.1	96.1	97.8	92.1	95.8	97.7

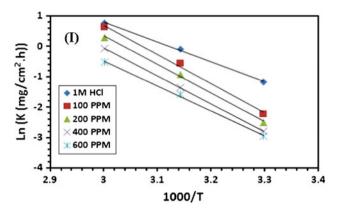


Fig. 2 Arrhenius plots of  $\ln (K)$  versus 1,000/T in the absence and presence of different concentrations of inhibitor I

weight). The lower values of the apparent activation energy obtained in the presence of triazole derivatives compounds (II and III) compared with those obtained in its absence. This means that this can be attributed to its chemisorption on the steel surface [35]. The inhibition efficiency also increased as the temperature increased (Table 2). The fact that  $\eta$  (%) increased with temperature was explained by Bouyanzer and Hammouti [36] and de Souza and Spinelli [37], as the likely specific interaction between the steel surface and the inhibitor. Ivanov [38] considers the increase in  $\eta$  (%) with temperature increases as the change in the nature of the adsorption mode. The inhibitor is being physically adsorbed at lower temperatures, while chemisorption is favored as the temperature increases. Noor and Al-Moubaraki [39]

**Table 2** Activation parameter values in the absence and presence ofdifferent concentrations of the synthesized triazole derivatives (I, II,III)

Inhibitor	Inhibitor conc. (ppm by weight)	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\frac{\Delta S^*}{(\text{J mol}^{-1} \text{ K}^{-1})}$
Blank 1 M	0.00	54.37689	51.73636	-84.0373
Ι	100	79.78114	77.14062	-8.62097
	200	78.15991	75.50027	-16.5359
	400	76.26598	73.62546	-25.3487
	600	68.12575	65.48605	-53.3254
II	100	77.34182	74.70129	-24.1432
	200	27.10031	24.46062	-190.609
	400	22.00716	19.36663	-211.154
	600	19.06317	14.80557	-227.097
III	100	76.69000	74.0503	-23.8772
	200	59.73858	57.09806	-99.1355
	400	27.57255	24.93202	-191.231
	600	19.55536	16.91566	-219.928

\* Standard value

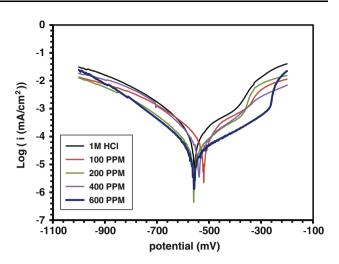


Fig. 3 Anodic and cathodic polarization curves obtained at 30  $^{\circ}$ C in 1 M HCl at different concentrations of inhibitor I

suggested that with an increase in temperature, some chemical changes occur in the inhibitor molecules, leading to an increase in the electron density at the adsorption centers of the molecule, which causes an improvement in inhibition efficiency. Al-Sabagh et al. [40] explained that, steel corrosion occurs at the uncovered part of the surface. Thus adsorption of inhibitors was assumed to occur at the higher energy sites. The presence of inhibitor compounds which result in the blocking of the active sites must be associated with an increase in the activation energy ( $E_a$ ) of steel in the inhibited sites. The relationships between the temperature dependence of the percentage IE of an inhibitor and the  $E_a$  can be classified into three groups according to temperature effects [40, 41].

- (i) IE decreases with an increase in temperature,  $E_a$  (inhibited solution) >  $E_a$  (uninhibited solution);
- (ii) IE increases with an increase in temperature,  $E_a$  (inhibited solution)  $< E_a$  (uninhibited solution);
- (iii) IE does not change with temperature,  $E_a$  (inhibited solution) =  $E_a$  (uninhibited solution).

#### Potentiodynamic Polarization

The polarization curves for carbon steel in 1 N HCl with the studied inhibitors, I, II and III at different concentrations at 30 °C are shown in Fig. 3 and (Figs. 4,5, supplementary file). The electrochemical corrosion kinetic parameters, i.e., anodic and cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ), corrosion current density ( $I_{corr}$ ) and inhibition efficiency ( $\eta_p$  %) are listed in Table 3. The surface coverage area  $\theta$ was calculated using Eq. (7):

$$\theta = 1 - (I_{\rm inh}/I_{\rm corr}) \tag{7}$$

where  $I_{corr}$  and  $I_{inh}$  are the uninhibited and inhibited corrosion current densities, respectively.

The inhibition efficiency  $(\eta_p \%)$  of this inhibitor was obtained from Eq. (8):

$$\eta_{\rm p}\% = \theta \times 100 \tag{8}$$

It is clear from the polarization curves that the increases in the inhibitor concentrations of I, II and III decrease the corrosion current density ( $I_{corr}$ ) which consequently increases the surface coverage values (Table 3). These inhibitors cause changes in the anodic and cathodic Tafel slopes and no definite trend was observed in the shift of  $E_{corr}$  values in the presence of different concentrations of the synthesized inhibitors, suggesting that these compounds behave as mixed-type inhibitors mainly anodic.

The results show that the most effective compound is II which has the hydrocarbon chain length C10. The maximum inhibition efficiencies were 83, 91 and 93 %, for compound I, III, and II, respectively [42–45].

#### Electrochemical Impedance Spectroscopy (EIS)

Results obtained from EIS can be interpreted in terms of the equivalent circuit of the electrical double layer shown in Fig. 6 in the supplementary file [46].

Figure 4 and (Figs. 7–8 supplementary file) show the Nyquist plots for carbon steel in 1 M HCl solution with and without different concentrations of the synthesized triazole compounds (I, II, and III) at 30 °C. The Nyquist plots were regarded as one part of a semicircle. The charge transfer resistance values ( $R_{ct}$ ) were calculated from the difference in impedance at lower and higher frequencies [47]. The

double layer capacitance  $(C_{dl})$ , values were calculated using Eq. (9) [48].

$$f(-Z_{\rm max}) = (2\pi C_{\rm dl} R_{\rm ct})^{-1}$$
(9)

where  $f(-Z_{\text{max}})$  is the frequency of maximum imaginary components of the impedance. The inhibition efficiency was calculated using charge transfer resistance using Eq. (10):

$$\eta \% = ((R_{\rm ct} - R_{\rm ct}^{\rm o})/R_{\rm ct}) \times 100$$
(10)

where  $R_{ct}$  and  $R_{ct}^{o}$  are the charge transfer resistance values with and without inhibitor for carbon steel in 1 N HCl, respectively. The electrochemical impedance parameters derived from the Nyquist plots and the inhibition efficiency are listed in Table 4. It was clear that,  $R_{ct}$  values in the presence of the inhibitor were always greater than their values in the absence of the inhibitor and also increase with increasing inhibitor concentration, which indicates a reduction in the steel corrosion rate. The capacitance,  $C_{dl}$ , values were lower due to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules acted by adsorption at the metal/solution interface [49]. The inhibiting efficiency was in the following order: II > III > I.

# Antimicrobial Activity Against Sulfate-Reducing Bacteria (SRB)

The antimicrobial activity of the three synthesized compounds (I, II, III) against SRB was determined by the serial dilution method at doses of 50, 100, 200 and 400 ppm and the results are listed in Table 5. The three synthesized

Table 3 Potentiodynamic polarization parameters of different concentrations of synthesized triazole derivatives (I, II, III) at 30  $^{\circ}$ C at a scanning rate of 2 mV s<sup>-1</sup>

Inhibitor	Inhibitor conc. (ppm by weight)	$E_{\rm corr}$ [mV (SCE)]	$I_{\rm corr} ({\rm mA} {\rm cm}^{-2})$	$\beta_a (\mathrm{mV}\mathrm{dec}^{-1})$	$\beta_{\rm c} \ ({\rm mV} \ {\rm dec}^{-1})$	θ	η %
	0.00	-558.4	0.266	318.2	-174.	_	_
Ι	100	-522.7	0.096	158	-152.7	0.637	63.7
	200	-560.1	0.066	209.2	-152.3	0.749	74.9
	400	-541.2	0.053	147	-104.5	0.800	80.0
	600	-560	0.042	260	-140.7	0.839	83.9
II	100	-494.5	0.049	100.3	-140.5	0.814	81.4
	200	-488.3	0.046	152.9	-206.3	0.824	82.4
	400	-511.2	0.023	118.5	-310.5	0.913	91.3
	600	-503.2	0.018	102.6	-293.7	0.931	93.1
III	100	-544.2	0.056	192	-132	0.789	78.9
	200	-520.4	0.046	142.9	-290.3	0.827	82.7
	400	-510.7	0.024	81.7	-209.3	0.908	90.8
	600	-508.4	0.021	126.5	-300	0.919	91.9

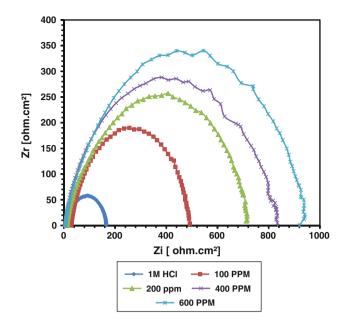


Fig. 4 Nyquist plots for carbon steel in 1 M HCl in the absence and presence of different concentrations of inhibitor I

compounds showed impressive results due to their relatively high efficiency against this type of bacteria. The results indicate that the three synthesized compounds have high antimicrobial activity against the SRB at relatively high doses (200–400 ppm), and that the three synthesized compounds were inactive at the lowest concentration (50–100 ppm). On the other hand, it was capable to killing all the bacteria within 3 h (as contact time) at the highest concentration. To decrease the effect of the microbial induced corrosion, the biocides should be used to inhibit SRB growth and other acid producing bacteria in the oil field.

Table 5 The bacterial count (cell/ml) of different doses of the synthesized compounds (I, II, III)

	Dose (ppm)				
	50	100	200	400	
Cpd (I)	1,000	100	10	Nil	
Cpd (II)	1,000	10	Nil	Nil	
Cpd (III)	100	10	Nil	Nil	

#### *Biodegradability*

The biodegradability of I, II and III was evaluated using the Die-away test as described in Ref. [50]. The results of the biodegradation using surface tension measurements for 7 days (Fig. 5) showed a gradual increase in the biodegradation extent of the different inhibitor solutions by increasing the time. The extent of the biodegradation values of the inhibitor solutions in the river water reached a maximum after 7 days. The gradual increase in biodegradation is ascribed to the loss of the surface activity of the inhibitors dissolved in the river water. The loss of surface activity may be due to the disruption of the inhibitor molecules [51]. The biodegradation products in the start of the test period (i.e., 1-3 days) have surface active characters, which retain the surface activity of the solutions. However, at the end of the test period (4-7 days), the products lose their surface activity due to the severe degradation. The biodegradation ratios of the inhibitor (Table 6) range between 35 and 53.8 % after 7 days. The biodegradation values of these inhibitors specified them as biodegradable compounds [52].

InhibitorInhibitor conc. (ppm) $R_{\rm s}$  (ohm cm2) $R_{\rm ct}$  (ohm cm2) $C_{\rm dl}$  ( $\mu \rm F \, cm^2$ ) $\theta$  $\eta$  %

Table 4 EIS parameters in the absence and presence of different concentrations of synthesized triazole derivatives (I, II, III) at 30 °C

mnibitor	Innibitor conc. (ppm)	$R_{\rm s}$ (onin cm )	$R_{\rm ct}$ (onlin clin )	$C_{dl}$ (µF cm )	0	η %
	0.00	4.9	160.7	221.8	_	_
Ι	100	28.21	463.9	24.42	0.653	65.3
	200	12.22	707.1	22.5	0.772	77.2
	400	1.96	829.5	15.34	0.806	80.6
	600	5.6	939.7	15.16	0.828	82.8
Π	100	15	873	14.58	0.815	81.5
	200	13	1,213	8.288	0.867	86.7
	400	8	1,726	6.56	0.906	90.6
	600	1.72	2,842	5.59	0.943	94.3
III	100	2.33	762.7	9.34	0.789	78.9
	200	-7	936.2	6.02	0.828	82.8
	400	5.69	1,330	5.9	0.879	87.9
	600	8.779	1,479	4.81	0.891	89.1

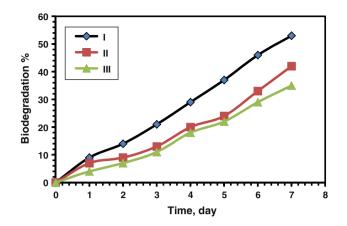


Fig. 5 Dependence of biodegradation (%) on the time for the synthesized inhibitors

 Table 6
 Biodegradation (%) of the synthesized inhibitors

Inhibitors	Biodegradation (%)
Cpd (I)	35.3
Cpd (II)	42.1
Cpd (III)	53.2

# Conclusions

From the above results it may be concluded that

- The synthesized triazole derivative compounds demonstrate good inhibition of the corrosion process of mild steel in 1 N HCl and they have a high capability to prevent SRB growth.
- The prepared compounds act as a mixed-type inhibitor in 1 N HCl. The weight loss and polarization curves are in good agreement.

#### References

- Soror TY, El-Dahan HA, El-Sayed Ammer NG (1999) Corrosion inhibition of carbon steel in hot hydrochloric acid solutions. J Mater Sci Technol 15:559–562
- Ashassi-Sorkhabi H, Majidi MR, Seyyedi K (2004) Investigation of inhibition effect of some amino acids against steel corrosion in HCl solution. Appl Surf Sci 225:176–185
- Sanad SH, Ismail AA, El-Meligi AA (2000) Indole and its derivatives as corrosion inhibitors for C-steel during pickling. J Mater Sci Technol 16:291–296
- Abd El-Maksoud SA, Fouda AS (2005) Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium. Mater Chem Phys 93:84–90
- Chetouani A, Medjahed K, Benabadji KE, Hammouti B, Kertit S, Mansri A (2003) Poly(4-vinylpyridine isopentyl bromide) as

inhibitor for corrosion of pure iron in molar sulphuric acid. Prog Org Coat 46:312–316

- Bouklah M, Benchat N, Aouniti A, Hammouti B, Benkaddour M, Lagrenée M, Vezine H, Bentiss F (2004) Effect of the substitution of an oxygen atom by sulphur in a pyridazinic molecule towards inhibition of corrosion of steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium. Prog Org Coat 51:118–124
- Chetouani A, Hammouti B, Aouniti A, Benchat N, Benhadda T (2002) New synthesised pyridazine derivatives as effective inhibitors for the corrosion of pure iron in HCl medium. Prog Org Coat 45:373–378
- Morad MS (1999) Influence of propargyl alcohol on the corrosion behaviour of mild steel in H<sub>3</sub>PO<sub>4</sub> solutions. Mater Chem Phys 60:188–195
- Bilgiç S (2002) The inhibition effects of benzoic acid and salicylic acid on the corrosion of steel in sulfuric acid medium. Mater Chem Phys 76:52–58
- Bentiss F, Traisnel M, Lagrenée M (2000) The substituted 1,3,4oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media. Corros Sci 42:127–146
- Quraishi MA, Khan MAW, Ajmal M, Muraidharan S, Iyer SV (1997) Influence of heterocyclic anils on corrosion inhibition and hydrogen permeation through mild steel in acid chloride environments. Corrosion 53:475–480
- Khamis E (1990) The effect of temperature on the acidic dissolution of steel in the presence of inhibitors. Corrosion 46:476–484
- Qafsaoui W, Takenouti H (2010) Corrosion protection of 2024-T3 aluminium alloy by electro-polymerized 3-amino 1,2,4triazole in sulphate solution containing chloride. Corros Sci 52:3667–3676
- Finsgar M, Milosev I (2010) Inhibition of copper corrosion by 1,2,3-benzotriazole: a review. Corros Sci 52:2737–2749
- Zheludkevich ML, Yasakau KA, Poznyak SK, Ferreira MGS (2005) Triazole and thiazole derivatives as corrosion inhibitors for AA2024 aluminium alloy. Corros Sci 47:3368–3383
- Bentiss F, Traisnel M, Gengembre L, Lagren'ee M (2000) Inhibition of acidic corrosion of mild steel by 3,5-diphenyl-4H-1,2,4triazole. App Surf Sci 161:194–202
- Gopi D, Govindaraju KM, Collins ArunPrakash V, Angeline Sakila DM, Kavitha L (2009) A study on new benzotriazole derivatives as inhibitors on copper corrosion in ground water. Corros Sci 51:2259–2265
- Wang L (2006) Inhibition of mild steel corrosion in phosphoric acid solution by triazole derivatives. Corros Sci 48:608–616
- Quraishi MA, Jamal D (2001) Corrosion inhibition of N-80 steel and mild steel in 15% boiling hydrochloric acid by a triazole compound—SAHMT. Mater Chem Phys 68:283–287
- Zhang S, Tao Z, Liao S, Wu F (2010) Substitutional adsorption isotherms and corrosion inhibitive properties of some oxadiazole-triazole derivative in acidic solution. Corros Sci 52:3126–3132
- Tawfik SM, Sayed A, Aiad I (2012) Corrosion inhibition by some cationic surfactants in oil fields. J Surfactants Deterg 15:577–585
- Hegazy MA, Zaky MF (2010) Inhibition effect of novel nonionic surfactants on the corrosion of carbon steel in acidic medium. Corros Sci 52:1333–1341
- Sherif ESM, El Shamy AM, Ramla MM, El Nazhawy AOH (2007) 5-(Phenyl)-4H-1,2,4-triazole-3-thiol as a corrosion inhibitor for copper in 3.5% NaCl solutions. Mater Chem Phys 102:231–239
- Zamani K, Faghihi K, Reza Sangi M, Zolgharnein J (2003) Synthesis of some new substituted 1,2,4-triazole and 1,3,4-thiadiazole and their derivatives. Turk J Chem 27:119–126
- 25. ASTM G31-72 (reapproved 2004) Standard practice for laboratory immersion corrosion testing of metal

- Lehr IL, Saidman SB (2006) Characterisation and corrosion protection properties of polypyrrole electropolymerised onto aluminium in the presence of molybdate and nitrate. Electrochim Acta 51:3249–3255
- Negm NA, Aiad I (2007) Synthesis and characterization of multifunctional surfactants in oil-field protection applications. J Surf Deterg 10:87–92
- 28. ASTM G3-89 (1994) standard practice for conventions applicable to electrochemical measurements in corrosion testing
- 29. ASTM D4412-84 (2009) Standard test methods for sulfatereducing bacteria in water and water-formed deposits
- EI-Sukkary MMA, Syed NA, Mad I, Helmy SM, EI-Azab WIM (2009) Aqueous solution properties, biodegradability, and antimicrobial activity of some alkyl polyglycosides surfactants. Tenside Surf Deterg 46:311–316
- Negm NA, Kandile NG, Mohamad MA (2011) Synthesis, characterization and surface activity of new eco-friendly Schiff bases vanillin derived cationic surfactants. J Surf Deterg 14:325–331
- Forland GM, Rahman T, Holand H, Borve KJ (1996) Adsorption of sodium dodecyl sulfate and butanol onto acidic and basic alumina. J Colloid Interface Sci 182:348–355
- 33. Nataraja SE, Venkatesha TV, Manjunatha K, Boja Poojary, Pavithra MK, Tandon HC (2011) Inhibition of the corrosion of steel in hydrochloric acid solution by some organic molecules containing the methylthiophenyl moiety. Corros Sci 53:2651–2659
- 34. Ahamad I, Gupta C, Prasad R, Quraishi MA (2010) An experimental and theoretical investigation of adsorption characteristics of a Schiff base compound as corrosion inhibitor at mild steel/ hydrochloric acid interface. J Appl Electrochem 40:2171–2183
- Popova A (2007) Temperature effect on mild steel corrosion in acid media in presence of azoles. Corros Sci 49:2144–2158
- Bouyanzer A, Hammouti B (2004) A study of anti-corrosive effects of Artemisia oil on steel. Pigment Resin Technol 33:287–292
- de Souza FS, Spinelli A (2009) Caffeic acid as a green corrosion inhibitor for mild steel. Corros Sci 51:642–649
- Ivanov ES (1986) Inhibitors for metal corrosion in acid media. Metallurgy, Moscow
- Noor EA, Al-Moubaraki AH (2008) Thermodynamic study of metal corrosion and inhibitor adsorption processes in mild steel/ 1-methyl-4[4'(-X)-styryl pyridinium iodides/hydrochloric acid systems. Mater Chem Phys 110:145–154
- Al-Sabagh AM, Kandil NGh, Ramadan O, Amer NM, Mansour R, Khamis EA (2011) Novel cationic surfactants from fatty acids and their corrosion inhibition efficiency for carbon steel pipelines in 1 M HCl. Egypt J Petrol 20:47–57
- Priya ARS, Muralidharam VS, Subramania A (2008) Development of novel acidizing inhibitors for carbon steel corrosion in 15% boiling hydrochloric acid. Corrosion 64:541–552
- Wu TX, Li ZJ, Zhao JC (1998) A facile method for the synthesis of 4-amino-5-hydrocarbon-2,4-dihydro-3H-1,2,4-triazole-3-thione Schiff bases. Chem J Chin Univ 19:1617–1619
- Wang J, Cao C, Chen J, Zhang M, Ye G, Lin H (1995) Anodic desorption of inhibitors. J Chin Soc Corros Prot 15:241–246
- 44. Lorenz WJ, Mansfeld F (1981) Determination of corrosion rates by electrochemical DC and AC methods. Corros Sci 21:647–672
- 45. Elkadi L, Mernari B, Traisnel M, Bentiss F, Lagrenee M (2000) The inhibition action of 3,6-bis(2-methoxyphenyl)-1,2-dihydro-1,2,4,5-tetrazine on the corrosion of mild steel in acidic media. Corros Sci 42:703–719
- 46. Prabhu RA, Venkatesha TV, Shanbhag AV, Kulkarni GM, Kalkhambkar RG (2008) Inhibition effects of some Schiff's bases on the corrosion of mild steel in hydrochloric acid solution. Corros Sci 50:3356–3362

- Tsurus T, Haruyama S (1978) Corrosion monitor based on impedance method. II. Construction and its application to homogeneous corrosion. J Jpn Soc Corros Eng 27:573–579
- Ramesh Saliyan V (2008) Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propanohydrazide as an effective inhibitor of mild steel corrosion in HCl solution. Corros Sci 50:55-61
- Atta AM, El-Azabawy OE, Ismail HS, Hegazy MA (2011) Novel dispersed magnetite core–shell nanogel polymers as corrosion inhibitors for carbon steel in acidic medium. Corros Sci 53:1680–1689
- Naylor CG, Williams JB, Varineau PT, Yunick RP, Serak K, Cady C, Severn DJ (1998) 19th annual society environmental toxicology and chemistry, Charlotte, NC
- Negm NA, El Farargy AFM, Mohammed DE, Mohamad HN (2012) Environmentally friendly nonionic surfactants derived from tannic acid: synthesis, characterization and surface activity. J Surf Deterg 15:433–443
- 52. Negm NA, El Farargy AF, Mohammad IA, Zaki MF, Khowdiary MM (2013) Synthesis and inhibitory activity of Schiff base surfactants derived from tannic acid and their Cobalt (II), Manganese (II) and Iron (III) complexes against bacteria and fungi. J Surf Deterg 16:767–777

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